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Accessing heavy allyl-analogous [(TerN)₂E][−] (E = Sb, Bi) ions and their reactivity towards ECl₃[†]

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The attempted preparation of the biradicaloid [E(μ-NTer)]₂ (E = Sb, Bi) yielded salts of the anion [(TerN)₂E][−]. These heteroatom allyl analogues could be further utilized in the reaction with pnictogen(III) chlorides to form the first 1,3-dichloro-1-bisma-3-stiba-2,4-diazane [ClSb(μ-NTer)₂BiCl].

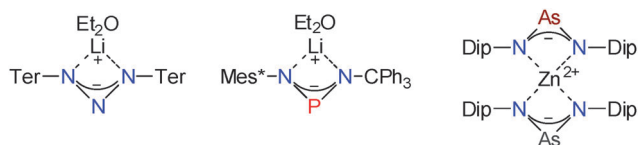
In recent research, allyl-analogous group 15 anions of the type [(R-E^{1,2})₂E][−] (E^{1,2} = N, P, As) have attracted great interest (Scheme 1). Triazenides, the lightest examples of such anions, were identified as redox-active ligands by Kaim *et al.* only in 2013.¹ For their structural aspects, Niemeyer *et al.* investigated several unsymmetrically substituted triazenides and found intriguing aggregation behaviour that shows dependence on the cation.^{2–4} In contrast, the heavier homologue, [(R-N)₂P][−], was targeted less often. The NPN anion was studied by Niecke *et al.* in the early 1990s^{5,6} and were recently utilized in the preparation of an arsa-phospha-diazane.⁷ Roesky *et al.* were the first to investigate [(R-N)₂As][−], which was obtained as salt of Zn²⁺ and Cd²⁺ upon deprotonation of the acid of [(R-N)₂As][−] with metal amine bases [MN(SiMe₃)₂₂] (M = Zn, Cd).⁸ Substitution of the pnictogens bearing the organic substituents from R-N to R-P

lead to the formation of highly sensitive compounds, of which several metal complexes were investigated by the groups of Niecke (NPP),⁹ Lerner (PPP),¹⁰ Jutzi (PPP, PAsP),¹¹ Scheer (PPP, PAsP),^{12,13} and Wright (PAsP).¹⁴ These highly reactive anions can be stabilized by bulky substituents, as for example *m*-terphenyls, which were systematically studied by Power *et al.* They have been employed frequently in both transition metal and main group element chemistry. The use of *m*-terphenyls enabled the study of several unusual bonding situations,^{15–17} ranging from Cr–Cr quintuple bonds¹⁸ to M–E triple bonds (Re≡Ge, Mo≡Si, W≡Sn)^{19–21} and several examples of multiple bonds between heavy main group elements.^{22,23} These heavy element multiply bonded species can exhibit biradical character, as was shown for the digermene in the reactions with small molecules.^{24–26} Complementing the variety of highly reactive species stabilized by *m*-terphenyls, Power *et al.* were able to synthesise heavy group 14 carbene analogs.²⁷

In the course of our investigations concerning small group 15 heterocycles, we succeeded in the preparation of the singlet biradicaloids [P(μ-NTer)]₂ and [As(μ-NTer)]₂ (Ter = 2,6-bis(2,4,6-trimethylphenyl)-phenyl).^{28–31} The chemistry of biradicaloids was recently reviewed by Abe and Breher.^{32,33} Computations predicted a considerably larger biradical character for the heavier congeners, [Sb(μ-NTer)]₂ and [Bi(μ-NTer)]₂,^{34,35} rendering them attractive preparative targets.^{36,37}

In this contribution, we present the first examples of group 15 heteroatom allyl-analogues featuring the heaviest pnictogens (Sb and Bi) and *m*-terphenyl substituents and investigated their reactivity towards pnictogen(III) halides.

The starting materials, [ClSb(μ-NTer)]₂ and [ClBi(μ-NTer)]₂, are already known^{38,39} and were reduced with utilizing magnesium in THF (Scheme 2), KC₈ in toluene or benzene, and the benzophenone ketyl radical in THF (*cf.* ESI[†]). Upon reduction with magnesium, the solution of the dichloro-cyclo-dipnictadiazanes **1E** turned dark blue for [(Ter-N)₂Sb]MgCl·THF (**2Sb**) and dark green for [(Ter-N)₂Bi]MgCl·THF (**2Bi**) from initially yellow and red, respectively. After workup, crystalline material of black appearance was obtained in both cases. Even though both compounds are



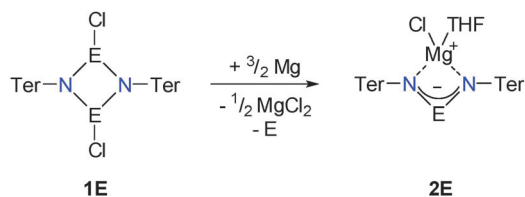
Scheme 1 Selected examples for known group 15 allyl-analogues (Ter = 2,6-bis(2,4,6-trimethylphenyl)-phenyl, Dip = 2,6-diisopropyl-phenyl, Mes* = 2,4,6-tri-*tert*-butyl-phenyl).

