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Supporting Information

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

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1. Experimental Section

1.1. General Methods

All the manipulations of air- and water-sensitive reactions were performed with rigorous exclusion of oxygen and moisture in flame-dried Schlenk-type glassware either on a dual manifold Schlenk line, interfaced to a high vacuum (10^{-3} torr) line (Figure S1) or in an argon-filled MBraun glove box. Hexane was distilled under nitrogen from potassium benzophenoneketyl before storage *in vacuo* over LiAlH₄. Toluene, diethylether, and *n*-pentane were dried by using an MBraun solvent purification system (SPS 800), degassed and stored *in vacuo* over LiAlH₄. Elemental analyses were carried out with an Elementar vario Micro cube. IR spectra were obtained on a Bruker Tensor 37 spectrometer equipped with a room temperature DLaTGS detector and a diamond ATR (attenuated total reflection) unit. ¹H, ¹³C{¹H}, and ³¹P{¹H} NMR spectra were recorded on a Bruker Avance III 400 (¹H: 400.30 MHz, ¹³C: 100.67 MHz, ³¹P: 162.04 MHz) or on a Bruker Avance III 300 (¹H: 300.13 MHz, ¹³C; 75.48 MHz, ³¹P: 121.50 MHz). The chemical shifts are reported in ppm relative to external TMS (¹H, ¹³C) and H₃PO₄ (85%) (³¹P). The designation of spin systems in the ³¹P{¹H} NMR spectra was performed by convention. [Cp*Fe(η^{5} -P₅)],¹ [K(dme)]₂[Cp*Fe(η^{5} -P₅)],² [LGeCI] (L = PhC(NtBu)₂),³ and [LGe-GeL]³ were synthesized according to literature procedures.

1.2. Synthesis and analytical data

1.2.1. Synthesis of 1 [(LGe)₂{(μ , η^{4} -P₅)FeCp*}]

Method A: Using a high-vacuum line, toluene (*ca*. 10 mL) was transferred under vacuum from a solvent storage flask and condensed over a mixture of [LGe-GeL] (150 mg, 0.246 mmol) and [Cp*Fe(η^{5} -P₅)] (85 mg, 0.246 mmol) (see Figure S1 for the reaction setup) at -78 °C. The reaction mixture was allowed to warm to room temperature over 30 minutes. All the volatiles were removed under vacuum after further stirring the reaction mixture for 30 minutes at room temperature. The residue was extracted with hexane (20 mL) and filtered. The filtrate was concentrated till incipient crystallization (overall workup time 2-3 hours) and subsequently stored at -30 °C for one day to obtained orange-coloured crystals of complex **1**. The crystals were separated from the mother liquor by decantation and dried *in vacuo*. (Yield: 70 mg, 0.146 mmol, 60%).



Figure S1: Reaction set-up for transfer of toluene under vacuum. A) toluene stored *in vacuo* over LiAlH₄, B) resealable reaction flask under vacuum, C) low temperature (-78 °C) bath, D) high vacuum (10⁻³ torr) line.

Method B: $[K(dme)]_2[Cp*Fe(\eta^5-P_5)]$ (181.3 mg, 0.3 mmol) was dissolved in dme and cooled to -50 °C. To this, a solution of [LGeCl] (203.7 mg, 0.6 mmol) in 10 mL dme pre-cooled at -50 °C was added. An immediate change in colour from dark green to brown/reddish was observed and a colourless solid was formed. The reaction mixture was allowed to reach room temperature within three hours and stirred for another 10 minutes at room temperature. All the volatiles were removed *in vacuo*. A dark red solution could be extracted with 3 x 10 mL of *n*-hexane and filtered over diatomaceous earth. The complex **1** was obtained as a dark red powder by slow evaporation of the solvent under reduced pressure (overall workup time: two to three hours). (Yield: 250.0 mg, 0.26 mmol, 87%).

