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Calculation of the Ligating Strength of N-Heterocyclic Germylenes – Extending the π-Acceptor Range

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The ligand behaviour of N-heterocyclic germylenes (NHGe) with respect to their σ-donor ability, π-acceptor strength and net electron donating ability is determined by calculating their molecular electrostatic potential (MEP). Correlation of the MEP to the Tolman Electronic Parameter (TEP) is achieved using a family of phosphite ligands. The results indicate that the π-acceptor strength of NHGe reaches significantly beyond that of phosphites.

Introduction

The first stable carbenes were synthesised by Arduengo et al. in 1991 using imidazolium salts as precursors.[1] Later, carbenes derived from benzimidazole[2] and acyclic representatives[3] were added to the list. These N-heterocyclic carbenes (NHC) and their acyclic counterparts derive their remarkable stability from the strong $N \rightarrow C_{carbene}$ π donation that leads to a largely filled p(π) orbital at the carbene carbon atom.[4] It is no coincidence that most applications of stable carbenes involve the Arduengo type imidazole-based carbenes as they are much more stable than the benzimidazole-based or acyclic representatives.[5]

The corresponding germylenes are considerably more stable and were synthesised in reverse order to the carbenes.[6] The first examples were the acyclic germylenes described by Lappert et al. in the 1970's,[7] the first N-heterocyclic germylene (NHGe) introduced by Veith[8] and Meller[9] in the 1980's and the first non-anellated NHGe by Herrmann et al. in 1992.[10]

In an earlier review article Petz described the chemistry of low-valent germanium(II) halides and amides briefly touching their coordination chemistry and ligating properties.[11] A key finding was the principle ability of germylenes to engage in metal-to-ligand back-bonding and to possess a π-acceptor strength comparable to that of triarylphosphanes. In the twenty years following Petz's landmark review article on acyclic germylenes, new classes of mainly heterocyclic germylenes were synthesised and described.[8,9,12]

We are very much interested in the synthesis of neutral electron-deficient germylenes and thus had to make an educated guess as to the relative stabilities of different germylene classes. From the chemistry of carbenes it is known, that anellated NHC are less stable than the non-anellated derivatives, and acyclic carbenes are thought to be less stable still.[5] If we assume this observation to be valid for the germylenes as well, then the NHGe should be more stable than Lappert's acyclic representatives. This assumption is corroborated by the annelation effect described by Heinicke and Kühl.[13] The annelation effect describes the influence of a conjugated unsaturated electron system on the bond order of the N–Ge bonds and thus on the π-acceptor strength of the germylene. As the anellated system is usually electron withdrawing, the annelation results in an increased π-acceptor strength of the NHGe (see Figure 1).

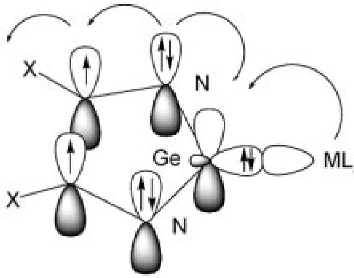

Figure 1. Backbonding in metal-germylene complexes.

One main aim of the current study is to identify germylenes possessing a π-acceptor strength rivalling or exceeding that of phosphites. Known examples for the ligating properties of germylenes include acyclic germanium(II) amides[11] and two representatives of NHGe, 1,3-$(But)_2C_2H_4N_2Ge$ (**1**) [14] and 1,3-$(CH_2But)_2C_2H_2N_2Ge$ (**2a**).[15] The electronic properties of ligands can easily be assessed by measuring the carbonyl stretching frequency of their metal-carbonyl

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complexes and comparing them to a common scale known as the Tolman Electronic Parameter (TEP)[16] (described below). If one converts the values found in Petz's review article to the TEP scale[17] and treats the two values for their NHGe counterparts similarly, one has established that the known examples for germylenes have a π-acceptor strength similar to that of triarylphosphanes. However, the application of the annelation effect would suggest that the substitution of the phenyl ring in 1,3-$(CH_2But)_2$-$C_6H_4N_2Ge$ (**3a**)[13b] by a pyrido,[13a] pyrazino- or quinoxalino-ring system would push the π-acceptor strength of the corresponding NHGe into the region of the phosphites.

Similarly, the substitution in 4,5-position of the five-membered ring or the respective position of the anellated NHGe should influence the π-acceptor strength of the germylene accordingly. Both effects are more easily monitored and compared in NHGe than in acyclic germylenes, where annelation is impossible and substitution rather difficult. In addition, it is assumed that NHGe are more stable than the corresponding acyclic germylenes and thus heterocyclic electron-deficient germylenes would stand a much greater chance to be synthesised.

