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Controlled introduction of functional groups at one P atom in [Cp*Fe(η^5-P_5)] and release of functionalised phosphines†

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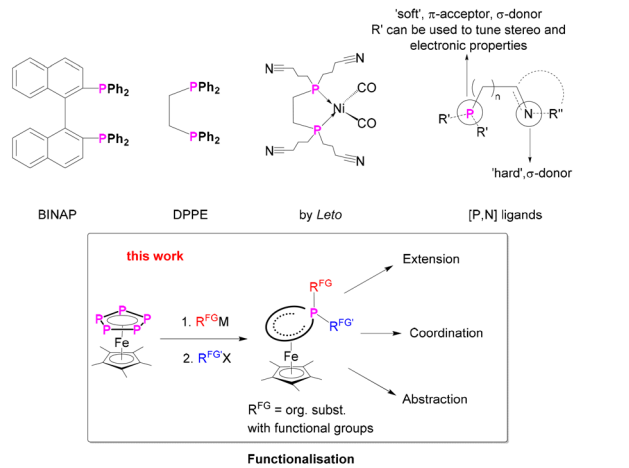
By salt metathesis reactions of the anionic complexes of the type [Cp*Fe(η^4-P_5R)]$^-$ (R = ^{t}Bu (**1a**), Me (**1b**), –C≡CPh (**1c**); Cp* = 1,2,3,4,5-pentamethylcyclopentadienyl) with organic electrophiles (XR^{FG}; X = halogen; R^{FG} = $(CH_2)_3Br$, $(CH_2)_4Br$, Me) a variety of organo-substituted polyphosphorus ligand complexes of the type [Cp*Fe(η^4-P_5RR^{FG})] (**2**) are obtained. Thereby, organic substituents with different functional groups (FG), such as halogens or nitriles, are introduced. In [Cp*Fe(η^4-P_5RR')] (**2a**: R = ^{t}Bu, R′ = $(CH_2)_3Br$), the bromine substituent can be easily substituted, leading to functionalized complexes [{Cp*Fe(η^4-P_5*t*Bu)}$(CH_2)_3${Cp*Fe(η^4-P_5Me)}] (**4**) and [Cp*Fe(η^4-P_5RR')] (**5**) (R = ^{t}Bu, R′ = $(CH_2)_3PPh_2$) or by abstraction of a phosphine to the asymmetric substituted phosphine *t*Bu(Bn)P$(CH_2)_3$Bn (**6**). The reaction of the dianionic species [K(dme)$_2$][Cp*Fe(η^4-P_5)] (**I′**) with bromo-nitriles leads to [Cp*Fe{η^4-$P_5((CH_2)_3CN)_2$}] (**7**), allowing the introduction of two functional groups attached to one phosphorus atom. **7** reacts with $ZnBr_2$ in a self-assembly reaction to form the supramolecular compound [Cp*Fe{η^4-$P_5((CH_2)_3CN)_2$}$ZnBr_2$]$_n$ (**8**).

Introduction

Chela originates from the ancient Greek language and means claw or pincer and is related to the word *chelos* – crab. Chelate ligands, similar to a crab's prey, surround the metal centre not with only one donor atom, but with two or more coordinating bonds separated from each other. The *chelate effect*[1] can be explained by using principles of thermodynamics and favours in general the chelated complex, featuring a two, tri or multidentate ligand. Chemists took advantage of this phenomenon and developed, synthesised and tuned a variety of different chelate or pincer ligands which are very important in coordination chemistry and catalysis.[2–8] Prominent classes are *e.g.* BINAP [2,2′-bis(diphenylphosphino)-1,1′-binaphthyl],[9] DPPE (1,2-bis(diphenylphosphino)-ethane),[10,11] DPPF (1,1′-bis(diphenylphosphino)ferrocene)[12] or [P,N][4,13] ligands (Scheme 1). These are used *e.g.* for asymmetric catalysis,[4,14] hydrogenation,[6,15,16] and coupling reactions.[17]