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[†] Electronic supplementary information (ESI) available: Experimental and computational details and information on X-ray structure elucidation. CCDC 1059323 (**2Sb**), 1059324 (**2Bi**), and 1059325 (**3**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5cc04355g



Scheme 2 Preparation of **2E** (E = Sb, Bi).

thermally stable (**2Sb**: $T_{\text{dec}} = 228$, **2Bi**: $T_{\text{dec}} = 246$ °C), they are very sensitive towards air and water. The use of KC_8 instead of magnesium as a reducing agent did not afford the heavy biradicaloids either. When utilized in a stoichiometric ratio, a dark greenish mixture of products was obtained. After fractional crystallisation, only considerable amounts of the starting material were obtained in numerous experiments, even though its colour ranged from nearly colourless *via* the expected yellow of $[\text{ClSb}(\mu\text{-Nter})]_2$, but even orange, green and black crystals were grown due to small amounts of highly coloured impurities. When an excess of KC_8 was used, colourless $[\text{K}(\mu\text{-N(H)Ter})]_2$ was obtained (*cf.* ESI†). Similar over-reduction occurred, when $[\text{ClBi}(\mu\text{-Nter})]_2$ and Mg were stirred for three days, affording colourless imido complex $[\text{TerN}(\text{MgCl})_2]_2 \cdot 4\text{THF}$ (*cf.* ESI†).

IR data for both **2Sb** and **2Bi** are very similar. The slight differences observed barely exceed the measurement accuracy. The in-plane N–E–N deformation vibration was observed at 876 cm^{-1} for **2Sb** and at 870 cm^{-1} for **2Bi**, respectively. The E–N stretch is observed at 686 (**2Sb**) and 676 cm^{-1} (**2Bi**) in good agreement with computed data (*cf.* ESI†).⁴⁰

The heavy allyl analogs **2Sb** and **2Bi** crystallise isotypically from benzene in the monoclinic space group $P2_1/n$. The molecular structures feature short N–E bonds, displaying considerable double bond character (Fig. 1, **2Sb**: 1.963, 1.971; **2Bi**: 2.075, 2.086, $\sum r_{\text{cov}}(\text{N} = \text{Sb}) = 1.93$, $\sum r_{\text{cov}}(\text{N} = \text{Bi}) = 2.01$, *cf.* $[\text{ClSb}(\mu\text{-Nter})]_2$ 2.051(2), 2.063(2); $[\text{ClBi}(\mu\text{-Nter})]_2$ 2.151(2), 2.169(3) Å).⁴¹ There are acute N–E–N angles in both species **2** (**2Sb**: $85.97(6)$; **2Bi**: $82.78(8)^\circ$) due to an s-type lone pair of the heavy pnictogen and bond orbitals mainly composed of p-atomic orbitals (*cf.* Table 1).

The intensive blue colour can be rationalized with the aid of DFT computations. The computed frontier orbitals are in good

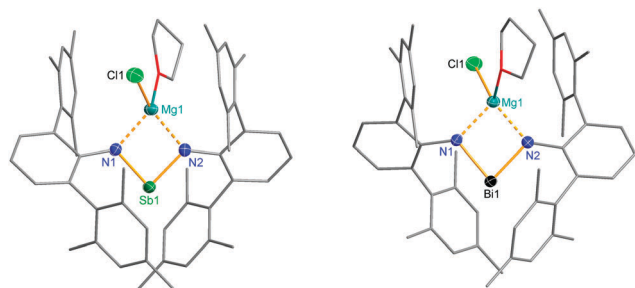


Fig. 1 Molecular structure of **2Sb** and **2Bi**. Thermal ellipsoids are drawn at 50% probability (173 K). Selected bond lengths [Å] and angles [°]: **2Sb**: Sb1–N1 1.963(1), Sb1–N2 1.971(1), Mg1–N1 2.080(1), Mg1–N2 2.092(2), N1–Sb1–N2 $85.97(6)$; **2Bi**: Bi1–N1 2.075(2), Bi1–N2 2.086(2), Mg1–N1 2.070(2), Mg1–N2 2.078(2), N1–Bi1–N2 $82.78(8)$.

