

Hot Paper

Nucleophilic Functionalization of a Cationic Pentaphosphole Complex—A Systematic Study of Reactivity

Maximilian Widmann,^[a] Christoph Riesinger,^[a] Alexey Y. Timoshkin,^[b] Philip M. Blank,^[a] and Manfred Scheer^{*[a]}*Dedicated to Professor Hubert Schmidbaur on the occasion of his 90th birthday*

The systematic nucleophilic functionalization of the cationic pentaphosphole ligand complex $[\text{Cp}^*\text{Fe}(\eta^4\text{-P}_5\text{Me})][\text{OTf}]$ (**A**) with group 16/17 nucleophiles is reported. This method represents a highly reliable and versatile strategy for the design of novel transition-metal complexes featuring twofold substituted end-deck cyclo- P_5 ligands, bearing unprecedented hetero-element substituents. By the reaction of **A** with classical group 16 nucleophiles, complexes of the type $[\text{Cp}^*\text{Fe}(\eta^4\text{-P}_5\text{MeE})]$ ($\text{E} = \text{OEt}$ (**1**), O^tBu (**2**), SPh (**3**), SePh (**4**)) are obtained. By transferring this protocol to group 17 nucleophiles, the highly sensitive complexes $[\text{Cp}^*\text{FeP}_5(\eta^4\text{-P}_5\text{MeX})]$ ($\text{X} = \text{F}$ (**5**), Cl (**6**), Br (**7**), I (**8**)) could be

isolated. All products show exclusively 1,1'-substitution at the cyclo- P_5 ring. Interestingly, further studies on the reactivity of the halogenated species revealed their ability to undergo ring-opening reactions with cyclic ethers such as THF and ethylene oxide yielding $[\text{Cp}^*\text{FeP}_5(\eta^4\text{-P}_5\text{MeOC}_4\text{H}_8\text{X})]$ ($\text{X} = \text{Br}$ (**9**), I (**10**)) or $[\text{Cp}^*\text{FeP}_5(\eta^4\text{-P}_5\text{MeOC}_2\text{H}_4\text{X})]$ ($\text{X} = \text{Br}$ (**11**), I (**12**)), respectively. Furthermore, the use of acyclic ethers such as dimethoxyethane led to the formation of $[\text{Cp}^*\text{FeP}_5(\eta^4\text{-P}_5\text{MeOC}_2\text{H}_4\text{OCH}_3)]$ (**13**) mediated by C–O bond cleavage, followed by subsequent P–O bond formation, as further enlightened by DFT calculations.

Introduction

Hydrocarbon-based aromatic compounds with the general formula C_nH_n are useful compounds in all areas of modern chemistry. One of the most decisive factors for their extraordinary stability as compared to their unsaturated analogs is aromaticity, based on the Hückel rule which states that compounds with delocalized $[4n+2]$ π -electrons are more stable than those that feature $4n$ π -electrons.^[1] In coordination chemistry, aromatic systems are commonly used as a broad ligand platform, found e.g. in the ubiquitous ferrocene $[\text{Cp}_2\text{Fe}]$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$),^[2] with all π -electrons homogenously participating in a symmetrical bonding towards the central iron atom.^[3] Additionally, due to the electron-rich character of ferrocenes', prototypical reactions of aromatic systems, such as electrophilic aromatic substitutions, are massively accelerated in comparison

