

Exploring Differences between Bis(aldimino)- and amino-aldimino-*N,C,N*-Pincer-Stabilized Pnictinidenes: Limits of Synthesis, Structure, and Reversible Tautomerization-Controlled Oxidation

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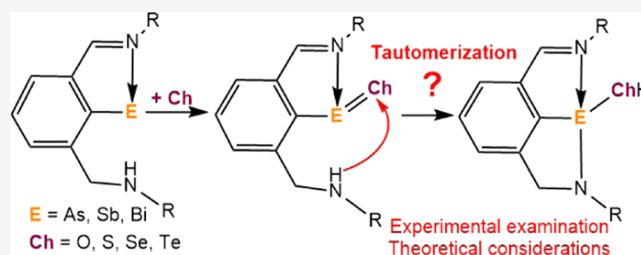
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ABSTRACT: Two types of *N,C,N*-chelated pnictinidenes, i.e., [2-(RNHCH₂)-6-(RN = CH)C₆H₃]*E* (**1-E-R**) and [2,6-(RN = CH)₂C₆H₃]*E* (**2-E-R**, where *E* = As, Sb, Bi), are targeted in this study. **2-E-R** could be obtained by simple reduction of respective precursors [2,6-(RN = CH)₂C₆H₃]*E*Cl₂ (i.e., (**2-E-R**)Cl₂) with KC₈ for *E* = As, Sb, or Bi with *R* being *t*Bu, Ad, or Dipp. By contrast, the utilization of a bulky hydride, i.e., K-selectride, allowed the isolation of **1-E-R** for *E* = As or Sb and *R* = Dipp, while the utilization of other pincer ligands, where *R* = *t*Bu or Ad, led only to mixtures of both **1-E-R** and **2-E-R**. For bismuth, even the Dipp-substituted pincer ligand provided a mixture of **1-Bi-Dipp** and **2-Bi-Dipp** only. The structures and chemical properties of these sets of compounds, i.e., **1-E-Dipp**, **2-E-*t*Bu**, and **2-E-Dipp**, were compared using X-ray diffraction analysis, UV–vis spectroscopy including an extensive theoretical study, and CV measurements. The oxidation of **2-E-Dipp** (*E* = As, Sb, Bi) by air resulted only in the formation of complicated mixtures, while oxidation of **1-E-Dipp** (*E* = As or Sb) cleanly produces (**1'-E-Dipp**)OH as a result of a tautomeric NH → OH shift at elusive oxides (**1-E-Dipp**)O under formation of a new E–N covalent bond. To examine the potential of such tautomerization-driven stabilization of oxidation products, the reactivity of **1-E-Dipp** (*E* = As or Sb) toward other chalcogens is also reported, including a theoretical study.

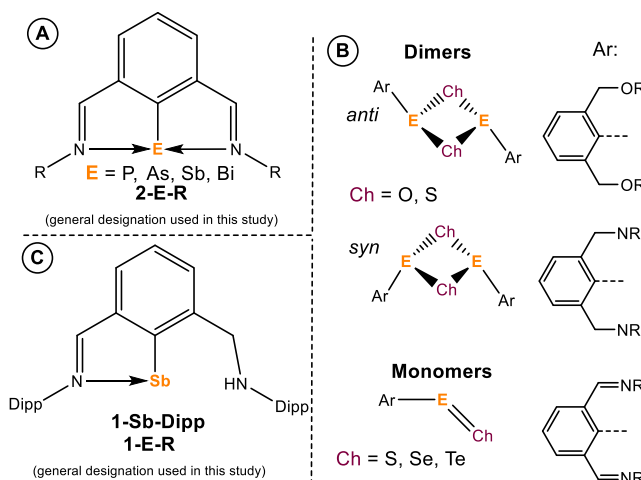


INTRODUCTION

Monomeric group 15 compounds bearing the pnictogen atom *E* in the +I oxidation state are known as pnictinidenes.¹ They represent very reactive R–*E* molecules (*E* = P, As, Sb or Bi); therefore, their synthesis is not trivial and still remains a challenging task. For a long time, these compounds could not be isolated and were studied especially as very reactive intermediates² or as ligands for transition metals that often exhibit interesting reactivity.^{1e,3} Lighter pnictinidenes, especially phosphinidenes, could be generated *in situ* from suitable metastable precursors and transferred to other substrates in a controlled manner as well.⁴

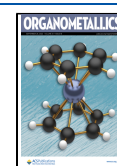
In 2010, monomeric antimony(I) and bismuth(I) compounds supported by an *N,C,N*-pincer ligand were reported at that time representing the first examples of such species stable at ambient conditions.⁵ Although these compounds are thermodynamically stabilized by rather strong intramolecular N → *E* interactions that significantly influence the bonding situation around the central atoms, they still behave and can be regarded as pnictinidenes.⁵ This concept built up on the pincer ligand platform for the stabilization of phosphinidenes,⁶ arsinidenes,⁷ stibinidenes,⁸ and bismuthinidenes⁹ has been later adopted by other groups as well (Chart 1A).

Chart 1

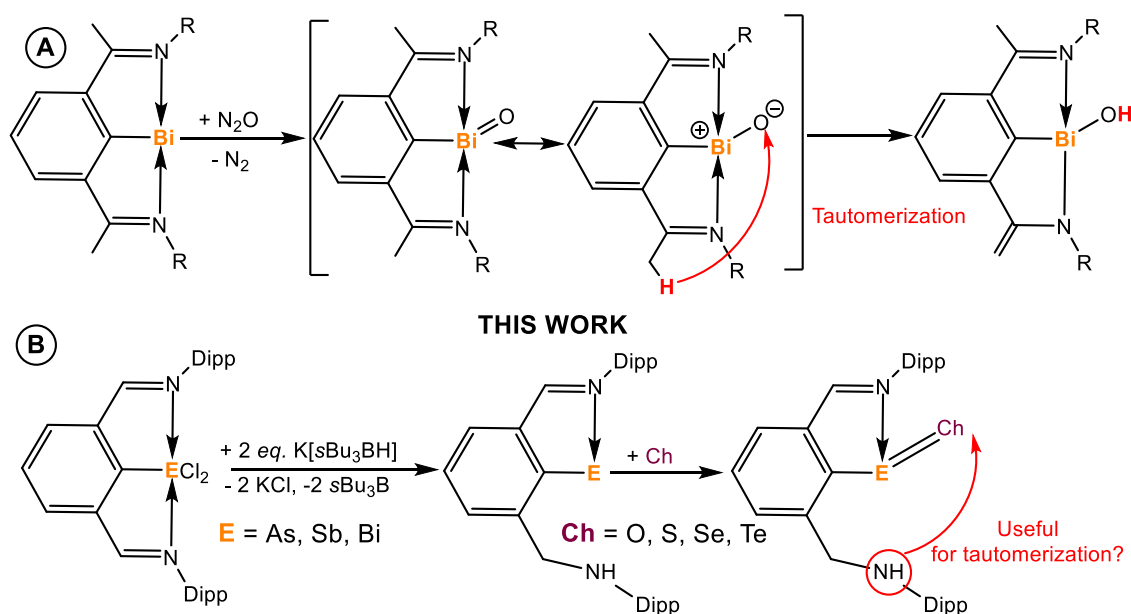


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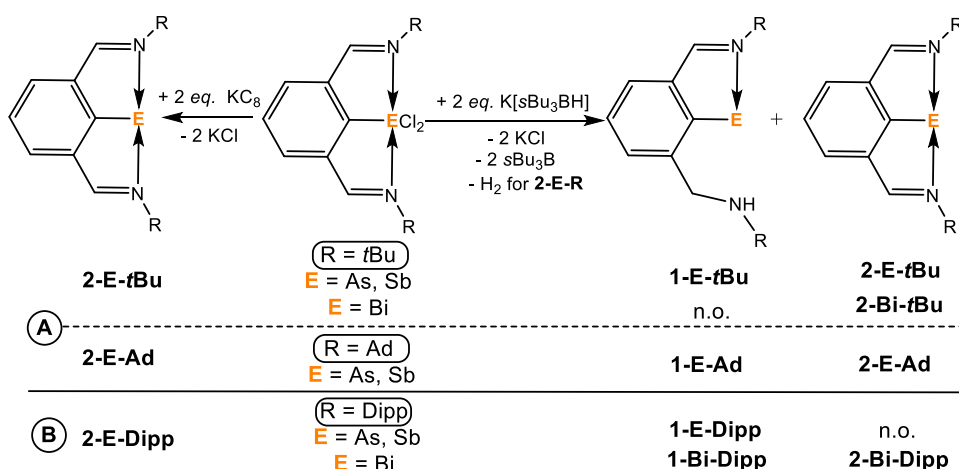
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Scheme 1. Spontaneous Tautomerization Observed for the Bi=O Terminal Bond (A) and Intended Reactivity in This Study (B)



Scheme 2. Comparison of the Obtained Products after the Reduction of Starting Trivalent Precursors either by KC_8 (left) or K-Selectride (right) Showing a Dependence on the Imino-Function R Substituent and the Pnictogen Atom



Due to the presence of two lone pairs at the pnictogen atom, these compounds have clearly demonstrated their potential as nonconventional ligands for transition metals.¹⁰ In addition to their coordination capabilities, these compounds have been shown to activate carbon–carbon multiple bonds via the element–ligand cooperative (ELC)^{11,12} mechanism, resembling thereby a hetero Diels–Alder reaction protocol.¹³ Related bismuthinidenes are also able to undergo an oxidative addition toward a variety of $\text{C}(\text{sp}^3)\text{--X}$ bonds ($\text{X} = \text{I}$ or OTf).¹⁴ Cornella et al. have very recently demonstrated that N,C,N -chelated bismuthinidenes are useful catalysts for a transfer hydrogenation of azo compounds by an amino-borane¹⁵ and hydrodefluorination of polyfluoroarenes.¹⁶ The same group also reported an interesting catalytic oxidation of pinacolborane (HBPin) by N_2O , where the bismuth(I) compounds serve as oxygen atom transfer agents. One of these catalytic systems exhibited an unusual tautomerization when hydrogen transfers from the methyl group to the elusive

terminal $\text{Bi}=\text{O}$ bond resulting in the formation of a $\text{Bi}=\text{OH}$ linkage and a new $\text{Bi}=\text{N}$ covalent bond (Scheme 1A).¹⁷

The other bismuth oxido-compounds described in Cornella's study form dimers with the central Bi_2O_2 ring or they are unstable at ambient conditions.¹⁷ This finding is in line with previous knowledge gained about oxides and sulfides bearing related pincer ligands that form similar dimers and can adopt *syn* or *anti* conformations.¹⁸ For heavier chalcogens, terminal $\text{E}=\text{Ch}$ bonds¹⁹ (Chart 1B) are accessible depending on the pincer ligand used.²⁰ By contrast, the isolation of terminal $\text{E}=\text{O}$ bonds for heavier pnictogens is quite rare and desires the coordination of an external Lewis acid such as $\text{B}(\text{C}_6\text{F}_5)_3$ ²¹ or protonation by strong Brønsted acids, e.g., HOTf .²² Nevertheless, the intramolecular tautomerization described above (Scheme 1A) represents a very promising alternative that may be useful for the stabilization of similar monomeric pnictogen compounds after oxidation by trapping the formally present terminal $\text{E}=\text{O}$ bond.

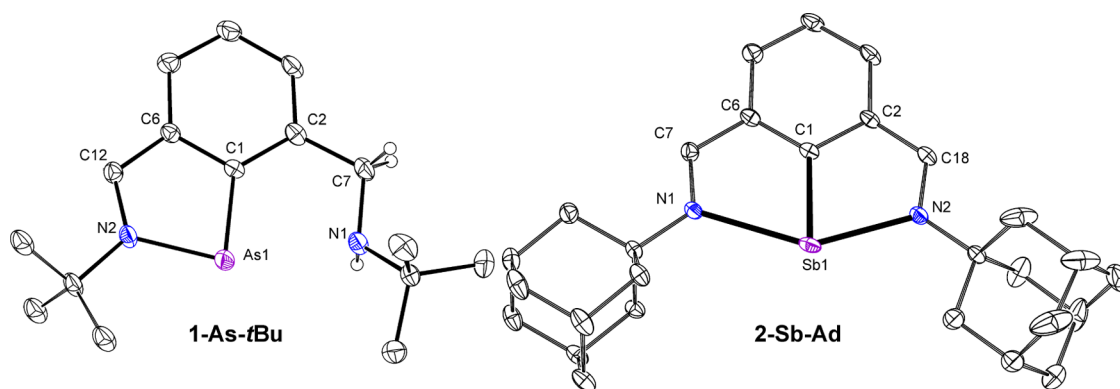


Figure 1. Molecular structures of **1-As-tBu** and **2-Sb-Ad** showing 30% probability ellipsoids and the crystallographic numbering scheme. Hydrogen atoms are omitted for clarity except for the CH₂NH group in the case of **1-As-tBu**.

In this regard, we have recently reported on an N,C,N -chelated stibinidene **1-Sb-Dipp** (Chart 1C) that bears a secondary amine function that is easily accessible by simple reduction of the parent chloride by K-selectride.⁸ The presence of this secondary amine function in the vicinity of the central atom seems to be promising for tautomerization after oxidation of the central pnictogen atom similar to the procedure described by Cornella et al.¹⁷

Thus, the main aim of this study is to examine the synthesis of heavier pnictinidenes structurally related to **1-Sb-Dipp** (**Chart 1C**), compare their structures and chemical behavior with those of previously described bis(imino) analogues (**Chart 1A**, **2-E-R**), and to prove their potential in oxidation reactions with chalcogens that might be influenced by the adjacent secondary amine functionality (**Scheme 1B**).

