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## 1 Introduction

# Promotion of $\mathrm{TH}_{3}$ ( $\mathrm{T}=\mathrm{Si}$ and Ge ) group transfer within a tetrel bond by a cation $-\pi$ interaction $\dagger$ 

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#### Abstract

The possibility of the transfer of the $\mathrm{TH}_{3}$ group across a tetrel bond is considered by ab initio calculations. The TB is constructed by pairing $\mathrm{PhTH}_{3}$ ( $\mathrm{Ph}=$ phenyl; $\mathrm{T}=\mathrm{Si}$ and Ge ) with bases $\mathrm{NH}_{3}$, $\mathrm{NHCH}_{2}$, and the $\mathrm{C}_{3} \mathrm{~N}_{2} \mathrm{H}_{4}$ carbene. The $\mathrm{TH}_{3}$ moves toward the base but only by a small amount in these dimers. However, when a $\mathrm{Be}^{2+}$ or $\mathrm{Mg}^{2+}$ dication is placed above the phenyl ring, the tetrel bond strength is greatly magnified reaching up to nearly $100 \mathrm{kcal} \mathrm{mol}^{-1}$. This dication also induces a much higher degree of transfer which can be best categorized as half-transfer for the two N -bases and a near complete transfer for the carbene.


Proton transfer is an important component in numerous chemical reactions and biological systems, and has accordingly attracted a great deal of attention over the years. ${ }^{1-5}$ Generally, proton transfer is facilitated by a strong H -bond, which is in turn dependent on both the acidity of the proton donor and the alkalinity of the acceptor, as well as substituent and cooperativity effects. Typically, electron-donating substituents on the proton acceptor and withdrawing units on the donor enhance the strength of the H-bond. ${ }^{6}$ There have been numerous demonstrations of H -bond cooperativity, both with other H -bonds and with other types of noncovalent interactions ${ }^{7-11}$ which can modulate the H -bond strength as well as the proton transfer occurring within. ${ }^{12-14}$ Recent work has demonstrated that many of these same principles, e.g. cooperativity and solvation effects, ${ }^{15,16}$ apply to the transfer of a halogen atom when it has replaced the proton in what have come to be called halogen bonds.

The tetrel bond, TB, is an attractive interaction between the $\sigma$ or $\pi$-hole on a group 14 atom, e.g. C or Si , and a base, quite similar in its foundations to both the hydrogen and halogen bonds. Because of its profound implications in various areas such as crystal materials, molecular recognition, chemical reactions, and biological systems, ${ }^{17-25}$ this noncovalent bond has engendered a rapidly growing list of theoretical and

[^0]experimental studies. Among some of the findings, the TB displays cooperativity with various sorts of other noncovalent interactions including hydrogen, halogen, chalcogen, triel, beryllium, and lithium bonds. ${ }^{26-31}$ While our understanding of proton transfer within H -bonds is fairly thorough and that of halogen transfer is now beginning to gel, one area that has escaped scrutiny to this point surrounds the question as to what conditions might promote the transfer of a tetrelcontaining group within the context of a tetrel bond.

The work described herein attacks this question for the first time. As the tetrel-containing Lewis acid, a $\mathrm{TH}_{3}$ group is attached to a phenyl group, where $\mathrm{T}=\mathrm{Si}$ and Ge . This system was chosen since aromatic compounds are ubiquitous in the fields of chemistry, materials, and biology. Aromatic units are versatile in that they can engage in various sorts of interactions such as $\pi-\pi$ stacking, ${ }^{32}$ cation $-\pi,{ }^{33}$ and anion $-\pi$ interactions. ${ }^{34}$ Three different bases were chosen to interact with the $\mathrm{PhTH}_{3}$ system. As N -bases, $\mathrm{NH}_{3}$ and $\mathrm{NHCH}_{2}$ place the N in sp ${ }^{3}$ and $\mathrm{sp}^{2}$ hybridizations, respectively, so can span a range of nucleophilicity. To further expand the scope of bases considered, the N heterocyclic $\mathrm{C}_{3} \mathrm{~N}_{2} \mathrm{H}_{4}$ carbene allows the lone pair of a C atom to interact with the tetrel atom. These bases have been shown earlier to form fairly strong tetrel bonds with a small model acid $\mathrm{SiH}_{3} \mathrm{~F},{ }^{35}$ so ought to exert a reasonable pull on the tetrel group. Very recently, such N -heterocycle carbenes have been used as electron donors to form carbon $\cdots$ carbon ${ }^{+}$tetrel bonds. ${ }^{36}$ The first issue concerns how much of a tetrel group transfer occurs in any of the dimers formed by each acid when paired with each base. In order to ramp up the tendency toward a transfer, a dication $\mathrm{Be}^{2+}$ or $\mathrm{Mg}^{2+}$ is placed above the phenyl ring of the acid. This choice is guided by an earlier work wherein the tetrel bond strength of $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{TH}_{3} \cdots \mathrm{NCX}$ ( $\mathrm{T}=\mathrm{Si}$ and $\mathrm{Ge} ; \mathrm{X}=\mathrm{H}, \mathrm{F}$ and OH ) was amplified by the presence of a monocation in a similar position. ${ }^{37}$ The central question
addressed is whether this cation can exert a strong enough force so as to push the $\mathrm{TH}_{3}$ group across to the base, and if so, would this be a full or only partial transfer?