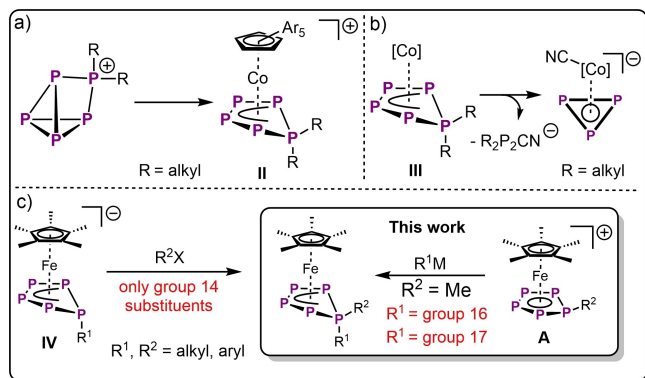
to other compounds containing aromatic ligands e.g. $[\text{Cr}(\eta^6\text{-arene})_2]$ complexes,^[4] which could be experimentally shown by for instance the protonation, acylation, or mercuration of ferrocene.^[5] Interestingly, the isolobal connection between the CH and the P fragment,^[6] as well as the diagonal relationship between phosphorus and carbon,^[7] relates aromatic hydrocarbons to cyclic, unsubstituted polyphosphorus (P_n) ligands. Despite numerous reports on complexes that feature various examples of P_n ligands,^[8] completely inorganic metallocenes still remain an exclusive class of compounds for which only $[\text{Ti}(\eta^5\text{-P}_5)_2]^{2-}$ ^[9] as well as the recently reported $[\text{Fe}(\eta^4\text{-P}_4)_2]^{2-}$ ^[10] are known to this date. "Semi-inorganic" metallocenes, however, as for example $[\text{Cp}^*\text{Fe}(\eta^5\text{-P}_5)]$ ^[11] ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$) (**I**), are considered to be a useful platform for reactivity studies on P_n ligands. Ferrocene shows simple oxidation when treated with one-electron oxidants.^[12] In contrast, **I** shows structural changes under participation of individual P-atoms according to spectro-electrochemical studies by Geiger^[13] which could later be proved experimentally by our group. Indeed, **I** shows the aggregation to $\{\text{P}_{10}\}^{2-/2+}$ complexes under reductive or oxidative conditions.^[14] Due to the absence of H^+ at the cyclo- P_5 ring of **I**, the substitution by e.g. organic groups is hindered. One approach for functionalization is the electrophilic activation yielding cationic—but still aromatic—pentaphosphole complexes $[\text{Cp}^*\text{Fe}(\eta^4\text{-P}_5\text{R})][\text{X}]$ ^[15,16] ($[\text{X}] = [\text{WCA}]$) (Scheme 1, **A**). To stabilize these reactive cationic species, the use of weakly coordinating anions (WCAs)^[17] is required. This principle could be extended to other polyphosphorus (P_n) complexes ($n = 2\text{--}8$), giving rise to several differently functionalized P_n ligand complexes.^[18] To introduce two organic substituents on polyphosphorus ligands, the complexation of cationic $[\text{P}_5\text{R}_2][\text{GaCl}_4]$ ^[19] ($\text{R} = \text{alkyl}$) with

[a] M. Widmann, Dr. C. Riesinger, P. M. Blank, Prof. Dr. M. Scheer
Department of Inorganic Chemistry
University of Regensburg
Universitätsstraße 31, 93053 Regensburg, Germany
E-mail: manfred.scheer@ur.de

[b] Prof. Dr. A. Y. Timoshkin
Institute of Chemistry
Saint Petersburg State University
Universitetskaya emb. 7/9, 199034 St. Petersburg (Russia)

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Scheme 1. a) Complexation of $[P_5R^1R^2]^+$ by $[Cp^{Ar}Co(COD)]$ (COD = 1,5-cyclo-octadiene, $Cp^{Ar} = \eta^5-C_5(C_6H_4-4-Et)_5$). b) Fragmentation towards cyanide addition; $[Co] = [(PHDI)Co]$ (PHDI = bis(2,6-diisopropylphenyl)phenanthrene-9,10-diimine). c) Nucleophilic functionalization of $[Cp^*Fe(\eta^5-P_5)]$ (I), yielding monoanionic $[Cp^*Fe(\eta^4-P_5R^1)]^-$ species (IV), and content of this work.

