Mixed-Metal Lanthanide–Iron Triple-Decker Complexes with a *cyclo*-P₅ Building Block**

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In memory of Oskar Glemser (1911-2005)

Triple- and multidecker sandwich complexes have been discussed in the last decades for their unique electrical and magnetic properties. The organic spacer between the metals may facilitate intermetallic electronic communication, which has a high potential for molecular electronics.^[1] A number of one-dimensional organometallic sandwich molecular wires (SMWs) have been extensively studied. Thus, the multilaver vanadium-arene (Ar) organometallic complexes $[V_n(Ar)_m]$, which can be produced in a molecular beam by laser vaporization, are a class of one-dimensional molecular magnets.^[2] Ferrocene-based molecular wires have been synthesized in the gas phase and characterized by mass spectroscopy.^[3] It was calculated that these compounds have half-metallic properties with 100 % negative spin polarization near the Fermi level in the ground state.^[4] In contrast to this investigation in the gas phase, studies on related organometallic triple- and multidecker sandwich complexes containing f-block elements (lanthanides or actinides) in condensed phase remain rare;^[5] studies were mostly on the cyclooctatetraene ligand and its derivatives. The only rare-earth-element triple-decker complex with heterocycles is the low-valent scandium 1,3,5-triphosphabenzene complex $[{(\eta^{5} P_3C_2tBu_2)Sc_2(\mu-\eta^6:\eta^6-P_3C_3tBu_3)$, which was obtained by cocondensation of scandium vaporized in an electron beam with an excess of the phosphaalkyne $tBuC = P^{[6]}$ Apart from organometallic compounds, triple- and multidecker sandwich complexes of the 4f elements consisting of "salen" type Schiff base ligands,^[7] phthalocyanines, and porphyrins have been

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extensively studied because these compounds exhibit tunable spectroscopic, electronic, and redox properties, and different extents of intramolecular π - π interactions.^[8] Despite these promising physical properties further investigations on 4f elements based triple- and multidecker sandwich complexes are obviously hampered by the limited variety of ligands that have been attached to the metal centers to date. Based on these considerations, we present herein mixed d/f-block-metal triple-decker complexes with a purely inorganic all-phosphorus middle deck.

In contrast to d-block chemistry, where purely inorganic ring systems of Group 15 elements such as P_5 and P_6 ,^[9] As₅,^[9c] and Sb₅^[10] are well-established, there is no analogy with the fblock elements to date. On the other hand, it was shown only recently that rare-earth elements can stabilize highly reactive main-group species such as N2^{3-.[11]} Although some heavier Group 15-lanthanide compounds, such as phosphides $(Ln-PR_2)$,^[12] arsenides $(Ln-AsR_2)$,^[12d,13] stibides $(Ln-Sb_3)$,^[14] and bismutides (Ln-Bi-Bi-Ln)^[15] are known, the first molecular polyphosphide of the rare-earth elements, $[(Cp*_2Sm)_4P_8]$ $(Cp^* = \eta^5 - C_5 Me_5)$, was recently synthesized.^[16] The structure of the complex is very rare and can be described as a realgartype P_8^{4-} ligand trapped in a cage of four samarocenes. As no triple-decker sandwich complex of the rare-earth elements with a polyphosphide middle-deck bridging the metal centers is known, we focused our interest on the cyclo-P₅ ligand. The structure and properties of this ligand are very similar to the well-known cyclopentadienyl anion (Scheme 1) and could therefore have many possible coordination modes.



Scheme 1. Comparison of the cyclo-P₅ and cyclopentadienyl ligands.