■ RESULTS AND DISCUSSION

Synthesis and Characterization. First, we have tried to adopt the synthetic protocol used for the synthesis of **1-Sb-Dipp** to less sterically hindered pnictogen(III) precursors (Scheme 2A). Thus, precursors $[2,6-(t\text{BuN}=\text{CH})_2\text{C}_6\text{H}_3]\text{-ECl}_2$ ²³ were treated with 2 equiv of K-selectride in a thf solution. Unfortunately, in the case of arsenic and antimony, only mixtures of earlier reported classical bis-(aldimino) pnictinidenes **2-E-*t*Bu** and the intended amino-aldimino-compounds **1-E-*t*Bu** could be obtained and characterized by NMR spectroscopy (see the Supporting information, SI). Yet, the molecular structure of manually selected single crystals of **1-As-*t*Bu** could be determined (Figure 1). This revealed a significant difference between both As–N distances 2.676 Å (N1) and 1.931 Å (N2), respectively, the latter approaching the single covalent bond (cf. $\Sigma_{\text{cov}}(\text{As}–\text{N}) = 1.92 \text{ Å}$).²⁴ Similarly, the As1–C1 bond of 1.871 Å is slightly shorter than $\Sigma_{\text{cov}}(\text{As}–\text{C}) = 1.96 \text{ Å}$. By contrast, the C12–N2 bond is elongated in comparison with the value expected for a double bond of $\Sigma_{\text{cov}}(\text{C}=\text{N}) = 1.27 \text{ Å}$.²⁵ All values together resemble those recently reported for an aromatic 2,1-benzazaarsole pointing to an aromatic nature of this cycle.⁷ It is worthy to note that for bismuth, the same reaction produced only **2-Bi-*t*Bu** that could be isolated or even detected as a sole product in the reaction mixture by NMR spectra (see Figure S31). Nevertheless, the utilization of a *t*Bu-substituted pincer ligand turned to be insufficient for selective synthesis of the remaining **1-E-*t*Bu** (E = Sb, As). Attempts to improve the selectivity of the reaction in the case of antimony and arsenic by the utilization of bulkier 1-adamantyl group attached to the imino-

function were made. The starting chlorides [2,6-(AdN=CH)₂C₆H₃]₂Cl₂ (E = As, Sb) were prepared by standard metathesis of lithium precursors with ECl₃ (see [SI](#)). Their reduction by KC₈ smoothly produced the expected products **2-As-Ad** or **2-Sb-Ad** and their structures were corroborated by ¹H and ¹³C NMR spectra showing one set of signals for the ligand backbone and for **2-Sb-Ad** additionally by single-crystal X-ray diffraction analysis ([Figure 1](#)). Nevertheless, the treatment of the adamantyl-substituted precursors with 2 equiv of K-selectride led to the entirely same failure in the isolation of **1-E-Ad** as in the case of *t*Bu analogues because they were obtained in mixtures with **2-E-Ad** only and thus **1-E-Ad** could not be isolated in a reasonable yield ([Scheme 2A](#)).

Therefore, we returned to Dipp-substituted compounds that were proven to cleanly produce **1-Sb-Dipp**.⁸ Necessary precursors $[2,6-(\text{DippN}=\text{CH})_2\text{C}_6\text{H}_3]\text{ECl}_2$ (E = As, Bi) were prepared by the salt metathesis method and characterized by ^1H and ^{13}C NMR spectra (see SI) and their molecular structures, which resemble related pincer compounds reported earlier, are depicted in Figures S9 and S14.²³ Both compounds were subsequently reduced by 2 equiv of KC_8 producing the expected pnictinidenes **2-As-Dipp** or **2-Bi-Dipp** as red and deep blue crystalline solids, respectively (Scheme 2) and their ^1H and ^{13}C NMR spectra proved the symmetric coordination of the ligand as expected. More importantly, the reaction of the arsenic precursor with 2 equiv of K-selectride in thf solution smoothly furnished the intended **1-As-Dipp** in very good yield (85%) as orange-red crystals. By contrast, a mixture of both possible products, i.e., **1-Bi-Dipp** and **2-Bi-Dipp**, could only be isolated despite many attempts and variations of experimental procedures (see SI). **1-As-Dipp** exhibited an expected set of signals in the ^1H NMR spectrum including a typical mutually coupled doublet and triplet for the CH_2NHDipp group (3.96 and 4.53 ppm, respectively, with $^3J(^1\text{H}, ^1\text{H}) = 10.2$ Hz) and similarly two diagnostic signals for both CH_2NHDipp (58.0 ppm) and $\text{CH}=\text{NDipp}$ (142.3 ppm) moieties were detected in the ^{13}C NMR spectrum. It is obvious that the presence of the aromatic Dipp group is sufficient for the successful isolation of amino-aldimino-pincer-substituted pnictinidenes. It is also to note that the electronic nature of the N-substituent is probably more important than its steric bulk as the N-aryl-imines are usually much easier to reduce than the N-alkylimines (see below also CV study). Therefore, the presence of the Dipp substituent allowed smooth formation of **1-As-Dipp** and **1-Sb-Dipp**, while it seems to be much more complicated for *t*Bu analogues.

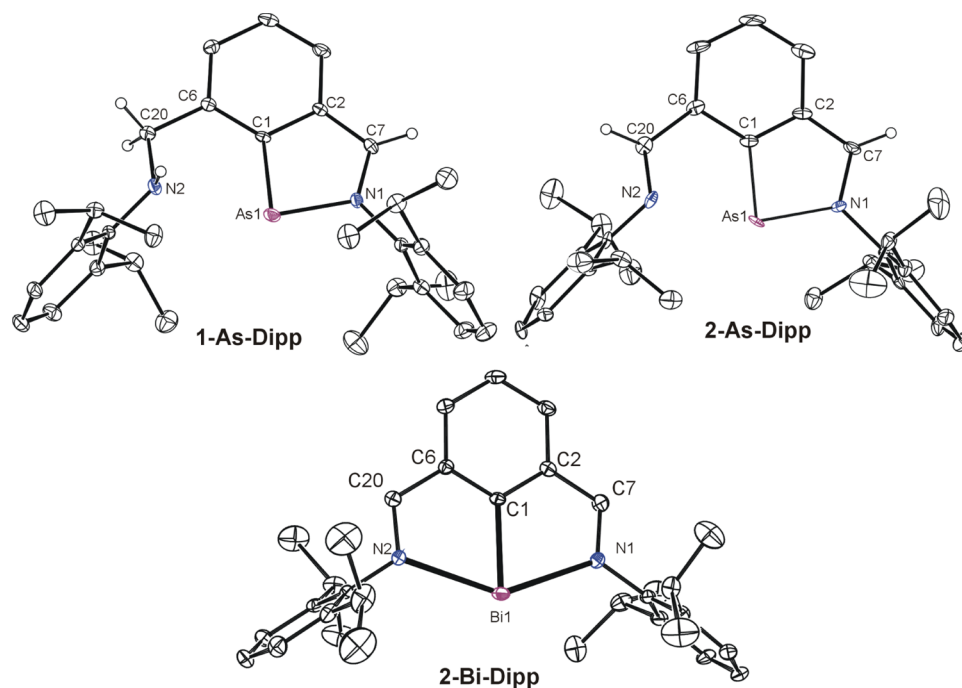


Figure 2. Molecular structures of **1-As-Dipp**, **2-As-Dipp**, and **2-Bi-Dipp** showing 30% probability ellipsoids and the crystallographic numbering scheme. Hydrogen atoms are omitted for clarity except for CH_2NH and $\text{CH}=\text{N}$ groups.

Table 1. Comparison of the Properties of E–N Bonds (d in Å) in a Series of 1-E-R and 2-E-R Compounds^a

E		1-E-R		2-E-R	
		E–N1 ^b	E–N2 ^b	E–N1 ^b	E–N2 ^b
As	d_{XRD} (R=Dipp)	1.900(3)	2.656(3)	1.933(9)	2.469(9)
	d_{DFT} (R=Dipp)	1.883	2.820	1.907	2.704
	d	1.875	2.867	1.891	2.770
	WBI	0.82	0.07	0.79	0.10
	ρ	0.133	0.019	0.129	0.022
	H	-6.5×10^{-2}	2.2×10^{-4}	-6.2×10^{-2}	1.6×10^{-4}
	E_{int}		1.7		7.0
Sb ^c	d_{XRD} (R=Dipp)	2.254(6)	2.534(6)	2.336(4)	2.373(3)
	d_{DFT} (R=Dipp)	2.123	2.810	2.303	2.400
	d	2.122	2.788	2.265	2.446
	WBI	0.66	0.12	0.48	0.32
	ρ	0.095	0.026	0.070	0.048
	H	-2.9×10^{-2}	-1.5×10^{-3}	-1.6×10^{-2}	-7.3×10^{-3}
	E_{int}		5.1		12.2
Bi	d_{XRD} (R=Dipp)			2.461(4)/2.469(4) ^e	2.561(4)/2.545(4) ^e
	d_{DFT} (R=Dipp)	2.270 ^d	2.827 ^d	2.448	2.481
	d	2.280	2.796	2.460	2.463
	WBI	0.56	0.14	0.36	0.36
	ρ	0.076	0.028	0.052	0.052
	H	-1.6×10^{-2}	-8.5×10^{-4}	-6.4×10^{-3}	-6.5×10^{-3}
	E_{int}		6.8		15.0

^aWBI, ρ (in a.u.), H (in a.u.), and E_{int} (in kcal/mol) values correspond to R=H (**1-E-H**). ^bPlease note that the numbering is adapted to that used for arsenic compounds. ^cReference 8. ^dThe data for **1-Bi-Dipp** are only based on theoretical studies. ^eValues for the second independent molecule in the unit cell.

Furthermore, the reduction of $[2,6-(\text{DippN}=\text{CH})_2\text{C}_6\text{H}_3]-\text{ECl}_2$ (E = As, Sb) was repeated using the deuteride $\text{Li}[\text{BEt}_3\text{D}]$ (*in situ* generated from LiD and Et_3B in thf) to prove the role of the K-selectride as the source of the hydrogen for the newly formed CH_2NH fragment. In both cases, the products contained the expected CHDN(D)Dipp moiety (for NMR spectra, see Figures S36–S39). The presence of deuterated

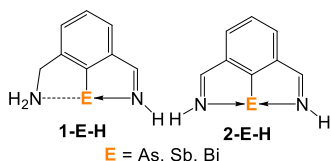
isotopologues in the product was also proved by vibrational spectra where weak bands of the N–D and C–D stretching modes were found at ~ 2511 and 2114 cm^{-1} , respectively. The observed $\nu_{\text{NH}}/\nu_{\text{ND}}$ and $\nu_{\text{CH}}/\nu_{\text{CD}}$ ratio of 1.351(4) is in good accordance with values reported for deuterated *N*-arylbenzamides and *N*-benzylanilines (Figures S68–S71).²⁶

Structure and Spectroscopic Properties. The molecular structures of **1-As-Dipp**, **2-As-Dipp**, and **2-Bi-Dipp** were established by single-crystal X-ray diffraction analysis (Figure 2). In Table 1, their structural parameters are compared with the earlier reported antimony analogues **1-Sb-Dipp** and **2-Sb-Dipp**.⁸ Unfortunately, for **1-Bi-Dipp** only the calculated values are available at the moment as this compound could not be isolated (see above).

It is evident that the As(1)–N(1) bond lengths shortened slightly going from **2-As-Dipp** (1.993 Å) to **1-As-Dipp** (1.899 Å), while the As(1)–N(2) bonds elongated cf. 2.469 and 2.656 Å, respectively. Nevertheless, in both cases, the value for the As(1)–N(1) bond resembles $\Sigma_{\text{cov}}(\text{As}–\text{N}) = 1.92$ Å; therefore, both rings might be regarded as 6π electron aromatic azapnictoles in regard to previous results.⁷ By contrast, the difference in E–N distances between **1-E-Dipp** and **2-E-Dipp** is significantly more pronounced for antimony and bismuth (Table 1). While both E–N bond lengths are equivalent in the case of **2-E-Dipp** and thus represent hypervalent Sb(I) and Bi(I) compounds, these become pronouncedly different for **1-E-Dipp** (Table 1) and this indicates the presence of aromatic azapnictole rings (see below).

To compare the electronic structures of compounds **1-E-R** and **2-E-R**, we carried out DFT calculations at the ω B97XD/def2-TZVP level (a comparable level of theory has been employed for similar chelate complexes⁹) and on the optimized geometries, natural bond orbital (NBO) analysis was performed. To gain insights into the bonding situations, Wiberg bond indices (WBI) and natural population analysis (NPA) charges were obtained, and atoms-in-molecules (AIM) analysis was also applied. In the following, we focus on the parent compounds shown as **1-E-H** and **2-E-H** (Chart 2),

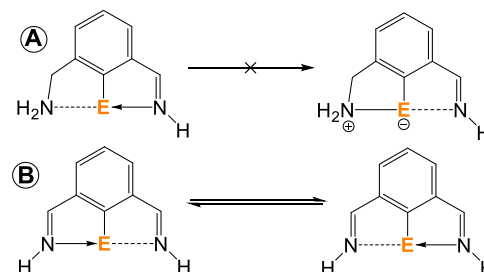
Chart 2



which contain H substituent at the nitrogen centers instead of the bulky *t*Bu or Dipp groups. The analogous computations on the experimentally obtained species with Dipp groups (i.e., **1-E-Dipp** and **2-E-Dipp**) indicate that the simplified models **1-E-H** and **2-E-H** are suitable for comparison (on the basis of very similar atomic distances, see Table 1 and SI for detailed results).