transition metal complexes to yield II (Scheme 1, a))^[20] was shown to be a reliable method, as demonstrated by the Wolf group. They also showed that the salt metathesis between R_2PCl and the anionic $[(L)Co(\eta^4-P_4)]$ ($L = PHDI = \text{bis}(2,6\text{-diisopropylphenyl})\text{phenanthrene-9,10-diimine}$, $R = \text{alkyl}$) can also effectively generate these motifs in III.^[21] Notably, the latter resulted in the formation of an $[(L)Co(\eta^3-P_3)(CN)]^-$ species upon reaction with cyanides (Scheme 1, b).^[21] Another possibility to introduce two organic substituents into a *cyclo*- P_5 ring of I is its nucleophilic functionalization yielding $[Cp^*Fe(\eta^4-P_5R^1)]^-$ (Scheme 1, IV),^[22] followed by subsequent quenching by organic electrophiles.^[23] Having such substitution patterns, the use of nucleophiles such as KBn or LiR ($R = \text{alkyl}$) produces unprecedented asymmetric phosphines $[PR^1R^2R^3]$ ($R^1 \neq R^2 \neq R^3 = \text{alkyl, aryl}$) within less than one hour in gram scale.^[23–26] However, the substitution patterns are so far limited to group 14 substituents due to the low nucleophilicity of heteroelement nucleophiles, which limits the nucleophilic functionalization of compound I. Introducing substituents from other main groups could significantly expand the scope of substitution, enabling more precise and diverse functionalizations. This raises the crucial question of whether two substituents of different main groups can be incorporated into the *cyclo*- P_5 framework as a necessary step for advancing further functionalization or facilitating the release of these functionalized phosphines, respectively. While the nucleophilic initiated release of asymmetric phosphines may be particularly challenging with electronegative group 16 or 17 substituents, the approach nonetheless enlarges the scope of functionalization significantly. Since the first report of the successful generation of the cationic pentaphosphole complexes $[Cp^*Fe(\eta^4-P_5R)]^+[WCA]$,^[15,16] no detailed studies on the quenching chemistry of $[Cp^*Fe(\eta^4-P_5R)]^+[WCA]$ and its respective follow-up chemistry except NHC reactions^[27] have been published. Due to its easy and scaleable synthesis, $[Cp^*Fe(\eta^4-P_5Me)]^+[OTf]^-$ ($[OTf]^- = [SO_3CF_3]^-$) (A) was selected for this investigation.

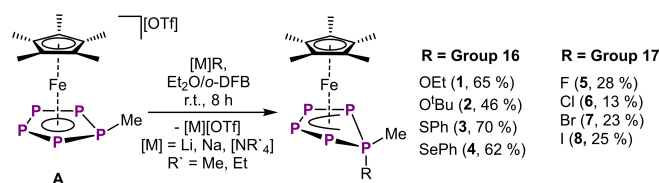
Herein, we present a systematic and innovative protocol for the generation of novel P_5R_2 ligands, significantly expanding

the scope of functionalization beyond the previously established group 14 elements to now include group 16 and 17 substituents, respectively. This approach introduces a robust and versatile strategy for the incorporation of a wide range of main group nucleophiles, establishing A as a powerful platform for in-depth studies of nucleophilic reactivity.

Results and Discussion

The conversion of A with group 16 salts seemed to be an ideal starting point for these investigations. For this purpose, the salts of standard reagents such as EtOH, ^tBuOH, PhSH as well as PhSeH, respectively, were selected. In all cases, the 1,1'-substituted products $[Cp^*Fe(\eta^4-P_5MeE)]$ ($E = \text{OEt}$ (1), O^tBu (2), SPh (3), SePh (4)) were isolated in yields of 65 % (1), 46 % (2), 70 % (3), and 62 % (4), respectively, after workup (Scheme 2). Interestingly, by transferring the developed reaction to group 17 salts, the corresponding halide-containing compounds $[Cp^*Fe(\eta^4-P_5MeX)]$ ($X = \text{F}$ (5), Cl (6), Br (7), I (8)) could be isolated using the soluble ammonium salts $[NR_4]X$ ($R = \text{Me}$, $X = \text{F, Cl}$; $R = \text{Et}$, $X = \text{Br, I}$) as halide transfer reagents. However, in contrast to the stable compounds 1–4, these complexes feature instability over time showing significant decomposition in solution after a few days. Still, the quantitative formation of 5–8 could nevertheless be monitored by ³¹P NMR spectroscopy of the reaction mixture. This aspect renders the nucleophilic quenching of A with halides a challenging reaction pathway. Furthermore, DFT computations indicate that compounds 6–8 are thermodynamically unstable with respect to MeX elimination. The activation energies for an intramolecular pathway are relatively high, but decrease in the order of $\text{F} > \text{Cl} > \text{Br} > \text{I}$, which is in line with reactivity trends experimentally observed (vide infra).

