


 Cite this: *Chem. Commun.*, 2020, 56, 10207

 Received 4th June 2020,
 Accepted 13th July 2020

DOI: 10.1039/d0cc03920a

rsc.li/chemcomm

Pentaphosphaferrocene, [Cp*Fe(η^5 -P₅)] (Cp* = η^5 -C₅Me₅), was used as a polyphosphorus source to obtain germylene–polyphosphide complexes. A stepwise reactivity was observed between the digermylene, [LGe–GeL] (L = {PhC(N^tBu)₂}), and [Cp*Fe(η^5 -P₅)]. Firstly, reductive homolytic cleavage of the Ge–Ge single bond in [LGe–GeL] led to [(LGe)₂(μ , η^4 -P₅)FeCp*]. This complex showed an unprecedented isomerization.

Phosphorus containing organo-heterocyclic compounds are very well documented¹ and have found applications in material science,² pharmaceutical industries,³ and ligand design for coordination chemistry.⁴ However, phosphorus heterocyclic compounds based on heavier group-14 elements are relatively scarce.⁵ Recently, direct functionalization of white phosphorus with low-valent species to access phosphorus heterocycles has attracted wide-spread attention.⁶ Low-valent main group compounds are usually highly susceptible towards redox reactions and have been efficiently utilized to reduce white phosphorus and generate phosphorus containing heterocyclic compounds.^{6a,7} For example, the reactions of different carbenes with white phosphorus resulted in organo-phosphorus cages, chains, and rings.⁸ Similarly, the reaction of white phosphorus with silylenes furnished sila-phospha cages and rings.^{7c,9} Also, low-valent germanium compounds have been reported to react with P₄ leading to germa-phospha heterocyclic compounds.¹⁰

The isolobality between [CH] and [P] fragments led to the prediction that the [*cyclo*-P₅][−] moiety may also be used to make sandwich compounds similar to ferrocene.¹¹ In 1987, Scherer and co-workers synthesized pentaphosphaferrocene, [Cp*Fe(η^5 -P₅)], in an elegant approach by co-thermolysis of white phosphorus and

A bis(germylene) functionalized metal-coordinated polyphosphide and its isomerization†

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[Cp*Fe(CO)₂]₂.¹² [Cp*Fe(η^5 -P₅)] has revealed to be a very useful metalloligand for further coordination chemistry due to the presence of a C₅ symmetric arrangement of lone pairs on the *cyclo*-P₅ ring. By using [Cp*Fe(η^5 -P₅)], one of us has carried out pioneering work in the field of inorganic supramolecular and polymer chemistry.¹³ Notably, the redox chemistry of [Cp*Fe(η^5 -P₅)] is different from that of ferrocene, due to the involvement of the *cyclo*-P₅ ring in redox events.¹⁴ Also, the reactivity of [Cp*Fe(η^5 -P₅)] towards main group nucleophiles and lanthanides has been investigated.¹⁵ Very recently, we have shown that [Cp*Fe(η^5 -P₅)] could be used as an air-stable polyphosphorus source to obtain silicon- or aluminium-polyphosphorus heterocyclic compounds.¹⁶

Interestingly, the reaction of [Cp*Fe(η^5 -P₅)] with different silylenes, *e.g.* [LSiCl],¹⁷ [LSi{N(SiMe₃)₂}],¹⁸ and [LSi–SiL]¹⁹ resulted in different reaction pathways such as substitution **A**, addition **B**, and ring expansion **C** reactions, respectively (Chart 1).^{16a} Such a rich reactivity of [Cp*Fe(η^5 -P₅)] with species featuring low-valent silicon prompted the question as to whether a similar reactivity would be observed with the heavier germylene analogues [LGeCl] and [LGe–GeL].²⁰ Low-valent Si species are prone to become Si(IV) *via* oxidation, however, this pathway is not obvious for low-valent Ge compounds, which may result in a different reactivity.²¹ Herein, we report on the

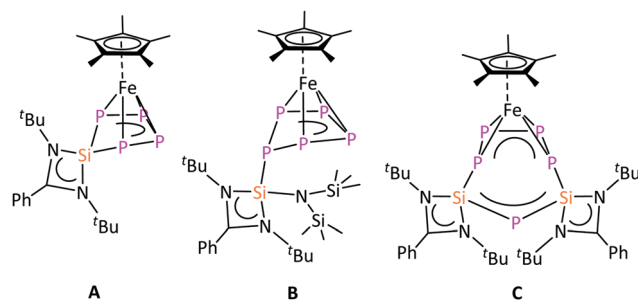


Chart 1 Selected products obtained from the reaction of [Cp*Fe(η^5 -P₅)] with different silylenes.^{16a}