The calculated geometrical parameters nicely agree with those observed in the X-ray diffraction measurements (except for the bismuth analogues for which no experimental structure is available); see Table 1. The geometries of bis(imino) compounds **2-As-H** and **2-Sb-H** are actually not symmetric due to the differing strengths of the two dative bonds between the pnictogen center and the nitrogen donor atoms (e.g., $d_{\text{N}–\text{E}}(\text{2-As-H}) = 1.891/2.770$ Å), albeit this difference in the bismuth-containing compound is negligible ($d_{\text{N}–\text{E}}(\text{2-Bi-H}) = 2.460/2.463$ Å). In “mixed” compounds **1-E-H**, the imino nitrogen forms a stronger bond than the strongest $\text{N}_{\text{imino}}–\text{E}$ bond in the case of the corresponding compound **2-E-H**. Although the amino-nitrogen is a stronger donor, the $\text{N}_{\text{amino}}–\text{C}$ bonds are longer and weaker, likely because the imino substituent offers the possibility of π -conjugation. This is

further bolstered by the decrease of the Wiberg bond indices for these bonds to close to zero ($\text{WBI}_{\text{N}_{\text{amino}}–\text{E}}(\text{1-As-H}) = 0.07$) and the increase of the bond length ($d_{\text{N}_{\text{amino}}–\text{E}}(\text{1-As-H}) = 2.867$ Å), leading to a difference of almost 1 Å in the case of the arsenic-containing compound ($d_{\text{N}_{\text{imino}}–\text{E}}(\text{1-As-H}) = 1.875$ Å). If compounds **1-E-H** and **2-E-H** are compared for a given pnictogen, the sum of the Wiberg bond indices of the N–E bonds is nearly equal (the more one strengthens, the more the other weakens), albeit these sums shrink as descending in the pnictogen group, indicating an increase in the polarity of the bonds. Based on relaxed scan calculations on compounds **2-E-H**, a bell-clapper-type rearrangement⁷ was observed (Scheme 3B and SI), except for **2-E-Bi**, where only one isomer exists. In

Scheme 3. Bell–Clapper-Type Isomerization Prohibited for **1-E-H** (A) and Obtained for **2-E-H** (B)

stark contrast, **1-E-H** compounds show a different behavior: if the distance between the pnictogen center and the amino-nitrogen is decreased, the energy grows monotonously. Therefore, the new type of complexes (**1-E-H**) are unable to undergo bell-clapper-type isomerization (Scheme 3A).

The electron density values at the bond critical points (ρ) also show differences: the markedly unequal electron density values indicate different $\text{N} \rightarrow \text{E}$ dative bonds in all complexes except for the **2-Bi-H** species in which the two values are practically the same. Furthermore, the total energy density (H) at the bond critical point is also indicative to distinguish between stronger dative bonding or weaker, noncovalent interactions: while for the former, the H value is negative, for the latter it has a positive sign. The values close to zero exclude a substantial covalent (dative) character. The amino-group can only form rather weak, noncovalent, so-called pnictogen interactions²⁷ in compounds **1-E-H**, which is supported by the positive or close to zero values of H , especially in case of **1-As-H**. In the direction of $\text{As} \rightarrow \text{Sb} \rightarrow \text{Bi}$, the $\text{N}_{\text{amino}}–\text{E}$ bond strength increases, which is clearly in line with increasing Lewis acidity of the pnictogen center E.²⁸ The bonds in the heavier analogues ($\text{E} = \text{Sb}, \text{Bi}$) are a rather dative type with substantially negative H values.

We have estimated the interaction energies for the $\text{N}_{\text{amino}}–\text{E}$ bond in **1-E-H** and for the weaker $\text{N}_{\text{imino}}–\text{E}$ bond in **2-E-H** by model calculations (Table 1; for details see Figure S90). These interaction energies are clearly larger in compounds **2-E-H** (7.0–15.0 kcal/mol), compared to compounds **1-E-H** (1.7–6.8 kcal/mol) and increase in the order $\text{As} < \text{Sb} < \text{Bi}$. To summarize, the traditional analogues can be described as pnictogen-chelated complexes (rather asymmetric for **2-As-H** or **2-Sb-H** and almost symmetric for **2-Bi-H**), while the new **1-E-H** compounds are rather azapnictole rings with flanking amino-groups serving as donors for weak, noncovalent interactions toward the pnictogen centers.

Table 2. Experimental and Calculated Spectral Data at the B3LYP/def2-TZVP Level for Compounds 1-E-R and 2-E-R^a

E	1-E-Dipp			2-E-Dipp		
	As	Sb	Bi	As	Sb	Bi
$\lambda_{\max}$ (experimental) [nm]/log $\epsilon_{\max}$ [–]	417 (3.67)	513 (3.61)	^b	500 (3.19)	675 (3.74)	712 (3.81)
$\lambda_{\max}$ (calculated) [nm]/ f [a.u.]	397 (0.148)	465 (0.151)	508 (0.136)	480 (0.126)	611 (0.102)	649 (0.092)
E	1-E-H			2-E-H		
	As	Sb	Bi	As	Sb	Bi
$\lambda_{\max}$ (calculated) [nm]/ f [a.u.]	386 (0.142)	452 (0.168)	493 (0.151)	465 (0.083)	601 (0.060)	642 (0.052)
$E(\text{HOMO})$ [eV]	–4.83	–4.45	–4.22	–5.07	–4.62	–4.42
$E(\text{LUMO})$ [eV]	–1.29	–1.40	–1.37	–1.85	–1.97	–1.88
$\Delta E(\text{LUMO} - \text{HOMO})$ [eV]	3.54	3.05	2.85	3.22	2.66	2.54

^aAbsorption wavelength ($\lambda_{\max}$, hexane), molar absorption coefficient (log $\epsilon_{\max}$), oscillation strength (f), and energies of frontier molecular orbitals (the latter only for the model species). ^bExperimental data for 1-Bi-Dipp are not available.

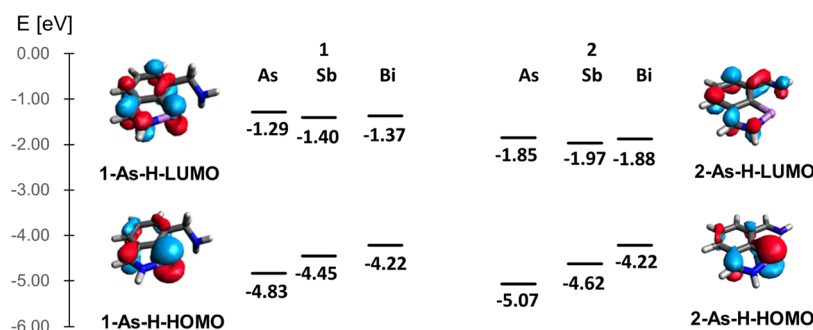


Figure 3. Energy diagram of frontier molecular orbitals of 1-E-H and 2-E-H.

Furthermore, compounds 1-E-Dipp, 2-E-Dipp, and 2-E-tBu were studied by UV–vis spectroscopy (Figures S77–S79). To gain insight into the nature of the excitations in the UV–vis spectra, TD-DFT calculations were performed. To find out which methods reproduce the experimental data the best, we examined several functionals: B3LYP, CAM-B3LYP, ω B97XD, and M06-2X. To simplify the calculations, we again focused on the model systems 1-E-H and 2-E-H at the nitrogen donor centers, which show good agreement with the analogues substituted with tBu and Dipp. All four of the studied functionals qualitatively describe the experimental spectra and the best match is observed using the B3LYP functional. Since the experimental spectra were recorded in hexane, we used the PCM model with the parameter for hexane. The average deviation of the calculations from the experimental excitation wavelengths is round 30–50 nm, which is rather typical for TD-DFT calculations. Due to their importance, only the $S_0 \rightarrow S_1$ excitations are discussed in detail; see Table 2.

In all of the cases, the lowest energy excitation corresponds to a HOMO $\rightarrow$ LUMO transition. Therefore, the relative energies of the HOMO and LUMO orbitals are of importance to describe the tendencies of these excitations. Clearly, a red shift is observed in the direction of As $\rightarrow$ Sb $\rightarrow$ Bi both for 1-E-H and 2-E-H sets of compounds. Based on Table 2 and Figure 3, for the same ligand type, the energy of the HOMO substantially increases in the As $<$ Sb $<$ Bi direction, but the LUMO energy is practically constant for a given type (1-E-H or 2-E-H). Thus, the HOMO–LUMO gap decreases in the order of As $>$ Sb $>$ Bi, and parallelly the excitation energy drops, resulting in a red shift of the spectra.

In the case of the new type of complexes 1-E-H, the HOMO and LUMO orbital energies are higher compared to the corresponding traditional analogues 2-E-H. Importantly, this difference is more significant for the LUMO, than for the

HOMO energies. Hence, for a given pnictogen, this results in a higher HOMO–LUMO gap for the new type of compounds 1-E-H compared to the corresponding 2-E-H analogues. Consequently, the excitation energy is larger for compounds 1-E-H than for the conventional counterparts, clearly leading to a blue shift in the spectra (e.g., 417 nm for 1-As-Dipp vs 500 nm for 2-As-Dipp).

To gain deeper understanding, we analyzed the contributions and energies of the FMO orbitals (see Figure 3 for arsenic as an example). In both types of compounds, the HOMO consists of mainly the p_z -type lone pair of the pnictogen center embedded into the π -system of the organic backbone. As the energy of the p_z -orbital (being the main contributor) clearly increases in the As $\rightarrow$ Sb $\rightarrow$ Bi order, the HOMO energies increase significantly in the same order. The LUMOs are of π^* -type: in the conventional complexes 2-E-H, both imino π -orbitals are involved, while in the new type of compounds 1-E-H, one imino group can contribute to the LUMO. As a difference, the pnictogen heteroatom is not involved in the LUMO of the 2-E-H complexes; however, it only has a small contribution in the LUMO of complexes 1-E-H. Therefore, the LUMO energies show negligible variation for a given type of compound. Importantly, due to the additional π bond, the degree of delocalization in the π -system is more extended in species 2-E-H compared to that in 1-E-H. Thus, the LUMOs of the traditional complexes are more stabilized (–1.85 to –1.97 eV) compared to 1-E-H (–1.29 to –1.40 eV), which is the main reason for the observed, blue-shifted spectra of compounds 1-E-H compared to those of compounds 2-E-H.

Finally, the redox behaviors of 1-E-Dipp, 2-E-Dipp, and 2-E-tBu were studied using CV measurements (Table 3). These CVs revealed one, in some cases two, redox process in the cathodic direction (see SI). For each type of compound, the

Table 3. Electrochemical Data of the Studied Compounds in THF

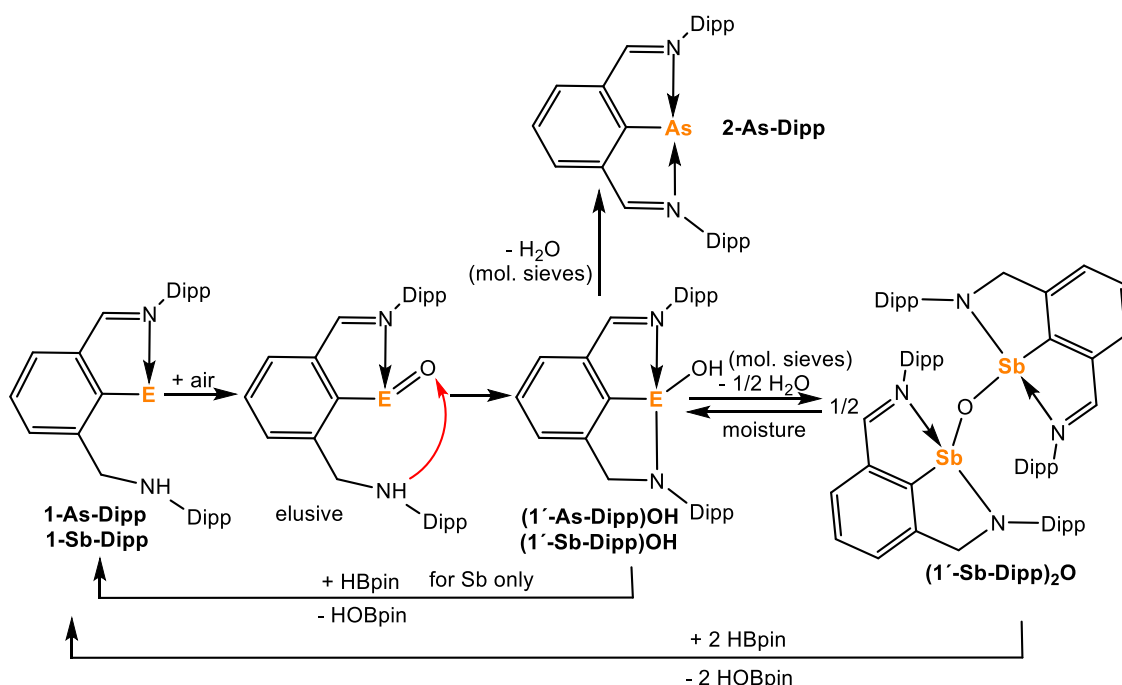
	$E_{1/2}(\text{ox1})$ [V]	$E_{1/2}(\text{ox2})$ [V]	$E_{1/2}(\text{red1})$ [V]	$E_{1/2}(\text{red2})$ [V]	ΔE [V] ^c
1-As-Dipp	0.62	0.88	−2.31		2.93
1-Sb-Dipp	0.29 ^a		−2.30 ^b		2.59
2-As-Dipp	0.83	1.02	−1.86	−2.62 ^b	2.69
2-Sb-Dipp	0.48		−1.79	−2.63 ^b	2.27
2-Bi-Dipp	0.28		−1.87	−2.64 ^b	2.15
2-As- <i>t</i> Bu	0.58 ^a	0.83	−2.13		2.84
2-Sb- <i>t</i> Bu	0.15 ^a		−2.01	−2.42	2.23
2-Bi- <i>t</i> Bu	0.01 ^a		−2.10		2.21

