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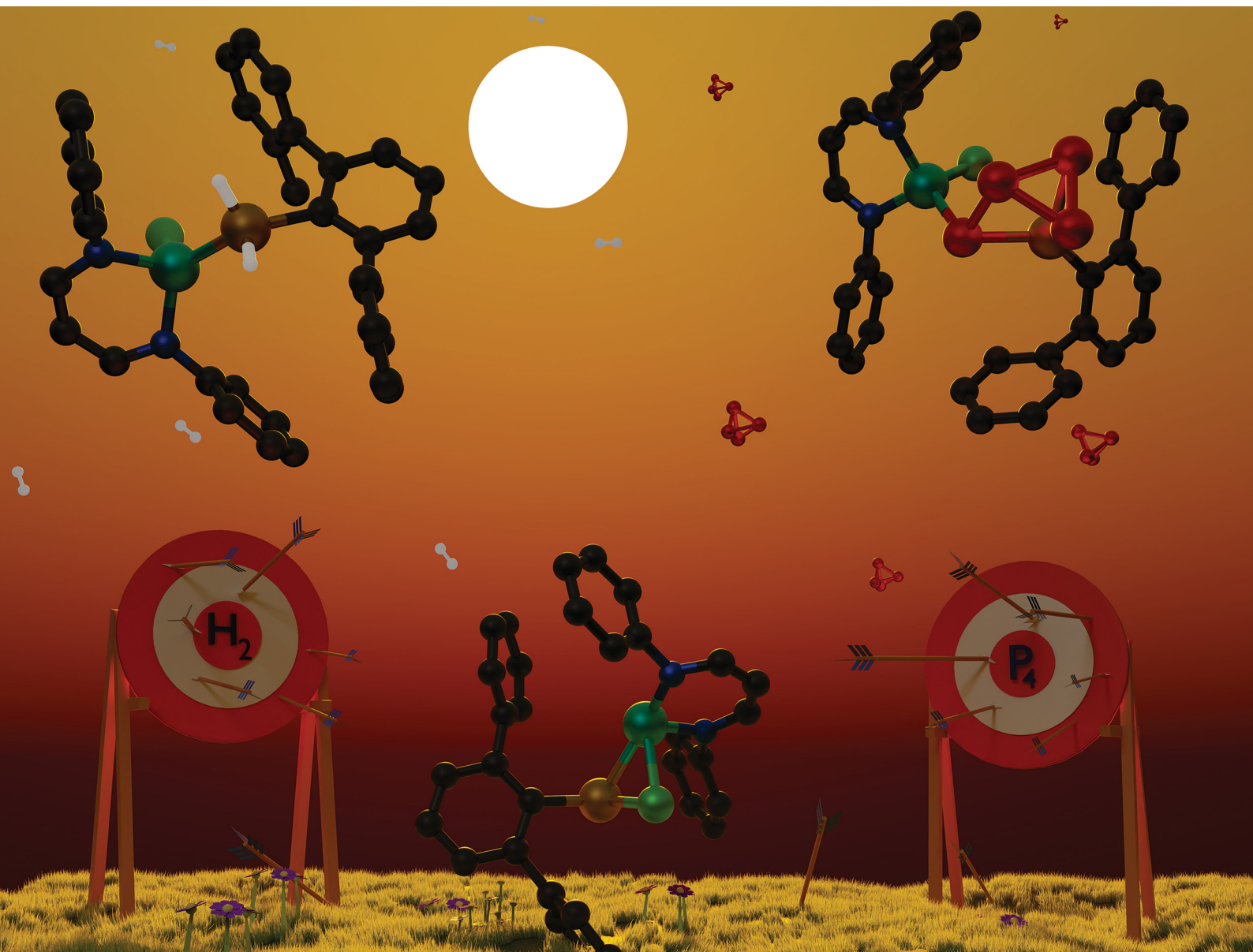
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Stephan Schulz *et al.*
Activation of non-polar bonds by an electron-rich
gallagermylene