The coordination of *cyclo*-P₅ ligand to an iron(II) center was first discovered by Scherer and Brück;^[9a] the structure^[17] and coordination and redox properties of pentaphosphaferrocene, [Cp*Fe(η^5 -P₅)], have been studied intensively. Electrochemistry studies by Geiger and Winter^[18] suggested that the redox properties of [Cp*Fe(η^5 -P₅)] were similar to those of ferrocene, giving one-electron oxidation/reduction steps. [Cp*Fe(η^5 -P₅)] is an attractive complex ligand owing to the possibility of using one or more of the lone pairs of electrons

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on the phosphorus atoms to coordinate additional metalligand fragments to form spherical molecules,^[19] or to take advantage of the aromatic π -electron system to coordinate a second metal moiety.^[20] Thus, several examples of transitionmetal triple-decker complexes containing the η^5 -bonded bridging *cyclo*-P₅ building block have been synthesized in which the *cyclo*-P₅ unit maintains its pentagonal-planar arrangement, even under harsh reaction conditions.^[9b,21] To the best of our knowledge, neither rare-earth metal *cyclo*-P₅ complexes nor polyphosphides bridging 4f- and 3d-metal triple-decker complexes have been reported.

The reaction of the samarium(II) complex $[(DIP_2pyr)SmI(thf)_3]^{[22]}$ ($DIP_2pyr = 2,5$ -bis{N-(2,6-diisopropylphenyl)iminomethyl}pyrrolyl) and $[Cp*Fe(\eta^5-P_5)]$ in toluene at elevated temperature resulted in a 1:1 mixture of the first 3d/4f-*cyclo*-P₅ sandwich complex $[Cp*FeP_5Sm-(DIP_2pyr)]_2$ (1) and the corresponding dimeric product $[(DIP_2pyr)SmI_2(thf)]_2$ (2) (Scheme 2).



Scheme 2. Synthesis of compounds **1** and **2**. The bonding situation is simplified.

In the reaction, two equivalents of $[(DIP_2pyr)SmI(thf)_3]$ each act as a one-electron reducing agent. One of the resulting samarium(III) ions is coordinated to the *cyclo*-P₅ unit and the other one is isolated as complex **2**. During the redox reaction one iodine atom was transferred between the two samarium atoms. As a result, the {(DIP_2pyr)Sm} subunit, which is coordinated to the *cyclo*-P₅ ligand, does not bear any iodine atom, whereas in compound **2** two iodine atoms are coordinated to the metal center. Compounds **1** and **2** were obtained as a mixture of crystals, which could be manually separated by using a microscope and characterized by X-ray single-crystal diffraction (Figure 1; Supporting Information, Figure S1).

To study the formation of 1 and 2 and to obtain analytically pure products of 1 and 2, the two complexes were prepared independently. Complex 2 was synthesized by the reaction of SmI_3 and $(DIP_2pyr)K$ in THF. Compound 1 could also be prepared by treatment of only one equivalent of



Figure 1. Solid-state structure of 1. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] or angles [°]: P1–P2 2.2043(10), P1–P5 2.1859(9), P2–P3 2.2158(10), P3–P4 2.1706(10), P4–P5 2.2216(11), Sm–P1 2.8658(8), Sm–P2 3.3803(7), Sm–P3 2.9643(7), Sm–P4 3.0184(7), Sm'–P1 2.9920(7), Sm'–P2 2.8933(7), Sm–N1 2.876(2), Sm–N2 2.338(2), Sm–N3 2.693(2), Fe–P2 2.2230(7), Fe–P3 2.3165(8), Fe–P4 2.3162(8), Fe–P5 2.2667(8); P1-P2-P3 110.39(4), P2-P3-P4 97.15(4), P3-P4-P5 100.33(4), P4-P5-P1 108.14(4), P5-P1-P2 80.79(3).

