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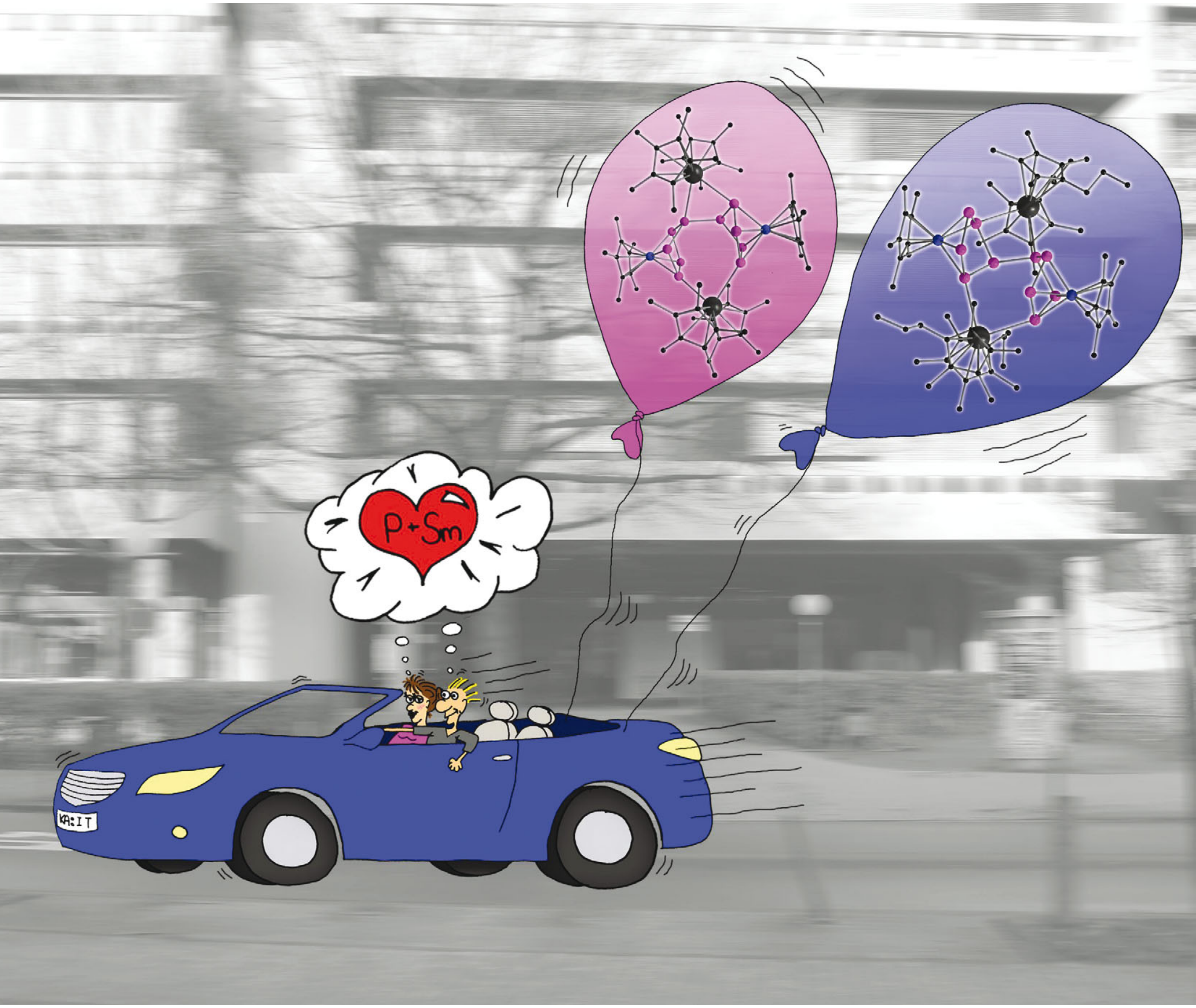

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P–P bond formation *via* reductive dimerization of $[Cp^*Fe(\eta^5\text{-}P_5)]$ by divalent samarocenes†

