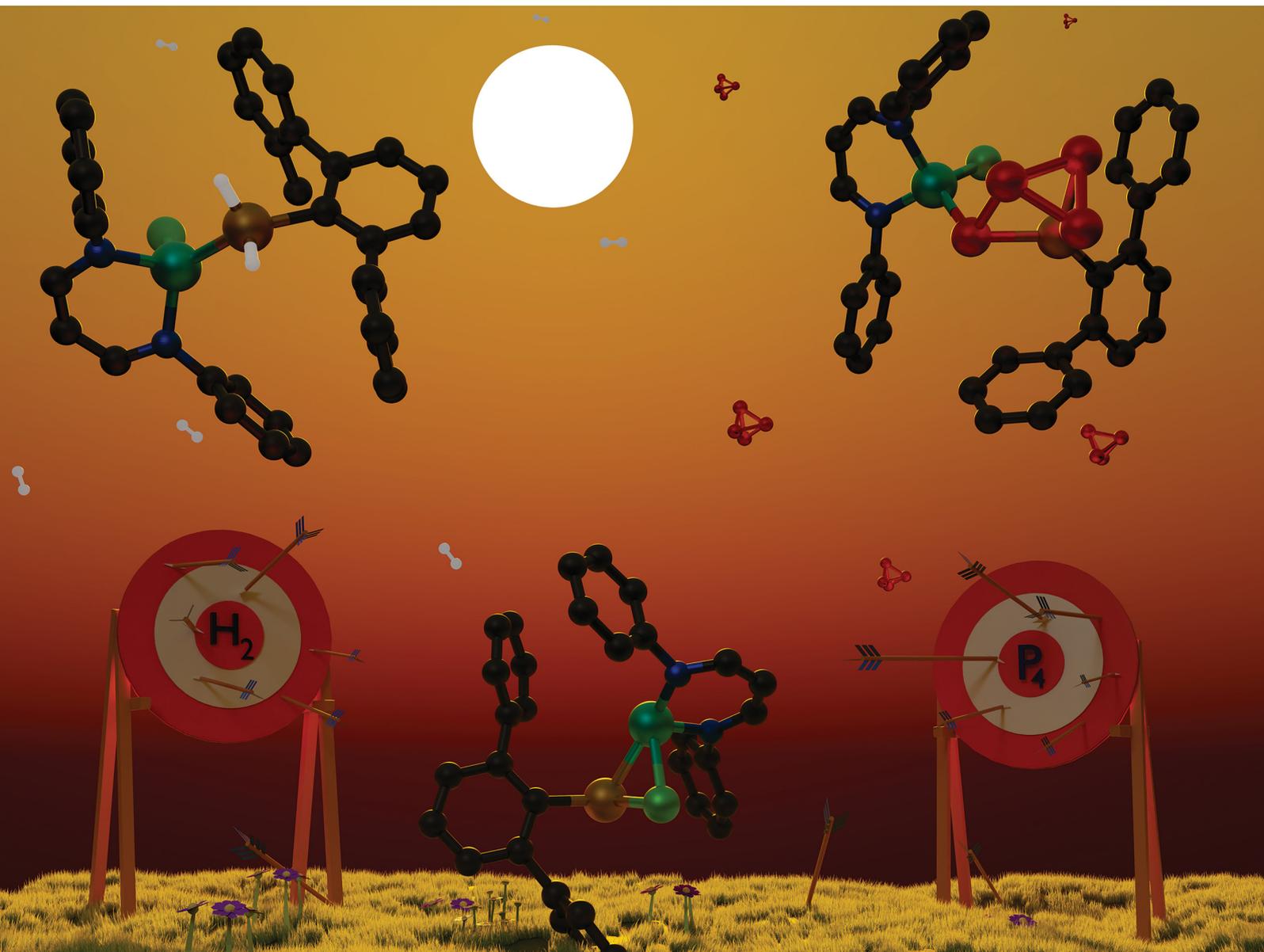


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Activation of non-polar bonds by an electron-rich gallagermylene†