## 2 Theoretical methods

All calculations were performed using the Gaussian 09 program. ${ }^{38}$ Geometries were optimized at the MP2 computational level with the aug-cc-pVTZ basis set. Frequency calculations at the same level confirmed that the structures obtained correspond to energetic minima. The interaction energy was calculated by the supermolecular method involving the energies of the monomers at the geometries they adopt within the complex. This quantity was corrected for the basis set superposition error (BSSE) by the counterpoise protocol proposed by Boys and Bernardi. ${ }^{39}$

Using the nature bond orbital (NBO) method ${ }^{40}$ within the Gaussian 09 program, charge transfer and second-order perturbation energy were obtained. The AIM All package ${ }^{41}$ was used to assess the topological parameters at each bond critical point (BCP) including electron density, its Laplacian, and energy density. Molecular electrostatic potentials (MEPs), and their extrema, were calculated on the $0.001 \mathrm{a} . \mathrm{u}$. isodensity surface at the MP2/ cc-pVTZ level using the WFA-SAS program. ${ }^{42}$

## 3 Results

### 3.1 Dyads

As depicted in the top two diagrams of Fig. 1, there is a $\sigma$-hole lying along the extension of the C-T bond for both $\mathrm{T}=\mathrm{Si}$ and Ge. The value of $V_{\max }$ on the $\rho=0.001$ a.u. isodensity surface is


Fig. 1 MEP maps of monomers and complexes. Color ranges are: red, greater than 12; yellow, between 12 and zero; green, between zero and -12 ; blue, less than -12 ; all in $\mathrm{kcal} \mathrm{mol}^{-1}$.
quite similar for the two molecules between 16 and $17 \mathrm{kcal} \mathrm{mol}^{-1}$. A nucleophile is drawn toward this $\sigma$-hole so as to form a tetrelbonded complex. The change in hybridization of the N from $\mathrm{sp}^{3}$ for $\mathrm{NH}_{3}$ to $\mathrm{sp}^{2}$ for $\mathrm{NHCH}_{2}$ enhances the interaction energy even though there is little difference in the values of $V_{\min }$ in Fig. S1 (ESI $\dagger$ ), which are within $2 \%$ of one another. Changing the interacting atom from N to C in the $\mathrm{C}_{3} \mathrm{~N}_{2} \mathrm{H}_{4}$ carbene magnifies $V_{\text {min }}$ to nearly $-50 \mathrm{kcal} \mathrm{mol}^{-1}$, and further strengthens the tetrel bond, albeit by only a small amount. There is also a trend for Si to engage in slightly stronger TBs than does Ge, despite their very similar $V_{\text {max }}$.

Fig. 2a depicts a typical such TB, in this case using $\mathrm{C}_{3} \mathrm{~N}_{2} \mathrm{H}_{4}$ as the base, and illustrates the definition of the geometrical parameters. $R_{1}$ and $R_{2}$ refer respectively to the distance of the central T to the nucleophilic atom N or C , and to the C of the phenyl group, while $\alpha$ is equal to the average of the three $\mathrm{C} \cdots \mathrm{T}-\mathrm{H}$ angles. Although the $\mathrm{C}-\mathrm{T}$ bond elongates by a certain amount upon formation of the TB (0.009-0.018 $\AA$ ) , $R_{1}$ is much longer than $R_{2}$ so one cannot speak of any appreciable transfer of the $\mathrm{TH}_{3}$ group in any of these dyads. This distinction is reflected in the $R_{2} / R_{1}$ ratio in Table 1, which is roughly 0.6 . The $\gamma_{1}$ and $\gamma_{2}$ quantities in the last two columns of Table 1 refer each distance to the sum of vdW radii. $\gamma_{2}$ is roughly 0.5 , which reflects its covalent nature, while the much larger $\gamma_{1}$ is consistent with a much weaker noncovalent bond. As a second consideration, $\alpha$ is close to the tetrahedral angle, so the TB has little effect on the pyramidal character of the $\mathrm{TH}_{3}$ group.

### 3.2 Triads

The ability of an external cation to promote a $\mathrm{TH}_{3}$ transfer was tested by placing either of two dications, $\mathrm{Be}^{2+}$ or $\mathrm{Mg}^{2+}$ directly above the phenyl ring, as exhibited in Fig. 2b. The position of the cation was optimized along with the remainder of the triad structure. One might expect that this dication would suck density out of the $\mathrm{PhTH}_{3}$ unit, and thereby accentuate the $\sigma$-hole on T. This hole deepening is illustrated by the large values of $V_{\max }$ in the last four panels of Fig. 1 which increases


Fig. 2 The geometries of (a) $\mathrm{PhTH}_{3} \cdots \mathrm{C}_{3} \mathrm{~N}_{2} \mathrm{H}_{4}$ and (b) $\mathrm{M}^{2+} \ldots \mathrm{PhTH}_{3} \cdots$ $\mathrm{C}_{3} \mathrm{~N}_{2} \mathrm{H}_{4}$.