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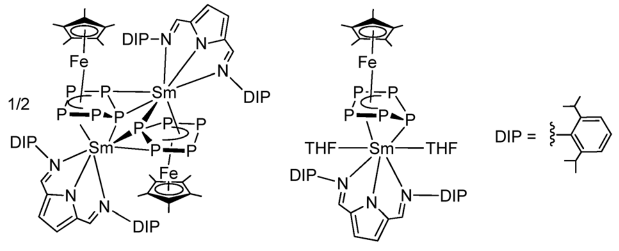
The two new 3d/4f polyphosphide complexes $[(Cp^*Fe)_2P_{10}\{Sm(\eta^5\text{-}C_5Me_4R)_2\}_2]$ ($Cp^* = \eta^5\text{-}C_5Me_5$; R = Me, *n*Pr) were prepared by reductive dimerization of $[Cp^*Fe(\eta^5\text{-}P_5)]$ with samarocenes. They are the first P_{10} bridging 3d/4f metal complexes and the first examples of reductive coupling of polyphosphide complexes by divalent lanthanides.

Metal-mediated white phosphorus (P_4) activation has been studied comprehensively and many metal polyphosphide complexes have been reported.[1] Due to the isolobal P and C–H relation, there is a similarity between phosphorous and carbon chemistry.[2] In rare earth element chemistry, polyphosphide complexes are still rare. In 2009, we reported the first molecular polyphosphide of rare-earth elements, $[(Cp^*_2Sm)_4P_8]$ ($Cp^* = \eta^5\text{-}C_5Me_5$), by diffusion of P_4 vapor into a toluene solution of solvate-free $[Cp^*_2Sm]$. In the reaction, each samarium atom transfers one electron to the phosphorus atoms to form a realgar-type P_8^{4-} ligand located in a cage of four samarocenes.[3] Another example of direct activation of P_4 to P_8^{4-} ligand stabilized by a scandium naphthalene complex has been recently reported by Huang and Diaconescu.[4] A phosphorus–phosphorus bond formation between the phosphaalkyne *t*BuC≡P molecules was accomplished in divalent samarium systems by reductive dimerization[5] and in the electron beam vaporized scandium system by cocondensation, which resulted in the low valent scandium 1,3,5-triphosphabenzene complex $[\{(\eta^5\text{-}P_3C_2\textit{t}Bu_2)Sc\}_2(\mu\text{–}\eta^6{:}\eta^6\text{-}P_3C_3\textit{t}Bu_3)]$.[6]

Our current interest is to create a new P–P bond between two polyphosphide metal complexes to create extended polyphosphorus d/f metal frameworks. Pentaphosphaferrocene, $[Cp^*Fe(\eta^5\text{-}P_5)]$,[7] which possesses lone pairs of electrons on the P-atoms, is a well-known complex ligand with multiple coordination sites for additional metal–ligand fragments.[1d] As we have already found, in the reaction of $[Cp^*Fe(\eta^5\text{-}P_5)]$ and Cu(I)Cl in CH_2Cl_2/CH_3CN, the pentagonal symmetric *cyclo*-P_5 rings are surrounded by six-membered P_4Cu_2 to form an entirely inorganic fullerene-like molecule $[\{Cp^*FeP_5\}_{12}\text{-}\{CuCl\}_{10}\{Cu_2Cl_3\}_5\{Cu(CH_3CN)_2\}_5]$ possessing 90 inorganic core atoms.[8] Since that, $[Cp^*Fe(\eta^5\text{-}P_5)]$ has become an efficient building block in crystal-engineering processes for spherical molecules and coordination polymers.[9] Recently, we have prepared the first polyphosphide bridging complexes of rare-earth elements and 3d transition metals, $[Cp^*FeP_5Sm(DIP_2pyr)]_2$ and $[Cp^*FeP_5Sm(DIP_2pyr)(THF)_2]$ (DIP_2pyr = 2,5-bis{*N*-(2,6-diisopropylphenyl)iminomethyl}pyrrolyl), that resulted from the reaction of divalent $[(DIP_2pyr)SmI(THF)_3]$ and $[Cp^*Fe(\eta^5\text{-}P_5)]$ in THF at an elevated temperature (Scheme 1).[10] They were the first mixed d/f metal triple-decker complexes with a purely inorganic middle deck which has the *cyclo*-P_5 unit in the center. As a result of the two electron reduction, the *cyclo*-P_5 is transformed from planar to an open envelope conformation, which links to the iron atom in an η^4-coordination mode and to the samarium atom in $[Cp^*FeP_5Sm(DIP_2pyr)(THF)_2]$ in an η^3-coodination mode. In these examples, there is no P–P bond formation during the reduction and reconfiguration of the polyphosphorus complex (Scheme 1).[10] Therefore, we decided to study



$[Cp^*FeP_5Sm(DIP_2pyr)]_2$ $[Cp^*FeP_5Sm(DIP_2pyr)(THF)_2]$

Scheme 1 Mixed d/f metal triple-decker complexes were formed without any P–P bond formation during the reduction.