^aAnodic (E_{pa}) peak potential. ^bCathodic (E_{pc}) peak potential; $E_{1/2} = (E_{\text{pa}} + E_{\text{pc}})/2$. ^c $\Delta E = E_{\text{pa}} - E_{\text{pc}}$. All potentials are given vs SCE.

first reversible reduction occurs at approximately the same negative potential, which is in accordance with the calculated LUMO energies showing only negligible variation. In terms of positive potentials, most of the studied compounds show one two-electron oxidation process corresponding to E(I) toward E(III). Generally speaking, the first oxidation of E(I) to E(III) in both series, i.e., **2-E-*t*Bu** and **2-E-Dipp**, is always most difficult for the lightest pnictogen ($E = \text{As}$), thereby showing a clear trend that when descending the group 15, the oxidation becomes easier. Such observation is in impeccable agreement with increasing energies of the calculated HOMO in the same order. When comparing both series **2-E-*t*Bu** and **2-E-Dipp**, the N-substituent has a significant effect on the E(I) → E(III) oxidation with N-*t*Bu substitute (i.e., **2-E-*t*Bu**) being about 0.3 V more easily oxidized. The lowest value of the first oxidation potential is found for **2-Bi-*t*Bu** (0.01 V vs SCE). In series **1-E-Dipp** and **2-E-Dipp**, **1-E-Dipp** compounds are about 0.2 V more easily oxidized, which is in accordance with

the calculated HOMOs being more stabilized for **2-E-Dipp**. Interestingly, the discussed E(I) → E(III) oxidation process for **1-Sb-Dipp** is, unlike all other compounds, irreversible. Finally, the electrochemical gap obtained from CV measurements in THF, the ΔE [V], is in an excellent correlation with the values of the HOMO–LUMO gap (λ_{max} converted to eV) from UV/vis measurement in hexane, see **SI**, taking minor discrepancies in absolute values to be attributed to solvent effects.

Oxidation. Based on the abovementioned results of CV measurements, the bis(aldimino)- (i.e., **2-E-Dipp**) and amino-aldimino-compounds (i.e., **1-E-Dipp**) should be oxidized quite easily by two electrons yielding the corresponding trivalent products. Therefore, a rather simple oxidation of these species by air was examined (**Scheme 4**). Treatment of **2-E-Dipp** resulted in a rapid decolorization of the reaction mixtures being indicative for a quick oxidation, but despite an immediate evaporation of the reaction mixtures, NMR analysis revealed the formation of rather complex mixtures for all pnictogens used (**Figures S40, S43, and S51**). This finding parallels that reported by Cornella for related bismuthindenes.¹⁷ By contrast, bubbling air through a benzene solution of **1-As-Dipp** (~2 h) or **1-Sb-Dipp** (<3 min) provided the corresponding oxidized products (**1'-As-Dipp**)OH and (**1'-Sb-Dipp**)OH in quantitative yields, both containing terminal E-OH moieties (**Scheme 4**). (**1'-Sb-Dipp**)OH is always contaminated by traces of the oxide (**1'-Sb-Dipp**)₂O (see below). This proves the tautomerization as a crucial step allowing isolation of the oxidized products. Albeit, we were not able to get single-crystalline material; the structures of (**1'-As-Dipp**)OH and (**1'-Sb-Dipp**)OH were only studied by ¹H NMR spectroscopy showing the presence of a typical AX pattern for the CH₂N group along with the singlet for the OH group (at 1.95 and 1.27 ppm, respectively). These signals are significantly shifted in comparison with the NH group present in the starting **1-As-Dipp** and **1-Sb-Dipp** (at 3.96 and 4.46

Scheme 4. Oxidation of 1-As-Dipp and 1-Sb-Dipp by Air and Their Recovery by the Reaction with HBpin

ppm, respectively). Furthermore, the obtained ^1H NMR chemical shifts for this OH group are also close to the terminal Bi–OH group (0.92 ppm) obtained in related pincer compounds.¹⁷ The presence of the terminal E–OH group gives a single absorption band at 3602 and 3616 cm^{-1} in the infrared spectra of (1'-As-Dipp)OH and (1'-Sb-Dipp)OH, respectively.

While (1'-As-Dipp)OH is stable for weeks under an inert atmosphere, the antimony analogue tends to eliminate water and condensates to the corresponding oxide (1'-Sb-Dipp)₂O. This can be isolated as yellow crystalline solid in very good yield, when a solution of (1'-Sb-Dipp)OH is treated with activated molecular sieves (3 Å) under inert conditions. It is to note that the process is reversible because when (1'-Sb-Dipp)₂O is dissolved in wet benzene, partial recovery of (1'-Sb-Dipp)OH could clearly be recognized by NMR spectroscopy (Figure S50). The molecular structure of (1'-Sb-Dipp)₂O is shown in Figure 4 and proves both the NH →

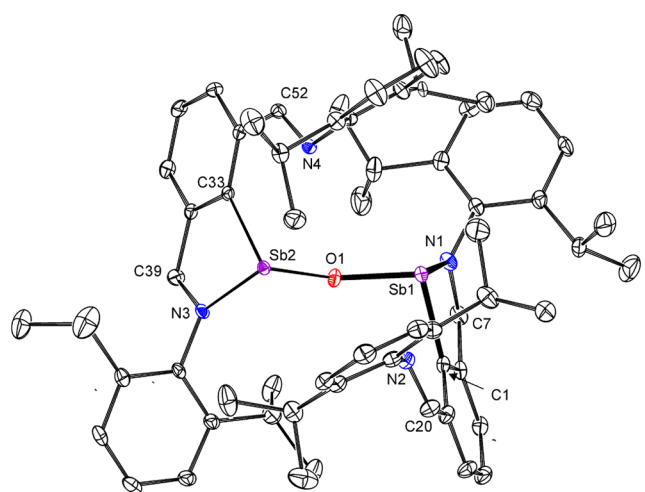


Figure 4. Molecular structure of (1'-Sb-Dipp)₂O showing 30% probability ellipsoids and the crystallographic numbering scheme. Hydrogen atoms are omitted for clarity.

OH tautomerization process and the subsequent condensation via dehydration. The central O1 atom bridges both Sb(1,2) atoms in a slightly nonsymmetric fashion (i.e., 1.968 vs 1.981 Å, cf. $\Sigma_{\text{cov}}(\text{Sb}-\text{O}) = 2.03$ Å) with Sb1–O1–Sb2 angle 131.22°, thus being similar to related dimeric N-coordinated oxides such as {[2,6-(Me₂NCH₂)₂C₆H₃]Sb(μ-O)}₂²⁹ or {[2-(Me₂NCH₂)C₆H₄]SbCl(μ-O)}₂³⁰. The Sb(1)–N(1) and Sb(2)–N(3) distances (i.e., 2.043 and 2.050 Å, respectively) are indicative for covalent single bonds ($\Sigma_{\text{cov}}(\text{Sb}-\text{N}) = 2.11$ Å), while N(2,4) atoms remain outside the primary coordination sphere of the Sb atoms (2.911 and 3.019 Å).

Strikingly, attempts to remove water from (1'-As-Dipp)OH by molecular sieves did not lead to the formation of the oxide; instead, 2-As-Dipp was formed (Scheme 4). The process could be completed within 24 h if a larger excess of molecular sieves was used (Figure S48). This reaction represents a remarkable example when the reduction of the central atom is accompanied by a water molecule elimination. Furthermore, it is to note that the whole process includes a C–H activation at the methylene group.

Another important question is the reversibility of oxidation. Therefore, (1'-As-Dipp)OH and (1'-Sb-Dipp)OH were treated with 1 equiv of HBpin in C₆D₆. While in the case of

arsenic, the reaction was quite sluggish and also produced a significant amount of side products (Figure S52), (1'-Sb-Dipp)OH was rapidly reduced by HBpin providing 1-Sb-Dipp along with a mixture of HOBpin and O(Bpin)₂ (Figures S53–S56) similarly to the results reported recently by Cornella et al.¹⁷ Furthermore, the same outcome could be obtained when (1'-Sb-Dipp)₂O was treated by 2 equiv of HBpin, but the reaction was slower and produced some minor impurities (Scheme 4). This process was also followed with time-resolved IR spectroscopy analyzing integral intensity of BH stretching at 2579 cm^{-1} . Additionally, this experiment also proves the robustness of the system that is able to oxidize additional dozens of HBpin added in a period of several hours (Figure S76).

The abovementioned results showed the potential of the tautomerization process and led us to further examine the oxidation of 1-As-Dipp and 1-Sb-Dipp reactivity toward other chalcogenes. Unfortunately, the oxidation by sulfur turned to be nonselective and provided complicated mixtures of products, albeit at early stages of the reaction the formation of only one oxidized product is evident from the ^1H NMR spectra (Figures S57 and S58). This finding well agrees with the results of our theoretical study (see further discussion). Furthermore, 1-As-Dipp was shown to be inert toward elemental tellurium even at an elevated temperature and the oxidation by selenium was also sluggish and heating of the reaction mixture produced only a mixture of products. By contrast, the 1-Sb-Dipp precursor was smoothly oxidized by both heavier chalcogens Se and Te (for Te, heating to 65 °C is necessary), and the corresponding compounds (1-Sb-Dipp)Se and (1-Sb-Dipp)Te bearing a terminal Sb=E bond could be isolated and structurally characterized. It is to note that both compounds did not show any tendency for tautomerization at room temperature and longer heating in benzene solution resulted in decomposition of the tellurium compound only (Figures S65 and S66). The ^1H and ^{13}C NMR spectra revealed one set of quite broad resonances for the ligand including the NH groups at 6.11 and 5.74 ppm for (1-Sb-Dipp)Se and (1-Sb-Dipp)Te, respectively. The ^{77}Se and ^{125}Te NMR spectra showed one signal in each case at −17.3 and −422.4 ppm, respectively, both values being comparable with other terminal Sb–Se and Sb–Te bonds in N-coordinated compounds.^{20a} The presence of the NH group in both (1-Sb-Dipp)Se and (1-Sb-Dipp)Te was evidenced by the absorption band of ν_{NH} mode at 3245 and 3237 cm^{-1} , respectively. We note that this band is split by ca. 20 cm^{-1} due to vibrational interaction in the solid state. The molecular structures are shown in Figures 5 and S67 and approved the monomeric forms, where Sb–Se (2.437 Å) and Sb–Te (2.661 Å) bonds are similar to those reported for the N-coordinated analogues [2,6-(Me₂NCH₂)C₆H₃]SbCh (Ch = Se 2.4396 and Te 2.6620 Å).^{20a} The central atom is coordinated by both nitrogen atoms in a slightly nonsymmetric manner (cf. 2.458 and 2.536 Å for (1-Sb-Dipp)Se and 2.406 and 2.540 Å for (1-Sb-Dipp)Te).

As both compounds 1-As-Dipp and 1-Sb-Dipp behave quite differently in the above-described oxidations in regard to both their feasibility and occurrence of tautomerization, we decided to perform an extensive theoretical study to shed more light on this phenomenon.

According to the experiments, it was found that the tautomerization markedly depends on the chalcogen atom attached to a given pnictogen center. Thus, the thermodynamic feasibility of the tautomerization reaction was examined computationally using the reaction in Scheme 5 (ΔE_{taut}) and

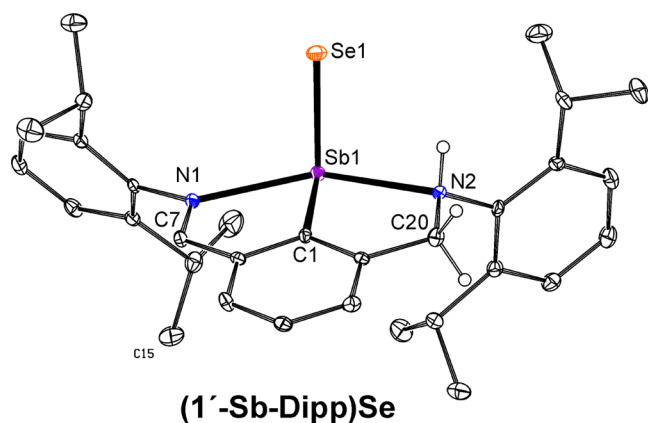
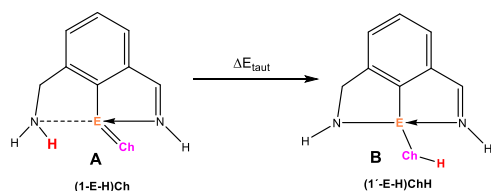


Figure 5. Molecular structure of (1'-Sb-Dipp)Se showing 30% probability ellipsoids and the crystallographic numbering scheme. Hydrogen atoms except CH₂NH are omitted for clarity.