During the course of the investigations a second aim presented itself. Up to date, theoretical studies of the electronic properties of ligands suffer from a systematic deviation from experimental values.[17] For instance, the calculated ν_{CO} values in transition-metal carbonyl complexes are typically 5–10% higher than the experimental values. The accuracy of theoretical calculations similar to the efforts for tertiary phosphanes,[18–20] amines[21] and DFT calculations on metal complexes[17,20] can be increased by the elimination of the transition metal as is the case in recent computations using the molecular electrostatic potential (MEP).[17–19] The second aim therefore is to arrive at a method that provides values that are directly comparable to experimental results without additional calibrations.

An added advantage of using MEP are the comparatively low system requirements and easy application as well as small expense involved in computing electronic properties of intended ligands. It should be possible to arrive at a meaningful value for the electronic properties of a ligand as easily as it is to calculate the "natural bite angle" of a bidentate ligand.[22]

Methodology

The Tolman Electronic Parameter (TEP) is based on transition-metal carbonyl complexes and in particular is defined as the ν_{CO} of the A_1 band in the IR spectrum of complex $[Ni(CO)_3L]$ were L is the monodentate ligand under investigation. Their IR spectra display very specific bands for the carbonyl groups. The resonances in the IR spectra for these groups are very sensitive towards alterations in tertiary phosphanes[23] and other ligands. The position of the ν_{CO} bands in the IR spectrum of a transition metal depends on the electronic situation at the metal. The CO ligand acts with its electron lone pair as a σ-donor towards the metal. The metal in turn can transfer electron density into the 2π antibonding orbital of the CO ligand, weakening the CO bond and shifting the ν_{CO} band towards lower wavenumbers.[24] If a CO ligand is replaced by a tertiary phosphane then the phosphane itself will act as a σ donor with its electron lone pair towards the metal. This renders the metal more electron rich. This increased electron density on the metal can then be transferred towards the CO groups and the phosphane ligands. The extent of this back bonding is dependent on the π-acceptor strength of the various ligands. As only the phosphane is altered and the other ligands (CO, Cp, etc.) remain constant, the system can be used to measure the electronic properties of a series of phosphane ligands. Of course, the phosphane ligands can be replaced by any other σ-donor ligand class such as sulfoxides and germylenes to determine their electronic properties. Good π-acceptor properties are indicated by a shift of the ν_{CO} frequency towards higher wavenumbers.[23] However, as the shift of ν_{CO} frequency is only an indication for the net electron donating ability of the ligand, this is not sufficient proof for good π-acceptor strength.

As this holds true for any transition-metal carbonyl complex, Tolman's famous statement "we could have chosen some other carbonyl complex, but $[Ni(CO)_3L]$ forms rapidly − even if L is very large" (L = tertiary phosphane) becomes understandable.[23] Indeed, before[25] and after[26–28] Tolman, other transition-metal carbonyl complexes were chosen for various reasons, propably the best known alternative system is the complex *cis*-$[Mo(CO)_4L–L]$ where L–L is a bidentate ligand,[26] developed by Crabtree to determine the electronic properties of chelating ligands. The Tolman scale originally reached from 2056 cm^{-1} (the value for the most basic phosphane $P\mathit{t}Bu_3$) to ca 2092 cm^{-1} (halogenated phosphites), but has been extended to lower wavenumbers with the advent of N-heterocyclic carbenes NHC.[29] This effectively means that the TEP spans a rather narrow range of some 40 wavenumbers making differences of 3–4 cm^{-1} very significant indeed.

The electrostatic potential of a molecule is a real physical property and can be determined experimentally by X-ray diffraction techniques or calculated computationally.[30] The MEP has its origin in the charge distribution within the molecule. The backbone is formed by the atoms whose nuclei are the centres of positive charge. The electrons (corresponding negative charge) are distributed around these nuclei occupying their respective orbitals. Thus, local minima V_{min} of the MEP indicate centres of negative charge on the molecule. These are quite frequently electron lone pairs. The absolute value of these minima can serve as a measure for the reactivity of the respective nucleophilic centre and hence for quantities such as the pK_a or the donor ability.