Table 1 Interaction energy of tetrel bond ( $E_{\text {int }}$, kcal $\mathrm{mol}^{-1}$ ), average of three $\mathrm{C} \ldots \mathrm{T}-\mathrm{H}$ angles ( $\alpha$, deg), intermolecular separation ( $R_{1}, \AA$ ), $\mathrm{C}-\mathrm{T}$ bond length ( $R_{2}, \AA$ ) and its change ( $\Delta R_{2}, \AA$ ) in the dyads and triads

| Complex | $E_{\text {int }}$ | $\alpha$ | $R_{1}$ | $R_{2}$ | $\Delta R_{2}$ | $R_{2} / R_{1}$ | $\gamma_{1}$ | $\gamma_{2}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{PhSiH}_{3} \cdots \mathrm{NH}_{3}$ | -1.94 | 108.1 | 3.112 | 1.886 | 0.009 | 0.61 | 0.853 | 0.496 |
| $\mathrm{PhSiH}_{3} \cdots \mathrm{NHCH}_{2}$ | -2.52 | 107.9 | 3.050 | 1.887 | 0.010 | 0.62 | 0.836 | 0.497 |
| $\mathrm{PhSiH}_{3} \cdots \mathrm{C}_{3} \mathrm{~N}_{2} \mathrm{H}_{4}$ | -3.90 | 106.1 | 2.942 | 1.895 | 0.018 | 0.64 | 0.770 | 0.499 |
| $\mathrm{PhGeH}_{3} \cdots \mathrm{NH}_{3}$ | -1.76 | 108.1 | 3.222 | 1.940 | 0.009 | 0.60 | 0.882 | 0.510 |
| $\mathrm{PhGeH}_{3} \cdots \mathrm{NHCH}_{2}$ | -2.22 | 107.9 | 3.123 | 1.940 | 0.009 | 0.62 | 0.856 | 0.510 |
| PhGeH3 $\cdots \mathrm{C}_{3} \mathrm{~N}_{2} \mathrm{H}_{4}$ | -3.19 | 107.3 | 3.092 | 1.945 | 0.014 | 0.63 | 0.814 | 0.512 |
| $\mathrm{Be}^{2+} \ldots \mathrm{PhSiH}_{3} \cdots \mathrm{NH}_{3}$ | -40.82 | 89.1 | 2.072 | 2.155 | 0.268 | 1.04 | 0.545 | 0.567 |
| $\mathrm{Be}^{2+} \ldots \mathrm{PhSiH}_{3} \cdots \mathrm{NHCH}_{2}$ | -44.56 | 88.8 | 2.031 | 2.161 | 0.274 | 1.06 | 0.534 | 0.569 |
| $\mathrm{Be}^{2+} \ldots \mathrm{PhSiH}_{3} \cdots \mathrm{C}_{3} \mathrm{~N}_{2} \mathrm{H}_{4}$ | -100.06 | 78.9 | 1.960 | 2.689 | 0.802 | 1.37 | 0.516 | 0.708 |
| $\mathrm{Be}^{2+} \ldots \mathrm{PhGeH}_{3} \cdots \mathrm{NH}_{3}$ | -34.71 | 89.7 | 2.182 | 2.276 | 0.345 | 1.04 | 0.574 | 0.599 |
| $\mathrm{Be}^{2+} \ldots \mathrm{PhGeH}_{3} \cdots \mathrm{NHCH}_{2}$ | -37.60 | 89.1 | 2.141 | 2.281 | 0.350 | 1.07 | 0.563 | 0.600 |
| $\mathrm{Be}^{2+} \ldots \mathrm{PhGeH}_{3} \cdots \mathrm{C}_{3} \mathrm{~N}_{2} \mathrm{H}_{4}$ | -94.49 | 76.3 | 2.023 | 2.850 | 0.919 | 1.41 | 0.532 | 0.750 |
| $\mathrm{Mg}^{2+} \ldots \mathrm{PhSiH}_{3} \ldots \mathrm{NH}_{3}$ | -20.88 | 91.5 | 2.123 | 2.084 | 0.197 | 0.98 | 0.558 | 0.548 |
| $\mathrm{Mg}^{2+} \ldots \mathrm{PhSiH}_{3} \cdots \mathrm{NHCH}_{2}$ | -30.01 | 91.2 | 2.078 | 2.087 | 0.200 | 1.00 | 0.547 | 0.549 |
| $\mathrm{Mg}^{2+} \ldots \mathrm{PhSiH}_{3} \cdots \mathrm{C}_{3} \mathrm{~N}_{2} \mathrm{H}_{4}$ | -66.10 | 86.5 | 2.018 | 2.220 | 0.333 | 1.10 | 0.531 | 0.584 |
| $\mathrm{Mg}^{2+} \ldots \mathrm{PhGeH}_{3} \ldots \mathrm{NH}_{3}$ | -24.14 | 93.0 | 2.260 | 2.174 | 0.243 | 0.96 | 0.598 | 0.572 |
| $\mathrm{Mg}^{2+} \ldots \mathrm{PhGeH}_{3} \cdots \mathrm{NHCH}_{2}$ | -27.34 | 92.5 | 2.215 | 2.176 | 0.245 | 0.98 | 0.583 | 0.573 |
| $\mathrm{Mg}^{2+} \ldots \mathrm{PhGeH}_{3} \cdots \mathrm{C}_{3} \mathrm{~N}_{2} \mathrm{H}_{4}$ | -69.56 | 83.0 | 2.072 | 2.504 | 0.573 | 1.21 | 0.545 | 0.715 |

Note: $\gamma$ is a ratio of $R_{1}$ or $R_{2}$ to the sum of the van der Waals radii of the two atoms.
this quantity by an order of magnitude up to the $200 \mathrm{kcal} \mathrm{mol}^{-1}$ range. The magnification is somewhat larger for the more compact $\mathrm{Be}^{2+}$ cation.

