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Substituted aromatic pentaphosphole ligands – a journey across the p-block†

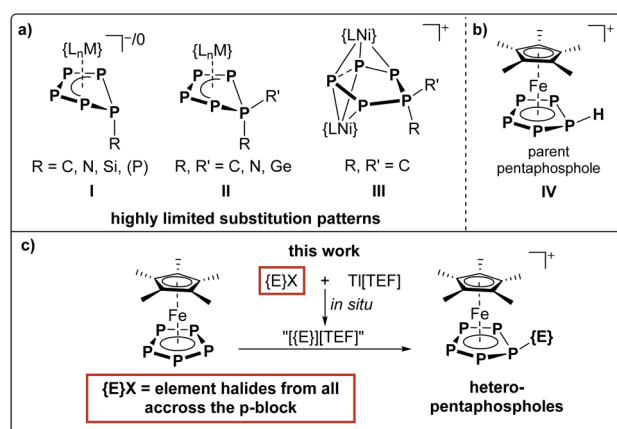
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The functionalization of pentaphosphaferrocene [$\text{Cp}^*\text{Fe}(\eta^5\text{-P}_5)$] (**1**) with cationic group 13–17 electrophiles is shown to be a general synthetic strategy towards P–E bond formation of unprecedented diversity. The products of these reactions are dinuclear [$\{\text{Cp}^*\text{Fe}\}_2\{\mu, \eta^{5.5}\text{-(P}_5)_2\text{EX}_2\}[\text{TEF}]$] ($\text{EX}_2 = \text{BBr}_2$ (**2**), GaI_2 (**3**), $[\text{TEF}]^- = [\text{Al}(\text{OC}(\text{CF}_3)_3)_4]^-$) or mononuclear [$\text{Cp}^*\text{Fe}(\eta^5\text{-P}_5\text{E})[\text{X}]$] ($\text{E} = \text{CH}_2\text{Ph}$ (**4**), CHPh_2 (**5**), SiHPh_2 (**6**), AsCy_2 (**7**), SePh (**9**), TeMes (**10**), Cl (**11**), Br (**12**), I (**13**)) complexes of hetero-bis-pentaphosphole ($(\text{cyclo-P}_5)_2\text{R}$) or hetero-pentaphosphole ligands ($\text{cyclo-P}_5\text{R}$), the aromatic all-phosphorus analogs of prototypical cyclopentadienes. Further, modifying the steric and electronic properties of the electrophile has a drastic impact on its reactivity and leads to the formation of [$\text{Cp}^*\text{Fe}(\mu, \eta^{5.2}\text{-P}_5)\text{Sb}(\text{Cp}^*)[\text{TEF}]$] (**8**) which possesses a triple-decker-like structure. X-ray crystallographic characterization reveals the slightly twisted conformation of the $\text{cyclo-P}_5\text{R}$ ligands in these compounds and multinuclear NMR spectroscopy confirms their integrity in solution. DFT calculations shed light on the bonding situation of these compounds and confirm the aromatic character of the pentaphosphole ligands on a journey across the p-block.

Introduction

Electrophilic aromatic substitution is one of the most basic and widely applied reactions for the functionalization of aromatic organic compounds. While Friedel–Crafts alkylation and acylation are in fact textbook examples for the reactivity of benzene derivatives,¹ they can also be applied to smaller ring systems.² In contrast, derivatives of the carbocyclic aromatic cyclopentadienide anion (Cp^- , C_5H_5^-) form non-aromatic cyclopentadiene derivatives (CpR , $\text{C}_5\text{H}_5\text{R}$) upon salt metathesis with element halogenides. Compared to their alkali metal salts, transition metal (TM) bound Cp^- ligands (e.g. in Cp_2Fe)³ exhibit a different reactivity towards electrophiles mimicking that of benzene derivatives (e.g. $(\text{C}_6\text{H}_6)\text{Cr}(\text{CO})_3$).⁴ The isolobal relationship between the CH fragment and the P atom⁵ and the diagonal relationship between carbon and phosphorus suggest a comparable reactivity for the pentaphospholide anion cyclo-P_5^- .⁶ However, investigations on the reactivity of the salts of cyclo-P_5^- towards alkylhalogenides showed further aggregation to polyphosphides,⁷ leaving the chemistry of pentaphospholes $\text{cyclo-P}_5\text{R}$ to theoretical studies for decades.⁸ Similar to Cp^- , cyclo-P_5^- can be stabilized within the coordination sphere of different TMs⁹ and is thus closely associated with the TM-mediated conversion of P_4 .¹⁰ One of the most prominent

examples of such complexes is pentaphosphaferrocene [$\text{Cp}^*\text{Fe}(\eta^5\text{-P}_5)$] (**1**).^{9a} While **1** readily reacts with various monovalent metal salts to form coordination compounds,¹¹ we could also demonstrate both its redox reactivity¹² and its behavior towards anionic¹³ and neutral nucleophiles.¹⁴ These reactions yielded complexes with bent $\text{cyclo-P}_5\text{R}$ ligands (**I**, Scheme 1),^{13,14} which are also accessible by the reaction of a niobium



Scheme 1 (a) Known substituted cyclo-P_5 ligand architectures I ($\{\text{L}_n\text{M}\} = \{(\text{Mes}^{\text{neo}}\text{PentN})_2\text{Nb}\}$ or $\{\text{Cp}^*\text{Fe}\}$), II ($\{\text{L}_n\text{M}\} = \{\text{Cp}^*\text{Fe}\}$, $\{\text{Cp}^{\text{PEt}}\text{Co}\}^+$, $\{(\text{BIAN})\text{Co}\}$), III ($\text{L} = \text{Cp}^{\text{PEt}}$); (b) the parent pentaphosphole complex IV; (c) targeted functionalization of an iron bound pentaphospholide ion with *in situ* generated cationic electrophiles from across the p-block to yield unprecedented coordinatively stabilized hetero-pentaphospholes.