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The electron-rich germylene $L\text{Ga}(\mu\text{-Cl})\text{GeAr}^{\text{Mes}}$ (**1**) ($L = \text{CH}[\text{C}(\text{Me})\text{N}(\text{Dipp})]_2$, $\text{Dipp} = 2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3$, $\text{Ar}^{\text{Mes}} = 2,6\text{-Mes}_2\text{C}_6\text{H}_3$, $\text{Mes} = 2,4,6\text{-Me}_3\text{C}_6\text{H}_2$) shows promising potential in the σ -bond activation of unpolar molecules as is shown in oxidative addition reactions with H_2 and P_4 , yielding $\text{L}(\text{Cl})\text{GaGe}(\text{H})_2\text{Ar}^{\text{Mes}}$ (**2**) and $\text{L}(\text{Cl})\text{Ga}(\text{P}_4)\text{GeAr}^{\text{Mes}}$ (**3**). Compounds **2** and **3** were characterised spectroscopically (^1H , $^{13}\text{C}\{^1\text{H}\}$, $^{31}\text{P}\{^1\text{H}\}$, IR) and by single-crystal X-ray diffraction (sc-XRD).

The activation of small molecules, *i.e.*, H_2 , CO, CO_2 , NH_3 , P_4 or ethylene, and their utilization for synthetic purposes including catalytic reactions is of fundamental importance in chemistry. While such reactions have been dominated by transition metal complexes for decades, the use of low valent main group complexes, whose electronic nature mimics that of transition metal complexes, has received increasing interest in recent years.¹ In particular the activation and cleavage of strong non-polar σ -bonds, *i.e.*, the H–H bond of H_2 , has received increasing attention. The reaction of the digermene $\text{Ar}^{\text{Dipp}}\text{GeGeAr}^{\text{Dipp}}$ ($\text{Ar}^{\text{Dipp}} = 2,6\text{-Dipp}_2\text{C}_6\text{H}_3$; $\text{Dipp} = 2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3$) with H_2 , which was reported by Power *et al.*, represents a milestone since the digermene $\text{Ar}^{\text{Dipp}}(\text{H})\text{Ge}=\text{Ge}(\text{H})\text{Ar}^{\text{Dipp}}$ and the germanes $\text{Ar}^{\text{Dipp}}(\text{H})_2\text{GeGe}(\text{H})_2\text{Ar}^{\text{Dipp}}$ and $\text{Ar}^{\text{Dipp}}\text{Ge}(\text{H})_3$ were formed under very mild reaction conditions.² Later on, the amido-substituted digermynes $[\text{L}^{1,2}\text{Ge}]_2$ ($\text{L}^1 = \text{N}(\text{SiMe}_3)(\text{Ar}^1)$, $\text{Ar}^1 = 2,6\text{-}(\text{CHPh}_2)_2\text{-4-MeC}_6\text{H}_2$; $\text{L}^2 = \text{N}(\text{Si}^i\text{Pr}_3)(\text{Ar}^2)$, $\text{Ar}^2 = 2,6\text{-}(\text{CHPh}_2)_2\text{-4-}^i\text{PrC}_6\text{H}_2$)³ were found to be active in H_2 activation, yielding $\text{L}^1\text{Ge}(\text{H})_2\text{GeL}^1$,^{3a} and $\text{L}^2(\text{H})\text{GeGe}(\text{H})\text{L}^2$,^{3b} respectively. Since then, reactions of H_2 with digermynes RGeGeR ,^{1a} digermavinylidene (L^3B)₂GeGe ($\text{L}^3\text{B} = [\text{HCN}(\text{Dipp})]_2\text{B}$), which reacted with

H_2 (4 atm) to the symmetric digermene $[\text{L}^3\text{BGe}(\text{H})_2]_2$,^{4a} and with a digermynyl aluminum complex, which slowly activated H_2 (1 atm) at ambient temperature,^{4b} have been reported.