The electrostatic potential $V(r)$ is closely related to the total charge density $D(r)$ through the Poisson Equation (1).

$$\nabla^2 V(r) = -4 \pi D(r) \qquad (1)$$

and plays a central role in the density functional theory (DFT). Therefore, the MEP is not an alternative to DFT dependent theoretical methods, but can be seen as one of the tools in this rapidly growing trade.

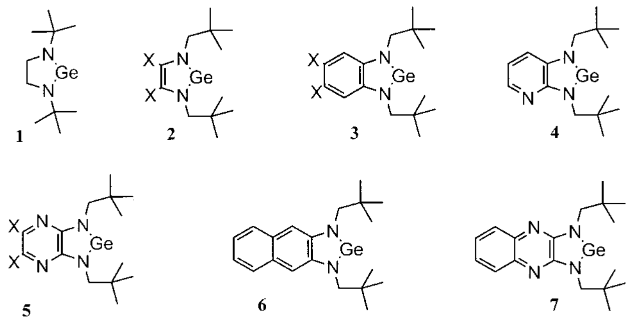
In a recent review, Politzer and Murray give a summary on the usefulness of MEP in determining nucleophilic areas and centres in molecules and to quantify their reactivity.[30a] Particularly instructive for our purposes are the sections on hydrogen bonding[31] and the basicity of amines. Here, the authors demonstrate how the hydrogen-bond acceptor strength can be calculated using MEP. As a hydrogen-bond acceptor is nothing else but a Brönstedt base, this is equivalent to calculating the pK_a for this nucleophilic centre.

Excellent correlation between measured pK_a's and calculated V_{min} values becomes even more apparent if MEP studies on azines, aliphatic amines, substituted pyridines and aniline derivatives are considered.[32] For all these nitrogen-containing nucleophiles, the V_{min} for the respective ring or amine nitrogen atoms has been shown to be a good measure for the pK_a.

Having demonstrated that MEP can indeed be used to calculate the pK_a and thus ν_{CO} of a nucleophilic ligand, one might be surprised why there shall be a controversy in the literature as to its applicability in determining the net donating ability of phosphanes. Suresh and Koga claim excellent correlation between the V_{min} of a phosphane and the frequency of the ν_{CO} band of the corresponding transition-metal carbonyl complex.[18] Giering et al., however, claim that such a correlation is not permissible as one can distinguish three families of phosphanes (alkyl, aryl and phosphite) that each correlate separately with the respective ν_{CO} band.[33]

The values for V_{min} are calculated in atomic units (au) and then transferred into [kcal/mol] for the convenience of the reader. Both units are given in Table 1 and Table 2.

A total of 13 phosphane ligands [P(O–*p*-Cl–*o*-tolyl)$_3$, PhOP(OMe)$_2$, P(O–2,4-Me$_2$–C$_6$H$_3$)$_3$, P(O–*p*-C$_6$H$_4$OMe)$_3$, P(*o*-tolyl)$_3$, P(OPh)$_3$, PPhCl$_2$, PMe$_2$CF$_3$, P(OCH$_2$)$_3$CEt, P(OCH$_2$)$_3$CPr, P(OCH$_2$)$_3$CMe, P(OCH$_2$CH$_2$CN)$_3$ and P(C$_6$F$_5$)$_3$] featuring a Tolman Electronic Parameter (TEP) of greater then 2080 cm^{-1}[16] (see Table 1) and seven NHGe ligand frameworks (see Scheme 1), six of which display neopentyl substituents on nitrogen were created using the program Cerius2–4.0.[34] The structure of **1** features *tert*-butyl substituents for comparison with experimental data.[10,14] A set of six substituents has been introduced to each of the three frameworks **2**, **3**, **5** to study the influence of donor and acceptor substituents on them. The structures were first relaxed using the force-field ESFF in Cerius2–4.0 and then further optimised by DFT under Gaussian 98[35] with the B3LYP functional and a 6-31G(d,p) basis set. The electrostatic potential was calculated for the final structure using the same functional and basis set, saved as cube files and analysed using the Gaussian interface of Cerius2–4.0. The precise value of the minimum of the molecular electrostatic potential (MEP) was obtained from the cube files by an automated procedure implemented as a script under scilab.[36]



X = H (**a**), F (**b**), Cl (**c**), CN (**d**), NO$_2$ (**e**), Me (**f**), OMe (**g**)

Scheme 1. Structures of the NHGe used for calculation.

For comparison with the data of Suresh and Koga[18] the MEP for three phosphorus ligands [PH$_3$, PPhCl$_2$, P(OPh)$_3$] were recalculated and yielded identical results. The data of these low electrostatic potentials are calculated with some uncertainty due to the influence of the positive ionic potential.