[(DIP₂pyr)SmI(thf)₃] and [Cp*Fe(η^5 -P₅)] for 15 h at elevated temperature in THF in the presence of potassium/naphthalene (Scheme 3). The potassium/naphthalene acted as a reductant and an iodine abstracting reagent. Single crystals of the dimeric complex **1** could be obtained by recrystallization from toluene and pentane. However, recrystallization of the product from THF and toluene gave a new monomeric samarium–iron *cyclo*-P₅ complex [Cp*FeP₅Sm(DIP₂pyr)-(thf)₂] (**3**; Scheme 3). In complex **3**, the two THF solvent molecules coordinate to the samarium atom and thus block the binding sites to prevent formation of the dimeric complex



Scheme 3. Synthesis of compounds 1 and 3. The bonding situation is simplified.

1. Recrystallization of complex 3 is more accessible than that of 1. Complex 3 is a more favorable and probable product than 1, and is even formed sometimes in toluene/pentane recrystallization. Thus, although we obtained compound 1 on two independent reaction pathways and present a full characterization, we consider this compound to be poorly reproducible.

To support the suggested formation pathway of compounds 1 and 3, the oxidation states of the samarium atoms were determined by magnetic measurements (SQUID) and NIR spectroscopy. A low paramagnetic susceptibility χ_{M} - $(290 \text{ K}) = 3649 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ and magnetic moment $\mu_{\rm eff}(\mu_{\rm B}) = 2.91$ for two samarium metal centers in 1 suggest that the oxidation state of samarium is +3. Similarly, the paramagnetic susceptibility χм $(290 \text{ K}) = 1232 \times$ $10^{-6} \text{ cm}^3 \text{mol}^{-1}$ and magnetic moment $\mu_{\text{eff}}(\mu_{\text{B}}) = 1.69$ of **3** are comparable to the literature values for Sm³⁺ complexes.^[23] Sm³⁺ complexes exhibit a characteristic absorption pattern in the NIR even in the presence of a strong visible absorption.^[24] The obtained spectra for compounds 1-3 show spectral patterns that are comparable to Sm3+/POCl₃/ZrCl₄^[25] and Sm3+/SeOCl2/SnCl4.[26]

Complexes **1–3** were characterized by analytical and spectroscopic methods and the solid-state structures were analyzed by single-crystal X-ray diffraction (Figure 1, Figure 2, and Supporting Information, S1). In the solid state, complexes **1** and **3** form a pseudo triple-decker structure in which the *cyclo*-P₅ unit forms the central moiety between the iron and the samarium atom. As a result of the twofold reduction, the *cyclo*-P₅ unit adopts an envelope conformation.^[27] In the thus-obtained {Cp*FeP₃}^{2–} anion, the phosphorus ligand may be considered as a formally *cyclo*-P₅^{3–} polyphosphide anion, which can be understood in the following way: One negative charge is localized on the phosphorus atom, which is bent out of plane, whereas the



Figure 2. Solid-state structure of **3**. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] or angles [°]: P1–P2 2.180(3), P1–P5 2.175(2), P2–P3 2.228(2), P3–P4 2.164(2), P4–P5 2.215(3), Sm–P1 2.847(2), Sm–P2 3.3385(15), Sm–P3 2.980(2), Sm–P4 3.0703(15), Sm–N1 2.769(5), Sm–N2 2.385(4), Sm–N3 2.770(5), Sm–O1 2.524(4), Sm–O2 2.496(4), Fe–P2 2.262(2), Fe–P3 2.291(1), Fe–P4 2.321(1), Fe–P5 2.255(2); P1-P2-P3 110.27(9), P2-P3-P4 99.32(10), P3-P4-P5 99.21(9), P4-P5-P1 110.08(9), P5-P1-P2 82.82(9).