Like the $\sigma$-hole depths, the interaction energies are also enhanced by approximately an order of magnitude by either of these two dications. $E_{\text {int }}$, which refers to the interaction of the base with the $\mathrm{M}^{2+} \ldots \mathrm{PhTH}_{3}$ pair, is particularly large for $\mathrm{C}_{3} \mathrm{~N}_{2} \mathrm{H}_{4}$, rising up to about $100 \mathrm{kcal} \mathrm{mol}^{-1}$, twice that for the two N-bases, which are themselves also magnified a great deal. The $\alpha$ angle lies in the vicinity of $90^{\circ}$ for these triads, indicating a relatively planar $\mathrm{TH}_{3}$ group. In fact, $\alpha$ correlates rather well with the interaction energy, with a correlation coefficient of 0.94, as shown in Fig. 3. A stronger TB diminishes $\alpha$, getting it below $90^{\circ}$ for the more strongly bound complexes. Such small angles are suggestive of an inversion of the $\mathrm{TH}_{3}$ group, which is itself associated with a certain degree of transfer of $\mathrm{TH}_{3}$ from the phenyl to the base.


Fig. 3 Average of three C...T-H angles ( $\alpha$ ) versus the interaction energy ( $E_{\text {int }}$ ) of tetrel bond in the triads.

The $R_{1}$ and $R_{2}$ distances in Table 1 bear out this idea. $R_{1}$ is roughly equivalent to $R_{2}$ for those triads with $\mathrm{NH}_{3}$ and $\mathrm{NHCH}_{2}$, with a ratio of just slightly larger than unity. It might thus be appropriate to consider the $\mathrm{TH}_{3}$ group as equally shared between the two subunits, a sort of half transfer. The degree of transfer is considerably larger for the carbene, where the $R_{2} /$ $R_{1}$ ratio has risen to well above 1 , particularly for the $\mathrm{Be}^{2+}$ dication, where it is 1.4. It would thus be fair to think of a $\mathrm{TH}_{3}$ transfer that exceeds a half transfer, even approaching a full transfer. Indeed, $R_{1}$ in the $\mathrm{Be}^{2+} \ldots \mathrm{PhSiH}_{3} \cdots \mathrm{C}_{3} \mathrm{~N}_{2} \mathrm{H}_{4}$ complex is $1.960 \AA$, only some $0.05 \AA$ longer than the $1.913 \AA$ for a fully optimized ${ }^{+} \mathrm{SiH}_{3}-\mathrm{C}_{3} \mathrm{~N}_{2} \mathrm{H}_{4}$ cation monomer. The triad and monomer values in the Ge analogues are 2.023 and $1.964 \AA$, respectively, a difference of only $0.06 \AA$. Another measure of the degree of transfer arises in the $\alpha$ angle. A value of $90^{\circ}$ might be thought of as a demarcation of half transfer as the $\mathrm{TH}_{3}$ group undergoes an inversion. According to Fig. 3, this line is crossed when the interaction energy exceeds about $36 \mathrm{kcal} \mathrm{mol}^{-1}$.

### 3.3 Degree of transfer

Other means of assessing the degree of transfer are derived from AIM analysis of the electron density topology. The data in the first six rows of Table 2 indicate a covalent $\mathrm{C}-\mathrm{T}$ bond in the six dyads, with bond critical point density $>0.1$, large density Laplacian and negative energy density $H$. The corresponding quantities for the $\mathrm{T} \cdots \mathrm{N} / \mathrm{C}$ bonds are clearly noncovalent: $\rho$ and $\nabla^{2} \rho$ are an order of magnitude smaller, and $H$ is slightly positive. The situation changes dramatically when the $\mathrm{M}^{2+}$ cations are added. All three AIM quantities are comparable for the two bonds but the balance shifts quite a bit toward a stronger and at least partially covalent $\mathrm{T} \cdots \mathrm{C} / \mathrm{N}$ bond for the $\mathrm{C}_{3} \mathrm{~N}_{2} \mathrm{H}_{4}$ base, while the C-T bond has weakened quite a bit. Note especially that the sign of H switches from slightly positive in the dyads to substantially negative in all of the triads, clear confirmation of a strengthened covalent nature.

Table 2 Electron density $(\rho)$, Laplacian $\left(\nabla^{2} \rho\right)$, and total energy density $(H)$ at the $C-T$ and $T \ldots N / C$ BCPs in the dyads and triads, all in a.u