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phosphorus triple bond complex with P_4 .¹⁵ Disubstituted *cyclo*- P_5R_2 moieties (**II** and **III**, Scheme 1) could be obtained *via* the coordination of the respective $[P_5R_2]^+$ cations¹⁶ to low-valent transition metal fragments.¹⁷ The formation of the structural motif **II** was also observed upon condensation of an anionic *cyclo*- P_4 complex with chlorophosphines.¹⁸ The introduction of germylene substituents has recently been achieved by the reaction of **1** with a digermylene.¹⁹ While their structural motifs are remarkable, the respective *cyclo*- P_5R_n ligands ($n = 1, 2$) within types **I–III** do not show any aromatic character, since they do not represent pentaphospholes (**IV**).⁸ Only recently, we succeeded in the synthesis of the first transition metal complexes $[Cp^*Fe(\eta^5-P_5R)][B(C_6F_5)_4]$ (**IV**, $R = H, Me, SiEt_3$) featuring such pentaphosphole ligands.²⁰ While our previous approach is well-suited to prepare the parent compound with a *cyclo*- P_5H ligand, it is limited to group 14 electrophiles (such as $CH_3/SiEt_3$) as introducible substituents.²¹

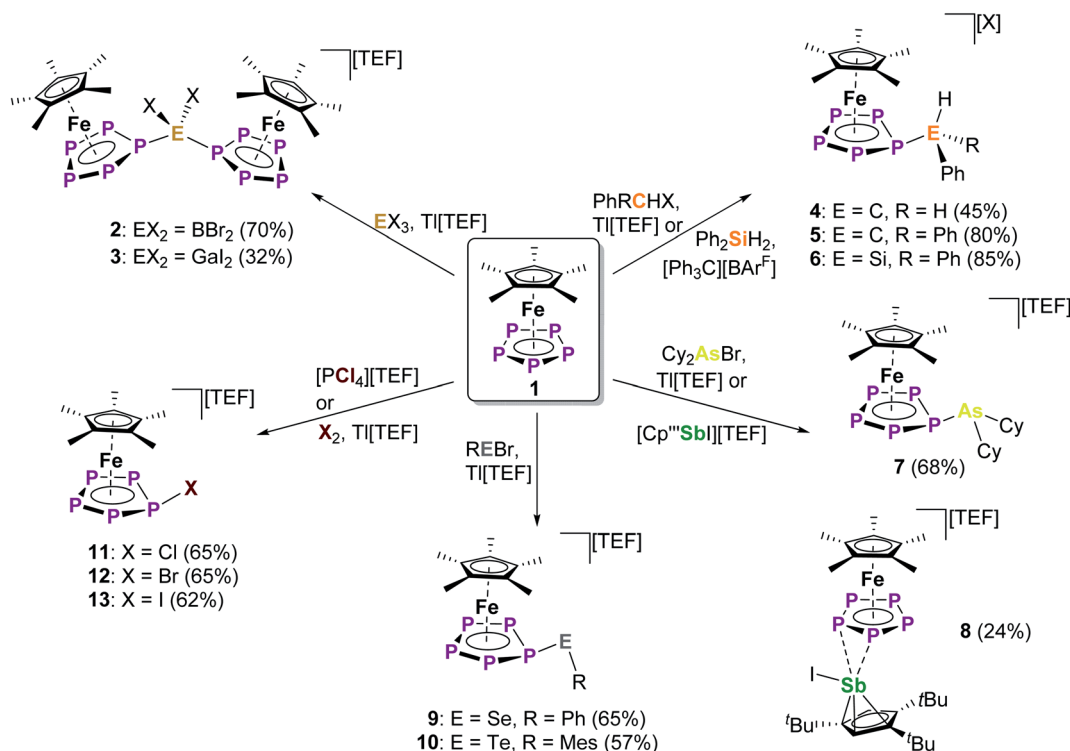
Thus, we sought a more general strategy to electrophilically functionalize **1** which may also be applicable beyond the synthesis of the targeted hetero-pentaphosphole complexes to other heteroaromatic ligands. Such a strategy would represent a valuable contribution to electrophilic substitution reactions in general. We hypothesized that the *in situ* generation of cationic electrophiles from p-block element halogenides and a suitable halide-abstracting reagent, as has for example been utilized for the functionalization of coordinated chlorophosphines,²² and subsequent reaction with **1** could provide this reactivity. Such an approach would allow P–E bond formation with a nearly unlimited choice of electrophiles and would thus overcome the limitations of known synthetic strategies towards the P–E bond formation in the vicinity of transition metals.^{14,15,23} Indeed, the major drawback of the so far used strategies is their immensely limited applicability to a very narrow range of electrophile/nucleophile combinations. This is usually reflected in the use of rather exotic low-valent main group species such as tetrylenes,^{14b,18} $\{Cp^*Al\}_4$,²⁴ or the utilization of highly reactive, *e.g.* anionic, polyphosphorus ligand complexes.^{23c,f} While our goal is the functionalization of **1** to obtain unprecedented hetero-pentaphosphole ligands, namely the aromatic all-P congeners of cyclopentadienes, we expect our approach to also be applicable to polyphosphorus ligand complexes of various sizes. Furthermore, this idea merges the functionalization of TM polyphosphorus complexes with the concept of electrophilic substitution,² a classic organic or organometallic (for *e.g.* Cp_2Fe (ref. 3) or $(C_6H_6)Cr(CO)_3$ (ref. 4)) reaction. Thus, it may be transferred back to these fields and allow the electrophilic functionalization of still challenging substrates such as multi-functionalized CpR derivatives.²⁵ To achieve the *in situ* generation of the desired electrophiles from the respective halogenides, $Tl[TEF]$ ($[TEF]^- = [Al\{OC(CF_3)_3\}_4]^-$)²⁶ was chosen to facilitate efficient halide abstraction and simultaneously introduce the weakly coordinating $[TEF]^-$ anion. However, for some cases, we also provide an easily accessible alternative avoiding Tl^+ salts by the reaction of simple element hydrides with $[Ph_3C][B(C_6F_5)_4]$ for *in situ* electrophile generation. This method has been employed *e.g.* for the generation of the highly reactive silylium ion precursor $[(Et_3Si)_2(\mu-H)][B(C_6F_5)_4]$.²¹