remaining negative charges are delocalized over the other four phosphorus atoms and the {Cp*Fe} fragment. Formally, the cyclo-P₅ unit binds in a η^4 -coordination mode to the iron atom. The iron part of compounds 1 and 3 thus obey the 18 valence-electron rule. The P3–P4 bond (2.1706(10) Å (1))and 2.164(2) Å (3)) is slightly shorter than the other P–P bonds (2.1859(9)–2.2216(11) Å (1) and 2.175(2)–2.228(2) Å (3)). P1 is bent out from the P₄ plane at an angle of 124.7° (1) and 127.6° (3). The Sm-P distances vary within a wide range. Three Sm-P distances in 1 and 3 are within the known bonding distances reported in the literature.^[12b, 16] They range from 2.8658(8) to 3.0184(7) Å (1) and 2.847(2) to 3.0703(15) Å (3). Formally, the η^3 -coordinated ligand binds with the negative charged phosphorus atom P1, P3, and P4 to the samarium center. In compound 1, an additional η^2 coordination of the second *cyclo*-P₅ unit is observed as a result of the dimerization. These two coordination sites are occupied by THF molecules in the monomeric compound 3.

To confirm the trivalent oxidation state of the samarium centers in complexes **1** and **3**, the Sm–N bonds were compared to similar samarium complexes containing the $(DIP_2pyr)^-$ ligand. For comparison we choose the divalent compound $[(DIP_2pyr)SmI(thf)_3]^{[22]}$ and the trivalent compound **2**. The distances of the samarium atom to the pyrrolyl nitrogen atom (Sm–N2) of compounds **1** (2.338(2) Å) and **3** (2.385(4) Å) are similar to the trivalent compound **2** (2.331(2) Å) and differ significantly in comparison with divalent $[(DIP_2pyr)SmI(thf)_3]$ (2.474(7) Å).^[22] Thus, the data is in agreement with the magnetic measurements and NIR spectroscopy.

To gain a better insight into the bonding in these novel monomeric triple-decker compounds, we performed quantum-chemical DFT calculations on 3. The calculated structure of 3 agrees well with its experimentally obtained parameters (Supporting Information, Table S2), which shows that the use of a special ECP and basis set for Sm³⁺ was a good choice (Supporting Information). In both 3 and the dianion [Cp*Fe- $(\eta^5 - \dot{P}_5)$]^{2-,[28]} the iron atom is connected to the P₅ ring in the way that only four instead of five phosphorus atoms are connected to iron owing to the bending of P1 out of the resulting P₄ plane. The Fe-P distances are comparable. The shape of the P_5 unit is expected for the formal reduction of P_5 to P_5^{3-} .^[29] However, the P–P distances in these anions differ significantly from those found in 3, so that the formulation of P₅ as trianion does not appear to be justified. A better (but not completely satisfactory) agreement is found for the P-P distances calculated for $[Cp*Fe(\eta^5-P_5)]^{2-}$. The samarium atom is threefold coordinated to the P₅ ligand. The calculated Sm-P distances agree well with the measured data. Based on population analyses (Supporting Information), compound 3 is best interpreted as a {Cp*FeP₅Sm}⁺ cation, which is basically electrostatically connected to the DIP₂pyr anion and two THF molecules.

In summary, the dimeric and the corresponding monomeric compounds 1 and 3 have certain hitherto unknown features. Compounds 1 and 3 can be considered as the first 3d/4f-metal triple-decker complexes with a polyphosphide bridging the metal centers. Both compounds are the first fblock element compounds ligated by the *cyclo*-P₅ unit. In both

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compounds reduction of the *cyclo*- P_5 unit leads to the {Cp*FeP₅}²⁻ subunit in which the phosphorus ligand may be considered as a formally *cyclo*- P_5^{3-} polyphosphide anion. Mixed 3d/4f-element triple-decker complexes raise fundamental questions about the formation of polyphosphides and other phosphorus derivatives^[30] within the coordination sphere of a metal center. Furthermore, they open new possibilities towards a better comprehension of intermetallic communication.