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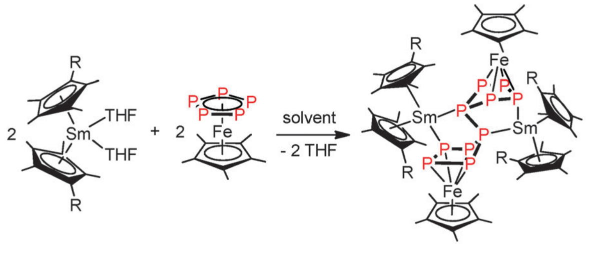
† Electronic supplementary information (ESI) available: Cif files of the structures and full experimental details of all compounds. CCDC 914587 (**1a**) and 914588 (**1b**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3cc38841g



R = Me (**1a**), solvent = toluene
R = *n*-Pro (**1b**), solvent = heptane

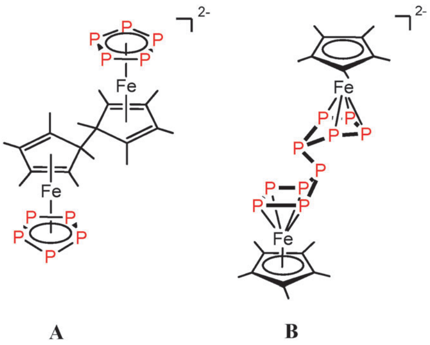
Scheme 2 Synthesis of **1a** and **1b**.

the reactivity of [Cp*Fe(η^5-P$_5$)] towards divalent samarocenes. The divalent samarocene [Cp*$_2$Sm(THF)$_2$] has been reported a few times in carbon–carbon bond formation, *e.g.* the dimerization of two terminal alkynes could be achieved[11] and it was also successfully used in P–P bond formation in [(Cp*$_2$Sm)$_4$P$_8$].[3] Here we report the first P–P bond formation between two transition metal polyphosphide complexes triggered by two divalent lanthanide complexes.

The two slightly different samarocenes, [Cp*$_2$Sm(THF)$_2$] and [(C$_5$Me$_4$(*n*-propyl))$_2$Sm],[12] were reacted with [Cp*Fe(η^5-P$_5$)] in toluene or heptane, correspondingly at an elevated temperature to give a brown colored solution. Recrystallization by slow evaporation in heptane afforded dark brown, air-sensitive crystals of the tetranuclear complexes [(Cp*Fe)$_2$P$_{10}${Sm(η^5-C$_5$Me$_4$R)$_2$}$_2$] (R = Me (**1a**), *n*Pr (**1b**)), containing a P$_{10}$ bridge (Scheme 2).

Complexes **1a** and **1b** were characterized by analytical and spectroscopic methods. The oxidation state of the samarium atom was determined by NIR, which exhibited a characteristic absorption pattern for Sm(III) complexes. Unlike the formation of [Cp*FeP$_5$Sm(DIP$_2$pyr)]$_2$ by a 2 : 1 ratio of [(DIP$_2$pyr)SmI(THF)$_3$] and [Cp*Fe(η^5-P$_5$)], **1a** and **1b** were synthesized in a 1 : 1 ratio of [(C$_5$Me$_4$R)$_2$Sm(THF)$_2$] and [Cp*Fe(η^5-P$_5$)]. Due to the different steric and electronic properties of the DIP$_2$pyr and two C$_5$Me$_4$R ligands on the samarium center, considerably different redox chemistry was shown for the two reactions. In contrast to the double reduction of a *cyclo*-P$_5$ unit by two [(DIP$_2$pyr)SmI(THF)$_3$] molecules, [Cp*Fe(η^5-P$_5$)] molecules received one electron each from the samarocene complex and formed a dimeric complex with the formation of a 2-center-2-electron P–P bond between two *cyclo*-P$_5$ units.