In marked contrast, H_2 activation reactions of germylenes R_2Ge have been reported only rarely.⁵ H_2 activation by aryl-substituted germylenes $\text{Ar}^{\text{Mes}}_2\text{Ge}$ (**A**) ($\text{Ar}^{\text{Mes}} = 2,6\text{-Mes}_2\text{-C}_6\text{H}_3$, $\text{Mes} = 2,4,6\text{-Me}_3\text{-C}_6\text{H}_2$) and $\text{Ar}^{\text{Dipp}}_2\text{Ge}$ proceeded either *via* the formation of the corresponding germane $\text{Ar}^{\text{Mes}}_2\text{GeH}_2$ or with the release of the ligand $\text{Ar}^{\text{Dipp}}\text{H}$ and $\text{Ar}^{\text{Dipp}}\text{GeH}_3$.^{6a} The crucial influence of the organic ligand on the germylene reactivity was demonstrated by Aldridge *et al.* by comparing different acyclic germylenes $\text{Ar}^{\text{Mes}}\text{GeR}'$ ($\text{R}' = \text{N}(\text{Dipp})\text{H}$, $\text{CH}(\text{SiMe}_3)_2$, $\text{P}(\text{SiMe}_3)_2$ and $\text{Si}(\text{SiMe}_3)_3$ (**B**)).^{6b} Electropositive ligands lead to smaller HOMO–LUMO gaps, resulting in an increased reactivity. This was further demonstrated by Jones *et al.* for the acyclic zinca-germylene $(\text{TBoN})(\text{L}^4\text{Zn})\text{Ge}$ ($\text{TBoN} = \text{N}(\text{SiMe}_3)\{\text{B}[\text{N}(\text{Dipp})\text{CH}]_2\}$; $\text{L}^4 = \text{N}(\text{Si}^i\text{Pr}_3)(\text{Ar}^1)$ (**C**), which reacted in toluene solution with H_2 at r.t. within five seconds to the corresponding germanium(IV) dihydride.^{6c} In contrast, the cationic tungstagermylene $[\text{Cp}^*(\text{CO})_3\text{WGe}(\text{IDipp})](\text{BAR}_4^{\text{F}})$ ($\text{IDipp} = [\text{HCN}(\text{Dipp})]_2\text{C}$; $\text{Ar}^{\text{F}} = 3,5\text{-}(\text{CF}_3)_2\text{C}_6\text{H}_3$) (1 atm, 60 °C, 24 h)^{6d} and a PMe_3 -coordinated cyclic (alkyl)(boryl)germylene (1 atm, 50 °C, 12 h) reacted with H_2 only at elevated temperatures to the corresponding germanes.^{6e}

Due to its fundamental interest, the activation of H_2 in reactions with metallylenes was further investigated by use of relativistic density functional theory (DFT), showing that the decreasing reactivity of tetrylenes from carbenes to stannylenes mainly results from a worsening of the back-donation from the tetrylene lone-pair orbital and the H_2 σ^* -orbital, despite an increase in interaction energy of the LUMO of the tetrylene and the HOMO of H_2 . However, decreasing the electronegativity of the tetrylene ligand resulted in significantly lower reaction barriers due to a reduced Pauli repulsion, which was identified as a main hindrance.⁷

In addition, the activation of non-polar P–P σ -bonds of white phosphorus (P_4) is also of broad interest.⁸ Among several pathways, oxidative addition reactions of P_4 to tetrylenes, in