Although polydentate ligands are an important class of ligands for the stabilisation of metal complexes and catalysis, their synthesis is not trivial. Specifically, phosphorus-based ligands[9,18,19] are synthesised from PCl_3, obtained by chlorinating of white phosphorus. By doing this, in general, PCl_3 is converted to the corresponding phosphine by stepwise salt metathesis with a suitable lithium-organyl/Grignard-reagent. The downsides of this route are the poor selectivity and the difficulties in the separation of the reaction mixture. Furthermore, this route does not commonly tolerate functional groups in the "backbone", which, however, is crucial when it comes to adapting the desired ligand properties. In principle, multidentate ligands are synthesised according to electronic and steric requirements in the first place, then coordinated to



Scheme 1 (Top) Selected bidentate phosphine ligands,[9–11,25] (bottom) functionalisation of pentaphosphaferrocene: introduction of functional groups and subsequent chemical reactions.

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a transition metal and, later, tested for their use in subsequent reactions and catalysis.[20–22] Especially the synthesis of new and particularly unsymmetrically substituted organophosphorus compounds is a challenge.[15] There are only very few poly- or especially cyclic phosphines known that carry functional groups and allow coordination and subsequent reactions.[23–26] Therefore, the search for alternative synthetic routes is an active topic in chemistry.[27]

This prompted us to study whether it is possible to tune and functionalise a polyphosphorus ligand, already in the coordination-sphere of a transition metal, and then use it for subsequent reactions. *Inter alia* different coordination sites towards other Lewis-acidic metals, synthetic modification and finally the removal of the prebuilt ligand from the transition metal complex were targeted (Scheme 1).

Pentaphosphaferrocene [Cp*Fe(η^5-P_5)] (**I**) as a carrier of plenty of P atoms seemed to be an ideal candidate for such an investigation[28] as this compound is readily accessible in a wide variety of different Cp^R ligands[29] and capable of releasing functionalised phosphines by abstraction.[28a,b]

Herein we report the synthesis of a large variety of neutral diorganyl-substituted complexes of the type [Cp*Fe(η^4-P_5RR')] (**2a**: R = ^{t}Bu, R′ = $(CH_2)_3$Br; **2b**: R = Me, R′ = $(CH_2)_3$Br; **2c**: R = –C≡CPh, R′ = $(CH_2)_3$CN; **2d**: R = Me, R′ = $(CH_2)_3$CN; **2e**: R = Me, R′ = $(CH_2)_4$Br) featuring functional groups, with ethynyl, nitrile and/or bromine substituents. The obtained complexes readily react with nucleophiles as *e.g.* $KPPh_2$ or KBn (Bn = benzyl), resulting in the selective formation of complexes in which the Br substituent is replaced by a terminal PPh_2 or Bn unit, which was exemplified for **2a**. Furthermore, complex **7** ([Cp*Fe{η^4-P_5($(CH_2)_3$CN)$_2$}]), containing two nitrile units, proved to be a versatile ligand towards $ZnBr_2$ leading to the unprecedented coordination polymer **8** ([Cp*Fe{η^4-P_5($(CH_2)_3$CN)$_2$}$ZnBr_2$]$_n$) in the solid state.

