Intramolecular donor-stabilized tetra-coordinated germanium(IV) di-cations and their Lewis acidic properties†

Balakrishna Peddi,‡a Souvik Khan,‡a Rajesh G. Gonnade,‡b Cem B. Yildiz‡bc and Moumita Majumdar‡a

We report the first examples of intramolecular phosphate-stabilized tetra-coordinated germanium(IV) dications: \([\text{LiPrF}_2\text{GeF}_2\text{CF}_3\text{SO}_3\text{]}_2\) and \([\text{LiPr}_2\text{GeF}_2\text{CF}_3\text{SO}_3\text{]}_2\) (LPr = 6-(disopropylphosphanyl)-1,2-di-hydroacenaphthenylene-5-ide; LPr = 6-(diphenylphosphanyl)-1,2-di-hydroacenaphthenylene-5-ide). The step wise synthetic strategy involves the isolation of neutral and mono-cationic Ge(IV) precursors: \([\text{LiPr}_2\text{GeCl}_{2}\text{]}_2\) (X = Cl, OTf) and \([\text{LiPr}_2\text{GeCl}_2\text{]}_2\text{Ph}\) and \([\text{LiPr}_2\text{GeCl}_2\text{]}_2\text{OTf}\). Both 3Pr and 3Ph exhibit constrained spiro-geometry. DFT studies reveal the dispersion of di-cationic charges over P–Ge–P sites. Anion or Lewis base binding occurs at the Ge site resulting in relaxed distorted trigonal bipyramidal/tetrahedral geometry. 3Pr and 3Ph activate the Si–H bond initially at the P-site. The hydride ultimately migrates to the Ge-site rapidly giving \([\text{LPh}_2\text{GeCl}_{2}\text{CF}_3\text{SO}_3\text{]}_2\) 3PhH, while sluggishly forming \([\text{LPh}_2\text{GeH}_{2}\text{CF}_3\text{SO}_3\text{]}_2\) and \([\text{LPh}_2\text{GeCl}_{2}\text{CF}_3\text{SO}_3\text{]}_2\). Compounds 3Pr and 3Ph were tested as catalysts for the hydrosilylation of aromatic aldehydes. While catalytic hydrosilylation proceeded via the initial Et3Si–H bond activation in the case of 3Pr, compound 3Ph as a catalyst showed a masked Frustrated Lewis Pair (FLP) type reactivity in the catalytic cycle.

Introduction

Germanium(IV) di-cations stabilized by neutral Lewis bases have been known for long, possessing inherent electrophilicity and rarely exhibiting nucleophilic behaviour. In contrast there are only very few examples of Ge(IV) di-cations known, which are stabilized by hyper-coordination involving neutral donors: \([\text{LGeF}_2\text{]}_2^\text{2+}\) \((\text{L} = \text{tris}(1\text{-ethylbenzoimidazol-2-ylmethyl})\text{amine})\) (Fig. 1A), \([\text{GeF}_2(\text{OTf})_2]\) \((\text{OTf} = \text{CF}_3\text{SO}_3\text{)}\) coordinated by two mono-dentate phosphate donors or bi-dentate chelating phosphine donors (Fig. 1B), and \([\text{Me}_2\text{Ge}(\text{OTf})_2]\) coordinated by two 4-N,N'-dimethylaminopyridine (DMAP) units or a 2,2'-bipyridine (Fig. 1C). Alongside in silicon chemistry, terpyridine-stabilized silicon(IV) di-cations \((\text{R}_2\text{Si}_2^\text{2+})\), tri-cations \((\text{R}_3\text{Si}^\text{3+})\), and silicon tetrakis(trifluoromethanesulfonate) have been established as Lewis superacids in recent times. The uses of Ge(IV) di-cations as Lewis acids hold immense potential; however they are yet to be unfolded. In general, while scheming Lewis acidic Ge(IV) polycations, an optimal balance between the stabilization of the polycationic species by neutral donors and accessibility of vacant orbitals is necessary. Therefore, focused investigations on the stabilization of Ge(IV) polycations using suitable donor groups that circumvent hyper-coordination are imperative for their potential Lewis acidity. Furthermore, isolation of such species has remained a worthwhile synthetic target on fundamental grounds.

As a matter of fact, compared to silicon analogues, there are scarce reports on Ge-based Lewis acids both in their neutral or cationic forms. Greb et al. have pioneered neutral bis(perchlorocatecholeto)germane as both hard and soft Lewis superacids (Fig. 1D). The bis(catecholeto)germane derivatives have been successfully implemented as Lewis acid catalysts. A significant example of the cationic form of Ge(IV) Lewis acid is \([\text{TPFC}\text{Ge(THF)}_2\text{]}_2^-\) \((\text{TPFC} = \text{tris(pentafluorophenyl)}\text{corrole}, \text{THF} = \text{tetrahydrofuran})\) (Fig. 1E). Recently, a Ge(IV) mono-cationic σ-donor ligand towards Ni(0) has been reported with simultaneous Lewis superacidity. It is worth mentioning that Gabba¨ et al. have demonstrated a formally cationic Ge(IV) σ-acceptor site in a dinuclear Pt–Ge(IV) complex.