However, the question arises as to how broad, if successful, the applicability of this approach would actually be, and which electrophiles could be introduced by employing it. We herein report on a synthetic strategy allowing the functionalization and P–E bond formation of **1** with twelve distinct cationic electrophiles all across the p-block elements and compare their structural and electronic properties.

Results and discussion

Starting with group 13 electrophiles, we investigated the reactivity of **1** towards BBr_3 in the presence of $Tl[TEF]$. However, performing the reaction in a 1 : 1 : 1 stoichiometry leads to a reaction of the *in situ* prepared borinium cation $[BBr_2]^+$ with the solvent, resulting in a mixture of products (see ESI†). Repeating the reaction in the presence of a second equivalent of **1** afforded the bimetallic compound $\{[Cp^*Fe]_2\{\mu, \eta^{5:5}-(P_5)_2BBr_2\}\}[TEF]$ (**2**), featuring an unprecedented $\{(cyclo-P_5)_2BBr_2\}$ ligand (Scheme 2). After workup, **2** could be isolated in 70% yield. To our pleasure, exchanging BBr_3 for the heavier analog GaI_3 affords the isostructural compound $\{[Cp^*Fe]_2\{\mu, \eta^{5:5}-(P_5)_2GaI_2\}\}[TEF]$ (**3**) in 32% yield. While we had already been able to demonstrate the silylation and methylation of **1**,²⁰ we now wanted to broaden the scope of group 14 functionalized pentaphosphole derivatives, by using better accessible and easier-to-handle electrophile precursors. In both cases, the reaction of **1** with $PhCH_2Br$ and Ph_2CHCl in the presence of $Tl[TEF]$ affords the pentaphosphole complexes $[Cp^*Fe(\eta^5-P_5CH_2Ph)][TEF]$ (**4**) and $[Cp^*Fe(\eta^5-P_5CHPh_2)][TEF]$ (**5**) in a yield of 45% and 80%, respectively. To demonstrate an easily accessible alternative pathway towards the electrophile generation avoiding the use of Tl^+ salts, we chose to react **1** with Ph_2SiH_2 in the presence of one equivalent of $[Ph_3C][B(C_6F_5)_4]$. A rapid reaction is indicated by the color change of the solution from green to greenish red and, after simple workup, the product $[Cp^*Fe(\eta^5-P_5SiHPh_2)][B(C_6F_5)_4]$ (**6**) could be isolated in an astonishing 85% yield. In principle, it should be possible to prepare phosphino-pentaphosphole complexes similarly well as they benefit from the additional stabilization caused by P–P bond formation. However, attempts to prepare such phosphino-functionalized species are seriously affected by the inherently high tendency of halogenophosphines to form phosphinophosphonium ions under Lewis acidic conditions.²⁷ We were able to observe the desired cation $[Cp^*Fe(\eta^5-P_5PBr_2)]^+$ spectroscopically only after reacting **1** with PBr_3 and $Tl[TEF]$ at $-80^\circ C$ (see ESI†). This cation, however, undergoes rapid fragmentation and rearrangement processes above $-60^\circ C$, affording a complex mixture of several polyphosphorus compounds and thus prohibiting its isolation even at low temperatures. In contrast, the reaction of **1**, Cy_2AsBr and $Tl[TEF]$ proceeds smoothly, and from the filtered solution, the arsino-pentaphosphole complex $[Cp^*Fe(\eta^5-P_5AsCy_2)][TEF]$ (**7**) could be isolated in 68% yield. When both the electronic and steric properties of the pnictogenium cation were changed and **1** was reacted with $Cp'''SbI_2$ ($Cp''' = 1,2,4\text{-}t\text{-}Bu_3C_5H_2$) and $Tl[TEF]$, the unique triple-decker-like complex $[Cp^*Fe(\mu, \eta^{5:2}-P_5)SbICp'''] [TEF]$ (**8**) with a P_5 middle deck could be obtained in 24% yield. The molecular