X-ray structural investigation of the products showed in all cases an intact *cyclo*- P_5R_2 end-deck ligand (Figure 1). However, compared to the pentaphosphole structure of A for which only a slightly bent *cyclo*- P_5 end-deck ligand is observed ($18.1(2)^\circ$ (A)),^[15,16] the further nucleophilic functionalization leads to a significant bending of the *cyclo*- P_5 ligand, forming an $\eta^4-P_5R_2$ structural motif ($133.00(3)^\circ$ (1), $132.58(5)^\circ$ (2), $133.89(13)^\circ$ (3), $133.9(3)^\circ$ (4), $137.02(19)^\circ$ (7), $136.2(4)^\circ$ (8)), which was also found for the mono-anionic complexes IV^[22] or the purely group 14/14-substituted complexes.^[23,24,26] For all products, the respective P–P bonds are very similar to each other ($2.106(5) \text{ \AA} - 2.152(10) \text{ \AA}$) and in the range of shortened P–P single bonds ($d(\text{P}–\text{P}) = 2.22 \text{ \AA}$).^[28–30] The found P–C as well as P–E bond



Scheme 2. Nucleophilic functionalization of the cationic pentaphosphole complex A with main group nucleophiles of group 16 and 17. Isolated yields are given in parentheses.

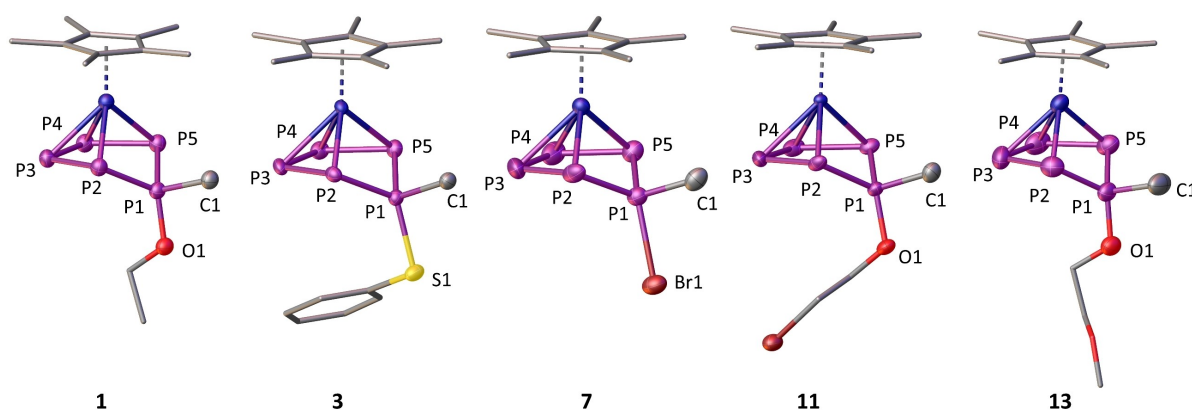


Figure 1. Molecular structures of the complexes **1**, **3**, **7**, **11** and **13** in the solid state. The structures of **2**, **4**, **8**, **9** and **12** are depicted in the SI; anisotropic displacement parameters are drawn at the 50% probability level and H atoms are omitted for clarity.