The redox properties of [Cp*Fe(η^5-P$_5$)] have been studied thoroughly by Winter and Geiger.[13] They suggested that [Cp*Fe(η^5-P$_5$)] could undergo monoelectronic reduction ($E_{1/2}$ = −2.00 V) to a 19 electron [Cp*Fe(η^5-P$_5$)]$^-$ anion, which dimerize to [Cp*$_2$Fe$_2$P$_{10}$]$^{2-}$. Based on the significant π character from the Cp* and *cyclo*-P$_5$ ligands, the possible structures of the dimeric ions **A** and **B** were proposed (Scheme 3).[13] The complexes **1a** and **1b** clearly provide the confirmation for the dimeric dianion **B** stabilized by two [(C$_5$Me$_4$R)$_2$Sm]$^+$ cations, which was recently experimentally confirmed by the reduction of [Cp*Fe(η^5-P$_5$)] with KH.[14] The reductive dimerization of [Cp*Fe(η^5-P$_5$)] is not fully unexpected because the reduction potential of samarocene[15] is sufficiently negative for [Cp*Fe(η^5-P$_5$)].



Scheme 3 The possible structures of the dimeric [Cp*$_2$Fe$_2$P$_{10}$]$^{2-}$ ion.

The solid state structures of **1a** and **1b** were established by single crystal X-ray diffraction (Fig. 1 and 2).‡ Compounds **1a** and **1b** crystallize in the triclinic space group $P\bar{1}$ and in the monoclinic space group $P2_1/c$, respectively. Both compounds have a non-crystallographic *C*2-axis through the newly formed P5–P6 bond. Each *cyclo*-P$_5$ unit has been reduced once to force one phosphorus atom to bend away from the iron center and changed confirmation from planar to open envelope shaped. The iron parts obey the 18 valent-electron rule. Besides coordination to the Cp* ligand, each iron atom binds in an η^4-fashion to the *cyclo*-P$_5$ unit. Formally, we consider the η^4-coordinated unit as a 6-electron donor ligand which can be considered as tetraphosphabutadiene dianion with two electrons to be delocalized around each of these units. The new P–P bonds with distances of P5–P6 2.2089(13) Å (**1a**) and 2.1998(14) Å (**1b**)

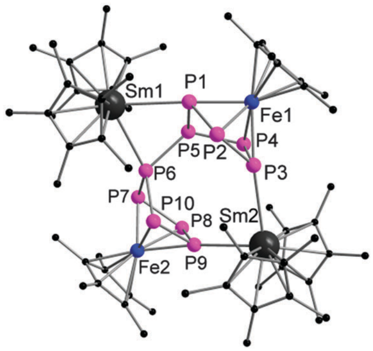


Fig. 1 Solid-state structure of **1a**, omitting hydrogen atoms.

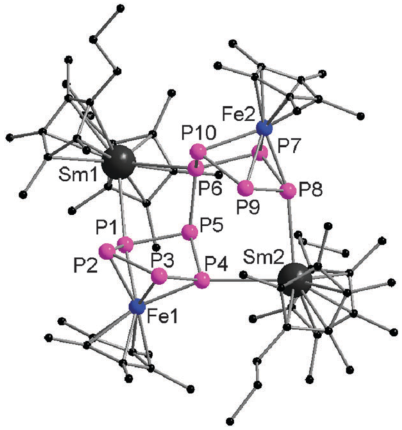
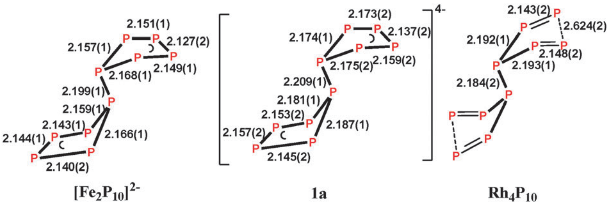


Fig. 2 Solid-state structure of **1b**, omitting hydrogen atoms.