Scheme 2 Reactivity of pentaphosphaferrocene **1** with different cationic p-block electrophiles; reactions were carried out in *o*-DFB and stirred at room temperature for several hours (for details see ESI[†]); while all other compounds are obtained as their [TEF][−] salt, **6** has a [B(C₆F₅)₄][−] counterion; [TEF][−] = [Al(OC(CF₃)₃)₄][−]; while all displayed reactions are quantitative (by NMR), the yields provided are those for the crystalline compounds.

structure of **8** may provide insight into the mechanism of the electrophilic functionalization of **1** which initially seems to occur through the π -system and not by the lone pairs of one of the P atoms of the *cyclo*-P₅ ligand. Functionalization of **1** with group 16 electrophiles could be achieved by the reaction with Tl[TEF] and PhSeBr or MesTeBr, respectively. The products [Cp*Fe(η^5 -P₅ER)] [TEF] (**9**: E = Se, R = Ph; **10**: E = Te, R = Mes) could be isolated in 65% and 57% yield, respectively, and reveal novel seleno- or telluro-pentaphosphole ligands. To date, there is no synthetic pathway for a rational and selective monohalogenation of unsubstituted polyphosphorus frameworks, although the products would provide both insight into the mechanism of P_n halogenation reactions²⁸ and a high potential for further functionalization. After recently investigating the complex iodination chemistry of **1** (ref. 29) and of the diphosphorus complex [{CpMo(CO)₂]₂(μ , $\eta^{2:2}$ -P₂)],³⁰ we were wondering if electrophilic halogen transfer could lead to the desired reactivity. Indeed, when a solution of [PCl₄][TEF] is added to **1** in *o*-DFB, the NMR spectra of the crude solution indicate the clean conversion to [Cp*Fe(η^5 -P₅Cl)] [TEF] (**11**) and PCl₃. After workup, **11** can be isolated in 65% yield. Similarly, the addition of X₂ to mixtures of **1** and Tl[TEF] leads to the formation of [Cp*Fe(η^5 -P₅X)] [TEF] (**12**: X = Br; **13**: X = I), which could be isolated in 65% and 62% yield, respectively. Notably, these halogenation reactions can be scaled up to at least 2 mmol, allowing the gram scale preparation of **11**–**13**, which opens broad perspectives for their further functionalization. While the

starting material **1** is comparably robust, the pentaphosphole complexes **2**–**13** are highly sensitive towards both moisture and air, while retaining decent thermal stability. All compounds **2**–**13** can be crystallized from mixtures of *o*-DFB or CH₂Cl₂ and *n*-hexane either at room temperature or at −30 °C. However, incommensurate modulation (**11**) or extreme disorder of anion and cation (**12**) within **11** and **12** prohibit a satisfactory refinement of their crystal structure. Compound **8** reveals a triple-decker-like arrangement (Fig. 1) of the cation [Cp*Fe(μ , $\eta^{5:2}$ -P₅)SbICp'']⁺ with elongated P–Sb interactions (3.236(2)/3.400(2) Å) and a planar P₅ ligand. The cations in **4**–**7** and **9**–**13** show the anticipated pentaphosphole complex structure with a slightly bent *cyclo*-P₅R ligand (Fig. 1). In contrast, the cations in **2** and **3** are dinuclear complexes in which two {Cp*Fe} units are bridged by the respective {(*cyclo*-P₅)₂EX₂} (**2**: E = B, X = Br, **3**: E = Ga, X = I) ligand. The P–P bond lengths within **2**–**13** are similar and in between the sum of the covalent radii of P–P single and double bonds.³¹ As observed for the parent compound [Cp*Fe(η^5 -P₅H)]⁺,²⁰ the substituents in the hetero-pentaphosphole complexes **2**–**7** and **9**–**13** are oriented in exo-fashion regarding the envelope of the P₅ ring (Fig. 1). The respective P–E bond lengths (**2**: 1.985(7) Å, **4**: 1.853(4) Å, **5**: 1.866(4) Å, **7**: 2.348(1) Å, **9**: 2.2234(7) Å, **10**: 2.438(2) Å, **13**: 2.385(1) Å) are in the range of single bonds, whereas those in **3** (2.410(1)/2.387(1) Å) and **6** (2.3053(8) Å) are elongated compared to the sum of the respective covalent radii (P–Ga: 2.35 Å, P–Si: 2.27 Å).³¹ The slight folding of the P₅ ring in these pentaphosphole complexes is far