lengths, respectively (see SI), deviate only very little from the reported values for P–C/E single bonds ($d(\text{P–C}) = 1.86 \text{ \AA}$, $d(\text{P–O}) = 1.74 \text{ \AA}$, $d(\text{P–S}) = 2.14 \text{ \AA}$, $d(\text{P–Se}) = 2.27 \text{ \AA}$, $d(\text{P–Br}) = 2.25 \text{ \AA}$, $d(\text{P–I}) = 2.44 \text{ \AA}$).^[28–30] To further elaborate the structures of **1–8** in solution, these products were investigated by multi-nuclear NMR spectroscopy. In the ^1H NMR spectra, all compounds show sharp signals for the Cp* ligand and corresponding signals for the substituents. Additionally, the Me substituents of **5–8** show significant broadening caused by additional couplings (see SI) to the adjacent P atoms (**6–8**) or the bound F substituent in **5**. When comparing the $^{31}\text{P}\{^1\text{H}\}$ spectra of the products, similar spectra with minor deviations in the chemical shifts of the respective signals are obtained. Compounds **1–5** show an AMM'XX' spin system which could be analyzed by simulation, proving the proposed structural motifs.^[22–24,26] Interestingly, for compounds **6–8**, a significant interference of the signals and therefore complicated ABB'XX' (**6**), AA'XX'Y (**7**), and AA'DD'X (**8**) spin systems, respectively, were detected (Figure 2). Furthermore, in the ^{31}P NMR, all compounds except **7** and **8** show a characteristic broadening of the signal, corresponding to the nucleus P1 (regarding the

labelling from Figure 1), which clearly indicates an additional $^2J_{\text{P–H}}$ coupling to the adjacent Me substituent.

Interestingly, in contrast to **A**, where a cationic THF polymerization^[31] was observed in combination with THF, it turned out that, in the presence of THF, compounds **7** and **8** tend to form ring-opened products of the type $[\text{Cp}^*\text{Fe}(\eta^4\text{-P}_5\text{MeOC}_2\text{H}_4\text{X})]$ ($\text{X} = \text{Br}$ (**9**), I (**10**)) (Scheme 3). A similar ring-opening reaction is found for the smaller ring-sized ethylene oxide, leading to the products $[\text{Cp}^*\text{Fe}(\eta^4\text{-P}_5\text{MeOC}_2\text{H}_4\text{X})]$ ($\text{X} = \text{Br}$ (**11**), $\text{X} = \text{I}$ (**12**)). In contrast to THF, ring-opening reactions with the considerably more ring-strained ethylene oxide only required a reaction time of two hours until the conversion is complete, which could be monitored by NMR spectroscopy. Remarkably, it turned out that this reactivity is not limited to cyclic ethers but could be extended to acyclic ethers such as dimethoxyethane (DME). Hereby, the formation of the complex $[\text{Cp}^*\text{Fe}(\eta^4\text{-P}_5\text{MeOC}_2\text{H}_4\text{OCH}_3)]$ (**13**) could be observed together with the elimination of an equivalent of the corresponding methyl halide, exemplarily shown for MeI by ^1H NMR monitoring (see SI). However, when using $\text{X} = \text{Br}$, the reaction time had to be increased to two days for a complete conversion to **13**.

In the solid-state structures of **10–13**, the *cyclo*- P_5R_2 ligand exhibits a pronounced bending, similar to what is observed in