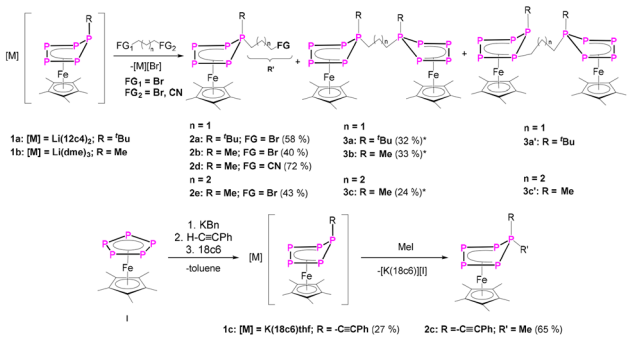
Results and discussion

In a first step, the scope of anionic starting materials [Cp*Fe(η^4-P_5R)]$^-$ (**1a**: R = ^{t}Bu; **1b**: R = Me) was extended by introducing an ethynyl group by synthesising the complex [K(18c6)(thf)$_2$][Cp*Fe(η^4-P_5-C≡CPh)] (**1c**) (Scheme 2). When ethynylbenzene is deprotonated with benzyl potassium and added to a solution of [Cp*Fe(η^5-P_5)] (**I**) in THF, a colour change from green to brown is observed. The $^{31}P\{^1H\}$ NMR spectrum of the reaction solution shows only one set of signals corresponding to an ABB′XX′ spin system of the anion of **1c** with resonances centred at 37.3, 27.9 and 58.4 ppm (Fig. 1 and S16†). Crystals of **1c** are obtained from a concentrated THF solution layered with *n*-hexane. Single crystal X-ray structure analysis revealed the molecular structure of the resulting product **1c** in the solid-state (Fig. 1 and S34†). The main structural feature of **1c** is an η^4-coordinated *cyclo*-P_5 ligand in an envelope conformation with a phenylethynyl substituent attached to the out-of-the-plane phosphorus atom. All P–P bonds are in the expected range and reveal double bond character with P–P bond lengths of 2.127(4)–2.187(3) Å,[30,31] whereas the newly formed P–C bond is with 1.782(7) Å in the range of a single bond.[30]

Similarly to **1c**, the anionic complexes [Cp*Fe(η^4-P_5R)]$^-$ (R = ^{t}Bu (**1a**) and R = Me (**1b**)) can be synthesised.[27] Due to the nucleophilic character of the out-of-plane phosphorus atom in these complexes, which possess a lone pair, **1a–c** were reacted with carbon-centred electrophiles, which, however, contain a functional group.

The reaction of **1a,b** with 1,3-dibromopropane results in the formation of a mixture of **2a,b** and **3a,b** (Scheme 2) which can be separated by column chromatography under an inert atmosphere. **2a,b** can be isolated as brown needles in moderate crystalline yields of 53% (**2a**) and 50% (**2b**), respectively, while **3a,b** afford yields of 32% (**3a**) and 33% (**3b**). Single crystal X-ray structure analyses show the expected structure of [Cp*Fe(η^4-P_5RR′)] (**2a**: R = ^{t}Bu, R′ = $(CH_2)_3$Br; **2b**: R = Me, R′ = $(CH_2)_3$Br) containing a 1-bromopropane substituent attached to the out-of-plane phosphorus atom (Scheme 2, Fig. 2). This simple method can be extended to introducing a nitrile group (**2d**) by using 4-bromobutyronitrile, or to increasing the alkyl chain length by using 1,4-dibromobutane (**2e**).

In all of these products **2a–e** (Fig. 2), the phosphorus-carbon distances are close to a single bond,[30] whereas the P–P bond lengths lie within the range of a single and double bond (Tables S20–29†).[30,31]



Scheme 2 Reaction of **1a,b** with 1,3-dibromopropane/1,4-dibromobutane/4-bromobutyronitrile (upper part) and **I** with 1. KBn, 2. ethynylbenzene and consecutive reaction with MeI (lower part), respectively. Yields are given in parentheses; *complexes **3** and **3′** co-crystallise, so the yields are summed up.

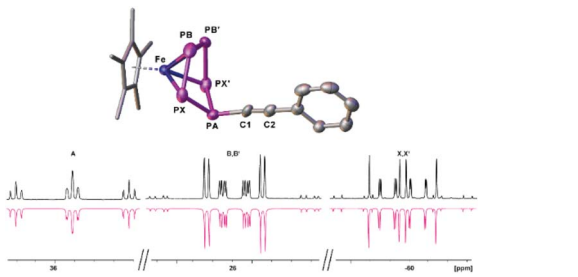


Fig. 1 (Top) Solid-state molecular structure of **1c** with thermal ellipsoids at 50% probability level. Cations and hydrogen atoms are omitted for clarity, the Cp* ligand is drawn in a wire frame model. (Bottom) Experimental (upwards) and simulated (downwards) $^{31}P\{^1H\}$ NMR (161.98 MHz, THF-d_8) spectrum of the anion of **1c**.