Anal Calcd. for C₄₀H₆₁N₄P₅Ge₂Fe (953.93): C, 50.36; H, 6.45; N, 5.87. Found: C, 49.62; H, 6.18; N, 5.60.

¹**H NMR** (400 MHz, 298 K, C₆D₆): δ [ppm] = 1.23 (s, 18 H, C(CH₃)₃), 1.32 (s, 18 H, C(CH₃)₃), 1.90 (s, 15 H, C(CH₃)), 6.89-7.02 (m, 6 H, *H*-Ph), 7.20 (t, 2 H, *H*-Ph, ³J_{HH} = 7.2 Hz), 7.65 (d, 1 H, *H*-Ph, ³J_{HH} = 6.5 Hz), 8.68 (d, 1 H, *H*-Ph, ³J_{HH} = 7.2 Hz).

³¹P{¹H} NMR (162 MHz, 298 K, C₆D₆): (AMM'XX') spin system δ [ppm] = -45.7 (m, 2 P, P_{XX}), 43.5 (m, 2 P, P_{MM}), 150.5 (m, 1 P, P_A) (See Section 4.1).

¹³C{¹H} NMR (100 MHz, 298 K, C₆D₆): δ [ppm] = 11.9 (C(CH₃)), 32.3 (C(CH₃)₃), 32.6 (C(CH₃)₃), 53.5 (C(CH₃)₃), 54.4 (C(CH₃)₃), 89.8 (C(CH₃)), 127.0 (C-Ph), 129.6 (C-Ph), 129.7 (C-Ph), 131.2 (C-Ph), 135.5 (C-Ph), 136.4 (C-Ph), signals for NCN could not be detected and recording the ¹³C{¹H} NMR spectrum with large numbers of scans *i.e.* during longer measurement times led to low quality spectra because of the isomerization product starting to appear.

IR (ATR): $\tilde{\nu}$ (cm⁻¹) = 2973 (s), 2960 (m), 2925 (m), 2900 (s), 2863 (s), 1646 (s), 1602 (s), 1578 (s), 1516 (s), 1474 (m), 1455 (m), 1412 (vs), 1389 (s), 1372 (s), 1359 (s), 1252 (s), 1221 (m), 1202 (s), 1177 (m), 1158 (m), 1140 (w), 1069 (m), 1063 (m), 1031 (m), 1019 (s), 925 (w), 898 (w), 849 (w), 791 (s), 741 (s), 706 (vs), 615 (w), 581 (m), 558 (w), 500 (w), 477 (m), 440 (m).

1.2.2. Isomerization of 1 to 2, [(LGe){(μ , η^3 -P₅)(η^1 -GeL)FeCp*}]

The isomerization of complex **1** to **2** was monitored by ¹H NMR spectroscopy (Section 3). In solution, complex **1** slowly isomerizes to complex **2** at room temperature *via* a **1**,2-migration of one [LGe]⁺ moiety and subsequent coordination to the [Cp*Fe]⁺ moiety. Despite several attempts, analytically pure complex **2** could not be isolated due to two main reasons: i) if the NMR scale reaction is carried out at room temperature, full conversion of complex **1** to complex **2** is impossible in a reasonable time scale (more than one month) (Section 3); ii) upon heating the reaction mixture to increase the rate of the reaction (40 °C for 24 h or 60 °C for 3 h), thermal decomposition is observed, resulting in a mixture of [Cp*Fe(η^5 -P₅)], **1**, **2**, and an unidentified product (Section 3). In addition, when the reaction is performed on a preparative scale, [LGe-GeL] (75 mg, 0.123 mmol) and [Cp*Fe(η^5 -P₅)] (42 mg, 0.123 mmol) in toluene at 40 °C for 24 h or 60 °C for 3 h, followed by filtration and slow evaporation of toluene, a mixture of brown (**2**), orange (**1**), and green ([Cp*Fe(η^5 -P₅)]) coloured crystals were obtained along with an unidentified red-brown amorphous solid. However, a few brown-coloured crystals of complex **2** could be manually separated from the mixture for NMR and X-ray diffraction studies. Furthermore, isolated crystals of complex **1** (50 mg) were heated at 40 °C for 24 h in toluene and the reaction mixture also showed a mixture of **1**, **2**, [Cp*Fe(η^5 -P₅)], and unidentified products according to the NMR results.