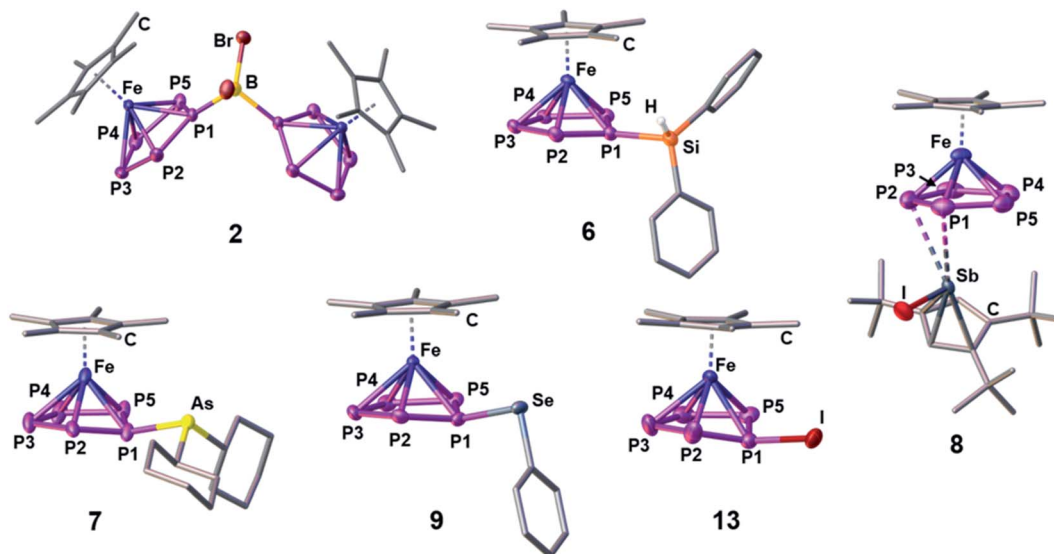


Fig. 1 Molecular structures of the cations in 2, 6, 7, 8, 9 and 13 in the solid state; Structural models for the cations in 3, 4, 5, 10 and 12 as well as a list of selected structural parameters (bond lengths and angles) for all compounds can be found in the ESI.†

less pronounced than in anionic or neutral substituted *cyclo*-P₅R ligands possessing an envelope structure (type I, Scheme 1).^{13,14} Interestingly, this slight folding, represented by the pyramidalization at the P₁ atom (359.94°(2) – 350.41°(13)), gradually increases when going from group 13 to group 17 substituents at the pentaphosphole ligand. To elaborate the molecular structure of the obtained pentaphosphole complexes 2–13 in CD₂Cl₂ solution, they were investigated by multinuclear NMR spectroscopy. In general, all of them reveal the expected signals for the Cp* ligand and the respective substituents in the ¹H NMR spectra. Furthermore, the signals for the benzylic hydrogen atoms in 4 (δ = 4.42 ppm) and 5 (δ = 5.93 ppm) show a coupling to the P₅ moiety (4: ²J_{H-P} = 11.2 Hz, ³J_{H-P} = 3.2 Hz, 5: ²J_{H-P} = 17.3 Hz). Interestingly, the isostructural 6 does not show a similar coupling for the hydrogen atom bound to silicon, which we attribute to the dynamic behavior of this compound in solution. Accordingly, the ¹³C{¹H} NMR spectra of 4 and 5 both reveal signals for the benzylic carbon atoms, which show ¹J_{C-P} coupling of 23 Hz for both compounds. The ³¹P{¹H} NMR spectra of most of the obtained products reveal complex AMM'XX' (4, 5), AA'BB'X (7), AA'MXX' (11), AA'MM'X (6, 9, 12) or even AA'M₂M'₂X₂X'₂ (2) spin systems (see ESI†). However, 3, 8, 10 and 13 show a highly dynamic behavior in CD₂Cl₂ solution which cannot be resolved, not even at –80 °C. Similar dynamic broadening of signals has been observed for the parent compound²⁰ and might be caused by a tumbling process of the respective substituent around the P₅ ring. When comparing the ³¹P{¹H} NMR spectra (Fig. 2), the signal assigned to P₁ (according to Fig. 1) gradually shifts to higher fields going from group 13 to group 17 substituents at the pentaphosphole moiety. Similarly, the signal assigned to P_{2/5} is downfield shifted following the same order, whereas the effect on the P_{3/4} signal is rather small (for assignment see Fig. 1). While this trend should depend on various electronic and steric factors, it correlates well

with the folding of the P₅ moiety (*vide supra*). The ⁿJ_{P-P} (n = 1–2) coupling constants for all compounds are within the expected range (see ESI†). Additional ¹J_{P-B} coupling of 64 Hz is clearly visible in the ³¹P NMR spectrum of 2 and is confirmed in its ¹¹B {¹H} NMR spectrum. While the dynamic behavior of the Si-substituted compound 6 in CD₂Cl₂ solution, even at –80 °C, does not allow for determination of P–P coupling constants, its ²⁹Si(DEPT 135) NMR spectrum shows a clear doublet of

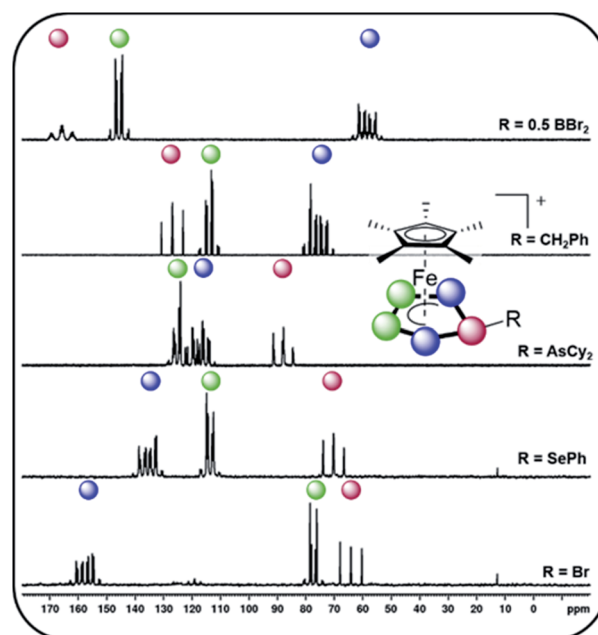


Fig. 2 ³¹P{¹H} NMR spectra of 2, 4, 7, 9 and 12 (from top to bottom, representing substitution with electrophiles from each group within the p-block) recorded in CD₂Cl₂ at room temperature and signal assignment according to the color code; respective NMR spectra of all other compounds are given in the ESI.†