Table 1 Computational data of **2Sb**, **2Bi** and the lighter homologues **2P** and **2As** for comparison

	2P	2As	2Sb	2Bi
$q(\text{E})$	+1.22	+1.23	+1.33	+1.40
$q(\text{N})$	−1.09	−1.09	−1.13	−1.15
s character of E lone pair [%]	70	77	82	86
HOMO–LUMO gap [kJ mol^{-1}]	361	306	267	251
λ_{max} [nm]	401	474	581	662

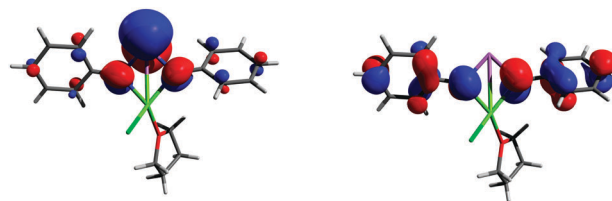
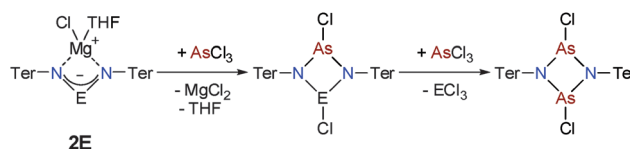


Fig. 2 Computed molecular orbitals of **2Sb** (HOMO left and LUMO right).⁴²

agreement with the ones sketched by Niecke *et al.* for $[(\text{R-N})_2\text{P}]^-$ ions.⁶ The HOMO \rightarrow LUMO excitation represents an $\pi \rightarrow \pi^*$ transition, with the π^* orbital featuring large coefficients for a p atomic orbital at the E center perpendicular to the N_2E plane (Fig. 2, **2Sb**: $\lambda_{\text{max}} = 585$; **2Bi**: $\lambda_{\text{max}} = 697$; computed: **2Sb**: $\lambda_{\text{max}} = 581$; **2Bi**: $\lambda_{\text{max}} = 662\text{ nm}$).

NBO analysis of the series of $[(\text{R-N})_2\text{E}]^-$ anions⁴² revealed clear trends. The E lone pair is of increasing s character in the sequence P (70%) < As (77%) < Sb (82%) < Bi (86%). In contrast, the N lone pairs possess considerable p orbital contributions ($\text{sp}^{1.7}$ hybrids). The NEN moiety is strongly polarized for which the charge distribution is a good estimate (E = P: $q(\text{N}) - 1.09$, $q(\text{P}) + 1.22$; E = As: $q(\text{N}) - 1.09$, $q(\text{As}) + 1.23$; E = Sb: $q(\text{N}) - 1.13$, $q(\text{Sb}) + 1.33$; E = Bi: $q(\text{N}) - 1.15$, $q(\text{Bi}) + 1.40$ e). The HOMO–LUMO gap decreases in the series towards heavier pnictogens (*cf.* Table 1).

Further investigations targeted the metathesis reaction of **2Sb** and **2Bi** with pnictogen(m) halides. The reaction of **2Sb** and **2Bi** with the chloride of the same pnictogen yielded the starting material, $[\text{ClSb}(\mu\text{-Nter})]_2$ and $[\text{ClBi}(\mu\text{-Nter})]_2$, respectively. This might be a useful approach to dichloro-cyclo-dipnictadiazanes, if another synthesis of the allyl-analogous anions **2E** can be found. When **2Sb** or **2Bi** was reacted with one equivalent of a AsCl_3 (Scheme 3), no clean reaction was observed. Upon employing an excess of AsCl_3 , substitution of the heavy pnictogen occurred, and $[\text{ClAs}(\mu\text{-Nter})]_2$ was obtained. However, by conversion of **2Sb** with BiCl_3 it was possible to synthesize the first 1,3-dichloro-1-bis-3-stiba-2,4-diazane (**3**), $[\text{ClSb}(\mu\text{-Nter})_2\text{BiCl}]$, in good yield as bright red crystals (Scheme 4).



Scheme 3 Reaction of **2Sb** with AsCl_3 .