Contemporary research in the field of main-group Lewis acids has introduced the concepts of geometrically constrained Lewis acids, main group Lewis acid/ligand assisted...
cooperative bond activation,\(^\text{19}\) hidden frustrated Lewis pair (FLP) chemistry\(^\text{20}\) in intra-molecular Lewis base stabilized Lewis acidic fragments.\(^\text{21}\) Taking advantage of the enforced proximity in peri-substituted acenaphthenes,\(^\text{22}\) herein we have established the unprecedented intramolecularly phosphine-stabilized tetra-coordinated di-cationic Ge(IV) compounds. The aptitude of these geometrically constrained Ge(IV) di-cationic species as Lewis acids has been assessed based on experimental findings and computational analyses. Non-innocent roles of the phosphines have been observed. The proclivity of Ge(IV) di-cationic compounds for Et\(_3\)Si–H bond activation coupled with FLP-type reactivity has been realized in a proof-of-concept catalytic hydrosilylation of \(p\)-methyl benzaldehyde.

**Results and discussion**

**Syntheses and characterization of intramolecular phosphine-stabilized Ge(IV) mono- and di-cationic compounds**

Intramolecular phosphine-stabilized Ge(IV) di-cationic compounds \(3^{\text{IPr}}\) and \(3^{\text{Ph}}\) were obtained in a step-wise manner as shown in Scheme 1. Initially, \(L^{\text{IPr}}\)-Br and \(L^{\text{Ph}}\)-Br were synthesized and characterized (see the ESI\(^\ddagger\) for Experimental procedures). Table 1 summarizes the NMR data for all compounds. The reaction between 1.5 equivalents of lithiated \(L^{\text{IPr}}\)-Br and GeCl\(_4\) at \(-78\) °C in a tetrahydrofuran (THF) medium, followed by extraction with dichloromethane (DCM), gave \(1^{\text{IPr}}\) (Scheme 1a). Structural elucidation of the single crystals of \(1^{\text{IPr}}\) obtained from acetonitrile (MeCN) reveals the formation of \(\left[L^{\text{IPr}}\right]_{2}\text{GeCl}_3\), interestingly possessing GeCl\(_3\) as a counter anion (Fig. S95, ESI\(^\ddagger\)). The formation of the GeCl\(_3\) anion stems from the reducing ability of phosphines.\(^\text{23}\) The mono-cationic compound \(1^{\text{IPr}}\) was characterized by the \(^{31}\text{P}\{\text{H}\}\) NMR chemical shift at \(-11.1\) ppm. An additional peak at \(-19.5\) ppm was observed in the \(^{31}\text{P}\{\text{H}\}\) NMR spectrum of the crude reaction mixture arising from the corresponding P(V) oxidized product (Fig. S7, ESI\(^\ddagger\)).\(^\text{24}\) Using straightforward
Table 1  NMR data for all compounds

<table>
<thead>
<tr>
<th>Compounds</th>
<th>$^{31}$P{H} in ppm (deuterated solvent)</th>
<th>$^{19}$F{H} in ppm (deuterated solvent)</th>
<th>$J$ values (Hz)</th>
<th>Compounds</th>
<th>$^{31}$P{H} in ppm (deuterated solvent)</th>
<th>$^{19}$F{H} in ppm (deuterated solvent)</th>
<th>$J$ values (Hz)</th>
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<tbody>
<tr>
<td>LiPrBr</td>
<td>$-1.58$ (CDCl$_3$)</td>
<td>$3iPrDMAP$</td>
<td>$+28.37 (3iPr), -13.19$</td>
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<td></td>
<td></td>
<td>$3iPrF$</td>
<td>$-79.21$ (CDCl$_3$)</td>
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<tr>
<td>LPhBr</td>
<td>$-9.40$ (CDCl$_3$)</td>
<td>$3Ph(DMAP)2$</td>
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<tr>
<td></td>
<td></td>
<td>$3Ph$</td>
<td>$J_{P-F} = 184.9$</td>
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</tr>
<tr>
<td>1Ph</td>
<td>$-34.79$ (CDCl$_3$)</td>
<td>$3PhF$</td>
<td>$-150.32$ (CDCl$_3$)</td>
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<td>$-10.77$ (CDCl$_3$)</td>
<td>$3Ph + Ph_3CClF$</td>
<td>$-6.31 (3Ph), -13.46 (2Ph)$</td>
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<td>3iPrF</td>
<td>$+73.4$ (bound Et$_3$PO), $-12.0$ (PPr$_2$) (CD$_2$Cl$_2$)</td>
<td>$+71.59$ (bound Et$_3$PO), $-6.30 (3iPr), -13.38$ (PPr$_2$) (CD$_2$Cl$_2$)</td>
<td>$3Ph + aldehyde$</td>
<td>$36.02$–$32.08$, $-19.26$ (CDCl$_3$)</td>
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<tr>
<td>3iPrOPEt$_3$</td>
<td>$+73.4$ (bound Et$_3$PO), $-12.0$ (PPr$_2$) (CD$_2$Cl$_2$)</td>
<td>$+71.59$ (bound Et$_3$PO), $-6.30 (3iPr), -13.38$ (PPr$_2$) (CD$_2$Cl$_3$)</td>
<td>$3Ph + aldehyde$</td>
<td>$36.02$–$32.08$, $-19.26$ (CDCl$_3$)</td>
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$^a$ Chemical shift values at room temperature. $^b$ Chemical shift values at low temperature. $^c$ In situ NMR. $^d$ Measured after 2 days. $^e$ Measured after one day.
lithiated Li\textsuperscript{IPr}-Br and GeCl\textsubscript{4} in a 2:1 ratio also led to the formation of 1\textsuperscript{IPr}. An anion exchange reaction of 1\textsuperscript{IPr} with one equivalent of trimethylsilyl trifluoromethane sulfonate (TMSOTf) followed by crystallization in DCM resulted in the isolation of 2\textsuperscript{IPr} (Scheme 1a). 2\textsuperscript{IPr} was characterized in the solution state using NMR spectroscopy displaying the characteristic \textsuperscript{31}P{\textsuperscript{1}H} NMR chemical shift at \(-10.8 \text{ ppm}\).