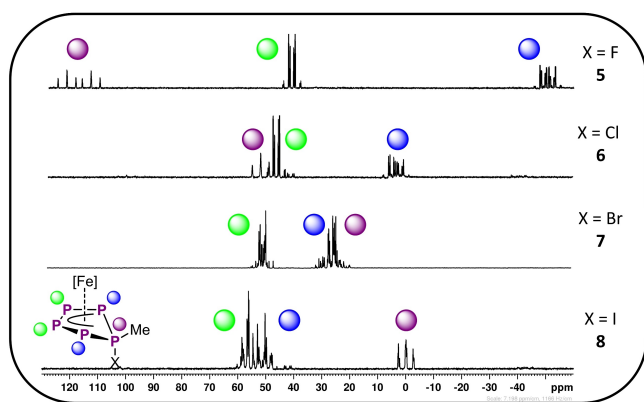
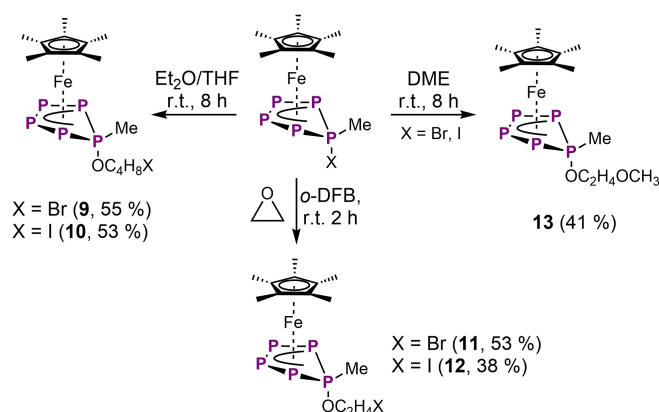
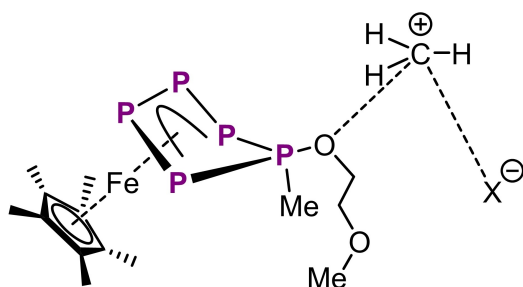


Figure 2. ^{31}P NMR spectra of the compounds **5–8** (from top to bottom), measured in C_6D_6 at room temperature with signals being assigned according to the color code; $[\text{Fe}] = [\text{Cp}^*\text{Fe}]$.



Scheme 3. Reactivity of **7** and **8** towards cyclic and acyclic ethers.



Scheme 4. Schematic representation of the TS leading to **13**.

1–8 (Figure 1). Specifically, the P1 atom is bent out of the plane spanned by the other P atoms in the *cyclo-P₅* ligand ($134.97(11)^\circ$ (**10**), $135.10(12)^\circ$ (**11**), $130.12(7)^\circ$ (**12**), $130.76(7)^\circ$ (**13**)). The P–P bond lengths of the compounds are very similar to each other ($2.1147(10)$ Å– $2.1416(13)$ Å) and are in the range of shortened P–P single bonds ($d(\text{P–P}) = 2.22$ Å).^[28–30] The found P–C ($1.814(5)$ Å (**10**), $1.811(5)$ Å (**11**), $1.819(4)$ Å (**12**), $1.812(3)$ Å (**13**)) as well as P–O ($1.617(3)$ Å (**10**), $1.631(4)$ Å (**11**), $1.641(8)$ Å (**12**), $1.6122(19)$ Å (**13**)) bond lengths, respectively, correlate with each other and lie in the range of regular P–C (1.86 Å) as well as P–O (1.74 Å) single bonds.^[28–30]

The ^{31}P NMR spectra of **9–13** show symmetrical AMM'XX' spin systems comparable to **1**, with chemical shifts and coupling constants strongly correlating with each other, further proving their identity in solution. In addition, the ^1H NMR spectra of the respective compounds also show the expected signals for the functional groups (see SI).

To obtain a deeper insight into a possible pathway of the formation of **13**, theoretical computations at the B3LYP^[32]/def2-TZVP(ECP on I)^[33,34] level of theory were performed for the reaction of DME with the more reactive heavier halogen derivatives **7** and **8**. A late transition state (TS) was located featuring P–O bond formation in tandem with C–O bond cleavage and significant lengthening of the P–X bond ($\text{X} = \text{Br}, \text{I}$) (Scheme 4). Positive atomic polar tensors (APT) charges on the leaving CH_3 group ($+1.07$ (Br); $+1.09$ (I)) and negative APT charges on the group 17 element (-1.01 (Br); -1.02 (I)) indicate that the key feature of this TS is the migration of a nearly planar CH_3^+ group from the oxygen center to the negatively charged halide ion (see SI; Table S17, Figure S56).