Scheme 4 The P–P bond distance (Å) comparison of the P_{10} frameworks. (left: in $[K_2(dme)_3][(Cp^*Fe)_2(P_{10})]$[14]; center: in **1a** ($[(Cp^*Fe)_2P_{10}(SmCp^*{}_2)_2]$); right: in $[((1,3\text{-}t\text{Bu}_2C_5H_3)Rh)_4P_{10}]$[24]).

in agreement with a single bond are created between the two off-plane phosphorus atoms. The core polyphosphide unit is formally considered as a $P_{10}{}^{4-}$ anion. The electron rich polyphosphide anion could be crucial for the bond formation of hard rare earth metals and phosphorus atom. The P–P bond distances around *cyclo*-P_5 rings are in the range of 2.137(2) to 2.1866(14) Å in **1a** and from 2.1146(16) to 2.189(2) Å in **1b**. The Sm–P bond distances range from 2.9758(10) to 3.1096(11) Å in **1a** and from 2.9613(12) to 3.1031(11) Å in **1b**.

Two related but different coordinated P_{10} frameworks from $[(Cp''M)_4P_{10}]$ (M = Rh, Cp″ = 1,3-tBu$_2C_5H_3$; M = Co, Cp″ = 1,3-$(SiMe_3)_2C_5H_3$) obtained in the direct P_4 activation by $[Cp''M(CO)_2]$ were previously reported by Scherer and coworkers.[16] The P_{10} frameworks were described as neutral double open-edged P_{10} dihydrofulvalenes. The P–P bond distances in **1a**, $[K_2(dme)_3][(Cp^*Fe)_2(P_{10})]$[14] and $[((1,3\text{-}t\text{Bu}_2C_5H_3)Rh)_4P_{10}]$ are shown in Scheme 4. The P_{10} systems in **1a** and $[K_2(dme)_3][(Cp^*Fe)_2(P_{10})]$ are comparable. The Sm coordinated compounds show slightly longer P–P bonds than the potassium salt of the dianion. There are two major differences between **1a** and $[((1,3\text{-}t\text{Bu}_2C_5H_3)Rh)_4P_{10}]$: (i) acyclic P_5-subunits with two shorter terminal P–P bonds and open edges are observed in $[(Cp''M)_4P_{10}]$, whereas closed *cyclo*-P_5-subunits with one short P–P bond in each ring are seen in **1a** and **1b**. (ii) The P_{10}-system is neutral in $[(Cp''M)_4P_{10}]$, whereas it possesses four negative charges in **1a** and **1b**.

In summary, we successfully synthesized and characterized two new 3d/4f polyphosphide complexes from reductive dimerization of $[Cp^*Fe(\eta^5\text{-}P_5)]$ by samarocenes. They are the first examples of reductive coupling of polyphosphide complexes by divalent lanthanides. They are also the first P_{10} bridging 3d/4f metal complexes. The $[Cp^*{}_2Fe_2P_{10}]^{2-}$ core in the complexes provides the experimental evidence for the proposed structure of the reduced form of $[Cp^*Fe(\eta^5\text{-}P_5)]$. The P–P bond formation between two polyphosphide complexes inspires the formation of additional polyphosphide building blocks by means of divalent f-elements.

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T. Wagner and S. Schneider are acknowledged for designing the inside cover.

Notes and references

‡ Crystal data for **1a**: $C_{60}H_{90}Fe_2P_{10}Sm_2$, M = 1533.42, triclinic, a = 14.8642(5) Å, b = 15.0687(5) Å, c = 17.7081(6) Å, α = 68.847(3)°, β = 77.695(3)°, γ = 63.804(2)°, V = 3312.3(2) Å^3, T = 200(2) K, space group $P\bar{1}$(2), Z = 2, μ(MoKα) = 2.45 mm^{-1}, 24 193 reflections measured, 11 914 independent reflections (R_{int} = 0.035). The final R_1 values were 0.030 ($I > 2\sigma(I)$). The final w$R(F^2)$ values were 0.069 (all data). The goodness of fit on F^2 was 0.99. **1b**: $C_{68}H_{106}Fe_2P_{10}Sm_2$, M = 1645.63, monoclinic, a = 14.357 (3) Å, b = 28.550 (6) Å, c = 17.985 (4) Å, β = 95.08 (3)°, V = 7343 (3) Å^3, T = 200(2) K, space group $P2_1/c$, Z = 4, μ(MoKα) = 2.22 mm^{-1}, 53 244 reflections measured, 13 335 independent reflections (R_{int} = 0.039). The final R_1 values were 0.034 ($I > 2\sigma(I)$). The final w$R(F^2)$ values were 0.087 (all data). The goodness of fit on F^2 was 0.97. CCDC 914587 (**1a**) and 914588 (**1b**).

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