| Complex | $\mathrm{C}-\mathrm{T}$ |  |  | $\underline{T} \cdots \mathrm{~N} / \mathrm{C}$ |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | $\rho$ | $\nabla^{2} \rho$ | H | $\rho$ | $\nabla^{2} \rho$ | H |
| $\mathrm{PhSiH}_{3} \cdots \mathrm{NH}_{3}$ | 0.1084 | 0.3729 | -0.0466 | 0.0091 | 0.0284 | 0.0008 |
| $\mathrm{PhSiH}_{3} \cdots \mathrm{NHCH}_{2}$ | 0.1084 | 0.3734 | -0.0466 | 0.0104 | 0.0319 | 0.0009 |
| $\mathrm{PhSiH}_{3} \cdots \mathrm{C}_{3} \mathrm{~N}_{2} \mathrm{H}_{4}$ | 0.1073 | 0.3679 | -0.0459 | 0.0133 | 0.0335 | 0.0007 |
| PhGeH3 $\cdots \mathrm{NH}_{3}$ | 0.1260 | 0.1507 | -0.0713 | 0.0082 | 0.0258 | 0.0009 |
| $\mathrm{PhGeH}_{3} \cdots \mathrm{NHCH}_{2}$ | 0.1259 | 0.1521 | -0.0712 | 0.0104 | 0.0307 | 0.0009 |
| PhGeH3 $\cdots \mathrm{C}_{3} \mathrm{~N}_{2} \mathrm{H}_{4}$ | 0.1242 | 0.1540 | -0.0696 | 0.0120 | 0.0333 | 0.0008 |
| $\mathrm{Be}^{2+} \ldots \mathrm{PhSiH}_{3} \cdots \mathrm{NH}_{3}$ | 0.0586 | 0.1775 | -0.0184 | 0.0590 | 0.2180 | -0.0130 |
| $\mathrm{Be}^{2+} \ldots \mathrm{PhSiH}_{3} \cdots \mathrm{NHCH}_{2}$ | 0.0577 | 0.1743 | -0.0180 | 0.0600 | 0.2537 | -0.0126 |
| $\mathrm{Be}^{2+} \ldots \mathrm{PhSiH}_{3} \cdots \mathrm{C}_{3} \mathrm{~N}_{2} \mathrm{H}_{4}$ | 0.0232 | 0.0395 | -0.0033 | 0.0892 | 0.3547 | -0.0294 |
| $\mathrm{Be}^{2+} \ldots \mathrm{PhGeH}_{3} \cdots \mathrm{NH}_{3}$ | 0.0602 | 0.1279 | -0.0191 | 0.0618 | 0.1814 | -0.0167 |
| $\mathrm{Be}^{2+} \ldots \mathrm{PhGeH}_{3} \cdots \mathrm{NHCH}_{2}$ | 0.0594 | 0.1278 | -0.0186 | 0.0661 | 0.2057 | -0.0184 |
| $\mathrm{Be}^{2+} \ldots \mathrm{PhGeH}_{3} \cdots \mathrm{C}_{3} \mathrm{~N}_{2} \mathrm{H}_{4}$ | 0.0192 | 0.0497 | 0.0001 | 0.1053 | 0.2152 | -0.0503 |
| $\mathrm{Mg}^{2+} \ldots \mathrm{PhSiH}_{3} \ldots \mathrm{NH}_{3}$ | 0.0695 | 0.2294 | -0.0227 | 0.0510 | 0.1746 | -0.0128 |
| $\mathrm{Mg}^{2+} \ldots \mathrm{PhSiH}_{3} \cdots \mathrm{NHCH}_{2}$ | 0.0690 | 0.2287 | -0.0225 | 0.0544 | 0.2069 | -0.0125 |
| $\mathrm{Mg}^{2+} \ldots \mathrm{PhSiH}_{3} \cdots \mathrm{C}_{3} \mathrm{~N}_{2} \mathrm{H}_{4}$ | 0.0527 | 0.1312 | -0.0174 | 0.0786 | 0.3006 | -0.0997 |
| $\mathrm{Mg}^{2+} \ldots \mathrm{PhGeH}_{3} \ldots \mathrm{NH}_{3}$ | 0.0766 | 0.1482 | -0.0305 | 0.0522 | 0.1504 | -0.0118 |
| $\mathrm{Mg}^{2+} \ldots \mathrm{PhGeH}_{3} \ldots \mathrm{NHCH}_{2}$ | 0.0763 | 0.1490 | -0.0303 | 0.0562 | 0.1692 | -0.0135 |
| $\mathrm{Mg}^{2+} \ldots \mathrm{PhGeH}_{3} \cdots \mathrm{C}_{3} \mathrm{~N}_{2} \mathrm{H}_{4}$ | 0.0396 | 0.0743 | -0.0070 | 0.0938 | 0.1531 | -0.0444 |

The NCI diagrams of the dyads and triads displayed in Fig. S2 (ESI $\dagger$ ) are a graphical way of looking at the electron density topology in a three-dimensional fashion. The green areas in the dyads are consistent with a weak $\mathrm{T} \cdots \mathrm{N} / \mathrm{C}$ tetrel bond, and the covalent $\mathrm{C}-\mathrm{T}$ bond to the phenyl group is signaled by the red and blue patterns. In the case of the triads, however, the patterns are similar on both sides of the $\mathrm{TH}_{3}$ group, consistent with an interpretation of some degree of $\mathrm{TH}_{3}$ transfer.

An important feature of tetrel and other noncovalent bond formation is the transfer of charge from Lewis base to acid. This charge transfer (CT) is reported in Table 3 and is fairly small in the dyads, 0.04 e or less. This quantity is greatly magnified in the triads, comporting with their much stronger tetrel bonds. CT rises to more than $0.4 e$ in several cases, the triads with the highest degree of $\mathrm{TH}_{3}$ transfer. When CT is calculated on base of Mulliken charge, its value becomes smaller, but the variation is similar to that with natural charge.

In addition to an overall transfer between the two subunits, the transfer can be further partitioned into pairs of orbitals. As is common to tetrel and related bonds, the largest transfer is that from the lone pair of the $\mathrm{C} / \mathrm{N}$ atom of the Lewis base into the $\sigma^{*}{ }_{(\mathrm{C}-\mathrm{T})}$ antibonding orbital of the acid. The overlap between these orbitals is illustrated in Fig. 4a. As seen in the fourth column of Table 3, the second-order perturbation energy associated with this transfer $E^{2}$ is between 5 and $10 \mathrm{kcal} \mathrm{mol}^{-1}$ for the various dyads. As the tetrel bond is strengthened in the triads, and the $\mathrm{TH}_{3}$ group moves closer to the base, this quantity is drastically enhanced, reaching the $88-400 \mathrm{kcal} \mathrm{mol}^{-1}$ range. Note also that due to the half transfer, there is a mirror image tetrel bond between the T and the phenyl group, exemplified by Fig. 4b. The NBO charge transfer energies for this second TB are listed in the last column of Table 3. In the $\mathrm{Be}^{2+}$ cases, this second quantity is smaller than the first, consistent with a transfer of the $\mathrm{TH}_{3}$ to the base. This same disparity occurs in the $\mathrm{Mg}^{2+}$ cases with