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† Electronic supplementary information (ESI) available: Experimental section, NMR spectra, IR spectra and X-ray crystallographic details of complexes **1** and **2**. CCDC 2007825 (**1**) and 2007826 (**2**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d0cc03920a

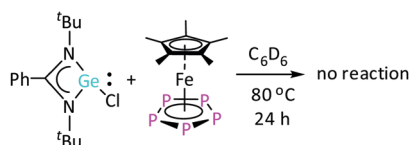


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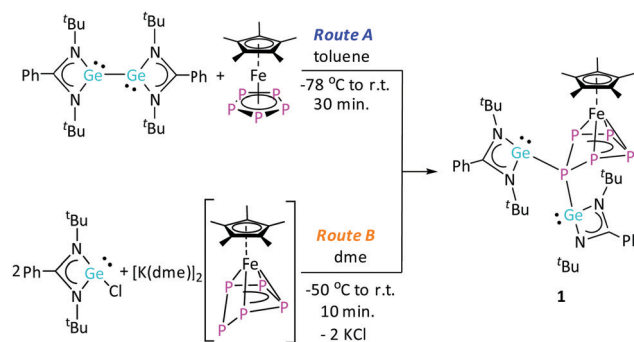
reactivity of $[\text{Cp}^*\text{Fe}(\eta^5\text{-P}_5)]$ with these germylenes and the isolation of the first example of a bis(germylene)-functionalized transition-metal polyphosphide complex. Furthermore, the isolated bis(germylene)-polyphosphide complex revealed an unprecedented constitutional isomerization.

In contrast to $[\text{LSiCl}]$, the heavier analogue of amidinate chloro-silylene, $[\text{LGeCl}]$, does not react with $[\text{Cp}^*\text{Fe}(\eta^5\text{-P}_5)]$ even after heating the reaction mixture at 80°C for 24 h (Scheme 1), as evidenced by ^1H NMR spectroscopy (Fig. S2, ESI†). This lack of reactivity can be explained by the lower oxidation potential (in absolute values) of $[\text{LGeCl}]$ compared to $[\text{LSiCl}]$. Since the di-silylene $[\text{LSi-SiL}]$ was found to be more reactive towards $[\text{Cp}^*\text{Fe}(\eta^5\text{-P}_5)]$ than $[\text{LSiCl}]$, as the Si atoms are formally in the +1 oxidation state in $[\text{LSi-SiL}]$,^{16a} the corresponding di-germylene, $[\text{LGe-GeL}]$, was employed for further investigations. The lower reactivity of $[\text{LGe-GeL}]$ compared to $[\text{LSi-SiL}]$ could be advantageously utilized to observe some intermediates that were anticipated to be also formed in the reaction with $[\text{LSi-SiL}]$, but could not be identified. The reaction between $[\text{LGe-GeL}]$ and $[\text{Cp}^*\text{Fe}(\eta^5\text{-P}_5)]$ at room temperature in toluene for 12 hours led to a mixture of products, as monitored by ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR studies. Interestingly, the intensity of the different resonances in the ^1H NMR spectra changed over time. Besides the starting material, $[\text{Cp}^*\text{Fe}(\eta^5\text{-P}_5)]$, some new compounds were formed. As outlined in the following sections, two of these compounds could be successfully identified.