multiplets at $\delta = -20$ ppm with a $^1J_{\text{Si-P}} = 239$ Hz coupling constant. Compared to the SiEt_3 -substituted derivative ($^1J_{\text{P-Si}} = 61$ Hz), this rather large $^1J_{\text{P-Si}}$ coupling constant may be the result of the difference in the substitution at Si and the resulting change in the orbital contribution to the P-Si bonding interaction. Furthermore, the ^{31}P NMR spectrum of **9** reveals ^{77}Se satellites for the P_X signal and a clear doublet ($^1J_{\text{P-Se}} = 418$ Hz) at $\delta = 287.3$ ppm in the $^{77}\text{Se}\{^1\text{H}\}$ NMR spectrum.

Computational studies

To attain a better understanding of the electronic structure of the obtained complexes **2–13**, computational analyses at the B3LYP³²/def2-TZVP³³ level of theory were performed.

Employing solvent correction,³⁴ the molecular structures, determined in the solid state, are well reproduced by these computations. NBO analysis³⁵ indicates the interaction between the $[\text{Cp}^m\text{SbI}]^+$ fragment and **1** in **8** to be of a mostly electrostatic and dispersive nature as shown by the absence of bonding MOs and the low charge transfer from the electrophile (see ESI[†]). Furthermore, the Wiberg Bond Indices (WBIs) for the P₁-E bonds in **3** (E = Ga, WBI = 0.58/0.57) and **6** (E = Si, WBI = 0.72) suggest these bonds to be of polar single bond character. This is substantiated by the respective orbital contributions to the P₁-E bonding (**3**: 79% P/21% Ga, **6**: 72% P/28% Si) and unoccupied antibonding (**3**: 21% P/79% Ga, **6**: 28% P/72% Si) molecular orbitals and agrees with the respective bond lengths determined for **3** (2.410(1)/2.387(1) Å) and **6** (2.3053(8) Å). In contrast, the WBIs of all other pentaphosphole complexes corroborate the P₁-E single bonds (WBI = 0.82–0.99) determined from their respective solid-state structures (Table 1, column 3). Accordingly, the orbital contributions to the respective P₁-E bonding and antibonding molecular orbitals (Fig. 3, left) are more balanced (Table 1, column 2), suggesting more covalent bonding in these cases. Analyzing the summed up natural charges for the fragments $\{\text{Cp}^*\text{Fe}(\eta^5\text{-P}_5)\}$ (**1**) and $\{\text{R}_n\text{E}\}$ (**E**, $n = 1-3$) (see ESI[†]) of **2–13** reveals correlation between the positive

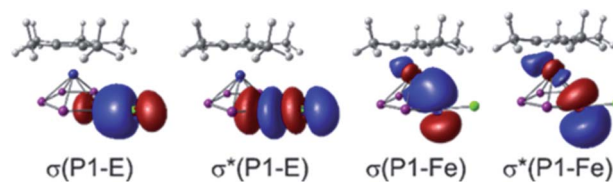


Fig. 3 Selected representative NBOs for the bonding and antibonding molecular orbitals for the P₁-E and P₁-Fe interactions found in the pentaphosphole complexes **2–7** and **9–13** exemplified at **11**; the σ^* orbitals are unoccupied.

charge accumulation at **1** and the electronegativity of the central atom of the electrophiles. As **3** and **6** incorporate the least electronegative central atoms in the respective electrophile, they show the lowest charge accumulation at **1** in the series of the herein reported pentaphosphole complexes (see Table S13[†]). The charge transfer from **1** to **E** (Table 1, column 5) obtained by an extended charge decomposition analysis (ECDA)³⁶ on the optimized structures of **2–13** shows a similar trend but hints towards other factors to be of relevance as well. Thus, effective charge transfer seems to be at least one of the governing factors for the formation of covalent P₁-E bonds and consequently less labile pentaphosphole ligands, which is in line with the highly dynamic behavior of **3** and **6** in CD_2Cl_2 solution (*vide supra*). Similar to the parent compound $[\text{Cp}^*\text{Fe}(\eta^5\text{-P}_5\text{H})]^+$,²⁰ the pentaphosphole complexes **2–7** and **9–13** exhibit a pronounced P₁-Fe bonding interaction (Fig. 3, right), which is represented by WBIs of 0.34–0.36. This interaction manifests their η^5 -binding mode and hints towards the aromatic character of the pentaphosphole ligands. To clarify the latter point, we computed the NICS(0/1/-1)_{zz}³⁷ values for the ligand geometries from the optimized structures of the cations **2–7** and **9–13** on the PBE0 (ref. 38)/aug-pcSseg-1 (ref. 39)/def2-TZVPPD^{33,40} level of theory. Consequently, these NICS(± 1)_{zz} values (Table 1) corroborate the aromaticity of the *cyclo*-P₅R ligands but are smaller than the ones for the *cyclo*-P₅⁻ ligand in