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† Electronic supplementary information (ESI) available: Experimental and analytical data (NMR, IR spectra, crystallographic data) and details from DFT calculations. CCDC 2321151 (**2**) and 2321152 (**3**) contain the supplementary crystallographic data for this paper. For ESI and crystallographic data in CIF or other electronic format see DOI: <https://doi.org/10.1039/d3cc06223f>



particular silylenes,⁹ have been reported. In contrast, reactions of heavier tetrylenes with P₄ are rather scarce.¹⁰ The acyclic germylene Ar^{Mes}₂Ge was found to reversibly activate P₄,^{10a} while we demonstrated the beneficial effect of electropositive metal-based ligands in L(Cl)M-SiL⁵ (L = HC[C(Me)N(Dipp)]₂, L⁵ = PhC[N(^tBu)]₂, M = Al, Ga), which reacted in an unprecedented [2+1+1] fragmentation reactions with P₄.^{9f} In addition, the reaction of L(Cl)Ga-SiL⁵ with Cp*Fe(η⁵-Pn₅) (Pn = P, As) resulted in Pn-Pn and Si-Ga bond cleavage, which is caused by the insertion of the silylene into the *cyclo*-Pn₅ rings.¹¹

We recently reported the synthesis of the unusual Cl-bridged gallagermylene LGa(μ-Cl)GeAr^{Mes} (Ar^{Mes} = 2,6-Mes₂C₆H₃, Mes = 2,4,6-Me₃C₆H₂) (**1**),^{12a} which reacted with CO₂ with activation of the polar C-O double bond (decarbonylation) to the germylene ether, whereas reactions with isocyanates and carbodiimides proceeded with insertion into the Ga-Ge bond.^{12b} In addition, **1** reacted with ethylene with insertion into the Ga-Ge bond followed by dimerization of the as-formed germylene to the corresponding digermene, which then reacted with ethylene in a [2+2] cycloaddition to the 1,2-digermacyclobutane.^{12c}

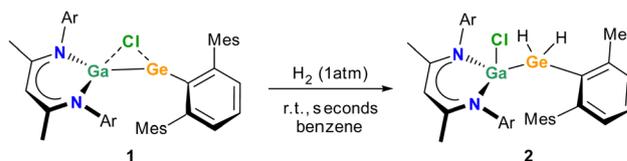
These promising reactivity studies prompted us to analyse the electronic structure of **1** in more detail by use of ORCA 5.0.4^{13a} and the NBO program package (version 7.0.10)^{13b} at the def2-TZVPP level of theory (def2-QZVP for E > Ne)^{13c} using the atom-pairwise dispersion correction based on tight binding partial charges (D4)^{13d,e} with the PBE0^{13f,g} functional and to compare the electronic structure of germylene **1** with that of the acyclic germylenes **A**, **B** and **C**, respectively. As we reported previously,^{12a} the geometry optimization resulted in a shift of the chlorine atom to the Ge atom (structure **1_{opt}**). Our computations (Table 1) indicate a decreasing natural partial charge of the Ge atom going from **A** to **1_{opt}**/C, which agrees with the increasing electropositive character of the respective ligands.

Although the electronic structures of the acyclic germylenes including the HOMO-LUMO gaps are comparable, an increase of the energy gap (ΔE_{HOMO-LUMO}) from **A** to **1_{opt}** is observed (Table 1). However, the relative energetic locations of the frontier orbitals indicate more destabilized orbitals of **1_{opt}**, which might enhance the relevant orbital interaction between the germylene lone-pair and the H₂ σ*-orbital. The activation of non-polar σ-bonds by use of germylene **1_{opt}** therefore seemed reasonable and we studied its reactions with H₂ and P₄, respectively.

The dark red solution solution of **1** in benzene-*d*₆ immediately turned colourless upon expose to a H₂ atmosphere at ambient temperature (Scheme 1). According to *in situ* ¹H NMR

Table 1 Natural partial charge *Q* of Ge [e], HOMO-LUMO (ΔE_{HOMO-LUMO}) [eV] and frontier orbital energies *E* [eV] of germylenes **A-C** and **1_{opt}**

	<i>Q</i> (Ge)	<i>E</i> _{HOMO}	<i>E</i> _{LUMO}	Δ <i>E</i> _{HOMO-LUMO}
A	+1.13	-5.25	-1.96	3.29
B	+0.78	-5.26	-2.13	3.13
C	+0.41	-5.15	-1.64	3.51
1_{opt}	+0.45	-4.98	-1.32	3.67



Scheme 1 Synthesis of **2** by reaction of germylene **1** with H₂.

spectroscopic studies, the formation of L(Cl)GaGe(H)₂Ar^{Mes} (**2**) is immediately completed (ESI,† Fig. S9) and the activation of H₂ proceeded much faster and under milder conditions than observed with germylenes **A** and **B** and almost as fast as **C** (Fig. 1). Even though the computed electronic structures of the germylenes **1** and **C** are hardly comparable, the significant faster reaction rate observed with germylene **1** compared to **A** and **B** can be attributed to a combination of reduced positive charge of the Ge atom and of destabilized frontier orbitals.