The relatively slow conversion observed when using $[\text{LGe-GeL}]$ prompted us to follow the reaction between $[\text{LGe-GeL}]$ and $[\text{Cp}^*\text{Fe}(\eta^5\text{-P}_5)]$ by starting the reaction at -78°C , warming up to room temperature and stirring for half an hour (route A; Scheme 2). After work-up, crystals of $[(\text{LGe})_2\{\mu, \eta^4\text{-P}_5\}\text{FeCp}^*]$ (**1**) were obtained in 60% yield. Interestingly, the same product **1** was formed in quantitative yield in the reaction of $[(\text{K}(\text{dme})_2)\text{Cp}^*\text{Fe}(\eta^5\text{-P}_5)]$ ¹⁴ with 2 equivalents of $[\text{LGeCl}]$ by salt elimination (route B, Scheme 2). The ^1H NMR spectrum of complex **1** showed two singlets at $\delta = 1.23$ and 1.32 ppm corresponding to the four ^tBu groups on the amidinate ligands, indicating different environments for the two $[\text{LGe}]$ moieties. The resonance corresponding to the methyl protons of the Cp^* group is downfield shifted to $\delta = 1.90$ ppm compared to $\delta = 1.08$ ppm in $[\text{Cp}^*\text{Fe}(\eta^5\text{-P}_5)]$. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum showed an AMM'XX' spin system corresponding to magnetically non-equivalent P atoms with chemical shifts at $\delta = -45.7$ ($\text{P}_{\text{XX}'}$), 43.5 ($\text{P}_{\text{MM}'}$), and 150.5 (P_{A}) ppm (Fig. 1), indicating the formation of an envelope shape for the *cyclo*- P_5 ring. The different J_{PP} coupling constants could be determined by iterative line fitting of the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (Section 4.1, ESI†) and are in the usual range of those observed for complexes containing an envelope-shaped *cyclo*- P_5 ring.¹⁶



Scheme 1 Reaction attempt between $[\text{LGeCl}]$ and $[\text{Cp}^*\text{Fe}(\eta^5\text{-P}_5)]$.



Scheme 2 Synthesis of complex **1**.

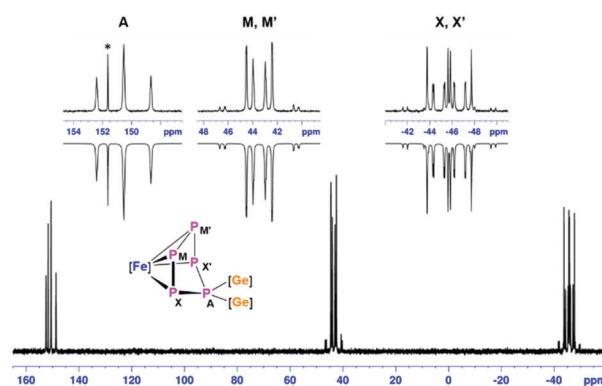


Fig. 1 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at 298 K of compound **1** in C_6D_6 with nuclei assigned to an AMM'XX' spin system; insets: extended signals (upward) and simulations (downward). See ESI† for details.

The molecular structure of complex **1** further confirmed the formation of an envelope-shaped *cyclo*- P_5 ring η^4 -coordinated to the $[\text{Cp}^*\text{Fe}]^+$ fragment (Fig. 2). The Fe-P bond distances (2.311(2)–2.357(2) Å) are in the usual range for similar compounds featuring an envelope-shaped *cyclo*- P_5 .^{14,15} The Ge1-P1 (2.4394(14) Å) and Ge2-P1 (2.4978(13) Å) bond lengths are similar to those in other tri-coordinated germylenes in a polyphosphide environment, for example, $[\text{RGe}(\mu\text{-P}_2)\text{-GeR}]$ ²² (2.439(1) Å) ($\text{R} = [(\textit{p}\text{-tolyl})_2\text{B}(1\text{-}(1\text{-adamantyl})\text{-3-yl-2-ylidene})_2]$) and $[\text{P}_7\text{Ge}(\text{N}(\text{SiMe}_3)_2)]^{2-}$ (2.504(1) and 2.526(1) Å).²³ The angles

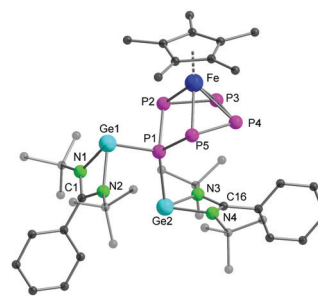


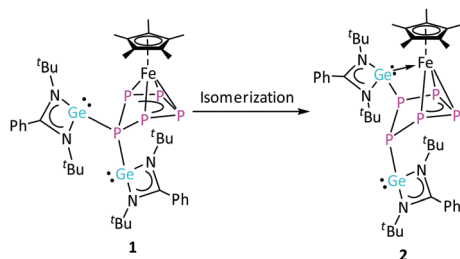
Fig. 2 The molecular structure of complex **1** in the solid state. The hydrogen atoms and the solvent molecule in the unit cell are omitted for clarity. Bond lengths and angles are given in ESI†.