Table 1 Selected computational and experimental parameters for the pentaphosphole complexes **2–7** and **9–13**

Compound	WBI (P ₁ -E)	Orbital contribution P ₁ -E	$d(\text{P}_1\text{-E})/\text{\AA}$		Charge transfer 1 → E ^b	NICS(± 1) _{zz} ^c
			Exp.	Theo.		
2 ^a	0.89	57/43	1.985(7)	2.01	0.57 ^d	-31.2/-30.5
3 ^a	0.58	79/21	2.399(1)	2.46	0.56 ^d	-34.7/-34.3
4	0.92	45/55	1.853(4)	1.86	0.85	-33.7/-32.8
5	0.88	45/55	1.866(4)	1.89	0.84	-31.2/-32.1
6	0.72	72/28	2.3053(8)	2.35	0.68	-34.3/-34.7
7	0.82	67/33	2.348(1)	2.38	0.63	-34.0/-33.4
9	0.98	53/47	2.2234(7)	2.25	0.83	-33.5/-32.6
10	0.92	62/38	2.438(2)	2.48	0.74	-34.9/-34.0
11	0.96	36/64	—	2.03	1.09	-31.0/-30.9
12	0.98	41/59	—	2.21	1.05	-31.8/-31.7
13	0.99	51/49	2.385(1)	2.42	0.94	-34.3/-34.2

^a As **2** and **3** are dinuclear complexes the average of the actual values is provided for clarity, NICS values have only been obtained on one the P₅ rings.

^b The charge transfer from fragment **1** to the respective fragments **E** is obtained by ECDA. ^c NICS(± 1)_{zz} values are computed on the ligand geometries from the optimized structures of the complexes **2–7** and **9–13** after removal of the $\{\text{Cp}^*\text{Fe}\}^+$ fragments. ^d The charge transfer is given per fragment **1**.



1 ($\text{NICS}(\pm 1)_{zz} = -40.5$). However, they compare well with that determined for the parent pentaphosphole complex $[\text{Cp}^*\text{Fe}(\eta^5\text{-P}_5\text{H})]^+$ ($\text{NICS}(\pm 1)_{zz} = -32.1/-31.2$).²⁰ A rough correlation between the pyramidalization at P_1 and the computed NICS values is observed, although this effect is not much accentuated and has minor exceptions (see ESI†).

Thus, we demonstrated the *in situ* electrophilic functionalization of **1** to be a highly versatile approach towards a variety of unprecedented hetero-pentaphosphole complexes. Moreover, to provide a first insight into the generality of this synthetic strategy, we extended our investigations to the electrophilic functionalization of $[\text{Cp}^*\text{Ta}(\text{CO})_2(\eta^4\text{-P}_4)]$ (**14**)⁴¹ bearing an aromatic tetra-phospha-*cyclo*-butadiendiide (*cyclo*- P_4^{2-}) ligand. First reactivity studies reveal that two equivalents of **14** react with BBr_3 in the presence of $\text{Ti}[\text{TEF}]$ to afford $[\{\text{Cp}^*\text{Ta}(\text{CO})_2\}_2\{\mu, \eta^{4:4}\text{-}(\text{P}_4)_2\text{BBr}_2\}][\text{TEF}]$ (**15**) in 74% yield (Fig. 4). Compound **15** crystallizes as orange blocks and shows a similar dinuclear structure as found in **2**, which was confirmed by X-ray structural analysis (Fig. 4). Interestingly, the metal fragments in **15** are rotated by nearly 180° compared to those in **2** and the P_1/P_5 atoms are bent out of the former P_4 plane by only $1.2(2)/0.7(2)^\circ$, respectively. The P–P bond lengths (2.124(4) – 2.171(4) Å) in the $\{\text{cyclo-P}_4\}_2\text{BBr}_2$ ligand are slightly shortened compared to the starting material **14** (2.1555(15) – 2.1800(15) Å),⁴¹ but still in-between covalent P–P single (2.22 Å) and double bonds (2.04 Å).³¹ The P_1/P_5 –B bond lengths (1.997(10)/1.996(9) Å) are within the expected range for P–B single bonds (1.96 Å) and the P_1 –B– P_5 angle of $112.3(5)^\circ$ leads to a slightly distorted tetrahedral geometry around the B atom. The ^{31}P NMR spectrum of **15** in CD_2Cl_2 reveals a complicated $\text{A}_2\text{A}'_2\text{MM}'\text{XX}'\text{Z}$ ($\text{Z} = \text{B}$) spin system with resonances located at -15.4 , -37.1 and -80.8 ppm, agreeing with its structure being retained in solution. $^1J_{\text{P-B}}$ coupling is clearly visible for the $\text{P}_{\text{M}}/\text{M}'$ resonance and consequently the respective $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum shows a triplet at -10.2 ppm with a $^1J_{\text{P-B}}$ coupling constant of 60 Hz.