Germane **2** is soluble in benzene, toluene and *n*-hexane, and its ¹H and ¹³C{¹H} NMR spectra show the expected resonances of the β-ketiminato and the terphenyl ligands. The characteristic Ge-H resonance was detected at 3.33 ppm, which is shifted to higher field compared to previously reported germanes (Ar^{Mes}₂GeH₂: 4.61 ppm^{6a} (Ar^{Mes})(Si(SiMe₃)₃)GeH₂: 3.90 ppm^{6b} (TBoN)(L²Zn)GeH₂: 3.88 ppm^{6c}). The FT-IR spectrum shows Ge-H stretching bands at ν = 2019 and 1942 cm⁻¹, respectively, which is in a comparable range reported for (TBoN)(L³Zn)GeH₂ (2054, 1995 cm⁻¹)^{6c} and Ar^{Mes}₂GeH₂ (2113, 1731 cm⁻¹).^{6a}

Crystals of **2** suitable for a single crystal X-ray diffraction (sc-XRD) study were grown from a saturated benzene solution at 6 °C. **2** crystallises in the triclinic space group *P* $\bar{1}$ as colourless blocks (Fig. 2).

The Ga-Ge (2.4381(3) Å) and Ge-C bond lengths (1.9725(16) Å) of **2** are slightly shortened compared to those of **1** (Ga-Ge: 2.4678(4) Å, Ge-C: 2.022(2) Å),^{12a} while the Ge-C bond lengths reported for (Ar^{Mes})(Si(SiMe₃)₃)GeH₂ (1.973(6) Å) and Ar^{Mes}₂GeH₂ (1.973(3) Å) are almost identical. The Ga-Cl bond length (2.2341(5) Å) of **2** is within the known range for L(Cl)Ga ligands but much shorter compared to the Cl-bridged complex **1** (Ga-Cl: 2.6076(6) Å).^{12a} The Ga-Ge-C bond angle is widened from 113.86(6)° in **1** to 129.19(5)° in **2** as was also observed for germanes (Ar^{Mes})₂GeH₂ (C-Ge-C: 127.9(2)°), [(Me₃Si)₃Si]Ge(H)₂(Ar^{Mes}) (Si-Ge-C: 125.8(2)°) and (TBoN)(L²Zn)GeH₂

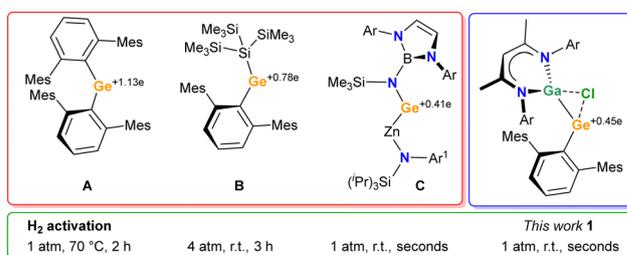


Fig. 1 Selected acyclic germylenes, which are active in H₂ activation, including computed natural charges. The natural charge of **1** refers to the charge of **1_{opt}** (*vide infra*). Mes = 2,4,6-Me₃C₆H₂, Ar = 2,6-ⁱPr₂C₆H₃, Ar¹ = 2,6-(CHPh)₂-4-MeC₆H₂.