between the N–Ge–P1 atoms, from $94.57(12)^\circ$ to $97.36(12)^\circ$, are in the typical range for tri-coordinated germlyenes.²⁴ The two germlyene moieties, $[\text{LGe}]^+$, in complex **1** are in a *trans*-conformation with respect to the orientation of the lone pairs on the Ge centres. Complex **1** results from the homolytic cleavage of the Ge–Ge single bond in $[\text{LGe–GeL}]$ and the two-electron reduction of $[\text{Cp}^*\text{Fe}(\eta^5\text{-P}_5)]$, and corresponds to a rare example of a germlyene in the coordination sphere of a polyphosphide.^{22,23,25} Furthermore, to the best of our knowledge, complex **1** is the first example of a bis(germlyene) functionalized transition-metal polyphosphide.²⁶

Interestingly, $[\text{LGe–GeL}]$ is reacting with exclusively one equivalent of $[\text{Cp}^*\text{Fe}(\eta^5\text{-P}_5)]$, even when the reaction is carried out in a 1:2 molar ratio, respectively. In this case, complex **1** together with one equivalent of unreacted $[\text{Cp}^*\text{Fe}(\eta^5\text{-P}_5)]$ are obtained. It should be noted that complex **1** is not stable in solution at room temperature and further reacts slowly. However, by careful control of the reaction time, complex **1** could be isolated in a pure form (details in ESI†). In order to identify the subsequent product(s) of the degradation of complex **1**, an NMR study of complex **1** was carried out. The ^1H NMR spectrum showed the conversion of **1** into new species (*vide infra*) along with re-formation of a small amount of $[\text{Cp}^*\text{Fe}(\eta^5\text{-P}_5)]$. However, the rate of the conversion at room temperature was found to be very slow, which prevented full conversion, even after one month (Fig. S8 and S9, ESI†). Therefore, to increase the rate, complex **1** was heated at 40°C for 48 h (Fig. S10, ESI†). On a preparative scale, the reaction between $[\text{LGe–GeL}]$ and $[\text{Cp}^*\text{Fe}(\eta^5\text{-P}_5)]$ was performed in toluene at 40°C for 24 h. As a result, after work-up, a mixture of crystals was obtained, consisting mostly of **1** and $[\text{Cp}^*\text{Fe}(\eta^5\text{-P}_5)]$ along with a few brown-coloured crystals of $[(\text{LGe})\{\mu, \eta^3\text{-P}_5\}(\eta^1\text{-GeL})\text{FeCp}^*]$ (**2**), which were identified by single crystal X-ray diffraction studies (for **2** cf. Scheme 3 and Fig. 3). Also, attempts to obtain pure complex **2** from isolated crystalline complex **1** in toluene at 40°C resulted in a mixture of **1**, **2**, $[\text{Cp}^*\text{Fe}(\eta^5\text{-P}_5)]$, and unidentified products according to the NMR investigations (Section 3, ESI†).

Complex **2** is an isomer of **1**, formed by an unprecedented 1,2-migration of one $[\text{LGe}]^+$ moiety on the *cyclo*- P_5 ring. Related 1,2-migration of a super-silyl moiety was observed during P_4 activation by an olefinic silylene.^{6e} The migrated $[\text{LGe}]^+$ entity further inserts into one of the Fe–P bonds, resulting in an unusual η^3 -coordination of the *cyclo*- P_5 ring to the $[\text{Cp}^*\text{Fe}]^+$ moiety. Despite several attempts, analytically pure complex **2**



Scheme 3 Isomerization of complex **1** to complex **2** via 1,2-migration of the $[\text{LGe}]^+$ moiety.

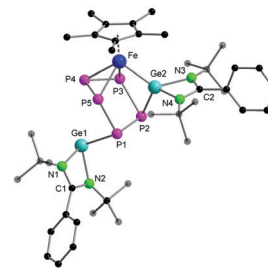


Fig. 3 The molecular structure of complex **2** in the solid state. The hydrogen atoms and the solvent molecule in the unit cell are omitted for clarity. Bond lengths and angles are given in ESI†