Table 1. Calculated molecular electrostatic potential MEP for electron poor phosphorus ligands.

Entry	Ligand	V_{min} [au]	V_{min} [kcal/mol]	Koga[a]	TEP [cm^{-1}][b]
1	P(OEt)$_3$			–27.85	2076.3
2	P(OMe)$_3$			–26.12	2079.5
3	P(O-*p*-Cl-*o*-Tolyl)$_3$	–0.0371	–23.2		2080.7
4	PhOP(OMe)$_2$	–0.0308	–19.3		2086.5
5	P(O-2,4-Me$_2$–C$_6$H$_3$)$_3$	–0.0285	–17.8		2083.2
6	P(O-*p*-C$_6$H$_4$OMe)$_3$	–0.0274	–17.1		2084.1
7	P(*o*-Tolyl)$_3$	–0.0255	–16.0		2084.1
8	P(OPh)$_3$	–0.0251	–15.7	–15.88	2085.3
9	PPhCl$_2$	–0.0148	–9.3	–9.38	2092.1
10	PH$_3$	–0.0447	–28.0	–28.2	
11	PMe$_2$CF$_3$	–0.0416	–26.0		2080.9
12	P(OCH$_2$)$_3$CEt	–0.0376	–23.5		2086.6
13	P(OCH$_2$)$_3$CPr	–0.0375	–23.5		2086.6
14	P(OCH$_2$)CMe	–0.0247	–15.4		2087.3
15	P(OCH$_2$CH$_2$CN)$_3$	–0.0104	–6.5		2087.6
16	P(C$_6$F$_5$)$_3$	–0.0223	–13.9		2090.9

[a] V_{min} in kcal/mol taken from ref.[18] [b] Ref.[16]

In most cases the electrostatic potential shows a well-defined minimum close to the position of the electron lone pairs on germanium or phosphorus. The withdrawal of electron density from the electron lone pair on Ge or P resulted in a very significant increase in the value of the minimum electrostatic potential in this region. In a few cases only a shallow minimum in a range of a positive potential was found at the position of the electron lone pairs.

Results and Discussion

From the available total set of phosphorus ligands, a ligand family comprising the Entries 3–9 in Table 1 was identified using the Quantitative Analysis of Ligand Effects (QALE) method developed by Giering, Prock and Fernandez.[37] This set of seven ligands was extended to nine by inclusion of $P(OEt)_3$ and $P(OMe)_3$ using the MEP values provided by Suresh and Koga.[18] Correlation of the MEP data for these nine ligands with their TEP values results in a correlation equation for electron-poor phosphorus ligands.

It should be mentioned that the Tolman Electronic parameter (TEP) was obtained empirically from the observed ν_{CO} bands in $[Ni(CO)_3L]$ (L = phosphane) complexes. They were listed by Tolman in order of increasing wavenumber. Later, several research groups published methods to derive quantitative information about the σ-donor and π-acceptor contributions that render the overall value.[17] QALE is the most accurate and widely accepted method. It uses four parameters to account for σ donor ability, steric and substituent effects, as well as π-acceptor strength. The σ-donor ability is the strongest effect by far, but the deviation from the reference value of 2056.1 cm^{-1} is usually attributed to the π-acceptor strength. This is not correct as this somewhat simplistic view neglects the other two QALE parameters and does not take into account those cases where the σ-donor ability is exceptionally weak[17] like in $P(CH_2CH_2CN)_3$.[38] The wealth of phosphorus ligands can be ordered in groups in such a way that each member behaves towards the four QALE parameters similar to all other members of the group, but different to other groups. Such a group is called a family in QALE terminology. As families are defined mathematically and not chemically, they often contain members that are chemically very different to other members. The ligands in Table 1 fall mainly into two groups, the unconstrained phosphites selected for further calculations and the constrained phosphites, where the three substituents on phosphorus bind to the same carbon bridge atom. There is an obvious geometrical constraint present in the second group that distinguishes this family from the second group of ligands.

It is also known from a recent study that a correlation between different transition-metal carbonyl complexes renders different linear-regression formulas for electron-rich and electron-poor ligand sets.[17] For this reason, only the electron-poor phosphites were selected.