Scheme 5. Tautomerization Reaction for the Studied Compounds



the corresponding energies are shown in Table 4. The value is negative when the tautomeric form B with hydrogen at the

Table 4. Calculated Tautomerization Reaction Energies Shown in Scheme 5 at the ω B97XD/def2-TZVP Level [kcal/mol]

Ch/E	As	Sb	Bi
O	−18.3	−20.0	−20.5
S	−4.0	2.6	4.8
Se	0.7	7.9	10.8
Te	5.5	12.5	16.1

chalcogen is more stable than the form A in which the hydrogen is on the nitrogen center. In the case of oxygen-containing analogues, the tautomeric forms B are favored by a substantial energy (18–20 kcal/mol) for each pnictogen center investigated. In stark contrast, the two tautomers of the sulfur-

containing species (and selenium-containing for the arsenic compound) have rather similar energies. This property is presumably responsible for the formation of complicated mixtures resulting from the oxidation of 1-As-Dipp by S or Se and 1-Sb-Dipp by S as mentioned above. These mixtures may contain both forms A and B, and the elimination of H₂S may lead to sulfur-bridged dimers analogous to (1'-Sb-Dipp)₂O (Scheme 4). Furthermore, formation of polysulfides, often obtained during sulfur oxidation of related low-valent main group compounds,^{18d,31} could not be ruled out. All of these circumstances most probably caused a failure in product isolation after oxidation of 1-As-Dipp and 1-Sb-Dipp by sulfur.

However, if the chalcogen is selenium or tellurium, the tautomerization is clearly disfavored and the compounds with terminal E=Ch bonds are more stable thermodynamically especially in the case of Sb and Bi (Table 4). In general, the tautomeric forms A get more stable compared to the B forms as descending the chalcogen group as well as by descending the pnictogen group (the only exception is for the oxygen-containing species, which show practically no change for the pnictogen element); see Figure 6.

The stability of the two tautomeric forms can be understood using the electrostatic potential map of the corresponding anions formed by deprotonation of the two tautomers shown in Figure 7. The red areas indicate attracting electrostatic potential toward a positive point charge, which is at O for [(1'-As-H)O][−] and at N for [(1-Bi-H)Te][−]. These statements also show good correlation with the Pauling electronegativity (EN) scale.³² Oxygen is more electronegative than nitrogen (cf. EN(O) = 3.44; EN(N) = 3.04), while the heavier chalcogens are more electropositive compared to nitrogen (cf. EN(S) = 2.58; EN(Se) = 2.55; EN(Te) = 2.10). Therefore, in the case of oxides, the tautomeric form B, i.e., (1'-E-H)OH, is favored, while for selenides and tellurides, the tautomeric form A, i.e., (1-E-H)Ch, is preferred. Importantly, the chalcogen centers have a deterministic role in preference of the two possible tautomers; however, pnictogens also have a special modulating role.

CONCLUSIONS

It has been demonstrated that the reduction of *N,C,N*-pincer-coordinated compounds by a bulky hydride, i.e., K-selectride, may lead to the formation of a new type of pnictinidene bearing a pendant secondary amino-function [2-(RNHCH₂)-6-(RN=CH)C₆H₃]₂E (1-E-R) (where E = As, Sb, Bi, R = *t*Bu, Ad, or Dipp). However, it turned out that this reaction is quite

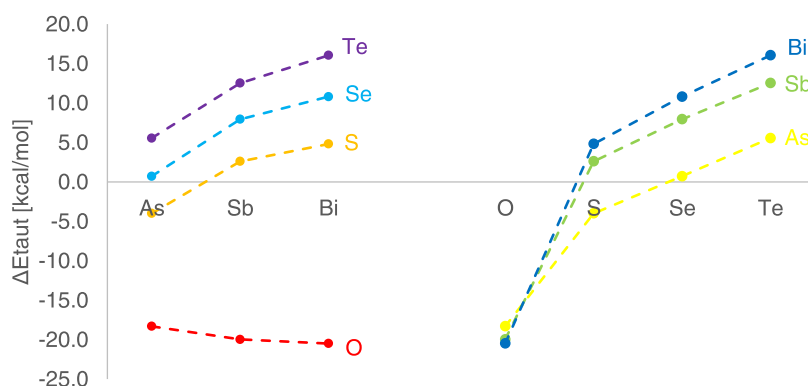


Figure 6. Tautomerization energy (ΔE_{taut} , Scheme 5) for different pnictogens (left) and chalcogens (right).

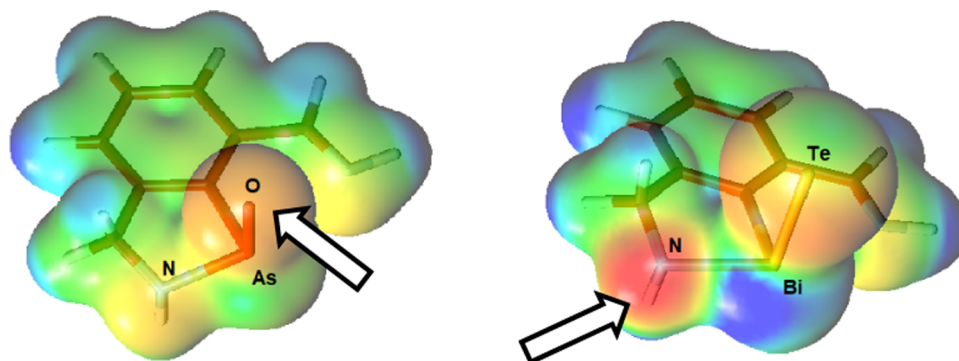


Figure 7. Molecular electrostatic potential for the anions obtained by deprotonation of $[(1'\text{-As-H})\text{O}]^-$ and $[(1\text{-Bi-H})\text{Te}]^-$ (left and right, respectively) at the ω B97XD/def2-TZVPD level.

sensitive toward the substitution at the nitrogen atom and clean formation of **1-E-R** is only accessible when R is a bulky aromatic Dipp group, but for the bismuth even in this case, the targeted bismuthinidene **1-Bi-Dipp** could not be isolated. The electronic nature of the N-substituent was recognized as an important factor because the N-aryl-imines seem to be better suited for stabilization of nonsymmetric compounds **1-E-R** than the corresponding N-aryl-imines, but a more detailed study has to be devoted to this topic in future.

The properties of new **1-E-Dipp** pnictinidenes were compared with the classical bis(imino)-ones, i.e., $[2,6\text{-(RN=CH)}_2\text{C}_6\text{H}_3]\text{E}$ (**2-E-R**) by a combined experimental/theoretical study, which revealed significant differences in their structures. While the **2-E-R** compounds may exhibit a so-called bell-clapper structure⁷ with the pnictogen atom moving between both imino-functionalities (except for bismuth, whose larger radius prevents the formation of two isomers), this type of fluxional behavior is prohibited in the case of new **1-E-Dipp** pnictinidenes. The latter compounds are better understood as azapnictoles bearing significant aromatic character and containing pendant amino-functions. As a consequence of these structural differences, **1-E-Dipp** pnictinidenes generally revealed higher values of HOMO–LUMO gap than **2-E-R**, but in both sets, these values gradually decrease in the order As $\rightarrow$ Sb $\rightarrow$ Bi.

Albeit in both cases, the CV measurements indicated smooth $2e^-$ oxidation, and the experimental air oxidation of **2-E-R** produced only complicated mixtures of products, most probably due to a labile behavior of the oxidized product containing terminal E–O bonds.¹⁷ Contrarily, straightforward oxidation using air as the oxidant was performed for (**1-E-Dipp**) (where E = As, Sb). In this case, a smooth $\text{NH} \rightarrow \text{OH}$ tautomerization at the pendant secondary amino-function was obtained, leading to the formation of hydroxides (**1'-E-Dipp**) **OH**. In the case of antimony, the tendency for condensation toward the corresponding oxide (**1'-Sb-Dipp**)₂O was observed, while attempts to remove a water molecule from the arsenic counterpart resulted in an unexpected reduction of the central element. In addition, a C–H bond activation at the ligand arm thereby produces bis(imino)-pnictinidene **2-As-Dipp**. Follow-up experiments also supported by theoretical considerations proved that similar tautomeric shift $\text{NH} \rightarrow \text{ChH}$ (Ch = S, Se, or Te) becomes less favorable in the case of antimony and bismuth compounds during oxidation by heavier chalcogens.

This type of tautomerization involving the pendant NH group in **1-E-Dipp** represents a remarkable example of the so-

called element–ligand-cooperation¹¹ like reactivity that seems to be promising for further studies in activation of other organic or inorganic molecules. Investigation in this direction is currently underway in our group.

EXPERIMENTAL SECTION

General Procedures. All air- and moisture-sensitive manipulations were carried out under an argon atmosphere using a standard Schlenk tube technique. Solvents were dried using a Pure Solv-Innovative Technology equipment. C_6D_6 and thf-d8 were dried by standard procedures and stored over a potassium mirror and molecular sieves, respectively. All reagents except those referenced in the main text were purchased from commercial sources and used as delivered. ^1H , $^{13}\text{C}\{^1\text{H}\}$, $^{11}\text{B}\{^1\text{H}\}$, $^{77}\text{Se}\{^1\text{H}\}$, and $^{125}\text{Te}\{^1\text{H}\}$ NMR spectra were recorded on Bruker Ascend 500 MHz and Bruker Ultrashield 400 MHz spectrometers using a 5 mm tunable broadband probe or a cryo-probe Prodigy. Appropriate chemical shifts in ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra are given relative to the residual signals of the solvent [C_6D_6 : $\delta(^1\text{H}) = 7.16$ ppm and $\delta(^{13}\text{C}) = 138.9$ ppm, thf-d8: $\delta(^1\text{H}) = 3.58$ ppm and $\delta(^{13}\text{C}) = 67.57$ ppm]. $^{11}\text{B}\{^1\text{H}\}$ NMR spectra were related to external $\text{B}(\text{OME})_3$ [$\delta(^{11}\text{B}) = 18.1$ ppm]. Infrared (single-bounce diamond or silicon ATR) and Raman (vacuum-sealed capillary, excitation laser 1064 nm) spectra were recorded on a Nicolet iS50 FTIR spectrometer equipped with an iS50 Raman module. The reactions with HBpin were continuously monitored using Si-ATR immersion probe and recorded as integral area intensity at $2530\text{--}2630\text{ cm}^{-1}$ vs time (Figure S76). Electronic absorption spectra (215–1100 nm) were run on a Maya2000Pro concave grating spectrometer using transmission dip probes with optical paths of 2 and 10 mm, respectively. Electrochemical measurements were carried out in THF containing 0.1 M Bu_4NPF_6 . Cyclic voltammetry (CV) and rotating disk voltammetry (RDV) were used in a three-electrode arrangement under an argon atmosphere (see SI). The working electrode was glassy carbon disc (2 mm in diameter) for CV and RDV experiments. Saturated calomel electrode (SCE) was used as the reference electrode and separated by a bridge filled with the supporting electrolyte. Platinum plate was used as an auxiliary electrode. All potentials are given vs SCE. Voltammetric measurements were performed using a potentiostat PGSTAT 128 N (AUTOLAB, Metrohm Autolab B.V., Utrecht, The Netherlands) operated via NOVA 1.11 software. Elemental analyses were performed on an LECO-CHNS-932 analyzer.

Preparation of a Mixture of $[2\text{-(tBuNHCH}_2\text{)}_2\text{-6-(tBuN=CH)-C}_6\text{H}_3]\text{As}$ (1-As-tBu**) and $[2,6\text{-(tBuN=CH)}_2\text{C}_6\text{H}_3]\text{As}$ (**2-As-tBu**).** A sample 2.82 mL of $\text{K}[\text{sBu}_3\text{BH}]$ solution in thf (1 M, 2.82 mmol) was added to a solution of 551 mg of $[2,6\text{-(tBuN=CH)}_2\text{C}_6\text{H}_3]\text{AsCl}_2$ (**2-As-tBu**) Cl_2 (1.42 mmol) in thf (50 mL) at -80°C . The temperature of the reaction mixture was maintained for 1 h, then warmed to r.t., and evaporated. The residue was extracted with pentane (60 mL), giving a red extract that was concentrated and stored at -30°C giving a mixture of both **1-As-tBu** and **2-As-tBu** (in ca. 1:0.2 mutual ratio as

determined by ^1H NMR spectroscopy). The NMR data for **2-As-tBu** are the same as reported elsewhere.^{10b} NMR data for **1-As-tBu**: ^1H NMR (500 MHz, C_6D_6) δ (ppm): 1.08 [9H, s, *t*Bu-*H*]; 1.14 [1H, t, $^3J(^1\text{H}, ^1\text{H}) = 8.3$ Hz, NH]; 1.51 [9H, s, *t*Bu-*H*]; 3.92 [2H, d, $^3J(^1\text{H}, ^1\text{H}) = 8.2$ Hz, CH_2]; 6.90 [1H, dd, Ar-*H*]; 7.19 [1H, m, Ar-*H*]; 7.89 [1H, d, $^3J(^1\text{H}, ^1\text{H}) = 8.2$ Hz, Ar-*H*]; 8.44 [1H, s, $\text{CH}=\text{N}$]. $^{13}\text{C}\{^1\text{H}\}$ NMR (125.76 MHz, C_6D_6) δ (ppm): 29.2 [*t*Bu- CH_3]; 33.3 [*t*Bu- CH_3]; 48.2 [CH_2]; 51.4 [*t*Bu-*C*]; 59.1 [*t*Bu-*C*]; 117.6 [Ar-*C*]; 121.8 [Ar-*C*]; 125.9 [Ar-*C*]; 133.6 [Ar-*C*]; 137.4 [Ar-*C*]; 141.8 [Ar-*C*]; 165.6 [$\text{CH}=\text{N}$].