Experimental Section

1: THF (10 mL) was condensed at -78 °C onto a mixture of $[(DIP_2pyr)SmI(thf)_3]$ (185 mg, 0.20 mmol), $[Cp*Fe(\eta^5-P_5)]$ (70 mg, 0.20 mmol), potassium metal (8 mg, 0.20 mmol), and naphthalene (30 mg, 0.24 mmol). The resulting reaction mixture was stirred for 16 h at 60 °C. The solvent of the dark-colored solution was evaporated to dryness. Toluene (5 mL) was condensed onto the dark residue to give a dark brown solution. The solution was filtered off and layered with pentane. Dark orange crystals and a pale precipitate were obtained at ambient temperature after three days. Yield: 35 mg, 16 % (single crystals). Magnetic susceptibility: χ_M (290 K) = 3649 × $10^{-6} \text{ cm}^3 \text{ mol}^{-1}$, $\mu_{\text{eff}}(\mu_{\text{B}}) = 2.91$. MIR (KBr): $\tilde{\nu} = 2958$ (m), 2902 (w), 1620 (s), 1587 (m), 1459 (m), 1439 (m), 1376 (m), 1309 (m), 1230 (m), 1155 (vs), 1022 (vs), 860 (m), 783 (s), 728 (s), 497 (w), 464 (s), 439 cm⁻¹ (m). NIR (KBr): $\tilde{\nu} = 9276 ({}^{6}F_{9/2}), 8155 ({}^{6}F_{7/2}), 7308 ({}^{6}F_{5/2}), 6786 ({}^{6}F_{3/2}),$ 6479 cm⁻¹ (${}^{6}F_{1/2}$). Anal. calcd (%) for Sm₂Fe₂P₁₀N₆C₈₀H₁₀₆ (1873.91 gmol⁻¹): C 51.28, H 5.70, N 4.48; found: C 51.16, H 5.82, N 4.03.

2: THF (10 mL) was condensed at -78 °C onto a mixture of SmI₃ (200 mg, 0.380 mmol) and (DIP₂pyr)K (180 mg, 0.375 mmol). The resulting reaction mixture was stirred for 16 h at 60 °C. The solvent of the orange solution was evaporated to dryness. Toluene (5 mL) was condensed onto the yellow residue to give yellow–orange solution and a pale precipitate. The mixture was filtered off into a 2-section ampoule to grow crystals by slow evaporation. Yellow crystals were obtained at ambient temperature. Yield: 320 mg, 92.7 %. ¹H NMR (300 MHz, C₆D₆): δ = 0.60 (brs, 4H, N = CH), 1.08 (d, 48H, *J* = 7 Hz, CH(CH₃)₂), 1.40 (brs, 8H, THF), 3.03 (sept, 8H, *J* = 7 Hz, CH(CH₃)₂), 3.59 (brs, 8H, THF), 6.37 (s, 4H, 3,4-pyr), 7.01–10.37 ppm (m, 12H, Ph). NIR (KBr): $\tilde{\nu}$ = 9211, (⁶F_{9/2}), 8021 (⁶F_{7/2}), 7148 (⁶F_{5/2}), 6360 (⁶F_{1/2}), 6246 cm⁻¹ (⁶H_{15/2}). Anal. calcd (%) for **1**·(2C₆H₅CH₃), Sm₂I₄N₆O₂C₈₂H₁₀₈ (2018.12 gmol⁻¹): C 48.80, H 5.39, N 4.16; found: C 48.54, H 5.68, N 3.917.