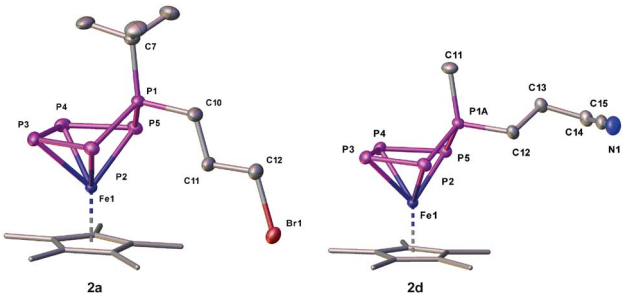


Fig. 2 Molecular structures of **2a** and **2d** with thermal ellipsoids at 50% probability level. Hydrogen atoms are omitted for clarity. The Cp* ligands are drawn in a wire frame model.

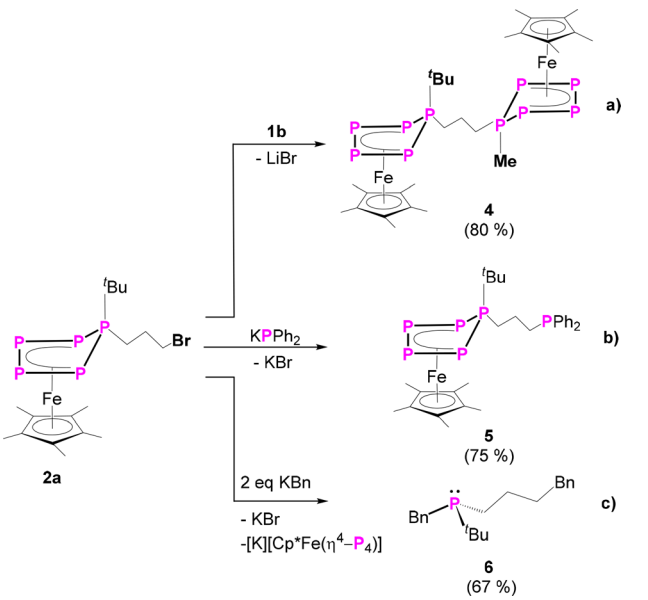
The second fraction of the chromatographic workup was identified as **3a** and **b**, revealing two [Cp*Fe(η^4-P_5)R] (**3a**: R = ^{t}Bu; **3b**: R = Me) moieties linked by a propane-1,3-diyl-group. In the major product **3a**, the *n*-propyl group is attached to the out-of-plane phosphorus atom P1 (Fig. S42†). In addition to **3a**, a minor product **3a'** co-crystallises in a ratio of 8 : 92. In **3a'**, the electrophile is attached to the P atom next to the out-of-plain P atom leading to a 1,2-substitution pattern, instead of the 1,1-substitution (for X-ray structure of **3a'** see Fig. S43†). However, the separation of **3a** and **3a'** *via* column chromatography or other methods failed. Therefore, it was investigated by ^{31}P NMR spectroscopy whether the reaction temperature, the order of addition of the starting materials or the chain length (1,4-dibromobutane instead of 1,3-dibromopropane) have an influence on the reaction progress. Unfortunately, it was not possible to completely hamper the formation of **3a'** as was possible for **3b**. But a minimum amount of **3a'** is formed when slowly adding 1,3-dibromopropane to a −80 °C pre-cooled solution of **1a** (Fig. S55†). Within the same reaction conditions, the amount of **2a** decreases significantly (Fig. S55†). DFT calculations (B3LYP/def2-TZVP level of theory) predict **3a** to be with 29 kJ mol^{-1} more stable than **3a'** (Table S46†). Since very little amount of **3a'** is formed when changing the starting material to [Li(dme)$_3$][Cp*Fe(η^4-P_5Me)] (**1b**) (Fig. S56†), the formation of **3a'** is probably also due to the steric bulk of the *tert*-butyl group in contrast to that of the significantly smaller methyl group in **3b**.