Synthesis of [2,6-(AdN=CH) $_2$ C $_6$ H $_3$]As (2-As-Ad). A solution of 807 mg of [2,6-(AdN=CH) $_2$ C $_6$ H $_3$]AsCl $_2$ (**2-As-Ad**)Cl $_2$ (1.48 mmol) in thf (50 mL) was added to freshly prepared KC $_8$ (140 mg K, 3.58 mmol; 312 mg C, 26 mmol) and stirred overnight at r.t. The reaction was evaporated and extracted by pentane (60 mL). The deep red extract was concentrated and stored at -30 °C giving **2-As-Ad** as a red powder that was collected by decantation and dried in vacuo. Yield: 365 mg, (52%), mp 260 °C (dec). Anal. calcd for C $_{28}$ H $_{35}$ AsN $_2$ (MW 474.52): C, 70.9; H, 7.4; N, 5.9%. Found: C, 70.6; H, 7.7; N, 6.2%. ^1H NMR (500 MHz, C_6D_6) δ (ppm): 1.58 [12H, s(br), Ad- CH_2]; 2.00 [6H, s(br), Ad-*CH*]; 2.14 [12H, s(br), Ad- CH_2]; 7.25 [1H, t, $^3J(^1\text{H}, ^1\text{H}) = 7.5$ Hz, Ar-*H*]; 7.72 [2H, d, $^3J(^1\text{H}, ^1\text{H}) = 7.5$ Hz, Ar-*H*]; 8.64 [2H, s, $\text{CH}=\text{N}$]. $^{13}\text{C}\{^1\text{H}\}$ NMR (125.76 MHz, C_6D_6) δ (ppm): 30.7 [Ad-*CH*]; 37.0 [Ad- CH_2]; 46.1 [Ad- CH_2]; 59.3 [Ad-*C*]; 120.5 [Ar-*C*]; 128.8 [Ar-*C*]; 134.4 [Ar-*C*]; 146.1 [Ar-*C*]; 161.2 [$\text{CH}=\text{N}$].

Preparation of a Mixture of [2-(AdNHCH $_2$)-6-(AdN=CH)-C $_6$ H $_3$]As (1-As-Ad) and [2,6-(AdN=CH) $_2$ C $_6$ H $_3$]As (2-As-Ad). A sample 2.72 mL of K[sBu $_3$ BH] solution in thf (1 M, 2.72 mmol) was added to a solution of 740 mg of [2,6-(AdN=CH) $_2$ C $_6$ H $_3$]AsCl $_2$ (**2-As-Ad**)Cl $_2$ (1.36 mmol) in thf (50 mL) at -80 °C. The temperature of the reaction mixture was maintained for 1 h and then slowly warmed to r.t. and stirred overnight. The reaction was evaporated and extracted with pentane (60 mL). The deep red extract was concentrated and stored at -30 °C giving a mixture of both **1-As-Ad** and **2-As-Ad** (in ca. 1:0.8 mutual ratio as determined by ^1H NMR spectroscopy). The NMR data for **2-As-Ad** are the same as mentioned above. NMR data for **1-As-Ad**: ^1H NMR (500 MHz, C_6D_6) δ (ppm): 1.18 [1H, t, $^3J(^1\text{H}, ^1\text{H}) = 8.2$ Hz, NH]; 1.52 [12H, m, Ad- CH_2]; 1.72 [6H, d, $^3J(^1\text{H}, ^1\text{H}) = 2.8$ Hz, Ad- CH_2]; 1.94 [6H, s, Ad-*CH*]; 2.23 [6H, d, $^3J(^1\text{H}, ^1\text{H}) = 3.0$ Hz, Ad- CH_2]; 4.01 [2H, d, $^3J(^1\text{H}, ^1\text{H}) = 8.2$ Hz, CH_2]; 6.96 [1H, dd, Ar-*H*]; 7.24 [1H, m, Ar-*H*]; 7.96 [1H, d, $^3J(^1\text{H}, ^1\text{H}) = 7.9$ Hz, Ar-*H*]; 8.57 [1H, s, $\text{CH}=\text{N}$]. $^{13}\text{C}\{^1\text{H}\}$ NMR (125.76 MHz, C_6D_6) δ (ppm): 30.4 [Ad-*CH*]; 30.9 [Ad-*CH*]; 36.9 [Ad- CH_2]; 37.4 [Ad- CH_2]; 43.0 [Ad- CH_2]; 46.4 [CH_2]; 47.2 [Ad- CH_2]; 51.8 [Ad-*C*]; 59.7 [Ad-*C*]; 117.6 [Ar-*C*]; 121.8 [Ar-*C*]; 126.0 [Ar-*C*]; 133.4 [Ar-*C*]; 135.9 [$\text{CH}=\text{N}$]; 142.2 [Ar-*C*]; 165.2 [Ar-*C*].

Preparation of a Mixture of [2-(*t*BuNHCH $_2$)-6-(*t*BuN=CH)-C $_6$ H $_3$]Sb (1-Sb-*t*Bu) and [2,6-(*t*BuN=CH) $_2$ C $_6$ H $_3$]Sb (2-Sb-*t*Bu). A sample 5.78 mL of K[sBu $_3$ BH] solution in thf (1 M, 5.78 mmol) was added to a solution of 1.26 g of [2,6-(*t*BuN=CH) $_2$ C $_6$ H $_3$]SbCl $_2$ (**2-Sb-*t*Bu**)Cl $_2$ (2.89 mmol) in thf (50 mL) at -80 °C. The temperature of the reaction mixture was maintained for 1 h and warmed to r.t. and evaporated. The residue was extracted with pentane (60 mL) giving a red extract that was evaporated, and the mixture was analyzed by NMR spectroscopy in C_6D_6 showing the presence of both **1-Sb-*t*Bu** and **2-Sb-*t*Bu** (in ca. 0.24:1 mutual ratio). The NMR data for **2-Sb-*t*Bu** are the same as reported elsewhere.^{10a} NMR data for **1-Sb-*t*Bu**: ^1H NMR (500 MHz, C_6D_6) δ (ppm): signals of *t*Bu and NH groups are overlapped by signals of the present sBu $_3$ B (see Figures S25 and 26), 3.75 [2H, d, $^3J(^1\text{H}, ^1\text{H}) = 8.4$ Hz, CH_2]; 6.90 [1H, d, $^3J(^1\text{H}, ^1\text{H}) = 6.9$ Hz, Ar-*H*]; 7.21 [1H, t, $^3J(^1\text{H}, ^1\text{H}) = 7.3$ Hz, Ar-*H*]; 7.93 [1H, d, $^3J(^1\text{H}, ^1\text{H}) = 7.9$ Hz, Ar-*H*]; 8.90 [1H, s, $\text{CH}=\text{N}$ signal overlapped with the major product **2-Sb-*t*Bu**]. $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, C_6D_6) δ (ppm): 29.1 [*t*Bu- CH_3]; 33.7 [*t*Bu- CH_3]; 48.5 [CH_2]; 52.2 [*t*Bu-*C*]; 59.6 [*t*Bu-*C*]; 117.2 [Ar-*C*]; 122.0 [Ar-*C*]; 129.7 [Ar-*C*]; 144.8 [Ar-*C*]; 147.9 [Ar-*C*]; 171.9 [$\text{CH}=\text{N}$].

Synthesis of [2,6-(AdN=CH) $_2$ C $_6$ H $_3$]Sb (2-Sb-Ad). A solution of 1.46 g of [2,6-(AdN=CH) $_2$ C $_6$ H $_3$]SbCl $_2$ (**2-Sb-Ad**)Cl $_2$ (2.47 mmol) in thf (50 mL) was added to freshly prepared KC $_8$ (210 mg K, 5.37 mmol; 520 mg C, 43 mmol) and stirred overnight at r.t. The reaction was evaporated and extracted by benzene (60 mL). The deep blue extract was concentrated and stored at 4 °C giving **2-Sb-Ad** as deep blue crystals that were collected by decantation and dried in vacuo. Yield: 480 mg, (37%), mp 307 °C (dec). Anal. calcd for C $_{28}$ H $_{35}$ SbN $_2$ (MW 521.36): C, 64.5; H, 6.8; N, 5.4%. Found: C, 64.6; H, 7.1; N, 5.6%. ^1H NMR (400 MHz, C_6D_6) δ (ppm): 1.58 [12H, s(br), Ad- CH_2]; 2.00 [6H, s(br), Ad-*CH*]; 2.13 [12H, s(br), Ad- CH_2]; 7.39 [1H, t, $^3J(^1\text{H}, ^1\text{H}) = 7.4$ Hz, Ar-*H*]; 7.87 [2H, d, $^3J(^1\text{H}, ^1\text{H}) = 7.4$ Hz, Ar-*H*]; 9.02 [2H, s, $\text{CH}=\text{N}$]. $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, C_6D_6) δ (ppm): 30.7 [Ad-*CH*]; 37.0 [Ad- CH_2]; 47.1 [Ad- CH_2]; 60.0 [Ad-*C*]; 120.5 [Ar-*C*]; 131.7 [Ar-*C*]; 137.4 [Ar-*C*]; 152.2 [$\text{CH}=\text{N}$]; 167.4 [Ar-*C*].

Preparation of a Mixture of [2-(AdNHCH $_2$)-6-(AdN=CH)-C $_6$ H $_3$]Sb (1-Sb-Ad) and [2,6-(AdN=CH) $_2$ C $_6$ H $_3$]Sb (2-Sb-Ad). A sample 1.28 mL of K[sBu $_3$ BH] solution in thf (1 M, 1.28 mmol) was added to a solution of 340 mg of [2,6-(AdN=CH) $_2$ C $_6$ H $_3$]SbCl $_2$ (**2-Sb-Ad**)Cl $_2$ (0.64 mmol) in thf (50 mL) at -80 °C. The temperature of the reaction mixture was maintained for 1 h and then slowly warmed to r.t. and stirred overnight. The reaction was evaporated and extracted by pentane (60 mL). The deep blue extract was concentrated and stored at -30 °C giving a mixture of both **1-Sb-Ad** and **2-Sb-Ad** (in ca. 0.5:1 mutual ratio as determined by ^1H NMR spectroscopy). The NMR data for **2-Sb-Ad** are the same as mentioned above. NMR data for **1-Sb-Ad**: ^1H NMR (500 MHz, C_6D_6) δ (ppm): 1.48 [6H, m, Ad- CH_2]; 1.57 [6H, m, Ad- CH_2]; 1.61 [1H, overlapped, NH based on H,H-COSY]; 1.62 [6H, m, Ad- CH_2]; 1.89 [3H, s(br), Ad-*CH*]; 1.98 [3H, s(br), Ad-*CH*]; 2.23 [6H, d, Ad- CH_2]; 3.86 [2H, d, $^3J(^1\text{H}, ^1\text{H}) = 8.1$ Hz, CH_2]; 6.83 [1H, d, $^3J(^1\text{H}, ^1\text{H}) = 6.9$ Hz, Ar-*H*]; 7.30 [1H, dd, Ar-*H*]; 8.04 [1H, d, $^3J(^1\text{H}, ^1\text{H}) = 7.9$ Hz, Ar-*H*]; 9.07 [1H, s, $\text{CH}=\text{N}$]. $^{13}\text{C}\{^1\text{H}\}$ NMR (125.76 MHz, C_6D_6) δ (ppm): 30.3 [Ad-*CH*]; 31.0 [Ad-*CH*]; 37.0 [Ad- CH_2]; 37.2 [Ad- CH_2]; 42.6 [Ad- CH_2]; 46.4 [CH_2]; 47.8 [Ad- CH_2]; 52.5 [Ad-*C*]; 60.1 [Ad-*C*]; 117.1 [Ar-*C*]; 122.0 [Ar-*C*]; 129.8 [Ar-*C*]; 137.2 [Ar-*C*]; 145.2 [Ar-*C*]; 146.2 [$\text{CH}=\text{N}$]; 171.0 [Ar-*C*].