The molecular structure\textsuperscript{25} of 1\textsuperscript{IPr} shows that the cationic part has an overall distorted trigonal bipyramidal (TBP) geometry with two pendant \textsuperscript{1}Pr\textsubscript{2}P groups occupying axial sites. Two Ge–C and one Ge–Cl bond constitute the trigonal plane with the sum of angles at the Ge atom close to 360°. The Ge1–P1 and Ge1–P2 bond lengths are 2.544(1) and 2.654(1) Å, respectively, which are longer than those of [GeF\textsubscript{3}(Ph\textsubscript{2}PCH\textsubscript{2}CH\textsubscript{2}PPh\textsubscript{2})(OTf)] (avg. Ge–P = 2.43 Å\textsuperscript{3} and diaminodiphosphine stabilized bis(chlorogermyliumylidene) (avg. Ge–P = 2.44–2.50 Å).\textsuperscript{26} The structural parameters of the cationic part in 2\textsuperscript{IPr} (Fig. 2a) are analogous to those of 1\textsuperscript{IPr}. The triflate counter anion in 2\textsuperscript{IPr} is located far away from the Ge cationic site (closest Ge–O contact being 5.7 Å).

The formation of 3\textsuperscript{IPr} can either proceed as a one-pot reaction between 1\textsuperscript{IPr} and two equivalents of TMSOTf in DCM or stepwise chloride abstraction from 1\textsuperscript{IPr} via the intermediacy of 2\textsuperscript{IPr} (Scheme 1a). Colourless crystals of 3\textsuperscript{IPr} were obtained from the concentrated THF solution. The characteristic \textsuperscript{31}P{\textsuperscript{1}H} NMR chemical shift values obtained for 3\textsuperscript{IPr} in CD\textsubscript{3}CN (+27.0 ppm) and CD\textsubscript{2}Cl\textsubscript{2} (+28.4 ppm) are similar, which invalidates possible solvent coordination.

The solid-state structure of 3\textsuperscript{IPr} (Fig. 3a) shows a spirocyclic geometry\textsuperscript{27} with the Ge atom at the nexus and having two non-coordinating triflate counter anions (closest Ge–O contact being 5.8 Å). Due to the presence of dipositive charges in 3\textsuperscript{IPr}, the Ge–C (avg. 1.92 Å) and Ge–P (avg. 2.36 Å) bond lengths are significantly shorter compared to those of 2\textsuperscript{IPr}. The strongly electron-donating nature of the two intramolecular \textsuperscript{1}Pr\textsubscript{2}P groups adequately stabilizes the Ge(m) di-cation in 3\textsuperscript{IPr} in an overall tetra-coordinated environment.

In the case of the diphenylphosphanyl donor, the neutral compound [\textsuperscript{1}IPr\textsubscript{2}GeCl\textsubscript{2}]\textsuperscript{1+} could be obtained from the reaction between lithiated Li\textsuperscript{IPh}-Br and GeCl\textsubscript{4} taken in a 2:1 ratio in a THF medium (Scheme 1b and Fig. S96, see the ESI for Experimental procedures). Chloride abstractions from 1\textsuperscript{IPh} using one and two equivalents of TMSOTf in DCM led to the formation of mono-cationic 2\textsuperscript{IPh} and di-cationic 3\textsuperscript{IPh} compounds, respectively (Scheme 1b). The characteristic peaks in \textsuperscript{31}P{\textsuperscript{1}H} NMR spectra for 2\textsuperscript{IPh} and 3\textsuperscript{IPh} appear at \(-13.2\) and \(-6.3 \text{ ppm}\) respectively.