However, the formation of **2a/b** can be completely suppressed in favour of **3a/b** by using a ratio of 2 : 1 in the reaction between **1a/b** and 1,3-dibromopropane at −80 °C. Increasing the carbon chain length, *i.e.* by using 1,4-dibromobutane, does have a relevant influence on the ratio of the 1,1- and 1,2-substitution products, according to ^{31}P NMR spectroscopic investigations (Fig. S57†), and favours the 1,2-substituted product **3c'**, although **3c** remains the major isomer. The reaction of compound **1b** with 1,4-dibromobutane still leads to the formation of **2e** (Scheme 2) and, as described above, to the bridged compounds **3c/c'** (Fig. S58†). The 1,2-substitution product **3c'** is formed in minor amounts only, but a minor amount of **2e'** can be observed in the crystal structure of **2e** (ratio 5 : 95, Fig. S41†). When the reaction is conducted at room temperature, **2e** can be isolated as a spectroscopically pure compound (Fig. S6 and S21†). Note, also **2b'** was detected as the 1,2-substituted minor product in a ratio of **2b : 2b'** = 90 : 10 (*cf.* Fig. S37†).

In order to extend the scope of functional groups, we used 4-bromobutyronitrile to attach an extra terminal nitrile group (Scheme 2). ^{31}P NMR spectroscopic investigations of the reaction mixtures of **1a–c** with 4-bromobutyronitrile show selective conversions. However, single crystals of **2d** (Scheme 2) could only be obtained by using **1b**. Compound **2d** can be isolated as dark brown blocks in 72% yield. **2d** co-crystalises with traces of **I** (5%), which can be washed with hexane to yield the spectroscopically pure compound **2d** (Fig. 2). The rather easy introduction of a CN functional group is very remarkable and shows the high potential of the presented method of functionalisation.

To prove the accessibility of the bromine functionality in **2a** for consecutive reactions, complex **2a** was reacted with the nucleophile **1b**. Indeed, this reaction leads to the formation of the asymmetric organo-substituted polypnictogen ligand complex **4** as dark green blocks in 80% yield (Scheme 3). The solid-state molecular structure is depicted in Fig. 4 and exhibits two organo-substituted [Cp*Fe(η^4-P_5R)] (R = ^{t}Bu, Me) moieties which are linked *via* an *n*-propyl group. The formation of different isomers by migration of the organic groups was not observed.

The ^{31}P{^{1}H} NMR spectrum of **4** reveals two different AMM′XX′ spin systems, corresponding to the two inequivalent P_5 units (Fig. 3). Based on the presence of different types of P–H coupling in the ^{31}P NMR spectrum, an unambiguous assignment of the spin systems to the differently substituted P_5 units could be made (Fig. S25 and S26†). Both spin systems show multiplets centred at −120.3, 41.0 and 164.3 ppm as well as at −129.9, 29.8 and 128.9 ppm, respectively.



Scheme 3 Consecutive reactions of **2a**: (a) reaction with **1b** to form **4**; (b) functionalisation with $KPPh_2$ to form **5**; (c) first reaction with one equivalent of KBn, then abstraction of the functionalised phosphine **6** by a second equivalent of KBn. Yields are given in parentheses.

