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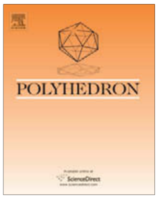

Novel highly electron-deficient quinoxaline-annulated 1,3,2-diazagermol- and diazastannol-2-ylidenes, stabilized as LiCl adducts

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ABSTRACT

Reaction of 2,3-bis(neopentylamino)quinoxaline (**1**) with *n*BuLi and $GeCl_4$ or $GeCl_2\cdot$(dioxane) (molar ratio 1:2:1) in THF furnished highly moisture-sensitive Ge(IV) and Ge(II) heterocycles **2a** and **3a**, respectively. The quinoxaline-annulated *N*-heterocyclic germylene (quinNHGe) **3a** is stable only in the presence of $Li(THF)_x$ and exhibits electrophilic properties associated with the strongly electron-withdrawing annulation. Coordination of chloride at Ge(II) and of Li^+ at nitrogen is assumed, as found in crystals of a bis(quinoxaline)-annulated eight-membered NHGe LiCl adduct. Addition of dineopentyl-benzimidazol-2-ylidene (bnNHC) provides a labile bnNHC-quinNHGe adduct **4** as indicated by strong downfield coordination shift of the NMR signal for the carbene donor atom. Attempts to grow single crystals led to decomposition and protonation of the carbene forming the bis(benzimidazolium) salt **5** with $Li_2(THF)_2Cl_4^{2-}$ anion. Introduction of 2-methoxyethyl or 2-dimethylaminoethyl side arms as chelating functional groups into the diaminoquinoxalines **6** and **7** and subsequent reaction with 2 *n*BuLi/$GeCl_2\cdot$(dioxane) did not markedly stabilize the resulting donor-substituted quinNHGe **8** and **9**. Related silicon (**2b**) and tin heterocycles (**3c**) were synthesised for comparison. The quinoxaline-annulated *N*-heterocyclic stannylene **3c** exhibits an extreme ^{119}Sn upfield shift compared to other *N*-heterocyclic stannylenes, suggesting higher coordination at tin.

1. Introduction

N-heterocyclic carbenes NHC are often used as mimics of the widely utilised phosphane ligands in coordination chemistry and catalysis [1]. Whereas trivalent phosphane ligands can be electronically modified from σ-basic to π-acidic by changing the substituents [2], modifying the NHC by virtue of their *N*-substituents results only in comparatively small alterations of their generally high donor strength [3]. More significant changes of the electronic properties are brought about by varying the NCN angle [4], saturation of imidazol-2-ylidenes [4,5] or annulation [6]. Strong shifts towards lower donor strengths and increasing acceptor properties occur by replacement of the divalent carbon with higher group 14 elements, e.g. in the homologous *N*-heterocyclic silylenes (NHSi) [7], germylenes (NHGe) and stannylenes (NHSn) [8]. The annulation effects in annulated higher homologues of NHC may further shift the ligand properties. This was shown recently by a method [9] to calculate the Tolman electronic parameters for a series of differently annulated NHGe from the local minimum of the molecular electronic potential and good agreement of calculated and experimental found ν_{CO} stretching frequencies of the corresponding NHGe metal carbonyl complexes [10]. The distinct coordination properties of NHC and their higher homologues is attributable to an inverse order of reactivity-relevant HOMOs, σ-orbitals for the carbon electron lone pair of non-, benzo- or pyrido[*b* or *c*]-annulated imidazol-2-ylidenes and π-orbitals for their homologous NHSi and NHGe [11]. *N*-Bridging annulation as in pyrido[*a*]-annulated NHC [12] raises the π-levels relative to the group 14 element(II) electron lone pair [13] whereas π-electron-withdrawing annulation as in pyrido[*b*]-NHE (E = C, Si, Ge) or pyrido[*c*]-NHC [11] cause the opposite effect. The electron withdrawal by annulation allows for better back bonding in electron-rich transition metal complexes as found e.g. in the series non-, benzo-, and naphtho-annulated *fac*-$(np_2NHGe)_3Mo(CO)_3$ complexes (np = *N*,*N*′-dineopentyl) [10a]. The strongest annulation effect within our longstanding studies on carbo- and *N*-heterocyclic annulated NHE (E = C, Si, Ge, Sn) (Fig. 1) [6b,10,11,13,14] was observed in quinoxaline-annulated NHC complexes. The parent NHC in this case was no longer isolable [14a] despite the constant presence of the sterically demanding *N*-neopentyl groups, which usually have a stabilizing effect. It attracted our interest to see whether higher homologues will be isolable following the general trend of increasing stability of the divalent compared to tetravalent species and if the ligand properties are more strongly shifted