The solid-state structure of **15** is well reproduced by DFT calculations (B3LYP³²/def2-TZVP,³³ PCM solvent correction for CH_2Cl_2) which give further insight into its electronic structure. The WBIs for the P_1/P_5 –B bonds (0.88/0.86) in **15** are in agreement with covalent P–B single bonds. Furthermore, the orbital

contributions to these P–B bonds (58% P/42% B%) are in line with this formulation. While the positive charge within **15** is distributed across both $\{\mathbf{14}\}$ fragments, the B atom shows negative charge accumulation (natural charge of -0.44), labelling the $\{\text{cyclo-P}_4\}_2\text{BBr}_2$ ligand in **15** a borate-bridged bis-tetra-phospha-butadiendiide. At last, the respective $\text{NICS}(\pm 1)_{zz}$ values indicate the aromaticity of the *cyclo*- P_4 ligand of **14** ($-3.3/-3.5$) to be preserved within the ligand geometry in **15** ($-9.5/-9.7$, $-10.8/-9.6$), although it is less pronounced than in the pentaphosphole complexes **2–7** and **9–13**.

Conclusions

In conclusion, we demonstrated a general synthetic strategy to obtain a broad range of hetero-pentaphosphole coordination complexes bearing substituents from across the whole p-block of the periodic table. While the group **14–17** substituted species $[\text{Cp}^*\text{Fe}(\eta^5\text{-P}_5\text{E})]^+$ ($\text{E} = \text{CH}_2\text{Ph}$ (**4**), CHPh_2 (**5**), SiHPh_2 (**6**), AsCy_2 (**7**), SePh (**9**), TeMes (**10**), Cl (**11**), Br (**12**), I (**13**)) reveal the desired mononuclear aromatic pentaphosphole complexes, the group **13** functionalized species result in unexpected dinuclear complexes $[\{\text{Cp}^*\text{Fe}\}_2\{\mu, \eta^{5:5}\text{-}(\text{P}_5)_2\text{EX}_2\}][\text{TEF}]$ ($\text{EX}_2 = \text{BBr}_2$ (**2**), GaI_2 (**3**)) with bridging bis-pentaphosphole $\{\text{cyclo-P}_5\}_2\text{EX}_2$ ligands. In contrast, the alternation of the electronic and steric properties of the employed electrophile, as in $[\text{Cp}^*\text{SbI}]^+$, leads to the formation of the triple-decker-like arrangement observed in $[\text{Cp}^*\text{Fe}(\mu, \eta^{5:2}\text{-P}_5)\text{SbICp}^*][\text{TEF}]$ (**8**). This paves the way towards the investigation of the chemical, physical and electronic properties of these all-P congeners of prototypical cyclopentadienes, which have raised considerable theoretical interest over the past decades.⁸ Furthermore, this report highlights the versatility of the electrophilic functionalization of transition metal-stabilized polyphosphorus frameworks. While some P–E bond formation processes at such compounds have been observed, these are highly specific towards certain electrophile/nucleophile combinations (*vide supra*). In contrast, our approach shows an unprecedented diversity and thus allows P–E bond formation for elements all across the p-block. The generality of this approach is proven by the additional electrophilic aromatic functionalization of the aromatic *cyclo*- P_4 ligand of **14**, which furnishes $[\{\text{Cp}^*\text{Ta}(\text{CO})_2\}_2(\mu, \eta^{4:4}\text{-}(\text{P}_4)_2\text{BBr}_2)][\text{TEF}]$ (**15**), bearing a unique borate-bridged bis-tetra-phospha-butadiendiide ligand. Finally, the obtained cationic pentaphosphole complexes **2–13** represent highly interesting starting materials (*e.g.* the halogen derivatives **11–13**) towards even further functionalized polyphosphorus frameworks, which is underlined by the gram scale synthesis of selected representatives (**5**, **11–13**).

Data availability

Crystallographic data for **2–10**, **13** and **15** has been deposited at the CCDC/ICSD under 2083554 (**2**), 2083555 (**3**), 2083556 (**4**), 2083557 (**5**), 2083558 (**6**), 2083559 (**7**), 2083560 (**8**), 2083561 (**9**), 2083562 (**10**), 2083563 (**13**) and 2101248 (**15**). All other data are provided in this article or in the ESI.†

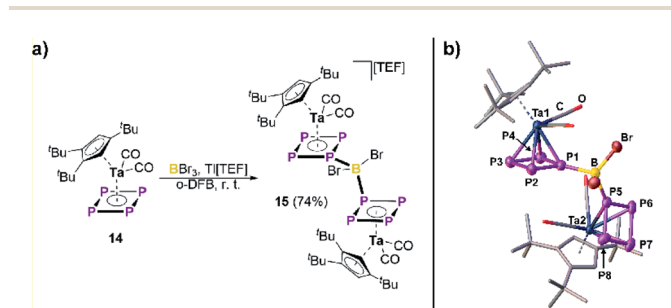


Fig. 4 (a) Reactivity of **14** towards the *in situ* formed dibromoboronium ion $[\text{BBr}_2][\text{TEF}]$; (b) molecular structure of **15** in the solid state (hydrogen atoms and the counter ion are omitted for clarity and thermal ellipsoids are drawn at the 50% probability level).



Author contributions

C. R. performed the experimental work and wrote the original draft. G. B. assisted in the performance of DFT calculations. M. Seidl assisted in the interpretation of X-ray structural data and M. Scheer supervised and acquired funding for the project. All authors contributed in preparing the final manuscript.

Conflicts of interest

There are no conflicts to declare.

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