The potential minima $V_{\min}$ on phosphorus for the nine selected phosphorus ligands are listed in Table 1 (Entries 1–9). The correlation (see Figure 2) with their TEP values yields Equation (2).

$$\nu CO_{Ni} = \left(\frac{V_{\min}}{1kcal/mol}\right)\cdot 0.73445\,cm^{-1} + 2097.6cm^{-1} \quad R = 0.939 \qquad (2)$$

Equation (2) was calculated using the $V_{\min}$ values in atomic units [au] having four significant digits and converted into kcal/mol (given with two digits behind the decimal point) for the convenience of the reader. The fifth digit in the equation is not considered to be significant, but serves to reduce the rounding error. The value of Equation (2) in [au] is: 458.72 [$V_{\min}$] cm^{-1} + 2097.6 cm^{-1}.

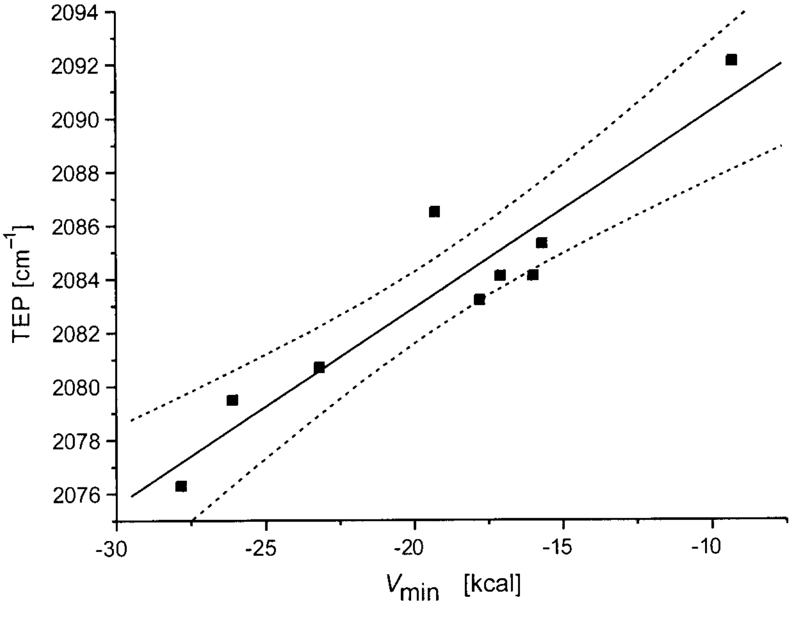


Figure 2. Calibration between TEP and $V_{\min}$ for Entries 1–9 in Table 1.

For the two NHGe ligands **1** and **2**, experimental TEP values of 2070[14] and 2073 cm^{-1},[17] respectively, are available. From Equation (2) values of 2081.2 and 2082.8 cm^{-1} are obtained, which are higher by about 10 cm^{-1} than the measured ones. This deviation of about 0.5% between calculated and measured TEP values is very modest compared to the 5–10% from DFT calculations on the entire metal-carbonyl complex.[17]

For a better understanding of error margins it should be remembered that we are looking at two different categories of differences in TEP values. The first is the experimental error encountered when the IR spectra of two different carbonyl complexes are measured. Here, the standard deviations are in the order of 0.1 cm^{-1} and the total range for accessible TEP values is approximately 40 cm^{-1} which makes a difference of 3–4 cm^{-1} for two different complexes very significant indeed.

The second category of differences is encountered with theoretical calculations. Calculated values are typically 5–10% above the respective experimental values.[17] This systematic deviation is addressed by a linear regression treatment correlating the experimental and theoretical values. An excellent correlation factor serves to validate theoretical values for complexes for which there are no experimental data. A deviation of 10 cm^{-1} as observed for the MEP values is therefore very modest compared to the 100–200 cm^{-1} observed for other theoretical methods. However, the raw data from MEP calculations is still not directly comparable to experimental values as here a deviation of 10 cm^{-1} is very large and equivalent to 25% of the entire experimental window.

Therefore, it seems desireable to refine the method sufficiently for the use as direct comparison between theoretical and experimental values and thus to eliminate the need for a correlation process. To be able to make semi-quantitative comparisons an error within 1 cm^{-1} seems appropriate.