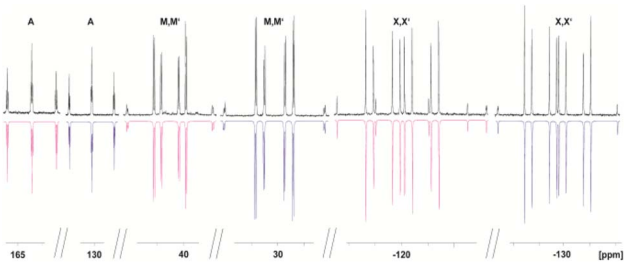


Fig. 3 Experimental (upwards) in CD_2Cl_2 at 293 K and simulated (downwards) $^{31}P\{^1H\}$ NMR spectrum of **4**.

Since compound **4** shows two different η^4-P_5RR' (R = Me, ^{t}Bu; R' = *n*-propyl) ligands, its cyclovoltammogram (CV) was measured to investigate the redox chemistry and check whether the two iron atoms are electrochemically inequivalent. Indeed, the CV (Fig. S63,† in *o*-DFB, referring to $[Cp_2Fe]/[Cp_2Fe]^+$) shows three oxidation processes, one of them reversible ($E_{rev} = -0.21$ V) and two irreversible ($E_{1irev} = 0.90$ V; $E_{2irev} = 1.01$ V), as well as two irreversible reductions ($E_{1irev} = -2.70$ V; $E_{2irev} = -2.57$ V), revealing the inequivalence of both Cp*Fe moieties.

Since the complexes **2** can be rationalised as formally being bromo-alkanes, their reactivity towards charged nucleophiles was investigated. Thus, compound **2a** was reacted with potassium diphenylphosphanide ($KPPh_2$) leading to the formation of complex **5** (Scheme 3, Fig. 4). The $^{31}P\{^1H\}$ NMR spectrum of the reaction solution shows an AMM'XX' spin system and an additional singlet located at $\delta = -17.9$ ppm, which evidences the formation of the desired product **5**, featuring a terminal phosphine unit. Crystallisation from *n*-pentane at r.t. under reduced pressure leads to pure **5** in 75% yield. The molecular structure proves the identity of **5** (Fig. 4). Note that the nature of the phosphanide can be varied. The use of $LiPCy_2$ (Cy = *cyclo*-hexyl) does also lead to the desired product, according to ^{31}P NMR spectroscopic (Fig. S59†) and mass spectrometric investigations.

Interestingly, the ^{31}P NMR spectrum of the reaction mixture does not show any signs of a phosphine abstraction or the formation of $[Cp^*Fe(\eta^4\text{-}P_4)]^-$ as reported for the reaction of $[Cp^*FeP_5R_2)]$ (R = Me, ^{t}Bu) with KBn.[27] Instead, $KPPh_2$ reacts selectively, under salt metathesis, with the bromine in **2a**. Formally, the functional group can be stated to act as a protecting group and to shield the P_5 ligand from a possible nucleophilic attack. Inspired by this observation and the reported phosphine abstraction,[27] compound **2a** was reacted with two equivalents (in portions) of benzyl potassium (KBn). According to $^{31}P\{^1H\}$ NMR spectroscopic investigations (Fig. S60†), the first equivalent of KBn reacts with **2a** *via* salt metathesis, *i.e.* the substitution of the bromine group, and the second equivalent leads to the elimination of the asymmetrically substituted phosphine ^{t}BuPBn($(CH_2)_3$Bn) **6** (Scheme 3 and Fig. S60†) and the formation of $[Cp^*Fe(\eta^4\text{-}P_4)]^-$. The identity of the phosphine **6** (Scheme 3) was proven by NMR spectroscopy ($\delta(^{31}P\{^1H\}) = 4.5$ ppm, which is in the typical range of phosphines)[32] and, after oxidation with sulphur to the corresponding phosphine sulphide **6'**, also by single-crystal X-ray diffraction analysis (Fig. 4). Note that **6** and **6'** are obtained as racemates.