¹**H NMR** (400 MHz, 298 K, C₆D₆): δ [ppm] = 1.10 (s, 9 H, C(CH₃)₃), 1.11 (s, 9 H, C(CH₃)₃), 1.43 (s, 9 H, C(CH₃)₃), 1.52 (s, 9 H, C(CH₃)₃), 1.91 (s, 15 H, C(CH₃)), 6.81-6.97 (m, 8 H, *H*-Ph), 7.06 (br, 1 H, *H*-Ph), 7.12 (br, 1 H, *H*-Ph).

³¹P{¹H} NMR (162 MHz, 298 K, C₆D₆): δ [ppm] = -43.0 (m, 1 P), -6.8 (m, 1 P), 72.4 (m, 1 P), 90.4 (m, 1 P), 252.5 (m, 1 P) (Details in section 4.2).

2. NMR Spectra



Figure S2: ¹H NMR (400 MHz, 298 K, C_6D_6) spectrum of the reaction mixture between LGeCl (+) and [Cp*Fe(η^5 -P₅)] (*).



Figure S3: ¹H NMR (400 MHz, 298 K, C₆D₆) spectrum of complex 1.



Figure S4: ${}^{31}P{}^{1}H{}$ NMR (162 MHz, 298 K, C₆D₆) spectrum of complex **1**; * = traces of [Cp*Fe(η^{5} -P₅)].



Figure S5: ¹³C{¹H} NMR (100 MHz, 298 K, C₆D₆) spectrum of complex **1**.



Figure S6: ¹H NMR (400 MHz, 298 K, C₆D₆) spectrum of complex **2**. A few crystals were manually separated to obtain the spectrum. **+** = grease, **\$** = $[Cp^*Fe(\eta^5-P_5)]$, ***** = toluene.



Figure S7: ³¹P{¹H} NMR (162 MHz, 298 K, C₆D₆) spectrum of complex **2**. A few crystals were manually separated to obtain the spectrum. + = [Cp*Fe(η^{5} -P₅)], * = traces of complex **1**.

3. Isomerization of complex 1 to 2



Scheme S1: NMR monitoring of the isomerization of complex 1 to complex 2 at room temperature.



Figure S8: Stacked ¹H NMR (400 MHz, <u>298 K</u>, C_6D_6) spectra of the aliphatic region for the conversion of isolated complex **1** to complex **2**. + = ^tBu group of **1**, * = Cp* group of **1**,~ = ^tBu group of **2**, ϕ = Cp* group of **2**, Δ = [Cp*Fe(η^5 -P₅)] and # = unidentified product(s).



Figure S9: Stacked ¹H NMR (400 MHz, <u>298 K</u>, C₆D₆) spectra of the aliphatic region for the formation of complex **1** and its subsequent conversion to complex **2**. Part **1** of the picture shows the ^{*t*}Bu signal of [LGe-GeL]. **+** = ^{*t*}Bu group of **1**, ***** = Cp* group of **1**, \sim = ^{*t*}Bu group of **2**, ϕ = Cp* group of **2**, Δ = [Cp*Fe(η^5 -P₅)] and **#** = unidentified product(s).



Scheme S2: NMR monitoring of isomerization of complex 1 to complex 2 at variable temperatures.