The error in transferring the method from phosphorus to germanium can be attributed to the differences between the third-row-element phosphorus and the fourth-row-element germanium. As Politzer and Murray have pointed out in a MEP study of the group 15 hydrides NH_3, PH_3 and AsH_3, V_{min} increases as one moves down the group from –44.9 for NH_3 via –22.3 for PH_3 to –16.3 kcal/mol for AsH_3.[19a] From these figures one would derive that an amine is always a better ligand than a phosphane, a conclusion that contrasts deeply with the experience of the synthetic chemist. The authors contribute this discrepancy to the local ionisation potential or polarisability.[19,21] The polarisability describes the ease to redistribute the electron density on the respective atom, whereas the local ionisation potential is a measure for the ability to transfer electrons from this atom. The MEP and the local ionisation potential are complementary with respect to electrophilic processes,[21a] such as the attack of a metal fragment (Lewis acid) on a ligand featuring an electron lone pair (ELP, Lewis base). Hence, one not only has to take into account the total electron density on the ligating atom as stated by the MEP, but also the ease of charge transfer on this site as indicated by the local ionisation potential or "softness of the ligand".[39] In practical terms, two ligands with a phosphorus and a germanium atom with the same MEP would have different TEPs, the one for the germanium compound being lower due to the higher polarisability of this atom (better σ-donor ability). One could account for this difference by multiplying the slope of the linear regression between V_{min} and TEP with an empirical factor of 1.7 based on the calculated and experimental TEP values for the ligands **1** and **2**. This transforms Equation (2) to Equation (3).

$$\nu CO_{Ni} = \left(\frac{V_{min}}{1 kcal/mol}\right) \cdot 1.2515\, cm^{-1} + 2097.6\, cm^{-1} \qquad (3)$$

Although the polarisability effect between phosphorus and germanium truly exists, quantification on the basis of only two data points can only be done tentatively. The empirical factor will have to be corrected once more experimental data are available, even though only comparatively small adjustments are likely to be necessary. However, as the adjustment is primarily for the difference between third-row- and fourth-row-elements, the resulting empirical factor should be valid for all fourth-row elements rather than only germanium.

The potential minima V_{min} on germanium for the seven selected NHGe ligands are listed in Table 2 (see also Figure 3) together with the results from Equation (3). These are denoted as "corrected TEP" values following the same trend as predicted by the annelation effect.[13] The hitherto unknown molecules **5a** and **7**[40] display TEP values in the expected order **7** > **5a** > **6**, the electron-acceptor effect of the two ring nitrogen atoms in **5a** being stronger than that of the additional ring in **6**.

For the three frameworks **2**, **3** and **5** representing the unsaturated non-anellated, benzo- and pyrazino-anellated NHGe, respectively, the influence of acceptor-(F, Cl, CN, NO_2) and donor-(Me, OMe) substituents on the backbone was investigated. The results are shown in Table 3 (see also

Table 2. V_{min} and TEP for the basic framework NHGe.

Structure	V_{min} [au]	V_{min} [kcal/mol]	Corr. TEP [cm^{-1}]	Structure	V_{min} [au]	V_{min} [kcal/mol]	Corr. TEP [cm^{-1}]
1	–0.0356	–22.27	2070	**5a**	–0.01567	–9.80	2085.3
2a	–0.0323	–20.20	2073	**6**	–0.02059	–12.88	2081.5
3a	–0.02535	–15.86	2077.8	**7**	–0.01411	–8.83	2086.6
4	–0.02199	–13.75	2080.4				