3: THF (10 mL) was condensed at -78°C onto a mixture of $[(DIP_2pyr)SmI(thf)_3]$ (375 mg, 0.40 mmol), $[Cp*Fe(\eta^5-P_5)]$ (140 mg, 0.40 mmol), potassium metal (19 mg, 0.49 mmol) and naphthalene (55 mg, 0.43 mmol) in a Schlenk tube. The resulting reaction mixture was stirred for 16 h at 60 °C. After the solvent was removed, the dark brown solid was washed with heptanes (20 mL) and dried under vacuum. THF (10 mL) was condensed onto the solid and stirred for 1 h. The mixture was filtered into a 2-section ampoule. Toluene (10 mL) was condensed to the filtrate to grow crystals in a 2-section ampoule. The dark orange crystals were obtained at ambient temperature after three days. Yield: 120 mg, 28% (single crystals). Magnetic susceptibility $\chi_{\rm M}$ (290 K) = 1232 × 10⁻⁶ cm³mol⁻¹, $\mu_{\rm eff}(\mu_{\rm B}) = 1.69$. MIR (KBr): $\tilde{v} = 2959$ (vs), 2900 (m), 1623 (m), 1568 (vs), 1449 (s), 1371 (m), 1333 (s), 1250 (m), 1162 (s), 1099 (m), 1050 (s), 927 (m), 846 (s), 768 (m), 735 (s), 564 (m), 463 cm⁻¹ (m). NIR (KBr): $\tilde{\nu} = 9216$ (${}^{6}F_{9/}$ 2), 7925 (${}^{6}F_{7/2}$), 7218 (${}^{6}F_{5/2}$), 6631 (${}^{6}F_{3/2}$), 6430 (${}^{6}F_{1/2}$), 6321 cm⁻¹ (${}^{6}H_{15/2}$) 2.). Anal. calcd (%) for SmFeP₅N₃O₂C₄₈H₆₉ (1081.17 g mol⁻¹): C 53.32, H 6.43, N 3.89; found: C 53.71, H 6.32, N 3.83.

Reaction of $[(DIP_2pyr)SmI (thf)_3]$ and $[Cp^*Fe(\eta^5-P_5)]$: Toluene (10 mL) was condensed at -78 °C onto a mixture of $[(DIP_2pyr)SmI(thf)_3]$ (108 mg, 0.12 mmol) and $[Cp^*Fe(\eta^5-P_5)]$ (20 mg, 0.058 mmol) in one side of a 2-section ampoule. The resulting reaction mixture was

stirred for 16 h at 60 °C. Both bright yellow crystals of 2 and dark orange crystals of 1 were obtained after the 2-section ampoule technique procedure. The crystals could be differentiated and separated under a microscope.

Crystal data for **1**: $C_{80}H_{106}Fe_2N_6P_{10}Sm_2\cdot3(C_7H_8)$, $M_r = 2150.21$, triclinic, a = 13.8374(7), b = 14.7963(10), c = 14.8908(8) Å, a = 65.526(4), $\beta = 70.167(4)$, $\gamma = 68.100(5)^\circ$, V = 2512.2(3) Å³, T = 150(2) K, space group $P\overline{1}$, Z = 1, $\mu(MoK_{\alpha}) = 1.642$ mm⁻¹, 18967 reflections measured, 9037 independent reflections ($R_{int} = 0.0353$). The final R_1 values were 0.0258 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.0432 (all data). The goodness of fit on F^2 was 0.998.

2: $C_{68}H_{96}I_4N_6O_2Sm_2\cdot 2(C_7H_8)$, $M_r = 2022.08$, triclinic, a = 15.1260(4), b = 16.6343(5), c = 18.9589(6) Å, $\alpha = 106.169(3)$, $\beta = 90.251(3)$, $\gamma = 110.110(2)^\circ$, V = 4275.7(2) Å³, T = 200(2) K, space group $P\bar{I}$, Z = 2, μ (Mo K_a) = 2.849 mm⁻¹, 32.012 reflections measured, 15.115 independent reflections ($R_{int} = 0.0350$). The final R_1 values were 0.0241 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.0552 (all data). The goodness of fit on F^2 was 1.003.

3: $2(C_{48}H_{69}FeN_3O_2P_5Sm)\cdot 3(C_7H_8)$, $M_r = 2438.63$, triclinic, a = 12.8658(8), b = 13.3175(9), c = 19.6233(13), a = 77.726(5), $\beta = 71.236(5)$, $\gamma = 66.402(5)^\circ$, V = 2903.7(3) Å³, T = 150(2) K, space group $P\overline{I}$, Z = 1, μ (MoK_a) = 1.432 mm⁻¹, 22189 reflections measured, 10330 independent reflections ($R_{int} = 0.0844$). The final R_1 values were 0.0540 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.1385 (all data). The goodness of fit on F^2 was 1.005.