00 1.95 1.90 1.85 1.80 1.75 1.70 1.65 1.60 1.55 1.50 1.45 1.40 1.35 1.30 1.25 1.20 1.15 1.10 1.05 1.00 0.95 0.90 0.85 0.80 0.75 f1 (ppm)

Figure S10: Stacked ¹H NMR (400 MHz, 313 & 323 K, C₆D₆) spectra of the aliphatic region for the conversion of isolated complex **1** to complex **2**. + = ^tBu group of **1**, * = Cp* group of **1**,~ = ^tBu group of **2**, ϕ = Cp* group of **2**, Δ = [Cp*Fe(η ⁵-P₅)], # = unidentified product(s).

4. Details of the simulation of the NMR spectra

Simulations of the ³¹P{¹H} NMR spectra were performed using the DAISY module of the Topspin 3.6 processing software (Bruker). The parameters chemical shift (∂), coupling constant (J) and linewidth ($\omega_{1/2}$) for the simulation of the phosphorus NMR spectra are compiled in the different tables.

4.1 Experimental and simulated spectra of 1 at 298 K

Two fragments were used for the simulation: complex **1** with a statistical weight of 1.000 and [Cp*Fe(η^{5} -P₅)] (corresponding to the singlet at δ 151.65) with a statistical weight of 0.027.



Figure S11: ³¹P{¹H} NMR spectrum at 298 K of complex 1 in C₆D₆ with nuclei assigned to an AMM'XX' spin system; insets: extended signals (upwards) and simulations (downwards); δ (P_A) = 150.5 ppm, δ (P_{MM'}) = 43.5 ppm, δ (P_{XX'}) = -45.7 ppm, ¹J_{MM'} = 406.8 Hz, ¹J_{MX} = ¹J_{M'X'} = 367.2 Hz, ¹J_{AX} = ¹J_{AX'} = 304.6 Hz, ²J_{XX'} = -39.0 Hz, ²J_{MX'} = ²J_{M'X} = -27.9 Hz, ²J_{AM} = ²J_{AM'} = 8.5 Hz, [Fe] = Cp*Fe, [Ge] = [LGe] The singlet at δ 151.64 ppm (*) corresponds to trace amounts of [Cp*Fe(η^{5} -P₅)].



Figure S12: Section of the ³¹P{¹H} NMR spectrum (162.04 MHz, 298 K, C₆D₆) of complex **1** with nuclei assigned to an AMM'XX' spin system; experimental (upwards) and simulation (downwards). The singlet at δ 151.64 ppm (*) corresponds to trace amounts of [Cp*Fe(η^5 -P₅)].

Table S1: Chemical shifts, couplings constants and linewidths from the iterative fit of the AMM'XX' spinsystem of 1 in C_6D_6 at 298 K and schematic representation of the FeP₅ core. [Fe] = Cp*Fe, [Ge] = [LGe].

Parameters	Iteration values		
δ (P _A)	150.53 ppm		
$\delta(P_{M}) = \delta(P_{M})$	43.46 ppm		
$\delta(P_{X}) = \delta(P_{X'})$	-45.72 ppm		
¹ <i>J</i> _{MM} ,	406.8 Hz		
${}^{1}J_{MX} = {}^{1}J_{M'X'}$	367.2 Hz		
${}^{1}J_{AX} = {}^{1}J_{AX},$	304.6 Hz		
² J _{XX} ,	-39.0 Hz		
${}^{2}J_{MX} = {}^{2}J_{M'X}$	-27.9 Hz		
${}^{2}J_{AM}={}^{2}J_{AM},$	8.5 Hz		
ω _{1/2} (A)	9.6 Hz		
$\omega_{1/2}(M) = \omega_{1/2}(M')$	8.5 Hz		
$\omega_{1/2}(X) = \omega_{1/2}(X')$	8.7 Hz		



4.2 Experimental and simulated spectra of 2 at 298 K

Three fragments were used for the simulation: complex **2** (statistical weight of 1.00), complex **1** (statistical weight of 0.42) and $[Cp^*Fe(\eta^5-P_5)]$ (singlet at δ 152.13 ppm, statistical weight of 0.38).