This result shows that is not only possible to selectively functionalise one phosphorus atom in $[Cp^*Fe(\eta^4\text{-}P_5)]$ (**I**) but also to introduce different substituents containing functional groups, which can be further converted to other functionalities and finally cleave off the corresponding phosphine or bisphosphine. In principle, this route represents an easy and convenient way to synthesise any desired functionalised phosphine.

To increase the number of functional groups attached to the P_5-platform, namely such that do not tolerate strong nucleophiles, the dianionic species $[K(dme)_2]_2[Cp^*Fe(\eta^4\text{-}P_5)]$ (**I'**) was reacted with two equivalents of 4-bromobutyronitrile (Scheme 4). This reaction results quantitatively in the formation of the desired product $[Cp^*Fe\{\eta^4\text{-}P_5((CH_2)_3CN)_2\}]$ (**7**) in 67% isolated yield. The solid-state molecular structure reveals an η^4-P_5 moiety, bearing two *n*-propyl substituents with terminal nitrile groups (Fig. S51†).

The presence of the nitrile functionalities in **7** renders it a suitable starting material for the synthesis of coordination compounds containing polyphosphorus units, with potentially uncommon structures. Based on our expertise in the supramolecular chemistry of polypnictogen ligand complexes,[29] coordinating groups, such as nitriles, are feasible ligands in self-assembly reactions with transition metal halides.[29] Therefore, in a preliminary study, **7** was reacted with zinc(II)bromide in THF (Scheme 4). After three days, green/brownish plate-shaped crystals of **8** were obtained in 81% yield, exhibiting a linear 1D structure in the solid state (Fig. 5). Within the strain, monomers of $[Cp^*Fe\{\eta^4\text{-}P_5((CH_2)_3CN)_2\}]$ are connected by zinc(II)bromide. That way, the endo-(with respect to the envelope P_5 unit) nitrile group coordinates to the zinc atom ($d_{N\text{-}Zn} = 2.053(6)$ Å) (Fig. 5, Table S44†). The latter is coordinated in a tetrahedral coordination environment on the opposite side

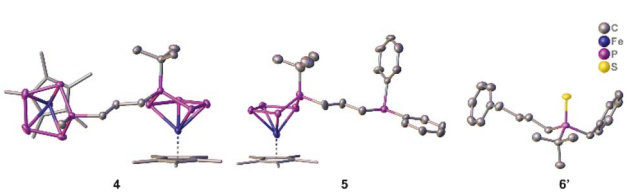
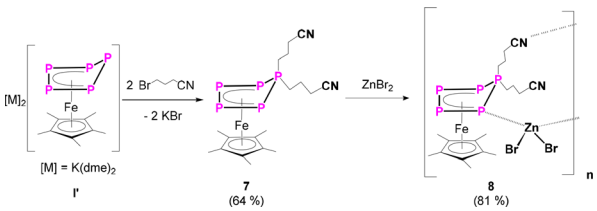


Fig. 4 Molecular structures of **4**, **5** and **6'** in the solid state with thermal ellipsoids at 50% probability level. Hydrogen atoms are omitted for clarity. The Cp* ligands are drawn in a wire frame model.



Scheme 4 Reaction of $[K(dme)_2]_2[Cp^*Fe(\eta^4\text{-}P_5)]$ (**I'**) with 4-bromobutyronitrile leading to complex **7** and consecutive reaction of **7** with zinc(II)bromide. Yields are given in parentheses.

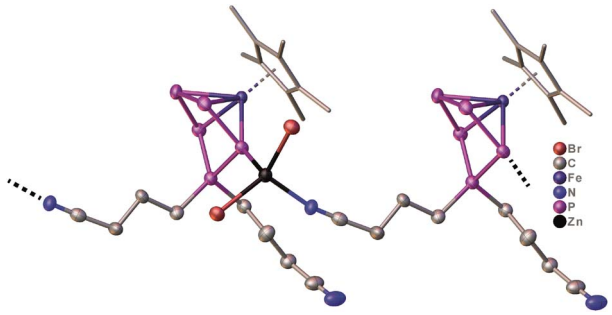


Fig. 5 Solid-State molecular structure of **8** with thermal ellipsoids at 50% probability level. Hydrogen atoms are omitted for clarity. The Cp* ligands are drawn in a wire frame model.