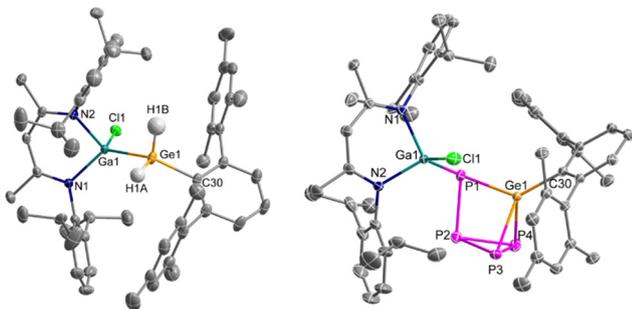


Fig. 2 Crystal structures of compounds **2** (left) and **3** (right) with thermal ellipsoid (50%); H atoms except for GeH₂, disorder and solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: **2**: Ga1–Ge1: 2.4381(3), Ge1–C30: 1.9725(16), Ga1–Cl1: 2.2341(5); Ga1–Ge1–C30: 129.19(5); **3**: Ga1–P1: 2.3486(3), Ga1–Cl1: 2.2018(4), P1–P2: 2.2557(5), P2–P3: 2.2154(5), P3–P4: 2.2694(6), P2–P4: 2.20879(5), P1–Ge1: 2.3165(3), P3–Ge1: 2.3001(4), P4–Ge1: 2.3344(4), Ge1–C30: 1.9600(11), Ga1–P1–Ge1: 107.142(14), P1–Ge1–P3: 96.355(13), P1–Ge1–P4: 89.406(14), P3–Ge1–P4: 58.633(15), P1–Ge1–C30: 132.63(3), P1–P2–P3: 100.612(18), P1–P2–P4: 94.237(19), P3–P2–P4: 61.720(17), P2–P3–P4: 59.000(17), P2–P4–P3: 59.280(16).

(Zn–Ge–N: 119.04(9)°), synthesised by oxidative addition of H₂ to the corresponding germylenes **A** (C–Ge–C: 114.4(2)°), **B** (Si–Ge–C: 112.7(1)°) and **C** (Zn–Ge–N: 107.8(1)°), respectively.

To further evaluate the reactivity of the electron-rich germylene **1** toward unpolar compounds, we reacted **1** with white phosphorus. The reaction of **1** with P₄ in benzene-*d*₆ solution is completed after one minute at r.t. according to *in situ* ¹H NMR spectroscopy (ESI,† Fig. S10) to yield compound **3** (Scheme 2). Compound **3** contains a P₄^{2−} moiety, which is formed by a consecutive activation/functionalization reaction of P₄, which occurred with the cleavage of two P–P bonds and the regioselective formation of three new Ge–P and one Ga–P bonds, respectively. A comparable 1,2-silyl migration was only once reported for the reaction of vinyl(silyl)silylene with P₄, which also occurred with formation of a P₄^{2−} unit.^{9c} However, in contrast to silylenes, which have been frequently reported to activate P₄,⁹ **1** belongs to the very short list of heavier tetrylenes capable for P₄ activation. Only the acyclic germylene **A**^{10a} and the acyclic stannylenes Ar^{Mes}SnSi^tBu₃^{10b} were found to react with white phosphorus with insertion into one P–P bond. However, both complexes were found to release P₄ under UV light irradiation. In addition, the distannyne {[(Dipp)NC(CH₃)₂C₆H₃Sn]₂}^{10c} has been reported to react with P₄.

3 is poorly soluble in *n*-hexane but well soluble in toluene and benzene. Its ¹H NMR and ¹³C{¹H} spectra show the expected resonances of the β-diketiminato and terphenyl ligands. The ³¹P NMR spectra of **3** shows four resonances

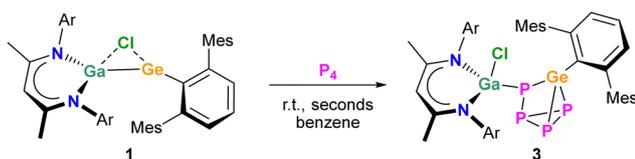
(198.5, −72.3, −378.6, −434.5 ppm) due to the magnetic inequivalency of the four P atoms, whereas three resonances (120.0, −181.0, −316.7 ppm) were reported for [Me^eIDippC(H)]-Si(P₄)[Si(SiMe₃)₃]^{9c} (Me^eIDipp = [(Me)CN(Dipp)]₂C).