Reaction of [2,6-(*t*BuN=CH) $_2$ C $_6$ H $_3$]BiCl $_2$ (2-Bi-*t*Bu)Cl $_2$ with K-Selectride. A sample 2.2 mL of K[sBu $_3$ BH] solution in thf (1 M, 2.2 mmol) was added to a suspension of 560 mg of [2,6-(*t*BuN=CH) $_2$ C $_6$ H $_3$]BiCl $_2$ (**2-Bi-*t*Bu**)Cl $_2$ (1.07 mmol) in thf (50 mL) at -80 °C. The temperature of the reaction mixture was maintained for 1 h and warmed to r.t. and evaporated. The residue was extracted with pentane (60 mL) giving a blue extract that was evaporated and the mixture was analyzed by NMR spectroscopy showing the presence of **2-Bi-*t*Bu** only. The NMR data for **2-Bi-*t*Bu** are the same as reported elsewhere.⁹

Synthesis of [2,6-(DippN=CH) $_2$ C $_6$ H $_3$]As (2-As-Dipp). A solution of 1.23 g of [2,6-(DippN=CH) $_2$ C $_6$ H $_3$]AsCl $_2$ (**2-As-Dipp**)Cl $_2$ (1.78 mmol) in thf (30 mL) was added to freshly prepared KC $_8$ (169 mg K, 4.32 mmol; 376 mg C, 31.3 mmol) and stirred overnight at r.t. The reaction was evaporated and extracted by pentane (60 mL). The deep red extract was stored at -30 °C giving **2-As-Dipp** as red crystals that were collected by decantation and dried in vacuo. Yield: 662 mg (71%), mp 217–222 °C. Anal. calcd for C $_{32}$ H $_{39}$ AsN $_2$ (MW 526.59): C, 73.0; H, 7.5; N, 5.3%. Found: C, 72.9; H, 7.3; N, 5.6%. ^1H NMR (500 MHz, C_6D_6) δ (ppm): 1.06 [24H, d(br), *i*Pr- CH_3]; 2.90 [4H, h, $^3J(^1\text{H}, ^1\text{H}) = 6.9$ Hz, *i*Pr-*CH*]; 7.00 [1H, t, $^3J(^1\text{H}, ^1\text{H}) = 7.5$ Hz, Ar-*H*]; 7.12 [4H, d, $^3J(^1\text{H}, ^1\text{H}) = 8.8$ Hz, Ar-*H*]; 7.21 [2H, m, Ar-*H*]; 7.52 [2H, d, $^3J(^1\text{H}, ^1\text{H}) = 7.5$ Hz, Ar-*H*]; 8.29 [2H, s, $\text{CH}=\text{N}$]. $^{13}\text{C}\{^1\text{H}\}$ NMR (125.76 MHz, C_6D_6) δ (ppm): 25.0 [*i*Pr- CH_3]; 28.8 [*i*Pr-*CH*]; 121.6 [Ar-*C*]; 123.8 [Dipp-*C*]; 126.8 [Ar-*C*]; 127.1 [Ar-*C*]; 130.8 [Ar-*C*]; 133.8 [Ar-*C*]; 141.9 [Ar-*C*]; 145.3 [Ar-*C*]; 153.1 [$\text{CH}=\text{N}$]; 164.9 [Ar-*C*].

Synthesis of [2-(DippNHCH $_2$)-6-(DippN=CH) $_2$ C $_6$ H $_3$]As (1-As-Dipp). A sample 4.1 mL of K[sBu $_3$ BH] solution in thf (1 M, 4.1 mmol) was added to a solution of 1.41 g of [2,6-(DippN=CH) $_2$ C $_6$ H $_3$]AsCl $_2$ (**2-Dipp-Ad**)Cl $_2$ (2.05 mmol) in thf (50 mL) at -80 °C. The temperature of the reaction mixture was maintained for

1 h and then slowly warmed to r.t. The reaction was evaporated and extracted by pentane (60 mL). The orange-red extract was concentrated and stored at -30°C giving **1-As-Dipp** in the form of orange crystals that were collected by decantation and dried in vacuo. Yield: 921 mg, (85%), mp 175°C . Anal. calcd for $\text{C}_{32}\text{H}_{41}\text{AsN}_2$ (MW 528.60): C, 72.7; H, 7.8; N, 5.3%. Found: C, 72.9; H, 7.3; N, 5.6%. ^1H NMR (500 MHz, C_6D_6) δ (ppm): 1.11 [6H, d, $^3J(\text{H},\text{H}) = 6.9$ Hz, $i\text{Pr-CH}_3$]; 1.21 [12H, d, $^3J(\text{H},\text{H}) = 6.8$ Hz, $i\text{Pr-CH}_3$]; 1.27 [6H, d, $^3J(\text{H},\text{H}) = 6.8$ Hz, $i\text{Pr-CH}_3$]; 2.76 [2H, h, $^3J(\text{H},\text{H}) = 6.9$ Hz, $i\text{Pr-CH}$]; 3.55 [2H, h, $^3J(\text{H},\text{H}) = 6.8$ Hz, $i\text{Pr-CH}$]; 3.96 [1H, t, $^3J(\text{H},\text{H}) = 10.2$ Hz, NH]; 4.53 [2H, d, $^3J(\text{H},\text{H}) = 10.2$ Hz, CH_2]; 6.90 [1H, d, $^3J(\text{H},\text{H}) = 6.7$ Hz, Ar-H]; 7.11 [1H, dd, Ar-H]; 7.16–7.21 [5H, m, Ar-H]; 7.29 [1H, t, $^3J(\text{H},\text{H}) = 7.6$ Hz, Ar-H]; 7.86 [1H, d, $^3J(\text{H},\text{H}) = 8.2$ Hz, Ar-H]; 8.19 [1H, s, $\text{CH}=\text{N}$]. $^{13}\text{C}\{^1\text{H}\}$ NMR (125.76 MHz, C_6D_6) δ (ppm): 24.9 [iPr-CH₃]; 25.4 [iPr-CH₃]; 26.0 [iPr-CH₃]; 28.6 [iPr-CH]; 28.7 [iPr-CH]; 58.0 [CH₂]; 119.3 [Ar-C]; 122.8 [Ar-C]; 123.9 [Ar-C]; 124.6 [Ar-C]; 125.2 [Ar-C]; 126.8 [Ar-C]; 129.0 [Ar-C]; 133.5 [Ar-C]; 139.6 [Ar-C]; 141.7 [Ar-C]; 142.3 [CH=N]; 142.9 [Dipp-C]; 143.0 [Dipp-C]; 145.3 [Dipp-C]; 169.1 [Ar-C]. IR (cm^{-1}): 3390w (ν_{NH}). Raman (cm^{-1}): 3390w (ν_{NH}). Deuterated isotopologue of **1-As-Dipp**: IR (cm^{-1}): 3390w (ν_{NH}), 2508w (ν_{ND}), 2113w (ν_{CD}). Raman (cm^{-1}): 3390w (ν_{NH}), 2512 (ν_{ND}), 2114w (ν_{CD}).

Synthesis of [2,6-(DippN=CH)₂C₆H₃]Bi (2-Bi-Dipp). A solution of 1.06 g of [2,6-(DippN=CH)₂C₆H₃]BiCl₂ (**2-Bi-Dipp**)Cl₂ (1.45 mmol) in thf (30 mL) was added to freshly prepared KC_8 (124 mg K, 3.2 mmol; 305 mg C, 25.4 mmol) and stirred overnight at r.t. The reaction was evaporated and extracted by hexane (60 mL). The deep green extract was concentrated and stored at 4°C giving **2-Bi-Dipp** as dark green crystals that were collected by decantation and dried in vacuo. Yield: 354 mg, (37%), mp 172°C (dec). Anal. calcd for $\text{C}_{32}\text{H}_{39}\text{BiN}_2$ (MW 660.66): C, 58.2; H, 6.0; N, 4.2%. Found: C, 58.5; H, 6.3; N, 4.5%. ^1H NMR (400 MHz, C_6D_6) δ (ppm): 1.06 [12H, d, $^3J(\text{H},\text{H}) = 6.9$ Hz, $i\text{Pr-CH}_3$]; 1.17 [12H, d, $^3J(\text{H},\text{H}) = 6.9$ Hz, $i\text{Pr-CH}_3$]; 3.08 [4H, h, $^3J(\text{H},\text{H}) = 6.9$ Hz, $i\text{Pr-CH}$]; 6.94 [1H, t, $^3J(\text{H},\text{H}) = 7.5$ Hz, Ar-H]; 7.11–7.17 [6H, m, Ar-H]; 7.85 [2H, d, $^3J(\text{H},\text{H}) = 7.5$ Hz, Ar-H]; 9.37 [2H, s, $\text{CH}=\text{N}$]. $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, C_6D_6) δ (ppm): 24.9 [iPr-CH₃]; 25.3 [iPr-CH₃]; 29.4 [iPr-CH]; 123.7 [Ar-C]; 123.9 [Ar-C]; 126.7 [Ar-C]; 136.4 [Ar-C]; 141.0 [Ar-C]; 145.6 [Ar-C]; 147.5 [Ar-C]; 171.2 [CH=N]; 211.9 [Ar-C].

Preparation of a Mixture of [2-(DippNHCH₂)-6-(DippN=CH)₂C₆H₃]Bi (1-Bi-Dipp) and [2,6-(DippN=CH)₂C₆H₃]Bi (2-Bi-Dipp). A sample 3.22 mL of $\text{K}[\text{sBu}_3\text{BH}]$ solution in thf (1 M, 3.22 mmol) was added to a solution of 1.176 g of [2,6-(DippN=CH)₂C₆H₃]BiCl₂ (**2-Bi-Dipp**)Cl₂ (1.61 mmol) in thf (50 mL) at -90°C . The temperature of the reaction mixture was maintained for 1 h and then slowly warmed to r.t. Then, the reaction was evaporated and extracted by hexane (60 mL). The deep blue extract was concentrated and stored at 4°C giving a mixture of both **1-Bi-Dipp** and **2-Bi-Dipp** (in ca. 1:0.9 mutual ratio as determined by ^1H NMR spectroscopy). The NMR data for **2-Bi-Dipp** are the same as mentioned above. NMR data for **1-Bi-Dipp**: ^1H NMR (500 MHz, C_6D_6) δ (ppm): 1.10 [12H, d, $^3J(\text{H},\text{H}) = 6.9$ Hz, $i\text{Pr-CH}_3$]; 1.14 [6H, d, $^3J(\text{H},\text{H}) = 6.9$ Hz, $i\text{Pr-CH}_3$]; 1.27 [6H, d, $^3J(\text{H},\text{H}) = 6.9$ Hz, $i\text{Pr-CH}_3$]; 3.12 [2H, h, $^3J(\text{H},\text{H}) = 6.9$ Hz, $i\text{Pr-CH}$]; 3.37 [2H, h, $^3J(\text{H},\text{H}) = 6.9$ Hz, $i\text{Pr-CH}$]; 4.42 [2H, d, $^3J(\text{H},\text{H}) = 8.2$ Hz, CH_2]; 4.80 [1H, t, $^3J(\text{H},\text{H}) = 10.2$ Hz, NH]; 6.27 [1H, dd, Ar-H]; 6.88 [1H, dd, Ar-H]; 7.05 [3H, m, Ar-H]; 7.18 [3H, m, Ar-H overlapped with signals of **2-Bi-Dipp**]; 7.95 [1H, d, $^3J(\text{H},\text{H}) = 7.6$ Hz, Ar-H]; 9.23 [1H, s, $\text{CH}=\text{N}$]. $^{13}\text{C}\{^1\text{H}\}$ NMR (125.76 MHz, C_6D_6) δ (ppm): 24.5 [iPr-CH₃]; 25.6 [iPr-CH₃]; 25.7 [iPr-CH₃]; 29.8 [iPr-CH]; 30.1 [iPr-CH]; 61.2 [CH₂]; 123.2 [Ar-C]; 123.8 [Ar-C]; 124.3 [Ar-C]; 125.1 [Ar-C]; 125.5 [Ar-C]; 127.4 [Ar-C]; 137.5 [Ar-C]; 140.9 [Ar-C]; 142.5 [Ar-C]; 142.7 [Ar-C]; 143.7 [Ar-C]; 146.1 [Ar-C]; 148.3 [Ar-C]; 175.0 [CH=N]; 207.9 [Ar-C].