Table 3 Charge transfer of tetrel bond (CT, e) based on natural charge $(N)$ and Mulliken charge $(M)$ and second-order perturbation energies ( $E^{2}$, kcal $\mathrm{mol}^{-1}$ ) in the dyads and triads

| Complexes | $\mathrm{CT}_{\mathrm{N}}$ | $\mathrm{CT}_{\mathrm{M}}$ | Types | $E^{2}$ | Types | $E^{2}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{PhSiH}_{3} \cdots \mathrm{NH}_{3}$ | 0.019 | 0.016 | $\mathrm{Lp}_{\mathrm{N}} \rightarrow \sigma^{*}{ }_{\mathrm{C}-\mathrm{Si}}$ | 5.22 |  |  |
| $\mathrm{PhSiH}_{3} \cdots \mathrm{NHCH}_{2}$ | 0.019 | 0.018 | $\mathrm{Lp}_{\mathrm{N}} \rightarrow \sigma^{*}{ }_{\mathrm{C}-\mathrm{Si}}$ | 5.35 |  |  |
| $\mathrm{PhSiH}_{3} \cdots \mathrm{C}_{3} \mathrm{~N}_{2} \mathrm{H}_{4}$ | 0.041 | 0.035 | $\mathrm{Lp}_{\mathrm{C}} \rightarrow \sigma^{*}{ }_{\mathrm{C}-\mathrm{Si}}$ | 10.66 |  |  |
| $\mathrm{PhGeH}_{3} \cdots \mathrm{NH}_{3}$ | 0.016 | 0.011 | $\mathrm{Lp}_{\mathrm{N}} \rightarrow \sigma^{*}{ }_{\text {C-Ge }}$ | 4.99 |  |  |
| $\mathrm{PhGeH}_{3} \cdots \mathrm{NHCH}_{2}$ | 0.018 | 0.015 | $\mathrm{Lp}_{\mathrm{N}} \rightarrow \sigma^{*}{ }_{\mathrm{C}-\mathrm{Ge}}$ | 5.13 |  |  |
| PhGeH3 $\cdots \mathrm{C}_{3} \mathrm{~N}_{2} \mathrm{H}_{4}$ | 0.037 | 0.026 | $\mathrm{Lp}_{\mathrm{C}} \rightarrow \sigma^{*}{ }_{\text {C-Ge }}$ | 10.37 |  |  |
| $\mathrm{Be}^{2+} \ldots \mathrm{PhSiH}_{3} \cdots \mathrm{NH}_{3}$ | 0.224 | 0.089 | $\mathrm{Lp}_{\mathrm{N}} \rightarrow \mathrm{p}^{*} \mathrm{Si}^{\text {i }}$ | 143.11 | $\mathrm{Lp}_{\mathrm{C}} \rightarrow \sigma^{*}{ }_{\text {Si- }}$ | 31.34 |
| $\mathrm{Be}^{2+} \ldots \mathrm{PhSiH}_{3} \cdots \mathrm{NHCH}_{2}$ | 0.235 | 0.094 | $\mathrm{Lp}_{\mathrm{N}} \rightarrow \mathrm{p}^{*} \mathrm{Si}$ | 162.27 | $\mathrm{Lp}_{\mathrm{C}} \rightarrow \sigma^{*}{ }_{\text {Si-N }}$ | 32.98 |
| $\mathrm{Be}^{2+} \ldots \mathrm{PhSiH}_{3} \cdots \mathrm{C}_{3} \mathrm{~N}_{2} \mathrm{H}_{4}$ | 0.422 | 0.297 | $\mathrm{Lp}_{\mathrm{C}} \rightarrow \mathrm{p}^{*} \mathrm{Si}$ | 400.69 | $\mathrm{Lp}_{\mathrm{C}} \rightarrow \sigma^{*} \mathrm{Si-C}$ | 24.64 |
| $\mathrm{Be}^{2+} \ldots \mathrm{PhGeH}_{3} \cdots \mathrm{NH}_{3}$ | 0.203 | 0.073 | $\mathrm{Lp}_{\mathrm{N}} \rightarrow \mathrm{p}^{*}{ }_{\text {Ge }}$ | 192.53 | $\mathrm{Lp}_{\mathrm{C}} \rightarrow \sigma^{*}{ }_{\text {Ge-N }}$ | 28.76 |
| $\mathrm{Be}^{2+} \ldots . \mathrm{PhGeH}_{3} \cdots \mathrm{NHCH}_{2}$ | 0.205 | 0.082 | $\mathrm{Lp}_{\mathrm{N}} \rightarrow \mathrm{p}^{*}{ }_{\text {Ge }}$ | 127.31 | $\mathrm{Lp}_{\mathrm{C}} \rightarrow \sigma^{*}{ }_{\text {Ge-N }}$ | 28.32 |
| $\mathrm{Be}^{2+} \ldots \mathrm{PhGeH}_{3} \cdots \mathrm{C}_{3} \mathrm{~N}_{2} \mathrm{H}_{4}$ | 0.426 | 0.350 | $\mathrm{Lp}_{\mathrm{C}} \rightarrow \mathrm{p}^{*} \mathrm{Ge}^{*}$ | 382.97 | $\mathrm{Lp}_{\mathrm{C}} \rightarrow \sigma^{*} \mathrm{Ge-C}$ | 21.93 |
| $\mathrm{Mg}^{2+} \ldots \mathrm{PhSiH}_{3} \cdots \mathrm{NH}_{3}$ | 0.205 | 0.055 | $\mathrm{Lp}_{\mathrm{N}} \rightarrow \mathrm{p}^{*}{ }^{\text {Si }}$ | 117.34 | $\mathrm{Lp}_{\mathrm{C}} \rightarrow \mathrm{p}^{*}{ }_{\text {Si }}$ | 235.74 |
| $\mathrm{Mg}^{2+} \ldots \mathrm{PhSiH}_{3} \cdots \mathrm{NHCH}_{2}$ | 0.215 | 0.061 | ${ }^{L} p_{N} \rightarrow \mathrm{p}^{*}{ }_{\text {Si }}$ | 134.56 | $\mathrm{Lp}_{\mathrm{C}} \rightarrow \mathrm{p}^{*}{ }_{\text {Si }}$ | 224.88 |
| $\mathrm{Mg}^{2+} \ldots \mathrm{PhSiH}_{3} \cdots \mathrm{C}_{3} \mathrm{~N}_{2} \mathrm{H}_{4}$ | 0.388 | 0.235 | ${ }^{L} p_{\mathrm{C}} \rightarrow \mathrm{p}^{*}{ }_{\text {Si }}$ | 307.92 | $\mathrm{Lp}_{\mathrm{C}} \rightarrow \sigma^{*}{ }_{\text {Si-C }}$ | 29.57 |
| $\mathrm{Mg}^{2+} \ldots \mathrm{PhGeH}_{3} \cdots \mathrm{NH}_{3}$ | 0.164 | 0.024 | $\mathrm{Lp}_{\mathrm{N}} \rightarrow \mathrm{p}^{*}{ }_{\text {Ge }}$ | 88.39 | $\mathrm{Lp}_{\mathrm{C}} \rightarrow \mathrm{p}^{*}{ }_{\mathrm{Ge}}$ | 222.85 |
| $\mathrm{Mg}^{2+} \ldots \mathrm{PhGeH}_{3} \cdots \mathrm{NHCH}_{2}$ | 0.172 | 0.041 | $\mathrm{Lp}_{\mathrm{N}} \rightarrow \mathrm{p}^{*}{ }_{\text {Ge }}$ | 104.90 | $\mathrm{Lp}_{\mathrm{C}} \rightarrow \mathrm{p}^{*}{ }_{\text {Ge }}$ | 209.10 |
| $\mathrm{Mg}^{2+} \ldots \mathrm{PhGeH}_{3} \cdots \mathrm{C}_{3} \mathrm{~N}_{2} \mathrm{H}_{4}$ | 0.321 | 0.191 | $\mathrm{Lp}_{\mathrm{C}} \rightarrow \mathrm{p}^{*}{ }_{\mathrm{Ge}}$ | 203.17 | $\mathrm{Lp}_{\mathrm{C}} \rightarrow \sigma_{\text {Ge-C }}^{*}$ | 19.43 |