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

Anna Bücker,[a] Alexander Gehlhaar,[a] Christoph Wölper[a] and Stephan Schulz ⓘ *[ab]

The electron-rich germylene LGa(μ–Cl)GeAr^{Mes} (**1**) (L = CH[C(Me)N(Dipp)]$_2$, Dipp = 2,6-^{i}Pr$_2$C$_6$H$_3$, Ar^{Mes} = 2,6-Mes$_2$C$_6$H$_3$, Mes = 2,4,6-Me$_3$C$_6$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 L(Cl)GaGe(H)$_2$Ar^{Mes} (**2**) and L(Cl)Ga(P$_4$)GeAr^{Mes} (**3**). Compounds **2** and **3** were characterised spectroscopically (^{1}H, ^{13}C{^{1}H}, ^{31}P{^{1}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 digermyne Ar^{Dipp}GeGeAr^{Dipp} (Ar^{Dipp} = 2,6-Dipp$_2$C$_6$H$_3$; Dipp = 2,6-^{i}Pr$_2$C$_6$H$_3$) with H$_2$, which was reported by Power *et al.*, represents a milestone since the digermene Ar^{Dipp}(H)Ge=Ge(H)Ar^{Dipp} and the germanes Ar^{Dipp}(H)$_2$GeGe(H)$_2$Ar^{Dipp} and Ar^{Dipp}Ge(H)$_3$ were formed under very mild reaction conditions.[2] Later on, the amido-substituted digermynes [L^{1,2}Ge]$_2$ (L^1 = N(SiMe$_3$)(Ar^1), Ar^1 = 2,6-(CHPh$_2$)$_2$-4-MeC$_6$H$_2$; L^2 = N(Si^{i}Pr$_3$)(Ar^2), Ar^2 = 2,6-(CHPh$_2$)$_2$-4-^{i}PrC$_6$H$_2$)[3] were found to be active in H$_2$ activation, yielding L^{1}Ge(H)$_2$GeL^1,[3a] and L^2(H)GeGe(H)L^2,[3b] respectively. Since then, reactions of H$_2$ with digermynes RGeGeR,[1a] digermavinylidene (L^{3}B)$_2$GeGe (L^{3}B = [HCN(Dipp)]$_2$B), which reacted with

H$_2$ (4 atm) to the symmetric digermane [L^{3}BGe(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$_2$Ge have been reported only rarely.[5] H$_2$ activation by aryl-substituted germylenes Ar^{Mes}Ge (**A**) (Ar^{Mes} = 2,6-Mes$_2$-C$_6$H$_3$, Mes = 2,4,6-Me$_3$-C$_6$H$_2$) and Ar^{Dipp}Ge proceeded either *via* the formation of the corresponding germane Ar^{Mes}GeH$_2$ or with the release of the ligand Ar^{Dipp}H and Ar^{Dipp}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 Ar^{Mes}GeR′ (R′ = N(Dipp)H, CH(SiMe$_3$)$_2$, P(SiMe$_3$)$_2$ and Si(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 (TBoN)(L^{4}Zn)Ge (TBoN = N(SiMe$_3$){B[N(Dipp)CH]$_2$}; L^4 = N(Si^{i}Pr$_3$)(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 tungstagermy-lene [Cp*(CO)$_3$WGe(IDipp)](BAr$_4$^{F}) (IDipp = [HCN(Dipp)]$_2$C; Ar^F = 3,5-(CF$_3$)$_2$C$_6$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 σ-lone-pair orbital and the H$_2$ σ*-orbital, despite an increase in interaction energy of the LUMO of the terylene 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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particular silylenes,[9] have been reported. In contrast, reactions of heavier tetrylenes with P_4 are rather scarce.[10] The acyclic germylene Ar^{Mes}_2Ge was found to reversibly activate P_4,[10a] while we demonstrated the beneficial effect of electropositive metal-based ligands in L(Cl)M-SiL[5] (L = HC[C(Me)N(Dipp)]$_2$, L[5] = PhC[N(^{t}Bu)]$_2$, M = Al, Ga), which reacted in an unprecedented [2+1+1] fragmentation reactions with P_4.[9f] In addition, the reaction of L(Cl)Ga-SiL[5] with Cp*Fe(η^5-Pn$_5$) (Pn = P, As) resulted in Pn–Pn and Si–Ga bond cleavage, which is caused by the insertion of the silylene into the *cyclo*-Pn$_5$ rings.[11]