Unlike 2\textsuperscript{IPr}, the molecular structure of 2\textsuperscript{IPh} depicts a distorted tetrahedral geometry (Fig. 2b). Compared to 2\textsuperscript{IPr}, the Ge1–P1 bond length has noticeably reduced in 2\textsuperscript{IPh} (2.357(1) Å). Another Ge1⋯P2 bond distance in 2\textsuperscript{IPh} is 3.012(1) Å. The trflate anion is far away from the Ge atom (closest Ge–O contact being 7.2 Å). The low temperature \textsuperscript{31}P{\textsuperscript{1}H} NMR for 2\textsuperscript{IPh} echoes the presence of two inequivalent phosphines exhibiting chemical shift values at \(-3.0\) and \(-20.5 \text{ ppm}\).

The solid-state structure of 3\textsuperscript{IPh} exhibits a spiro-geometry with similar bond parameters to those in 3\textsuperscript{IPr} (Fig. 3b). There are two non-coordinating triflate anions (closest Ge–O contact being 4.2 Å) present in the asymmetric unit. Both 3\textsuperscript{IPr} and 3\textsuperscript{IPh} in
the solid-state show no sign of decomposition when exposed to air for a day.

The optimized geometries of 20
\textsuperscript{iPr}, 20
\textsuperscript{Ph}, 30
\textsuperscript{iPr} and 30
\textsuperscript{Ph} at the TPSS-D3(BJ)/def2-TZVPP level of theory are in close agreement with the X-ray parameters (see the ESI† for the detailed theoretical part). On par with the experimental findings, Natural Bond Orbital (NBO) analyses for 20
\textsuperscript{iPr} suggest significant donor–acceptor (D–A) interactions (avg. 125 kcal mol\(^{-1}\)) for LP\(_{P1} \rightarrow \)LP\(_{Ge}\) and LP\(_{P2} \rightarrow \)LP\(_{Ge}\). However, dissimilar bonding situations in 20
\textsuperscript{Ph} between Ge1–P1 (covalent) and Ge1–P2 (D–A interaction) were confirmed by NBO and Atoms in Molecules analyses. The calculated Wiberg bond index (WBI) values for Ge1 and Ge2 in 20
\textsuperscript{Ph} possess dative nature with a value of 0.183 (0.712 for Ge1 in the Gutmann edge). The Laplacian values re
\textsuperscript{ex}ect similar contributions in terms of Ge
\textsuperscript{3d} partial charges and the electrostatic potential map analyses (Fig. 4a and b). The orbital scenario is analogous to those observed in the catecholato phosphonium ion or stibonium salt. There is no pure vacant p-orbital available from induced\(^{31}\)P NMR shifts (0.183 for Ge1–P1 and 0.712 for Ge1–P1). Additionally, no bonding orbital for Ge1–P2 was observed from the NBO analyses. Instead, only one D–A interaction (LP\(_{P2} \rightarrow \)LP\(_{Ge}\)) is determined in 20
\textsuperscript{Ph} with a stabilization energy of 32 kcal mol\(^{-1}\). Furthermore, we have performed AIM analyses. A negative Laplacian value at the BCPs (bond critical points) is associated with shared interactions, indicating covalent bonds, and positive Laplacian values reflect closed shell interactions such as ionic or dative bonds. In the case of 20
\textsuperscript{Ph}, the higher positive \(\nabla^2\rho(r)\) value on Ge2 shows dative bonding character.

The frontier molecular orbitals (FMOs) of 30
\textsuperscript{iPr} and 30
\textsuperscript{Ph} reflect similar contributions in terms of Ge–C and Ge–P σ* orbitals (Fig. 4a and b). The orbital scenario is analogous to those observed in the catecholato phosphonium ion or the central Ge atom in both cases. WBI calculations predict the values of 0.804 (30
\textsuperscript{iPr}) and 0.770 (30
\textsuperscript{Ph}) for Ge–P bonds, displaying a mostly covalent bonding situation. The dispersion of positive charges among the P (+1.161, +1.145 for 30
\textsuperscript{iPr}; +1.174, +1.174 for 30
\textsuperscript{Ph}) and Ge (+1.136 for 30
\textsuperscript{iPr}; +1.157 for 30
\textsuperscript{Ph}) sites is evident from NBO partial charges and the electrostatic potential map analyses (Fig. 4c and d). Canonical forms describing the dispersion of positive charges in 30
\textsuperscript{iPr} and 30
\textsuperscript{Ph} (F) are depicted in Fig. 1.