towards one phosphorus atom ($d_{P\text{-}Zn} = 2.430(2)$ Å) (Fig. 5, Table S44†) next to the P atom that is out of the plane which bears the nitrile linking unit. The zinc-phosphorus/nitrogen distances and angles are in line with similar complexes.[33,34] The sum of the covalent radii corresponds approximately to the bond distances in the solid state, indicating a bonding interaction between phosphorus-zinc and nitrogen-zinc, respectively.[33] To the best of our knowledge, compound **8** represents the first complex featuring a $ZnBr_2$ unit, which is coordinated by a phosphorus atom and a nitrile group. Surprisingly, the exo nitrile group does not coordinate (Fig. 5). This opens the way for further coordination reactions, by using *e.g.* a different stoichiometry or reactions with *e.g.* copper halides. As this would go beyond the scope of this report, it will be topic of future work. Nevertheless, the reaction of **7** with zinc(II)bromide shows the versatility of the system and the possibility for consecutive reactions in which other than [Cp*Fe(η^5-P_5)] (**I**) are used, which does not reveal any reactivity towards zinc(II)bromide.

The composition of **8** was also proven by elemental analysis and NMR spectroscopy, with the latter showing an AMM′XX′ spin system in THF-d_8 at room temperature (Fig. S31†). The ^{31}P and ^{1}H NMR spectra are similar to those of complex **7** but slightly shifted (Fig. S61 and S62†), indicating no phosphorus-zinc-interaction, but a nitrogen-zinc-coordination in solution which is in accordance with the HSAB principle.[35] Notably, after crystallisation, complex **8** is completely insoluble in non-coordinating solvents such as CH_2Cl_2, but highly soluble in coordinating ones as for instance THF and DME which indicates a partial depolymerization and a coordination of the solvent towards the zinc atom. This is in agreement with ESI-MS (in DME) which exclusively shows a molecular ion peak at m/z = 482.03, corresponding to complex **7**.

Conclusions

In summary, it was shown that pentaphosphaferrocene (**I**) represents a very versatile platform for the successful functionalisation of the *cyclo*-P_5 ligand. In alternating reactions with nucleophiles and electrophiles, a variety of functional groups can be easily introduced to one P atom at this polyphosphorus ligand complex, which had not been achieved before. Thus, a range of different compounds were obtained containing various functional groups (**2a–e**) including *e.g.* bromides and nitriles. This new modular system can even be further modified synthetically by using a Br-substituted derivative such as **2a** to introduce afterwards additional functional groups like phosphines and others (**4** and **5**) but remain coordinated in the coordination sphere of Cp*Fe. Moreover, in a consecutive nucleophilic attack, the functionalised phosphine can be finally abstracted from the Cp*Fe unit to give access to an unprecedented, functionalised phosphine (**6**) demonstrating the versatility of this method. In addition, it was possible to synthesise polyphosphorus ligand complexes that bear two functional groups at one P atom (**7**), which can be used for consecutive reactions in supramolecular chemistry as was exemplified in the yield of a first unique $ZnBr_2$ 1D-coordination polymer **8**. Current investigations focus on the introduction of different functional groups as well as their modifications and final release from the complex.

Data availability

All experimental procedures, spectroscopic data, information on the theoretical calculations and crystallographic data can be found in the ESI.†

Author contributions

The conceptualization (together with GB and MS), experimental work assisted by FR and MP and writing of the manuscript of this work were achieved by SR. M. Seidl accomplished the solution and refinement of X-ray structural data. MP and GB performed the DFT calculations. The entire work was supervised, guided, and revised by MS, who also acquired funding for the project. The final manuscript was reviewed and edited by SR, GB and MS.

Conflicts of interest

There are no conflicts to declare.

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