Figure S13: ³¹P{¹H} NMR spectrum at 298 K of the isomerization of complex **1** into complex **2** in C_6D_6 recorded after the letting the NMR tube stand for *ca*. 1 month at room temperature. Part **A**: simulation spectrum showing only the complex **2**, part **B**: simulation spectrum showing all the species in solution (*i.e.* **2**, **1** and [Cp*Fe(η^5 -P₅)] with statistical weights of 1.00, 0.42 and 0.38, respectively), part **C**: experimental spectrum. The numbering P₁-P₅ has been established arbitrarily and does not necessarily reflect the numbering on the X-ray structure.

Figure S14: Sections of the ³¹P{¹H} NMR spectrum (162.06 MHz, 298 K, C_6D_6) of complex **2** with assignment of the nuclei; experimental (upwards) and simulation (downwards). The numbering P_1-P_5 does not necessarily reflect the numbering on the X-ray structure.

Table S2: Chemical shifts, couplings constants and linewidths from the iterative fit of the P₅ spin system of **2** in C₆D₆ at 298 K and schematic representation of the P₅ core. [Fe] = Cp*Fe, [Ge] = [LGe]

Parameters	Iteration values	Parameters	Iteration values
$\delta(P_1)$	252.54 ppm	² J _{P1-P2}	-4.2 Hz
$\delta(P_2)$	90.43 ppm	² J _{P1-P3}	22.1 Hz
δ(P ₃)	72.42 ppm	² J _{P2-P5}	17.2 Hz
$\delta(P_4)$	-6.84 ppm	² Ј _{РЗ-Р4}	31.9 Hz
$\delta(P_5)$	-43.01 ppm	² J _{P4-P5}	8.8 Hz
¹ J _{P1-P4}	265.7 Hz	$\omega_{1/2}(P_1)$	6.4 Hz
¹ J _{P1-P5}	333.3 Hz	ω _{1/2} (P ₂)	6.4 Hz
¹ J _{P2-P3}	112.1 Hz	$\omega_{1/2}(P_3)$	7.4 Hz
¹ J _{P2-p4}	277.1 Hz	ω _{1/2} (P ₄)	6.1 Hz
¹ Ј _{РЗ-Р5}	416.2 Hz	ω _{1/2} (P ₅)	7.3 Hz

$$P - P_3$$

5. IR Spectrum of 1

Figure S15: IR spectrum of complex 1.

6. Single crystal X-ray diffraction

A suitable crystal was covered in mineral oil (Aldrich) and mounted on a glass fiber. The crystal was transferred directly to the cold stream of a STOE IPDS 2 or a STOE StadiVari diffractometer. All structures were solved by using the program SHELXS/T⁴ and Olex2.⁵ The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least-squares techniques on F^2 by using the program SHELXL.⁴ In each case, the locations of the largest peaks in the final difference Fourier map calculations, as well as the magnitude of the residual electron densities, were of no chemical significance.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as a supplementary publication no. 2007825-2007826. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+(44)1223-336-033; email: deposit@ccdc.cam.ac.uk).

Refinement details

The crystal structure of **1** contains one and a half molecules of toluene in the asymmetric unit. The half molecule could not be modeled satisfactorily and was therefore removed from the electron density map using the Olex2 solvent mask routine.⁵ Also, the Cp* molety is strongly disordered and therefore only refined isotropically.