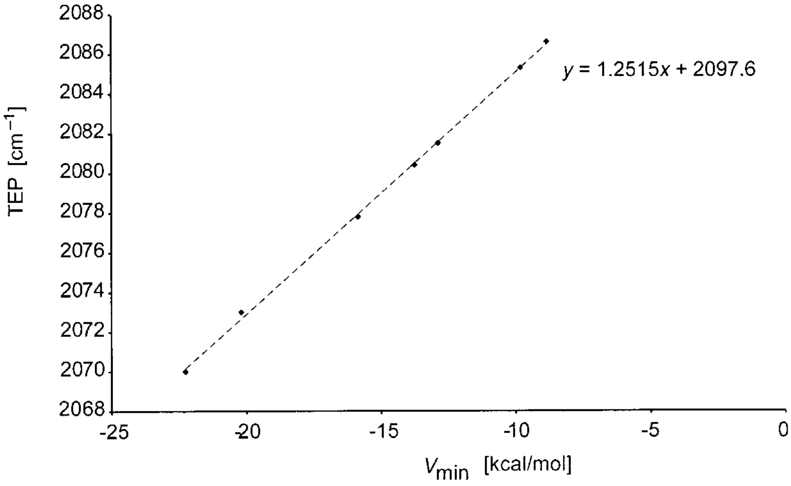


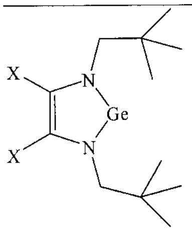
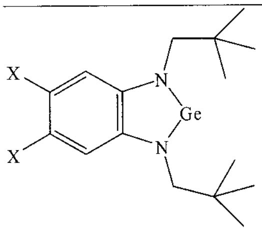
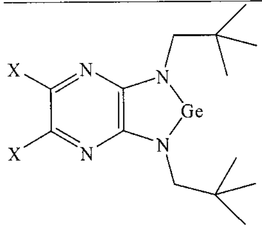
Figure 3. Visualisation of the relation between V_{min} and TEP for the basic framework NHGe. No correlation factor is given as the graph uses the output data from Equation [(3)].

Figure 4). The corrected TEP are in the expected order, but with Me having a greater donor effect than OMe and the two halogen atoms F and Cl reversed. Fluorine shows a weaker acceptor effect than Cl, probably due to the mesomeric effect not present in the chlorine compounds.[41] By the same argument MeO should have a stronger donor effect than Me. The reason for the opposite trend in the calculated values remains unclear. As expected, the effect of the substituent on the electronic properties of the germanium centre grows, if the substitution takes place closer to it, being larger in **2** than in **3**, **4** or **5**. In a few cases including **2e**, **5d** and **5e**, the MEP on germanium is slightly positive. Here, the calculation of a corrected TEP was no longer meaningful as the empirical factor *f* would have served to increase the TEP value rather than to decrease it with respect to the phosphorus ligands. With the advent of positive values for the MEP on germanium, the method reaches its mathematical limits, but the trend for the substituents is still valid. Here too, additional experimental data will lead to greater precision without altering the trends.

The TEP value steadily increases in the order Me < OMe < H < F < Cl < CN < NO_2 as well as in the order **1** < **2** < **3** < **4** < **6** < **5** < **7**. Both trends comply with expectation, the effect of substitution being in general more important. Annelation of **2a** with quinoxaline, the most electron-withdrawing ring system investigated, results in a corrected TEP value of 2086.6 cm^{-1} (**7**) being only 1.3 cm^{-1} higher than that found for chlorine substitution (2085.3 cm^{-1}, **2c**). Cyano and nitro substitution render ligands with corrected TEP values approaching 2100 cm^{-1} similar to the phosphorus trihalide ligands PCl_3 and PF_3 having values of 2097.3 and 2110.8 cm^{-1},[16] respectively.

The main point in understanding these high corrected TEP values that occur in substituted and anellated NHGe ligands is the ability of the germanium centre to act as a Lewis base while displaying a positive MEP. It is generally understood that the stability of the germylenes is derived from the interaction of the empty p orbital on Ge with the filled p orbitals of the neighbouring nitrogen atoms. Because the NHGe is a singlet germylene, the Ge atom retains the lone pair and forms two σ bonds to nitrogen with its two remaining electrons. Due to the relative electronegativities of germanium and nitrogen, the electron density on Ge will be reduced.[42]

Table 3. V_{min} and TEP for the substituted NHGe; uncorrected TEP in brackets.

Structure			V_{min} [au]	V_{min} [kcal/mol]	corr TEP [cm^{-1}]
	**2b**	F	– 0.01976	– 12.36	2082.1
	2c	Cl	– 0.01581	– 9.89	2085.3
	2d	CN	– 0.00103	– 0.66	2096.8
	2e	NO_2	0.00350	2.19	(2099.2)
	2f	Me	– 0.03590	– 22.46	2069.6
	2g	MeO	– 0.03246	– 20.30	2072.2
	**3b**	F	– 0.01719	– 11.20	2083.6
	3c	Cl	– 0.01328	– 8.31	2087.2
	3d	CN	– 0.00028	– 0.18	2097.4
	3e	NO_2	– 0.00040	– 0.25	2097.3
	3f	Me	– 0.02701	– 16.89	2076.5
	3g	MeO	– 0.02410	– 15.07	2078.8
	**5b**	F	– 0.01002	– 6.27	2089.8
	5c	Cl	– 0.00557	– 3.48	2093.2
	5d	CN	0.00806	5.04	(2101.3)
	5e	NO_2	0.02000	12.51	(2106.8)
	5f	Me	– 0.02000	– 12.51	2082.0
	5g	MeO	– 0.02010	– 12.57	2081.9