Lewis acidic properties of Ge\((n)\) di-cationic compounds

We have studied the effective Lewis acidity of both 3\textsuperscript{iPr} and 3\textsuperscript{Ph} from induced \(^{31}\)P\{\(^{1}\)H\} NMR shift of triethylphosphine oxide (Et\(_3\)PO) in the Gutmann–Beckett (GB) method (see the ESI† for details).\(^{29}\) Et\(_3\)PO adducts were targeted by employing varying equivalents of Et\(_3\)PO (0.2 to 3.0 equivalents) in deuterated solvents. The addition of 0.2 equivalents of Et\(_3\)PO to 3\textsuperscript{iPr} gave numerous peaks at +75.7, +74.2, −12.3 and −18.2 ppm. The complexity of the \(^{31}\)P\{\(^{1}\)H\} NMR spectra at room temperature impedes the Lewis acidity scaling of 3\textsuperscript{iPr} by the GB method. However, we have observed peaks appearing at +73.4 and −12.0 ppm in the \(^{31}\)P\{\(^{1}\)H\} NMR spectrum, when a 1:1 mixture of 3\textsuperscript{iPr} and Et\(_3\)PO was prepared in CD\(_2\)Cl\(_2\) at −78 °C and subsequently raised to room temperature. This gave an induced \(^{31}\)P\{\(^{1}\)H\} NMR chemical shift of Et\(_3\)PO for 3\textsuperscript{iPr} (Δ\(^{31}\)P = 21.3 ppm) with respect to the free Et\(_3\)PO (δ for free Et\(_3\)PO in the same solvent is 52.1 ppm).

In the case of 3\textsuperscript{Ph}, we have noticed the induced \(^{31}\)P\{\(^{1}\)H\} NMR chemical shift from the addition of 0.2 equivalents of Et\(_3\)PO in CD\(_2\)Cl\(_2\) (Δ\(^{31}\)P = 21.6 ppm, δ for free Et\(_3\)PO in the same solvent is 50.0 ppm); without any complexity observed in the NMR spectrum at room temperature. These Δ\(^{31}\)P values are close to the values reported for the Si(IV) di-cations (Δ\(^{31}\)P = 23.5 ppm for [P\(_2\)\text{Si(terpy)}\text{]2}^{+}\)). Both 3\textsuperscript{iPr} and 3\textsuperscript{Ph} exhibit similar effective Lewis acidity as obtained following the GB method. The peak at +71.6 ppm in the \(^{31}\)P\{\(^{1}\)H\} NMR spectrum assigned to the bound Et\(_3\)PO is shifted up-field upon increasing the amount of Et\(_3\)PO. This obvious shift is due to the expected weak acceptor ability upon further Et\(_3\)PO coordination at the cationic site.\(^{29}\) We have crystallized the mono-adduct 3\textsuperscript{iPr}OPEt\(_3\) (Fig. S97†) under low temperature conditions from the reaction between 3\textsuperscript{iPr} and Et\(_3\)PO. The molecular structure of 3\textsuperscript{iPr}OPEt\(_3\) shows a pentacoordinated Ge site. Interestingly, the solution-state NMR study of 3\textsuperscript{Ph}OPEt\(_3\) shows characteristic \(^{31}\)P\{\(^{1}\)H\} NMR chemical shifts at +68.5 and −20.5 ppm along with a peak at −6.3 ppm assigned to the \textit{in situ} generated free 3\textsuperscript{Ph}. This observation reflects the presence of the equilibrium in the solution-state.

Despite the dispersion of dipositive charges over the P–Ge–P sites in 3\textsuperscript{iPr} and 3\textsuperscript{Ph}, we have observed the preferential binding of Lewis bases such as Et\(_3\)PO and 4-N,N-dimethylaminopyridine (DMAP) at the Ge site (Scheme 2). The reaction between 3\textsuperscript{iPr} and DMAP taken in a 1:1 ratio gave 3\textsuperscript{iPr}DMAP, which was crystallized in small amounts from DCM/hexane layering at room temperature (Scheme 2). Single crystals of dimethylamino pyridinium triflate were obtained in large amounts, which were separated from the 3\textsuperscript{iPr}DMAP crystals. The molecular structure of 3\textsuperscript{iPr}DMAP from X-ray analysis reveals an overall TBP geometry with the DMAP coordination at one of the trigonal planar equatorial sites of the Ge atom (Fig. S98†). However, 3\textsuperscript{iPr}DMAP is unstable under room temperature conditions in the solution state. The \(^{31}\)P\{\(^{1}\)H\} NMR of \textit{in situ} generated 3\textsuperscript{iPr}DMAP at −40 °C in CD\(_2\)Cl\(_2\) shows a peak at −13.2 ppm in addition to the uncoordinated 3\textsuperscript{iPr} peak (+28.4 ppm) present in the reaction medium. These peaks gradually disappeared upon warming to room temperature, ultimately giving new peaks at +75.7 ppm and −18.2 ppm (vide supra). We have observed a peak at +12.9 ppm in the \(^{1}\)H NMR spectrum corresponding to the formation of the conjugate acid dimethylamino pyridinium triflate. Similar side-reactions might be involved in the reaction between 3\textsuperscript{iPr} and donors (Et\(_3\)PO and DMAP), as was reported earlier by Stephan et al.\(^{29}\)
A dynamic process\(^1\) between mono- and bis-adduct formation was observed upon reacting 3\(^{\text{ph}}\) with one equivalent of DMAP at room temperature. The NMR scale reaction in CDCl\(_3\) shows a peak at −18.5 ppm and a broad peak centered at −27.0 ppm in the \(^{31}\text{P}\{^1\text{H}\}\) NMR spectrum. The gradual decrease in temperature up to −50 °C resulted in a complete disappearance of the peak at −18.5 ppm. Concurrently two close sharp peaks at ∼−29 ppm appeared along with the generation of the peak for 3\(^{\text{ph}}\) at −6.3 ppm. Inferring from this NMR study, a bis-adduct was isolated (corresponding peak at ∼−29 ppm) from the reaction between DMAP and 3\(^{\text{ph}}\) at −35 °C. The crystallization from DCM/pentane layering at the same temperature gave single crystals of the trans bis-adduct 3\(^{\text{ph}}\)(DMAP)\(_2\) (Fig. S99†). As a matter of fact, in this case we find the spontaneous formation of the more favourable hexa-coordinated bis-adduct over the mono-adduct at lower temperatures.\(^{1\text{d}}\) The octahedral coordination type at the Ge atom of 3\(^{\text{ph}}\)(DMAP)\(_2\) comprises two \(\text{L}^{\text{ph}}\) in the equatorial plane and two DMAPs occupying the axial sites. Thus, dynamic processes were observed for the adducts formed between 3\(^{\text{ph}}\) and donors.