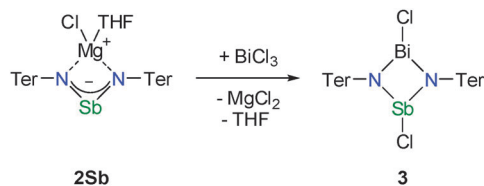
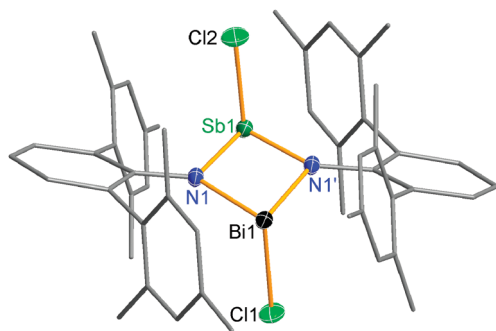
Scheme 4 Preparation of **3**.

Fig. 3 Molecular structure of **3**. Thermal ellipsoids are drawn at 50% probability (173 K). Selected bond lengths [Å] and angles [°]: Bi1–N1' 2.183(3), Bi1–N1 2.196(3), Sb1–N1' 2.034(4), Sb1–N1 2.045(4), Bi1–Cl1 2.55(2), Sb1–Cl2 2.44(2), N1–Bi1–N1' 73.9(1), N1–Sb1–N1' 80.4(1). Symmetry code: (') 2 – x, 1 – y, 1 – z.

Compound **3** crystallized isotypic to $[\text{ClSb}(\mu\text{-Nter})]_2$ and $[\text{ClBi}(\mu\text{-Nter})]_2$ in the orthorhombic space group *Pbca*. The molecular structure features the *trans* isomer with N–E and E–Cl single bonds (Fig. 3, **2Sb**: N–Sb 2.037, 2.038, **2Bi**: N–Bi 2.193, 2.183; **3**: Sb1–Cl2 2.44(2), Bi1–Cl1 2.55(2) Å) in good agreement with the values observed for $[\text{ClSb}(\mu\text{-Nter})]_2$ and $[\text{ClBi}(\mu\text{-Nter})]_2$ (cf. Sb–Cl 2.4321(4), Bi–Cl 2.537(2) Å).

The bisma-stiba-diazane **3** is thermally stable ($T_{\text{dec}} = 266^\circ\text{C}$) and can be prepared in bulk. The solution ^1H and ^{13}C NMR spectra indicate the exclusive existence of the *trans* isomer, in which all *ortho*-CH₃ groups are equivalent in solution at ambient temperature due to intramolecular dynamics. The $\nu(\text{E-Cl})$ vibrations were found at 280 and 265 cm^{-1} , which compares well with the known values for $[\text{ClSb}(\mu\text{-Nter})]_2$ (284, 258 cm^{-1}) and $[\text{ClBi}(\mu\text{-Nter})]_2$ (274, 256 cm^{-1}). The in-phase combination of E–N–E deformation vibrations was observed at 188 cm^{-1} for **3** (Sb, Bi), while the respective vibration was found at 216 cm^{-1} in $[\text{ClSb}(\mu\text{-Nter})]_2$ and at 150 cm^{-1} in $[\text{ClBi}(\mu\text{-Nter})]_2$. At higher wavenumbers, the combination of in-phase N–E–N deformation vibrations was assigned (**3**: 888; $[\text{ClSb}(\mu\text{-Nter})]_2$ 894; $[\text{ClBi}(\mu\text{-Nter})]_2$ 876 cm^{-1}).

In conclusion, the reduction of the heavy dichlorodipnictadiazanes did not lead to the desired biradicaloids, which we assess to be beyond the reach of synthetic methods at the moment. Possibly, other substituents feature suitable steric and electronic properties will enable the stabilisation of the heavy biradicaloids $[\text{Sb}(\mu\text{-Nter})]_2$ and $[\text{Bi}(\mu\text{-Nter})]_2$, which remains a challenge. However, the synthesis of **2Sb** and **2Bi** filled a gap in main group chemistry in the heavy group 15 allyl-analogues and enabled the synthesis of the first dichloro-cyclobisma-stiba-diazane, which may prove a suitable starting material

for the generation of reactive cations, radicals or Sb/Bi nitrides.⁴³ The metathesis reactivity of cyclic N–E bonded species was previously utilised in the preparation of $[\text{ClSb}(\mu\text{-Nter})]_2$ and $[\text{ClBi}(\mu\text{-Nter})]_2$ from $[\text{Sn}(\mu\text{-Nter})]_2$, a preparative method which we could extend to metathesis from $[\text{ClSb}(\mu\text{-Nter})]_2$ and $[\text{ClBi}(\mu\text{-Nter})]_2$ to the lighter congener $[\text{ClAs}(\mu\text{-Nter})]_2$.

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