Computations in the framework of the polarized continuum model (PCM) in THF indicate larger positive charges on the CH_3^+ group as well as larger negative charges on the X anion as compared to the gas phase, which leads to the lowering of the activation energies by $16\text{--}23\text{ kJ mol}^{-1}$. However, the absolute values of activation energies are relatively large (see SI; Table S17).

In contrast to the thermodynamically unstable compounds **6–8**, **13** features both kinetic and thermodynamic stability at room temperature with respect to the $\text{MeOC}_2\text{H}_4\text{OMe}$ elimination. The decomposition of **13** is endergonic by 7.4 kJ mol^{-1} in the gas phase and by 4.4 kJ mol^{-1} in THF solution (see SI; Table S15).

Conclusions

In summary, we developed a method for the nucleophilic functionalization of the cationic pentaphosphole complex **A**, leading to the synthesis of novel transition metal complexes with selectively 1,1'-functionalized P_5R_2 ligands, incorporating previously uncharted group 16 and 17 substituents. This novel approach significantly broadens the scope of the existing methods, successfully incorporating classical group 16 nucleophiles to generate complexes such as $[\text{Cp}^*\text{Fe}(\eta^4\text{-P}_5\text{MeE})]$ ($\text{E} = \text{OEt}$ (**1**), OtBu (**2**), SPh (**3**), SePh (**4**)) as well as group 17 nucleophiles yielding $[\text{Cp}^*\text{Fe}(\eta^4\text{-P}_5\text{MeX})]$ ($\text{X} = \text{F}$ (**5**), Cl (**6**), Br (**7**), I (**8**)). The latter products feature an extremely high sensitivity against air and moisture. DFT computations further revealed that complexes **6–8** are kinetically stabilized by an exergonic dissociation pathway under MeX elimination. The trend for activation barriers was observed to decrease from **5** to **8**, highlighting the increasing reactivity of the heavier halogen derivatives, which was experimentally confirmed by their reactions with ethers. For instance, nucleophilic ring opening of cyclic ethers produced $[\text{CpFe}(\eta^4\text{-P}_5\text{MeOC}_4\text{H}_8\text{X})]$ ($\text{X} = \text{Br}$ (**9**), $\text{X} = \text{I}$ (**10**)) and $[\text{CpFe}(\eta^4\text{-P}_5\text{MeOC}_2\text{H}_4\text{X})]$ ($\text{X} = \text{Br}$ (**11**), $\text{X} = \text{I}$ (**12**)), while the acyclic ether dimethoxyethane yielded $[\text{Cp}^*\text{Fe}(\eta^4\text{-P}_5\text{MeOC}_2\text{H}_4\text{OMe})]$ (**13**) via MeX elimination, as detected by NMR spectroscopy. Thus, complex **A** has been demonstrated to be a versatile platform for introducing a diverse array of main group nucleophiles, resulting in the design of novel, selectively functionalized polypnictogen complexes.

Experimental Section

Experimental procedures for the synthesis of all compounds, analytical data, quantum chemical computations, and X-ray crystallographic details are summarized in the Supporting Information. The authors have cited additional references within the Supporting Information (^[11,15,33,34,35]). Deposition Number(s) 2382932–2382941 contain(s) the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

Date Availability

The data that support the findings of this study are available in the supplementary material of this article.

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Conflict of Interests

There are no conflicts to declare.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: iron · nucleophilic functionalization · main group chemistry · phosphorus

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*M. Widmann, Dr. C. Riesinger,
Prof. Dr. A. Y. Timoshkin, P. M. Blank,
Prof. Dr. M. Scheer**

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**Nucleophilic Functionalization of a
Cationic Pentaphosphole Complex—A
Systematic Study of Reactivity**