b)


Fig. 4 Diagrams of orbital interactions in (a) $\mathrm{PhSiH}_{3} \cdots \mathrm{C}_{3} \mathrm{~N}_{2} \mathrm{H}_{4}$ and (b) $\mathrm{Be}^{2+}$ .. $\mathrm{PhSiH}_{3} \cdots \mathrm{C}_{3} \mathrm{~N}_{2} \mathrm{H}_{4}$.
the carbene base; NBO suggests the bond to the phenyl group remains stronger than that to the base for $\mathrm{NH}_{3}$ and $\mathrm{NHCH}_{2}$.

With specific regard to the motion of the central $\mathrm{TH}_{3}$ between the phenyl and base, this issue can be alternately viewed by considering the energy of the system with respect to both $R_{2}$ and its sum with $R_{1}$. Fig. 5 plots the total energy of the system as cuts through this two-dimensional surface for the $\mathrm{PhSiH}_{3} \cdots \mathrm{C}_{3} \mathrm{~N}_{2} \mathrm{H}_{4}$ dyad in 5 a and the same system but with $\mathrm{Be}^{2+}$ added in 5 b. Each colored curve was computed by fixing the intermolecular distance between the acid and base $R(\mathrm{C} \cdots \mathrm{C})=$ $R_{1}+R_{2}$ to a particular value. Then a $\mathrm{SiH}_{3}$ transfer potential was computed by altering the $\mathrm{C}-\mathrm{Si}$ bond length within the $\mathrm{PhSiH}_{3}$ unit, holding the intermolecular distance fixed. In the $\mathrm{PhSiH}_{3} \cdots \mathrm{C}_{3} \mathrm{~N}_{2} \mathrm{H}_{4}$ dyad, all curves of Fig. 5a contain a single well with a relatively short $\mathrm{R}(\mathrm{C}-\mathrm{Si})$, thus signaling no transfer. But after the $\mathrm{Be}^{2+}$ has been added, each curve in Fig. 5b contains two wells, suggesting a transfer is possible at any particular frozen intermolecular distance. The two wells are of different energy, with the untransferred $\mathrm{PhSiH}_{3} \cdots \mathrm{C}_{3} \mathrm{~N}_{2} \mathrm{H}_{4}$ more stable than $\mathrm{Ph} \cdots \mathrm{SiH}_{3} \mathrm{C}_{3} \mathrm{~N}_{2} \mathrm{H}_{4}$. They are separated by an energy barrier of variable height. For example, with $R(C \cdots C)$ fixed at $4.6 \AA$, an energy barrier of $9.4 \mathrm{kcal} \mathrm{mol}^{-1}$ separates the two minima. The barrier is sensitive to the intermolecular distance, increasing quickly as $\mathrm{R}(\mathrm{C} \cdots \mathrm{C})$ is elongated, with some of these values contained in Table S1 (ESI $\dagger$ ).