The preferential binding of donor groups at the Ge site is associated with the relief in constraint on going from a strained spiro-geometry in 3\(^{\text{ipr}}\) and 3\(^{\text{ph}}\) to the relaxed TBP (3\(^{\text{ipr}}\)DMAP) and distorted tetrahedral geometry (3\(^{\text{ph}}\)OPET\(_3\)) in the adducts, respectively. Notably, this results in a handful of penta-coordinated Ge compounds obtained having TBP geometry which are uncommon in Ge chemistry.\(^{1\text{d}}\) The viable expansion of the peri-distances\(^2\) in the two intramolecular P–Ge bonds in 3\(^{\text{ipr}}\) and 3\(^{\text{ph}}\) allows smooth structural rearrangements with the addition of nucleophiles.

We have validated the above understanding from the deformation energy\(^9,^{29}\) values obtained in the spiro- to TBP geometric transformation. We have prepared 3\(^{\text{ipr}}\)F from the addition of one equivalent of KF to 3\(^{\text{ipr}}\) (Scheme 2), which exhibits a distorted TBP geometry (Fig. 5a) like 2\(^{\text{pp}}\)F in the solid state. DFT calculations reveal that the fluoride ion binding to 3\(^{\text{ipr}}\) involves a low deformation energy \(E_{\text{def}} = 126 \text{ kJ mol}^{-1}\), falling within the range reported in the literature.\(^{19,^{29}}\) 3\(^{\text{ipr}}\)F was characterised by NMR spectroscopy in the solution state showing a characteristic triplet at −141.0 ppm \(\langle J_{\text{F-P}} = 185 \text{ Hz} \rangle\) in the \(^{19}\text{F}\{^1\text{H}\}\) NMR spectrum and a corresponding doublet in the \(^{31}\text{P}\{^1\text{H}\}\) NMR spectrum (−10.2 ppm).

Like 3\(^{\text{ipr}}\), the addition of one equivalent of KF led to the formation of 3\(^{\text{ph}}\)F (Scheme 2) showing similar characteristic peaks in NMR spectra \((\delta \text{ }^{19}\text{F}\{^1\text{H}\}: −150.3 \text{ ppm, triplet, and } \delta \text{ }^{31}\text{P}\{^1\text{H}\}: −17.5 \text{ ppm})\). The molecular structure of 3\(^{\text{ph}}\)F (Fig. 5b) resembles that of 2\(^{\text{ph}}\). The low temperature \(^{31}\text{P}\{^1\text{H}\}\) NMR spectrum reveals the presence of inequivalent phosphines in 3\(^{\text{ipr}}\)F. In this case, the release of the structural constraint occurs on going from spirocyclic 3\(^{\text{ph}}\) to the relaxed geometry in 3\(^{\text{ph}}\)F involving a deformation energy value of 148 kJ mol\(^{-1}\).\(^{19,^{29}}\)

The calculations on the gas-phase fluoride ion affinity (FIA)\(^{31}\) at the Ge sites give very high values of 873 kJ mol\(^{-1}\) and 859 kJ mol\(^{-1}\) for 3\(^{\text{ipr}}\) and 3\(^{\text{ph}}\) respectively (gas-phase FIA for reference SbF\(_3\) is 497 kJ mol\(^{-1}\)) (see the ESI† for details).
However, the calculated FIA values in DCM solvated models decreased significantly giving the values of 194 kJ mol\(^{-1}\) and 190 kJ mol\(^{-1}\) for 3\(^{\text{IV}}\) and 3\(^{\text{III}}\), respectively (solvent corrected FIA for reference SbF\(_5\) is 331 kJ mol\(^{-1}\)). This is a common phenomenon observed due to solvation damping, being more pronounced with a cationic Lewis acid.\(^{3,4}\) Both 3\(^{\text{IV}}\) and 3\(^{\text{III}}\) did not abstract the fluoride anion when reacted with [PPh\(_4\)][SbF\(_6\)] and hence are not Lewis superacids. The chloride ion affinity study using triyl chloride shows that only 3\(^{\text{III}}\) abstracts chloride with characteristic coloration\(^{10,8}\) and the NMR data reveal the formation of 2\(^{\text{IV}}\) (Scheme 2 and Fig. S62, ESI†).