Crystals of **3** suitable for sc-XRD analysis were obtained from a solution in hot *n*-hexane. **3** crystallises in the monoclinic space group *C2/c* as light-yellow platelets (Fig. 2). The Ge–P bond lengths are almost identical (2.3001(4) Å, 2.3165(3) Å, 2.3344(4) Å) and comparable to the Ge–P bond lengths reported for (Ar^{Mes})₂Ge(P₄) (2.3433(7) Å, 2.3509(9) Å). The Ge–C bond length of 1.9600(11) Å in **3** is slightly shorter compared to those in (Ar^{Mes})₂Ge(P₄) (Ge–C: 1.9975(12) Å, 1.9932(12) Å),^{10a} and the P–P bond lengths (2.2557(5) Å, 2.2089(5) Å, 2.154(5) Å, 2.2694(6) Å) vary in a slightly larger range compared to the P–P bond lengths [Me^eIDippC(H)]Si(P₄)[Si(SiMe₃)₃] (P–P: 2.2555(12) Å, 2.2262(12) Å, 2.2057(13) Å, 2.2615(10) Å).^{9c} The Ga–P bond length (2.3486(3) Å) is within the typical range of gallandiyl coordinated compounds (2.343(9)–2.405(8) Å) obtained from the reaction of LGa with P₄.¹⁴ In contrast, the Ga–P bond length (2.2510(3) Å) in [L(Cl)GaPSi(L⁵)P]₂, which formed in the [2+1+1] fragmentation reaction of P₄ with L(Cl)Ga-SiL⁵, is significantly shorter.^{9f} The P2–P3–P4 bond angle (59.000(17)°) is almost identical to the corresponding angle in [Me^eIDippC(H)]Si(P₄)-[Si(SiMe₃)₃] (58.96(4)°).^{9c}

The marked reactivity differences between the gallagermylene **1** and (Ar^{Mes})₂Ge **A** in the P₄ activation reaction point to a beneficial effect of the electropositive L(Cl)Ga substituent, which results in a lower formal charge of the Ge atom in **1** (*vide supra*). The oxidative addition of one P–P bond of P₄ to the germylene centre in **1** proceeded much faster than observed with germylene **A**, which required four days at r. t. to achieve 75% yield.^{10a} Moreover, gallagermylene **1** not only reacted with insertion of the germylene unit into one P–P bond, which is typically observed in reactions of tetrylenes with P₄, but with additional 1,2-migration of the L(Cl)Ga substituent from the Ge to the P atom. The migration of the L(Cl)Ga substituent was also recently observed in the P–P bond activation of the P₅ ring in Cp*Fe(η⁵-P₅) upon reaction with L(Cl)Ga-SiL⁵,¹¹ whereas heavier analogue L(Cl)Ga-GeL⁵ failed to activate Cp*Fe(η⁵-P₅), clearly demonstrating the higher reactivity of Cl-bridged gallagermylene **1** compared to L(Cl)Ga-GeL⁵.

To conclude, the gallagermylene **1** shows promising potential in the activation of stable, non-polar σ-bonds of small molecules as was exemplarily demonstrated in the σ-bond activation reaction of H₂, which is completed at ambient conditions within seconds. The high reactivity of **1** most likely results from the destabilisation of the HOMO and the beneficial effect of the electropositive L(Cl)Ga ligand. In addition, **1** represents a very rare example of a germylene that activates P₄ in an unusual activation/functionalization manner, resulting in formation of a P₄^{2−} unit as was previously only observed with an electron-rich vinyl(silyl)silylene.

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Scheme 2 Synthesis of **3** by reaction of germylene **1** with P₄.



Conflicts of interest

There are no conflicts to declare.

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