## 4 Discussion

It would thus appear that the degree of transfer of the $\mathrm{TH}_{3}$ group from the phenyl ring to any of several bases is rather small for both Si and Ge in the dimers. The $\mathrm{C}-\mathrm{T}$ distance stretches by less than $0.02 \AA$, and in some cases less than


Fig. 5 Energy profiles for $\mathrm{SiH}_{3}$ transfer between two carbon atoms in (a) $\mathrm{PhSiH}_{3} \cdots \mathrm{C}_{3} \mathrm{~N}_{2} \mathrm{H}_{4}$ and (b) $\mathrm{Be}^{2+} \ldots \mathrm{PhSiH}_{3} \cdots \mathrm{C}_{3} \mathrm{~N}_{2} \mathrm{H}_{4}$.
$0.01 \AA$. This minimal transfer is understandable since a full transfer would lead to an ion pair involving $\mathrm{C}_{6} \mathrm{H}_{5}{ }^{-}$and ${ }^{+} \mathrm{TH}_{3}{ }^{-}$ Nuc. This reluctance for an overall neutral complex to engage in more than a small amount of transfer places the $\mathrm{TH}_{3}$ group in the same category as the closely related proton transfer in H -bonded systems, according to an extensive body of literature that has accumulated over the years. ${ }^{43-45}$ And more recent examination of the closely related halogen transfer ${ }^{46-49}$ has arrived at a similar conclusion as the tetrel transfer here.

Again for both H -bonds and halogen bonds, the situation changes when the entire system contains either an overall positive or negative charge. In such a case, the transfer no longer transitions the system from a neutral to a much less stable ion pair. Instead, the $\left(\mathrm{AH}^{+} \cdots \mathrm{B}\right) \rightarrow\left(\mathrm{A} \cdots \mathrm{H}^{+} \mathrm{B}\right)$ reaction simply changes an ion-neutral complex to a very similar neutral-ion dimer, with no obvious or dramatic change in energy. Work over the years has shown that systems of this type, whether H - or halogen-bonded, are characterized by a double-well potential, with an energy barrier that rises quickly as the distance between the A and B subunits is stretched. ${ }^{50-56}$

The calculations described above show how the presence of a cation can act to push a $\mathrm{TH}_{3}$ group across a tetrel bond. This finding conforms to earlier work, for example in that a proton transfer can be promoted by the presence of an ion ${ }^{57-60}$ as can the presence of neighboring dipoles. ${ }^{61}$ There are environments which might enable the transfer within a neutral system.

Solvation for example, helps to stabilize the ion pair thus facilitating the proton transfer within a neutral complex ${ }^{62}$ and can perturb the potential within a charged system as well. ${ }^{55}$ There are also cooperative effects that can push an ionic entity across an existing noncovalent bond ${ }^{63}$ as did the dications here.

It is worth mentioning that the half transfer of any of these $\mathrm{TH}_{3}$ groups would correspond approximately to the transition state in a $\mathrm{S}_{\mathrm{N}} 2$ reaction. In contrast, though, these complexes where $\alpha$ is roughly $90^{\circ}$ correspond to minima, not a transition state. The $\mathrm{S}_{\mathrm{N}} 2$ reaction is usually discussed in the context of $\mathrm{T}=$ C, but the systems contained here did not contain the methyl group, i.e. T was not set equal to C . In the $\mathrm{S}_{\mathrm{N}} 2$ reaction involving the $\mathrm{CH}_{3}$ group, an anion is often taken as nucleophile, wherein the $\mathrm{CH}_{3}$ group transfers from a weak nucleophile to a strong one. When $\mathrm{PhCH}_{3}$ pairs with $\mathrm{NH}_{3}, \mathrm{NHCH}_{2}$, and $\mathrm{C}_{3} \mathrm{~N}_{2} \mathrm{H}_{4}$, the interaction is very weak, less than $1 \mathrm{kcal} \mathrm{mol}^{-1}$. However, no TB is obtained even when a dication is added. In future work, we intend to focus on the $\mathrm{CH}_{3}$ transfer through the intermediacy of a tetrel bond.

## 5 Conclusions

The transfer of a $\mathrm{TH}_{3}$ group ( $\mathrm{T}=\mathrm{Si}$ and Ge ) can be realized, even though this group is much heavier than a proton and is in principle much more difficult to accomplish. The ease of this transfer is closely related to the strength of the tetrel bond within the complex. Even when paired with any of three strong bases, $\mathrm{NH}_{3}, \mathrm{NHCH}_{2}$, and the carbene $\mathrm{C}_{3} \mathrm{~N}_{2} \mathrm{H}_{4}$, the $\mathrm{TH}_{3}$ group of $\mathrm{PhTH}_{3}$ will not transfer, due in part to its shallow $\sigma$-hole. On the other hand, introduction of a $\mathrm{Be}^{2+}$ or $\mathrm{Mg}^{2+}$ dication above the phenyl ring deepens the $\sigma$-hole, and greatly strengthens the tetrel bond, up to the $100 \mathrm{kcal} \mathrm{mol}^{-1}$ range. In such a situation, the $\mathrm{TH}_{3}$ group transfers roughly halfway for the two N -bases, and more completely for the carbine.

## Conflicts of interest

There are no conflicts to declare.

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