We recently reported the synthesis of the unusual Cl-bridged gallagermylene LGa(μ–Cl)GeAr^{Mes} (Ar^{Mes} = 2,6-Mes$_2$C$_6$H$_3$, Mes = 2,4,6-Me$_3$C$_6$H$_2$) (**1**),[12a] which reacted with CO_2 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 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 ($\Delta E_{HOMO-LUMO}$) 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 H_2 σ*-orbital. The activation of non-polar σ-bonds by use of germylene **1_opt** therefore seemed reasonable and we studied its reactions with H_2 and P_4, respectively.

The dark red solution solution of **1** in benzene-d_6 immediately turned colourless upon expose to a H_2 atmosphere at ambient temperature (Scheme 1). According to *in situ* ^1H NMR
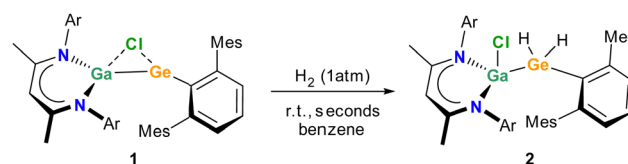
Scheme 1 Synthesis of **2** by reaction of germylene **1** with H_2.

spectroscopic studies, the formation of L(Cl)GaGe(H)$_2$Ar^{Mes} (**2**) is immediately completed (ESI,† Fig. S9) and the activation of H_2 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 ^{13}C{^{1}H} NMR spectra show the expected resonances of the β-ketiminate 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$^{Mes}_2$GeH$_2$: 4.61 ppm[6a] (Ar^{Mes})(Si(SiMe$_3$)$_3$)GeH$_2$: 3.90 ppm[6b] (TBoN)(L^{2}Zn)GeH$_2$: 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)(L^{3}Zn)GeH$_2$ (2054, 1995 cm^{-1})[6c] and Ar$^{Mes}_2$GeH$_2$ (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(SiMe$_3$)$_3$)GeH$_2$ (1.973(6) Å) and Ar$^{Mes}_2$-GeH$_2$ (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})$_2$GeH$_2$ (C-Ge-C: 127.9(2)°), [[Me$_3$Si]$_3$Si] Ge(H)$_2$(Ar^{Mes}) (Si-Ge-C: 125.8(2)°) and (TBoN)(L^{2}Zn)GeH$_2$

Fig. 1 Selected acyclic germylenes, which are active in H_2 activation, including computed natural charges. The natural charge of **1** refers to the charge of **1_opt** (*vide infra*). Mes = 2,4,6-Me$_3$C$_6$H$_2$, Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$, Ar^1 = 2,6-(CHPh$_2$)$_2$-4-MeC$_6$H$_2$.

Table 1 Natural partial charge Q of Ge [e], HOMO–LUMO ($\Delta E_{HOMO-LUMO}$) [eV] and frontier orbital energies E [eV] of germylenes **A–C** and **1_opt**