Gas-phase hydride ion affinity (HIA)\(^{10}\) calculations also give very high values of 949 kJ mol\(^{-1}\) and 928 kJ mol\(^{-1}\) for 3\(^{\text{IV}}\) and 3\(^{\text{III}}\), respectively (gas-phase HIA for reference B(C\(_6\)F\(_5\))\(_3\)) is 517 kJ mol\(^{-1}\)) (see the ESI† for details). Reasonable HIA values are obtained after considering the solvation in DCM: 254 kJ mol\(^{-1}\) and 269 kJ mol\(^{-1}\) for 3\(^{\text{IV}}\) and 3\(^{\text{III}}\), respectively (solvent corrected HIA for reference B(C\(_6\)F\(_5\))\(_3\)) is 270 kJ mol\(^{-1}\)). Thus, both 3\(^{\text{IV}}\) and 3\(^{\text{III}}\) are hydrophilic in nature. 3\(^{\text{IV}}\) efficiently abstracts the hydride from Li\(\text{Et}_2\text{H}\) at room temperature leading to the formation of 3\(^{\text{III}}\)H (Scheme 2). The \(^1\)H NMR spectrum of 3\(^{\text{III}}\)H reveals the Ge–H resonance as a triplet (\(J_{\text{Ge–H}} = 36\) Hz) at \(+7.2\) ppm; the chemical shift value falls within the range of reported Ge-hydrides.\(^{12}\) The molecular structure of 3\(^{\text{III}}\)H attains a distorted TBP geometry (Fig. S100†) analogous to 2\(^{\text{II}}\). The Ge–H bond length of 1.540 Å in the optimized geometry agrees well with that found in the molecular structure of 3\(^{\text{III}}\)H (1.54(3) Å) (see the ESI† for details). The reaction of 3\(^{\text{III}}\)H with two equivalents of Li\(\text{Et}_2\)\(\text{H}\) gave the neutral 3\(^{\text{II}}\)H\(_2\) (Scheme 2). The molecular structure of 3\(^{\text{II}}\)H\(_2\) is shown in Fig. S101.† The Ge–P distances in 3\(^{\text{II}}\)H\(_2\) are close to 3 Å; however they fall within the sum of van der Waal’s radii VdW(Ge–P) = 3.91 Å.\(^{12}\) The \(^1\)H NMR spectrum of 3\(^{\text{II}}\)H\(_2\) reveals a Ge–H resonance at 6.4 ppm as a triplet (\(J_{\text{Ge–H}} = 20\) Hz). The reaction between 3\(^{\text{III}}\) and one equivalent of Li\(\text{Et}_2\)\(\text{H}\) followed by crystallization from different solvent combinations gives the single crystals of 3\(^{\text{II}}\)Et and 3\(^{\text{II}}\)H(Et) (Scheme 2 and Fig. S102, S103, ESI†), confirming B–C bond activation.\(^{13}\) Thus, preliminary reactivity studies identify 3\(^{\text{III}}\) as a highly reactive di-cation.

### Catalytic hydrosilylation of an aromatic aldehyde by the Ge(IV) di-cationic compounds

Given the hydrophilicity of the soft Ge-based Lewis acids 3\(^{\text{IV}}\) and 3\(^{\text{III}}\), we targeted the activation of the Si–H bond in Et\(\text{SiH}\) (see the ESI† for details).\(^{14}\) Monitoring the reaction between 3\(^{\text{IV}}\) and excess Et\(\text{SiH}\) at room temperature using \(^{31}\)P NMR displays the formation of two new peaks at +20.3 ppm and +12.2 ppm along with retention of 3\(^{\text{IV}}\). The peak at +20.3 ppm showed a coupling of \(J_{\text{Ge–H}} = 476\) Hz. Furthermore, \(^1\)H–\(^{31}\)P 1D and 2D Heteronuclear Single Quantum Coherence (HSQC) NMR measurements (CNS2 optimized at 480 Hz) confirm that \(J_{\text{Ge–H}} = 476\) Hz.\(^{15}\) Thus, the Si–H bond activation and hydride binding occur preferentially at the P-site over the Ge-site giving 3\(^{\text{IV}}\)–PH. This is in contrast to 3\(^{\text{IV}}\)H formed by hydride abstraction from Li\(\text{Et}_2\)\(\text{H}\) (vide supra). Notably, although Si–H bond activation occurs at the P-site of 3\(^{\text{IV}}\), standing of the reaction mixture for 14 days ultimately led to Ge–H bond formation (\(J_{\text{Ge–H}} = 36\) Hz at +7.2 ppm) giving 3\(^{\text{II}}\)H.