CCDC 822355 (1), CCDC 822356 > (2), and CCDC 822357(3) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/ cif.

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- a) D. Astruc, Acc. Chem. Res. 1997, 30, 383–391; b) P. Nguyen, P. Gomez-Elipe, I. Manners, Chem. Rev. 1999, 99, 1515–1548.
- [2] a) K. Miyajima, A. Nakajima, S. Yabushita, M. B. Knickelbein,
 K. Kaya, J. Am. Chem. Soc. 2004, 126, 13202-13203; b) J. Wang,
 P. H. Acioli, J. Jellinek, J. Am. Chem. Soc. 2005, 127, 2812-2813.
- [3] S. Nagao, A. Kato, A. Nakajima, K. Kaya, J. Am. Chem. Soc. 2000, 122, 4221–4222.
- [4] L. Zhou, S.-W. Yang, M.-F. Ng, M. B. Sullivan, Tan, L. Shen, J. Am. Chem. Soc. 2008, 130, 4023 – 4027.
- [5] F. T. Edelmann, New J. Chem. 2011, 35, 517-528.
- [6] P. L. Arnold, F. G. N. Cloke, P. B. Hitchcock, J. F. Nixon, J. Am. Chem. Soc. 1996, 118, 7630–7631.
- [7] X. Yang, R. A. Jones, J. Am. Chem. Soc. 2005, 127, 7686-7687.
- [8] J. Jiang, D. K. P. Ng, Acc. Chem. Res. 2008, 42, 79-88.
- [9] a) O. J. Scherer, T. Brück, Angew. Chem. 1987, 99, 59; Angew. Chem. Int. Ed. Engl. 1987, 26, 59; b) O. J. Scherer, T. Brück, G. Wolmershäuser, Chem. Ber. 1989, 122, 2049–2054; c) O. J. Scherer, H. Sitzmann, G. Wolmershäuser, Angew. Chem. 1985, 97, 358–359; Angew. Chem. Int. Ed. 1985, 24, 351–353.
- [10] H. J. Breunig, N. Burford, R. Rösler, Angew. Chem. 2000, 112, 4320–4322; Angew. Chem. Int. Ed. 2000, 39, 4148–4150.
- [11] M. Fang, D. S. Lee, J. W. Ziller, R. J. Doedens, J. E. Bates, F. Furche, W. J. Evans, J. Am. Chem. Soc. 2011, 133, 3784–3787.
- [12] a) H. Schumann, E. Palamidis, G. Schmid, R. Boese, Angew. Chem. 1986, 98, 726-727; Angew. Chem. Int. Ed. 1986, 25, 718-719; b) G. W. Rabe, G. P. A. Yap, A. L. Rheingold, Inorg. Chem. 1997, 36, 3212-3215; c) M. R. Douglass, C. L. Stern, T. J. Marks, J. Am. Chem. Soc. 2001, 123, 10221-10238; d) W. J. Evans, J. T.

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Leman, J. W. Ziller, S. I. Khan, Inorg. Chem. 1996, 35, 4283-4291.