	Q(Ge)	E_{HOMO}	E_{LUMO}	$\Delta E_{HOMO-LUMO}$
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
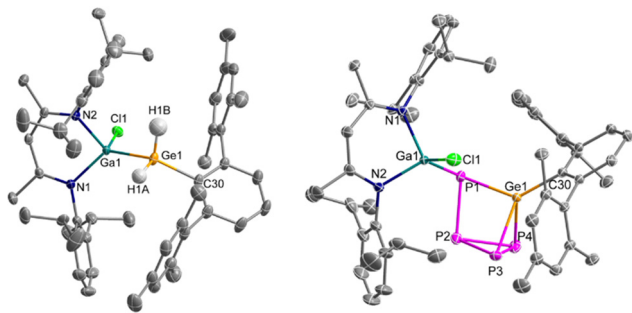
Fig. 2 Crystal structures of compounds **2** (left) and **3** (right) with thermal ellipsoid (50%); H atoms except for GeH$_2$, disorder and solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: **2**: Ga1–Ge1: 2.4381(3), Ge1–C30: 1.9725(16), Ga1–Cl1: 2.2341(5); Ga1–Ge1–C30: 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: 2.208.79(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 H$_2$ 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 P$_4$ in benzene-d_6 solution is completed after one minute at r.t. according to *in situ* ^{1}H NMR spectroscopy (ESI,† Fig. S10) to yield compound **3** (Scheme 2). Compound **3** contains a P$_4^{2-}$ moiety, which is formed by a consecutive activation/functionalization reaction of P$_4$, 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 P$_4$, which also occurred with formation of a P$_4^{2-}$ unit.[9c] However, in contrast to silylenes, which have been frequently reported to activate P$_4$,[9] **1** belongs to the very short list of heavier tetrylenes capable for P$_4$ activation. Only the acyclic germylene **A**[10a] and the acyclic stannylene Ar^{Mes}SnSi^{t}Bu$_3$[10b] were found to react with white phosphorus with insertion into one P–P bond. However, both complexes were found to release P$_4$ under UV light irradiation. In addition, the distannyne {[[(Dipp)NC(CH$_3$)]$_2$C$_6$H$_3$Sn}$_2$[10c] has been reported to react with P$_4$.

3 is poorly soluble in *n*-hexane but well soluble in toluene and benzene. Its ^{1}H NMR and ^{13}C{^{1}H} spectra show the expected resonances of the β-diketiminate and terphenyl ligands. The ^{31}P 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}IDippC(H)]-Si(P$_4$)[Si(SiMe$_3$)$_3$][9c] (^{Me}IDipp = [(Me)CN(Dipp)]$_2$C).

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})$_2$Ge(P$_4$) (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})$_2$Ge(P$_4$) (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}IDippC(H)]Si(P$_4$)[Si(SiMe$_3$)$_3$] (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 gallandiyle coordinated compounds (2.343(9)–2.405(8) Å) obtained from the reaction of LGa with P$_4$.[14] In contrast, the Ga–P bond length (2.2510(3) Å) in [L(Cl)GaPSi(L^5)P]$_2$, which formed in the [2+1+1] fragmentation reaction of P$_4$ with L(Cl)Ga-SiL^5, is significantly shorter.[9f] The P2–P3–P4 bond angle (59.000(17)°) is almost identical to the corresponding angle in [^{Me}IDippC(H)]Si(P$_4$)-[Si(SiMe$_3$)$_3$] (58.96(4)°).[9c]

The marked reactivity differences between the gallagermylene **1** and (Ar^{Mes})$_2$Ge **A** in the P$_4$ 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 P$_4$ 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 P$_4$, 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 P$_5$ ring in Cp*Fe(η^5-P$_5$) upon reaction with L(Cl)Ga-SiL^5,[11] whereas heavier analogue L(Cl)Ga-GeL^5 failed to activate Cp*Fe(η^5-P$_5$), clearly demonstrating the higher reactivity of Cl-bridged gallagermylene **1** compared to L(Cl)Ga-GeL^5.

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 H$_2$, 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 P$_4$ in an unusual activation/functionalization manner, resulting in formation of a P$_4^{2-}$ unit as was previously only observed with an electron-rich vinyl(silyl)silylene.
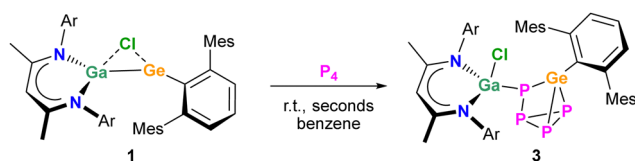
Scheme 2 Synthesis of **3** by reaction of germylene **1** with P$_4$.

Conflicts of interest

There are no conflicts to declare.

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