Compound	1*toluene	2 *2(toluene)
Formula	C47H69FeGe2N4P5	C54H77FeGe2N4P5
D_{calc} / g cm ⁻³	1.236	1.346
μ/mm^{-1}	1.492	1.500
Formula Weight	1045.94	1138.07
Colour	clear orange	clear brown
Shape	plate	plate
Size/mm ³	0.23×0.14×0.03	0.33×0.20×0.07
T/K	100	150
Crystal System	triclinic	triclinic
Space Group	<i>P</i> -1	<i>P</i> -1
a/Å	12.9054(14)	12.1225(10)
b/Å	13.5536(14)	14.174(2)
c/Å	17.432(3)	16.7654(17)
$\alpha/^{\circ}$	98.830(10)	84.679(10)
β/°	110.410(10)	79.665(7)
$\gamma/^{\circ}$	92.274(9)	83.291(10)
V/Å ³	2809.5(6)	2807.1(6)
Z	2	2
Z'	1	1
Wavelength/Å	0.71073	0.71073
Radiation type	MoKα	ΜοΚα
$\Theta_{min}/^{\circ}$	1.711	1.717
$\Theta_{max}/^{\circ}$	31.153	29.504
Measured Refl.	26911	28119
Independent Refl.	14041	15293
Reflections with $I > 2(I)$	8228	9972
R _{int}	0.0493	0.0387
Parameters	591	742
Restraints	468	468
Largest Peak	0.924	0.767
Deepest Hole	-0.964	-0.427
GooF	1.030	1.016
wR_2 (all data)	0.1873	0.0854
wR_2	0.1597	0.0748
R_1 (all data)	0.1253	0.0834
R_1	0.0679	0.0396

6.2. Crystal structures

Figure S16: The molecular structure of complex **1** in the solid state with thermal ellipsoids at 40% probability. The hydrogen atoms and the solvent molecule in the unit cell are omitted for clarity. Selected bond distances (Å) and angles [°]: Ge1-P1 2.4394(14), Ge1-N2 2.020(4), Ge1-N1 2.040(4), Ge2-P1 2.4978(13), Ge2-N3 2.016(4), Ge2-N4 2.010(4), Fe-P2 2.311(2), Fe-P3 2.357(2), Fe-P4 2.339(2), Fe-P5 2.321(2), P1-P2 2.196(2), P2-P3 2.152(3), P3-P4 2.159(3), P4-P5 2.176(2), P5-P1 2.209(2), N3-C16 1.350(6), N2-C1 1.348(6), N1-C1 1.354(6); Ge1-P1-Ge2 114.28(5), N2-Ge1-P1 95.61(12), N2-Ge1-N1 65.1(2), N1-Ge1-P1 94.57(12), N3-Ge2-P1 95.80(11), N4-Ge2-P1 97.36(12), N4-Ge2-N3 65.4(2).

Figure S17: The molecular structure of complex **2** in the solid state with thermal ellipsoids at 40% probability. The hydrogen atoms and the solvent molecule in the unit cell are omitted for clarity. Selected bond distances (Å) and angles [°]: Ge1-P1 2.4286(7), Ge1-N1 2.020(2), Ge1-N2 2.030(2), Ge2-Fe 2.2768(5), Ge2-P2 2.3142(7), Ge2-P3 2.7938(7), Ge2-N3 1.995(2), Ge2-N4 2.002(2), Fe-P3 2.3934(8), Fe-P4 2.3404(7), Fe-P5 2.3318(8), P1-P2 2.1875(10), P2-P3 2.3208(11), P3-P4 2.1195(10), P4-P5 2.1584(10), P5-P1 2.2153(10), N1-C1 1.324(3), N2-C1 1.330(3), N3-C2 1.326(3), N4-C2 1.329(3); N1-Ge1-P1 96.49(6), N1-Ge1 N2 64.58(8), N2-Ge1-P1 95.23(6), Fe-Ge2-P2 100.73(2), Fe-Ge2-P3 55.20(2), P2-Ge2-P3 53.04(2), N3-Ge2-Fe 131.92(6), N3-Ge2-P2 117.13(6), N3-Ge2-P3 170.14(6), N3-Ge2-N4 65.81(8), N4-Ge2-Fe 130.32(6), N4-Ge2-P2 108.14(6), N4-Ge2-P3 116.09(6), Ge2-Fe-P3 73.44(2), Ge2-Fe-P4 110.88(3), Ge2-Fe-P5 85.13(2).

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