- [13] H. Schumann, E. Palamidis, J. Loebel, J. Pickardt, Organometallics 1988, 7, 1008–1010.
- [14] W. J. Evans, S. L. Gonzales, J. W. Ziller, J. Chem. Soc. Chem. Commun. 1992, 1138–1139.
- [15] W. J. Evans, S. L. Gonzales, J. W. Ziller, J. Am. Chem. Soc. 1991, 113, 9880–9882.
- [16] S. N. Konchenko, N. A. Pushkarevsky, M. T. Gamer, R. Koeppe, H. Schnöckel, P. W. Roesky, J. Am. Chem. Soc. 2009, 131, 5740– 5741.
- [17] M. Scheer, L. J. Gregoriades, A. V. Virovets, W. Kunz, R. Neueder, I. Krossing, *Angew. Chem.* 2006, *118*, 5818–5822; *Angew. Chem. Int. Ed.* 2006, *45*, 5689–5693.
- [18] a) R. F. Winter, W. E. Geiger, Organometallics 2003, 22, 1948– 1952; b) R. F. Winter, W. E. Geiger, Organometallics 1999, 18, 1827–1833.
- [19] a) J. Bai, A. V. Virovets, M. Scheer, *Science* 2003, *300*, 781–783;
 b) S. Welsch, C. Gröger, M. Sierka, M. Scheer, *Angew. Chem.* 2011, *123*, 1471–1474; *Angew. Chem. Int. Ed.* 2011, *50*, 1435–1438;
 c) M. Scheer, A. Schindler, J. Bai, B. P. Johnson, R. Merkle, R. Winter, A. V. Virovets, E. V. Peresypkina, V. A. Blatov, M. Sierka, H. Eckert, *Chem. Eur. J.* 2010, *16*, 2092–2107;
 d) M. Scheer, *Dalton Trans.* 2008, 4372–4386.
- [20] M. Caporali, L. Gonsalvi, A. Rossin, M. Peruzzini, *Chem. Rev.* 2010, 110, 4178–4235.
- [21] a) A. R. Kudinov, D. A. Loginov, Z. A. Starikova, P. V. Petrovskii, M. Corsini, P. Zanello, *Eur. J. Inorg. Chem.* 2002, 3018–3027;

b) B. Rink, O. J. Scherer, G. Heckmann, G. Wolmershäuser, *Chem. Ber.* **1992**, *125*, 1011–1016; c) A. R. Kudinov, P. V. Petrovskii, M. I. Rybinskaya, *Russ. Chem. Bull.* **1999**, *48*, 1362–1364.

- [22] J. Jenter, M. T. Gamer, P. W. Roesky, Organometallics 2010, 29, 4410–4413.
- [23] F. T. Edelmann, P. Poremba in Synthetic Methods of Organometallic and Inorganic Chemistry, Vol. 6 (Ed.: W. A. Herrmann), Georg Thieme Verlag, Stuttgart, 1997.
- [24] a) H. D. Amberger, C. Hagen, Spectrochim. Acta Part A 1994, 50, 1267–1275; b) H.-D. Amberger, H. Reddmann, W. J. Evans, Inorg. Chem. 2009, 48, 10811–10818.
- [25] K. Bukietynska, B. Radomska, Polyhedron 1983, 2, 1297–1299.
- [26] Y. C. Ratnakaram, S. Buddhudu, Mater. Chem. Phys. 1985, 12, 443-448.
- [27] Other envelope-shaped compounds were obtained by the reactions of $[Cp^*Fe(\eta^5-P_5)]$ with the organometallic compounds $[(\eta^5-C_3H_3tBu_2)Ta(CO)_4]$ and $[\{Cp^*Ir(CO)\}_2]$: M. Detzel, T. Mohr, O. J. Scherer, G. Wolmershäuser, *Angew. Chem.* **1994**, *106*, 1142–1144; *Angew. Chem. Int. Ed.* **1994**, *33*, 1110–1112.
- [28] The ground state of the dianion of $[Cp*FeP_5]$ is a singlet. Geometry optimization of the lowest-lying 3A" state (disfavored by 49 kJ mol⁻¹) leads to separated Cp* and FeP₅⁻ anions. For this reason, we did not consider this state in the discussion.
- [29] The 1A' and 3A" states of P_5^{3-} are of comparable energy; the 3A" state is disfavored by 12 kJ mol⁻¹.
- [30] N. A. Piro, J. S. Figueroa, J. T. McKellar, C. C. Cummins, *Science* 2006, 313, 1276–1279.