The π donation from nitrogen transfers additional electron density onto the germanium atom lowering the V_{min} value. Annelation and substitution changes the N–Ge $(p\text{-}p)_\pi$ interaction so efficiently that only a single bond is

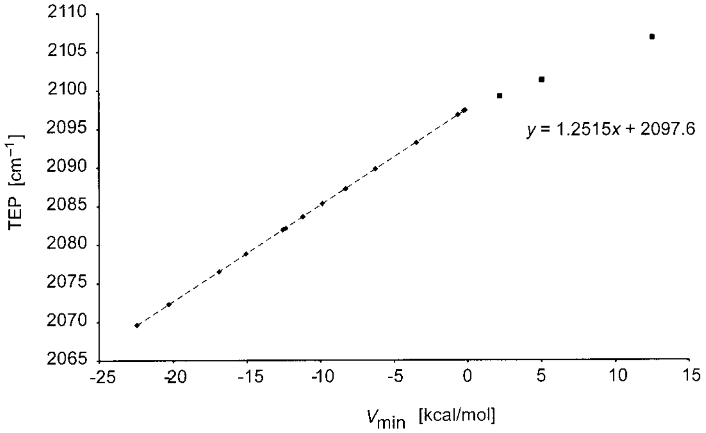
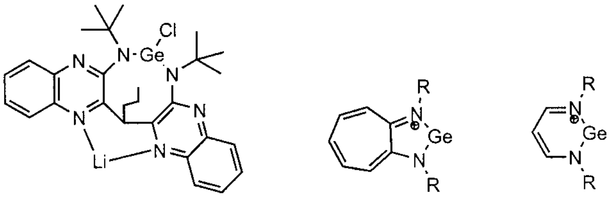


Figure 4. Visualisation of the relation between V_{min} and TEP for the substituted NHGe; uncorrected TEP shown as unconnected dots. No correlation factor is given as the graph uses the output data from Equation (3).

formed in some systems such as in the doubly quinoxalino-anellated NHGe **8**[43] (see Scheme 2). The existing experimental data is still insufficient to decide whether stabilisation by a Lewis base such as a chloride ion is a general trend for electron-deficient germylenes.



8 **9** **10**

Scheme 2. Structures of some electrophilic and cationic NHGe.

The weakening of the N–Ge $(p\text{–}p)_\pi$ interaction itself results in an increase in V_{min} attaining slightly positive values in extreme cases. Even then the germanium atom still possesses an ELP suitable to serve as a Lewis base towards a transition metal fragment.

Annelation and substitution enhance the π-acceptor strength of NHGe and presumably weaken their σ-donor potential by making the ELP less available for ligation. This behaviour has a parallel in phosphorus chemistry. As Burford et al. have shown, phosphorus ligands can act as Lewis acids if an anionic substituent is removed leaving a phosphenium cation,[44] or when a chelate ligand is exploited as is the case for the ß-diketiminate ligands.[45] There is evidence that for cationic NHGe systems like **9** and **10** the ELP might have greater s character resulting in contraction of the orbital and reduced σ-donor properties.[46]

During the preparation of this manuscript Barrau et al. published an article concerning the synthesis of cationic tungsten and iron complexes containing the cationic NHGe **10**.[47] Synthesis was achieved by silver or sodium salt metathesis from the neutral transition-metal complex containing the corresponding monoiminogermylene ligand, or directly between the triflate of the NHGe and a $W(CO)_5$ precursor. Although, the anion was in all cases still weakly coordinated to the cation, this work proves that cationic NHGe can act as donor ligands to transition metals.

Conclusions

Whereas NHC are electron-rich ligands, their germylene counterparts can be electron-poor with TEP values in the same range as phosphites. The introduction of acceptor substituents like halides, cyano or nitro groups render NHGe very electron-deficient with corrected TEP values approaching or even exceeding 2100 cm^{-1}, which make their synthesis an interesting and rewarding challenge for the synthetic chemist. They then have electronic properties similar to phosphorus trihalides without displaying their disadvantageous reactivity. NHGe compounds can serve as electron-poor neutral ligands with unique steric and electronic properties. Their potential in coordination chemistry and catalysis is very promising, but widely unexploited.

The molecular electrostatic potential (MEP) is a very convenient and accurate method to calculate the electronic properties of germylene ligands. If the effect of polarisability is taken into account by using an empirical factor, the method can in principle be fine-tuned to calculate the carbonyl vibration frequencies of respective transition-metal carbonyl complexes accurately without additional calibration processes. However, at present more data are required to calculate said empirical factor with the necessary precision.

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