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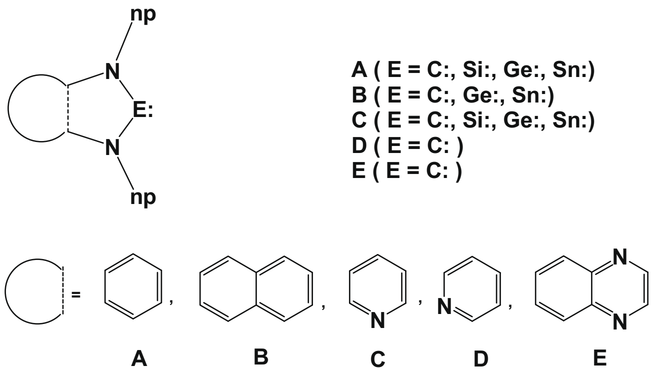
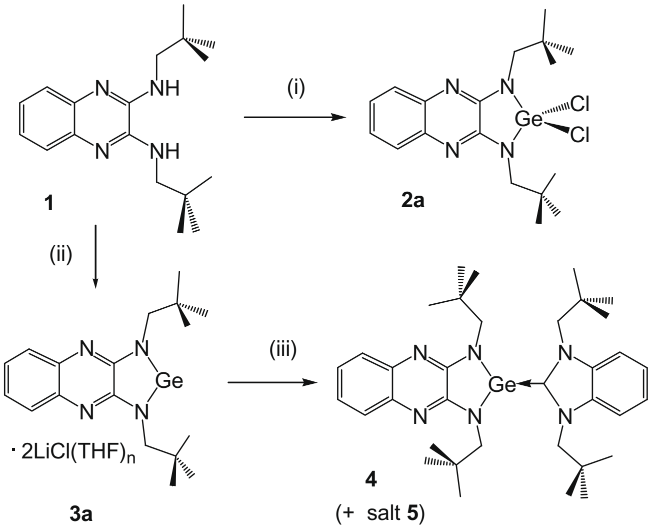


Fig. 1. A series of annulated NHCs and their heavier homologues.

towards acceptor properties than observed for the aforementioned carbocyclic annulation.



Scheme 1. Synthesis of **1**–**5**; (i) THF −40 °C, 2 *n*-BuLi, $GeCl_4$, reflux; (ii) THF −75 °C, 2 *n*-BuLi, $GeCl_2$ (dioxane), −75 to 20 °C; (iii) *N,N′*-dineopentyl benzmidazol-2-ylidene, THF, 20 °C.