could not be isolated in meaningful yield. Nevertheless, a few crystals of complex **2** were manually separated from the mixture of crystals (**1**, **2** and $[\text{Cp}^*\text{Fe}(\eta^5\text{-P}_5)]$) for NMR investigations and single crystal X-ray diffraction analysis. The Fe–P5 ($2.3318(8)\text{ \AA}$) and Fe–P4 ($2.3404(7)\text{ \AA}$) bond distances in complex **2** are similar to the Fe–P bond lengths in **1**. On the other hand, the Fe–P3 ($2.3934(8)\text{ \AA}$) bond distance is significantly longer, which could be attributed to the insertion of the $[\text{LGe}]^+$ moiety into the adjacent Fe–P2 bond. The Ge2–Fe bond length ($2.2768(5)\text{ \AA}$) is similar to the literature reported values.²⁷ The Ge1–P1 bond length ($2.4286(7)\text{ \AA}$) in complex **2** is slightly shorter than the Ge–P distance in complex **1** (average 2.4686 \AA). The distance of the newly formed Ge2–P2 bond ($2.3142(7)\text{ \AA}$) is on the shorter end of the reported Ge–P bond lengths.^{26,28} The P1–P2 ($2.1875(10)\text{ \AA}$), P3–P4 ($2.1195(10)\text{ \AA}$), and P4–P5 ($2.1584(10)\text{ \AA}$) bond distances are in between P–P single and double bonds. The P1–P5 ($2.2153(10)\text{ \AA}$) and P2–P3 ($2.3208(11)\text{ \AA}$) distances are consistent with a single and elongated single bond, respectively.^{16a,29}

The ^1H NMR spectrum of **2** showed a very slight downfield shift of the Cp^* -methyl protons upon isomerization of **1** to **2** (δ 1.90 vs. 1.91, respectively) (Fig. S6, ESI†). In addition, four new resonances at $\delta = 1.10, 1.11, 1.42,$ and 1.52 ppm were detected in the aliphatic region, corresponding to the ^tBu groups of complex **2**. Notably, the presence of four resonances indicates the non-equivalence of the ^tBu groups, which suggests a rigid conformation and restricted rotation of the $[\text{LGe}]$ units. In agreement with the molecular structure of **2**, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum showed a set of five multiplets at $\delta = -43.0, -6.8, 72.4, 90.4,$ and 252.5 ppm , corresponding to five chemically non-equivalent P atoms. The different coupling constants were successfully assigned by iterative simulations of the spectrum (Section 4.2, ESI†).

In conclusion, we have investigated the reactivity of base-stabilized chloro-germlyene and di-germlyene with $[\text{Cp}^*\text{Fe}(\eta^5\text{-P}_5)]$ and $[\text{K}(\text{dme})_2\text{Cp}^*\text{Fe}(\eta^5\text{-P}_5)]$. In contrast to the chlorosilylene $[\text{LSiCl}]$, the corresponding heavier analogue, $[\text{LGeCl}]$, did not show any reaction with $[\text{Cp}^*\text{Fe}(\eta^5\text{-P}_5)]$. However, a stepwise reaction was observed for the di-germlyene $[\text{LGe–GeL}]$. In the first step, the reductive homolytic cleavage of the Ge–Ge single bond in $[\text{LGe–GeL}]$ resulted in a two-electron reduction of $[\text{Cp}^*\text{Fe}(\eta^5\text{-P}_5)]$ yielding complex **1**. Complex **1** is the first example of a bis(germlyene)-functionalized transition metal polyphosphide complex. Interestingly, NMR monitoring



of the reaction showed that complex **1** isomerizes to a new complex, **2**, even at room temperature. Complex **2** is formed by an unprecedented 1,2-migration of one [LGe]⁺ moiety on the *cyclo*-P₅ ring. The formation of **1** and its subsequent isomerization leading to **2** sheds light on potential elusive intermediates that were not identified using the more reactive silicon analogues [LSiCl] and [LSi-SiL], because such intermediates were too reactive to be isolated.^{16a} On the other hand, the reactivity observed clearly shows the difference in the reactivity of low-valent Si compounds in comparison to that of the corresponding Ge derivatives towards a metal-coordinated polyphosphide. Compounds with low-valent Si atoms were transformed into Si(IV) species by reducing *cyclo*-P₅, however, the Ge homologues stayed at a low oxidation state, Ge(II), and displaced one P atom of the *cyclo*-P₅ ring coordinated to the [Cp*Fe]⁺ moiety.

The authors are grateful to the Deutsche Forschungsgemeinschaft (DFG) (No. 266153560, Ro2008/17-2 and Sche 384/33-2).

Conflicts of interest

There are no conflicts to declare.

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