In contrast, 3\(^{\text{III}}\) activates the Si–H bond in Et\(\text{SiH}\) giving 3\(^{\text{II}}\)H (Scheme 3a) as the product within 24 hours (see the ESI† for details). However, the time dependent \(^{31}\)P NMR monitoring of the initial reaction mixture displays a minor peak at +10.0 ppm with a coupling of \(J_{\text{Ge–H}} = 534\) Hz corresponding to the P–H formation, which subsequently disappeared giving 3\(^{\text{II}}\)H within 24 hours. The \(^1\)H NMR spectrum of 3\(^{\text{II}}\)H discloses the Ge–H resonance at +7.0 ppm as a triplet (\(J_{\text{Ge–H}} = 30\) Hz) and a corresponding doublet at −19.0 ppm in the \(^{31}\)P\(^{1}\)H NMR spectrum. The \(^{29}\)Si\(^{1}\)H NMR of the reaction mixture shows the corresponding formation of Et\(\text{SiOEt}\) (\(\delta = +45.0\) ppm).
The above-mentioned observations suggest that the hydride binding initially occurs at the P-site due to the dispersion of dipositive charges over P-Ge-P units in these di-cationic species. Computational investigations done on the hydride migration from P to Ge for both 3\textsuperscript{iv} and 3\textsuperscript{ph} reveal the involvement of a relatively higher transition state energy barrier in the case of the former (Fig. S112, ESI†). The hydride migration mechanism proposed based on the DFT calculations performed on the cationic part of the compounds proves only the trends of the hydride shifts from P to Ge. Nonetheless, the very low energy barriers obtained are inadequate to support the longer time requirements for hydride migrations observed experimentally. Probably, the inclusions of the solvent models and counter anions to the systems would be able to resolve the disagreement at an associated extremely high computational cost. Thus, the hydride migration mechanism proposed herein is rather based on the experimentally observed data. Additionally, the strong electron donating nature of iPr\textsubscript{2}P compared to Ph\textsubscript{2}P pushes the carbonyl-FLP insertion product taking place at the initial stage of the catalytic cycle. Notably, no Et\textsubscript{3}SiOTf formation is detected in the reaction mixture containing 3\textsuperscript{ph} (Fig. S104, ESI†). Thus, a masked frustrated Lewis pair (FLP) type behavior\textsuperscript{1,10} of 3\textsuperscript{ph} was observed, which is unsurprising due to the adaptability of the P-Ge bond in peri-systems. The NMR spectrum recorded immediately after the addition of 3\textsuperscript{ph} to the reaction mixture of the aldehyde and Et\textsubscript{3}SiH also displays similar chemical shift values (–19.3 ppm and around +36 ppm in the \textsuperscript{31}P{\textsuperscript{1}H} NMR study). The NMR study did not show any peak arising from Si–H bond activation by 3\textsuperscript{ph}. This suggests the formation of the carbonyl-FLP insertion product taking place at the initial stage of the catalytic cycle. Notably, no Et\textsubscript{3}SiOTf formation is detected from the \textsuperscript{29}Si{\textsuperscript{1}H} NMR monitoring (Fig. S93, ESI†). Thus, the catalytic hydrosilylation is likely to proceed via the carbonyl insertion followed by Et\textsubscript{3}Si–H addition across the carbonyl functional group (Scheme 4). The catalyst 3\textsuperscript{ph} is clearly observed after complete consumption of the reactants.

Thus, both 3\textsuperscript{iv} and 3\textsuperscript{ph} show different pathways catalysing the hydrosilylation of the aldehyde. Based on our experimental findings, while the former proceeds through the Si–H bond activation at the Lewis acidic site, the latter utilizes the masked FLP for the aldehyde insertion followed by Et\textsubscript{3}Si–H addition to the C=O bond.

**Conclusion**

In this study, we have established the first examples of tetra-coordinated Ge(iv) di-cationic compounds 3\textsuperscript{iv} and 3\textsuperscript{ph}. This was achieved through the intramolecular stabilization of the Ge di-cationic site using a phosphate donor in peri-substituted...
The strong P–Ge bonds led to the dispersion of di-cationic charges over Ge and P sites. The simple anion binding or Lewis base coordination occurs exclusively at the Ge site owing to the release of the geometric constraint on going from the spiro-geometry of the di-cation to the distorted TBP/tetrahedral geometry of the resultant species. Although the Si–H bond activation occurs initially at the P site for both the di-tetrahedral geometry of the resultant species. Although the Si site owing to the release of the geometric constraint on going di-cationic charges over Ge and P sites. The simple anion tuning the donor group properties in such charged initiated with Et3SiH hydrosilylation product formation for Chem. Sci.

References


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