2. Results and discussion

2.1. Preparation and characterization of quinoxalino-1,3,2-diazagermoles

The synthesis of quinoxaline[2,3-*d*]-annulated diazagermoles started from 2,3-dichloroquinoxaline [15], which by heating with excess ammonia in an autoclave was converted to 2,3-diaminoquinoxaline, followed by dipivaloylation and subsequent reduction with $LiAlH_4$ to 2,3-di(neopentylamino)-quinoxaline (**1**). This was lithiated with 2 equiv. of butyllithium (hexane) in THF, and the resulting pale yellow **$1Li_2$** was reacted with the germanium chlorides. For comparison of the products with di- and tetravalent germanium, both $GeCl_2$ and $GeCl_4$ were utilised in the cyclization study. The reaction with $GeCl_4$ proceeded rapidly, as seen by the immediate colour change. Removal of the solvents in vacuum and extraction of the product with diethyl ether gave the cyclic dichlorogermole **2a** as a yellow-orange, highly moisture-sensitive viscous oil in good yield. The substance is easily soluble in diethyl ether or in THF. It is also soluble in C_6D_6 but a precipitate forms after 1 h in this solvent. Solution NMR spectra are in accordance with a monomeric structure of the dissolved molecules. EI mass spectra exhibit the peaks for the molecular ion ($[M]^+$ $m/z = 442$) and for the typical fragmentation product $[M-t\mathrm{Bu}]^+$ ($m/z = 387$), both with correct isotopic distribution. The corresponding germylene, quinoxalino[2,3-*d*]-1,3,2-diazagermole-2-ylidene **3a**, was obtained in the conversion of **$1Li_2$** with 1 equiv. of $GeCl_2$(dioxane) in the aprotic donor solvent THF. The LiCl generated in the reaction remains soluble and stabilizes **3a**. Removal of THF in vacuum at room temperature is incomplete and shows that this solvent also coordinates to lithium. Redissolution of the extremely moisture-sensitive red oil in D_8-THF did not cause substantial decomposition under dry conditions; NMR spectra indicated only a small amount of an as yet unidentified decomposition product. Repeated experiments using solvents other than THF (e.g. benzene, diethyl ether, and toluene) for synthesis of **3a** proved unsuccessful. Similarly, attempts to extract **3a** by toluene or C_6D_6 after removal of uncoordinated THF in vacuum, the usual procedure in the synthesis of the stable benzo- [10b,c], pyrido[*b*]- [11b] or naphtho-annulated [14e] diazagermol-2-ylidenes, showed only signals of decomposition products in the NMR spectra. This indicates that the presence of $LiCl(THF)_x$ is crucial for the stability of **3a** and likewise that the adduct is not sufficiently stable to withstand the extraction experiments. The decomposition after removal from $LiCl(THF)_x$ indicates destabilization of the molecule, i.e., the parent diaminogermylene in the adduct **3a** (Scheme 1) is no longer sufficiently stabilized by π bond interactions to the neighbouring electron lone pairs of nitrogen. This is attributed to a strong shift of π-electron density into the competing, strongly electron-withdrawing annulated quinoxaline ring. This changes the ambiphilic properties of the five-membered cyclic diaminogermylene moiety from mainly nucleophilic to mainly electrophilic, so that it acts as a Lewis acid towards the chloride anion of LiCl. Coordination of lithium at nitrogen amplifies this effect.

The structure of an unusual, electrophilic, doubly quinoxaline-annulated eight-membered NHGe, stabilized by LiCl, has already been reported from our group (Fig. 2) [16] whereas a standard Meller-type five-membered NHGe requiring LiCl for stability has not been reported yet. We suppose that the stabilization principle in **3a** is very similar to that illustrated in Fig. 2. Several attempts were made to crystallize compound **3a** by using the layering technique with solvents of different polarity but all led to rapid formation of a precipitate accompanied by a change of colour from the characteristic red of **3a** to orange or yellow, which along with the NMR spectra indicates decomposition of the germylene.

The ^1H and ^{13}C NMR spectra of **3a** show the expected signals for the NCH_2 and *tert*-butyl groups and the remaining aromatic protons or ^{13}C nuclei. The ^1H NMR signals for the NCH_2 protons are almost unchanged from compound **1**; only the proton splitting pattern changes from doublet to singlet upon cyclization in line with the substitution of the NH protons by a germanium atom. The very small downfield shift of the NCH_2 protons upon cyclization suggests lack of a ring current effect in the quinoxaline-annu-

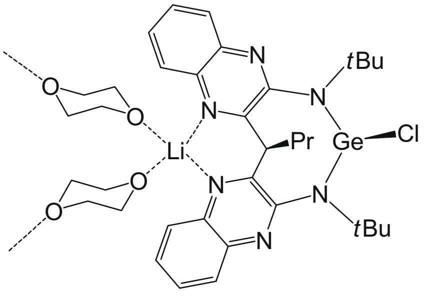


Fig. 2. Stabilisation of a bis(quinoxaline)-annulated heterocyclic diaminogermylene by LiCl and THF (monomer unit) [16].