Synthesis of [2-(DippN-CH₂)-6-(DippN=CH)₂C₆H₃]AsOH (1'-As-Dipp)OH. A solution of 557 mg of **1-As-Dipp** (1.05 mmol) dissolved in benzene (10 mL) was stirred and air was bubbled through the solution for 2 h. During this period, an intensive orange-

red color turned to pale yellow. The reaction mixture was evaporated producing the product (**1'-As-Dipp**)OH as a fine yellowish powder in a quantitative yield. mp $222\text{--}224^{\circ}\text{C}$ (becomes red). Anal. calcd for $\text{C}_{32}\text{H}_{41}\text{AsN}_2\text{O}$ (MW 544.60): C, 70.6; H, 7.6; N, 5.1%. Found: C, 70.7; H, 7.8; N, 5.4%. ^1H NMR (400 MHz, C_6D_6) δ (ppm): 1.10 [3H, d, $^3J(\text{H},\text{H}) = 6.9$ Hz, $i\text{Pr-CH}_3$]; 1.16 [6H, d, $^3J(\text{H},\text{H}) = 6.9$ Hz, $i\text{Pr-CH}_3$]; 1.20 [6H, d, $^3J(\text{H},\text{H}) = 6.8$ Hz, $i\text{Pr-CH}_3$]; 1.24 [3H, d, $^3J(\text{H},\text{H}) = 6.8$ Hz, $i\text{Pr-CH}_3$]; 1.33 [6H, m, $i\text{Pr-CH}_3$]; 1.95 [1H, s(br), OH]; 3.10 [1H, h, $^3J(\text{H},\text{H}) = 6.9$ Hz, $i\text{Pr-CH}$]; 3.21 [2H, h, $^3J(\text{H},\text{H}) = 6.8$ Hz, $i\text{Pr-CH}$]; 3.99 [1H, h, $^3J(\text{H},\text{H}) = 6.9$ Hz, $i\text{Pr-CH}$]; 4.40 [1H, d, $^3J(\text{H},\text{H}) = 16.3$ Hz, CH_2]; 5.10 [1H, d, $^3J(\text{H},\text{H}) = 16.3$ Hz, CH_2]; 7.04–7.24 [9H, Ar-H]; 8.07 [1H, s, $\text{CH}=\text{N}$]. $^{13}\text{C}\{^1\text{H}\}$ NMR (125.76 MHz, C_6D_6) δ (ppm): 24.0 [iPr-CH₃]; 24.4 [iPr-CH₃]; 25.1 [iPr-CH₃]; 25.7 [iPr-CH₃]; 25.9 [iPr-CH₃]; 26.2 [iPr-CH₃]; 28.6 [iPr-CH]; 28.7 [iPr-CH]; 29.0 [iPr-CH]; 64.5 [CH₂]; 123.8 [Ar-C]; 124.5 [Ar-C]; 124.6 [Ar-C]; 125.4 [Ar-C]; 126.5 [Ar-C]; 127.5 [Ar-C]; 130.1 [Ar-C]; 130.6 [Ar-C]; 137.6 [Ar-C]; 138.4 [Ar-C]; 142.6 [Ar-C]; 147.1 [Ar-C]; 148.5 [Ar-C]; 149.2 [Ar-C]; 149.9 [Ar-C]; 150.7 [Ar-C]; 162.5 [CH=N]. IR (cm^{-1}): 3602m (ν_{OH}). Raman (cm^{-1}): 3598w (ν_{OH}).

Synthesis of [2-(DippN-CH₂)-6-(DippN=CH)₂C₆H₃]SbOH (1'-Sb-Dipp)OH. A solution of 557 mg of **1-Sb-Dipp** (1.05 mmol) dissolved in benzene (10 mL) was stirred and air was bubbled through the solution for 3 min. During this period, an original intensive violet color turned to pale yellow. The reaction mixture was evaporated producing the product (**1'-Sb-Dipp**)OH as a fine yellowish powder in a quantitative yield. ^1H NMR (500 MHz, C_6D_6) δ (ppm): 1.17 [18H, m, $i\text{Pr-CH}_3$]; 1.27 [1H, s(br), OH]; 1.37 [6H, m, $i\text{Pr-CH}_3$]; 3.16 [2H, s(br), $i\text{Pr-CH}$]; 3.22 [1H, h, $^3J(\text{H},\text{H}) = 7.0$ Hz, $i\text{Pr-CH}$]; 4.00 [1H, h, $^3J(\text{H},\text{H}) = 7.0$ Hz, $i\text{Pr-CH}$]; 4.56 [1H, d, $^3J(\text{H},\text{H}) = 17.2$ Hz, CH_2]; 5.27 [1H, d, $^3J(\text{H},\text{H}) = 17.2$ Hz, CH_2]; 7.04 [2H, m, Ar-H]; 7.15 [5H, m, Ar-H]; 7.25 [2H, m, Ar-H]; 8.00 [1H, s, $\text{CH}=\text{N}$]. $^{13}\text{C}\{^1\text{H}\}$ NMR (125.76 MHz, C_6D_6) δ (ppm): 24.3 [iPr-CH₃]; 24.9 [iPr-CH₃]; 25.2 [iPr-CH₃]; 25.8 [iPr-CH₃]; 26.1 [iPr-CH₃]; 26.7 [iPr-CH₃]; 28.4 [iPr-CH]; 28.6 [iPr-CH]; 28.8 [iPr-CH]; 67.2 [CH₂]; 124.0 [Ar-C]; 124.3 [Ar-C]; 124.5 [Ar-C]; 125.9 [Ar-C]; 126.5 [Ar-C]; 128.2 [Ar-C]; 130.1 [Ar-C]; 130.3 [Ar-C]; 139.2 [Ar-C]; 139.3 [Ar-C]; 145.8 [Ar-C]; 147.7 [Ar-C]; 147.9 [Ar-C]; 150.1 [Ar-C]; 151.8 [Ar-C]; 154.2 [Ar-C]; 163.8 [CH=N]. IR (cm^{-1}): 3602m (ν_{OH}). Raman (cm^{-1}): 3598w (ν_{OH}).

Reaction of (1'-As-Dipp)OH with Molecular Sieves. A sample of 150 mg of (**1'-As-Dipp**)OH (0.28 mmol) was dissolved in dry C_6D_6 and transferred to activated molecular sieves (3 Å) in Young-valved Schlenk tube. The original pale-yellow solution starts to change the color to orange immediately and after 24 h, a dark violet solution was obtained (Figure S48). This solution was transferred to an NMR tube and its analysis revealed the presence of (**2-As-Dipp**) as the major product. The NMR data were consistent with those mentioned above.

Synthesis of [2-(DippN-CH₂)-6-(DippN=CH)₂C₆H₃]Sb₂O (1'-Sb-Dipp)₂O. A solution of 332 mg of (**1'-Sb-Dipp**)OH (0.56 mmol) dissolved in benzene (10 mL) was treated with activated molecular sieves (3 Å) for 1 week. The reaction mixture was filtered and the yellow filtrate was evaporated to give the product (**1'-Sb-Dipp**)₂O based on NMR analysis. It can be recrystallized from benzene to give single crystals of (**1'-Sb-Dipp**)₂O. Yield: 256 mg, (78%), mp 220°C (dec). Anal. calcd for $\text{C}_{64}\text{H}_{80}\text{N}_4\text{OsB}_2$ (MW 1164.89): C, 66.0; H, 6.9; N, 4.8%. Found: C, 66.2; H, 7.3; N, 4.6%. ^1H NMR (400 MHz, C_6D_6) δ (ppm): 0.59 [3H, d, $^3J(\text{H},\text{H}) = 6.5$ Hz, $i\text{Pr-CH}_3$]; 0.80 [12H, s(vbr), $i\text{Pr-CH}_3$]; 1.00 [3H, d, $^3J(\text{H},\text{H}) = 6.9$ Hz, $i\text{Pr-CH}_3$]; 1.06 [3H, d, $^3J(\text{H},\text{H}) = 6.8$ Hz, $i\text{Pr-CH}_3$]; 1.18 [3H, d, $^3J(\text{H},\text{H}) = 6.8$ Hz, $i\text{Pr-CH}_3$]; 2.71 [1H, h, $^3J(\text{H},\text{H}) = 6.9$ Hz, $i\text{Pr-CH}$]; 2.71 [2H, s(vbr), $i\text{Pr-CH}$]; 3.93 [1H, h, $^3J(\text{H},\text{H}) = 6.9$ Hz, $i\text{Pr-CH}$]; 4.37 [1H, d, $^3J(\text{H},\text{H}) = 17.1$ Hz, CH_2]; 5.62 [1H, d, $^3J(\text{H},\text{H}) = 17.1$ Hz, CH_2]; 7.03 [4H, m, Ar-H]; 7.09 [1H, m, Ar-H]; 7.15 [2H, m, Ar-H]; 7.21 [1H, t, $^3J(\text{H},\text{H}) = 7.5$ Hz, Ar-H]; 7.30 [1H, d, $^3J(\text{H},\text{H}) = 7.6$ Hz, Ar-H]; 7.96 [1H, s, $\text{CH}=\text{N}$]. $^{13}\text{C}\{^1\text{H}\}$ NMR (125.76 MHz, C_6D_6) δ (ppm): 24.1 [iPr-CH₃]; 24.2 [iPr-CH₃]; 25.2 [iPr-CH₃]; 25.6 [iPr-CH₃]; 26.3 [iPr-CH₃]; 28.5 [iPr-CH]; 29.0 [iPr-CH, overlap of two signals]; 68.8 [CH₂]; 123.4 [Ar-C]; 124.4 [Ar-C]; 125.4 [Ar-

C]; 126.0 [Ar-C]; 127.4 [Ar-C]; 128.9 [Ar-C]; 129.4 [Ar-C]; 130.9 [Ar-C]; 139.5 [Ar-C]; 148.2 [Ar-C]; 148.8 [Ar-C]; 149.4 [Ar-C]; 150.0 [Ar-C]; 155.3 [Ar-C]; 155.5 [Ar-C]; 165.7 [CH=N].

Synthesis of [2-(DippNHCH₂)-6-(DippN=CH)C₆H₃]SbSe (1-Sb-Dipp)Se. To a sample of 384 mg of (1-Sb-Dipp) (0.67 mmol) dissolved in benzene (15 mL), a solid sample of 79 mg of Se (1 mmol) was added. The reaction mixture was stirred for 30 min at r.t., then it was concentrated and layered with pentane. Storage of this brownish solution at 4 °C produced single crystals of (1-Sb-Dipp)Se that were collected by decantation and dried. Yield: 288 mg, (66%), mp 117 °C (dec). Anal. calcd for C₃₂H₄₁N₂SbSe (MW 654.43): C, 58.7; H, 6.3; N, 4.3%. Found: C, 59.0; H, 6.4; N, 4.6%. ¹H NMR (500 MHz, C₆D₆) δ (ppm): 1.04 [9H, s(br), iPr-CH₃]; 1.16 [12H, s(br), iPr-CH₃]; 1.49 [3H, s(br), iPr-CH₃]; 3.02 [1H, s(br), iPr-CH]; 3.27 [2H, s(br), iPr-CH]; 3.75 [1H, s(br), iPr-CH]; 3.88 [1H, s(br), CH₂]; 4.59 [1H, s(br), CH₂]; 6.11 [1H, t, ³J(¹H,¹H) = 8.0 Hz, NH]; 6.81 [1H, d, ³J(¹H,¹H) = 7.4 Hz, Ar-H]; 7.00–7.13 [7H, m, Ar-H]; 7.19 [1H, d, ³J(¹H,¹H) = 7.0 Hz, Ar-H]; 8.02 [1H, s, CH=N]. ¹³C{¹H} NMR (125.76 MHz, C₆D₆) δ (ppm): 24.7 [iPr-CH₃]; 25.2 [iPr-CH₃]; 29.1 [iPr-CH]; 29.4 [iPr-CH]; 57.8 [CH₂]; 123.8 [Ar-C]; 125.3 [Ar-C]; 126.5 [Ar-C]; 128.0 [Ar-C]; 128.9 [Ar-C]; 129.2 [Ar-C]; 129.3 [Ar-C]; 132.2 [Ar-C]; 140.3 [Ar-C]; 140.5 [Ar-C]; 140.8 [Ar-C]; 142.3 [Ar-C]; 142.7 [Ar-C]; 142.9 [Ar-C]; 146.0 [Ar-C]; 164.3 [Ar-C]; 169.1 [CH=N]. ⁷⁷Se{¹H} NMR (125.76 MHz, C₆D₆) δ (ppm): −17.3. IR (cm^{−1}): 3254w-br, 3236w-br (ν_{NH}). Raman (cm^{−1}): 3256vw (ν_{NH}).

Synthesis of [2-(DippNHCH₂)-6-(DippN=CH)C₆H₃]SbTe (1-Sb-Dipp)Te. To a sample of 268 mg of (1-Sb-Dipp) (0.47 mmol) dissolved in benzene (15 mL), a solid sample of 89 mg of Te (0.7 mmol) was added. The reaction mixture was stirred for 2 days at 65 °C, and then it was filtered. The filtrate was concentrated to ca. 1/2 of the original volume and layered with pentane. Storage of this violet solution at 4 °C produced single crystals of (1-Sb-Dipp)Te that were collected by decantation and dried. Yield: 205 mg, (63%), mp 116 °C (dec). Anal. calcd for C₃₂H₄₁N₂SbTe (MW 703.05): C, 54.7; H, 5.9; N, 4.0%. Found: C, 54.4; H, 6.1; N, 4.3%. ¹H NMR (500 MHz, thf-d₈) δ (ppm): 1.13 [6H, d, ³J(¹H,¹H) = 6.8 Hz, iPr-CH₃]; 1.23 [18H, d, ³J(¹H,¹H) = 6.6 Hz, iPr-CH₃]; 3.19 [2H, s(br), iPr-CH]; 3.22 [2H, s(br), iPr-CH]; 4.70 [2H, s(vbr), CH₂]; 5.74 [1H, t, ³J(¹H,¹H) = 8.5 Hz, NH]; 7.13 [3H, m, Ar-H]; 7.22 [3H, m, Ar-H]; 7.38 [1H, d, ³J(¹H,¹H) = 7.6 Hz, Ar-H]; 7.55 [1H, t, ³J(¹H,¹H) = 7.6 Hz, Ar-H]; 7.95 [1H, d, ³J(¹H,¹H) = 7.5 Hz, Ar-H]; 8.82 [1H, s, CH=N]. ¹³C{¹H} NMR (125.76 MHz, thf-d₈) δ (ppm): 25.3 [iPr-CH₃, overlapped with signals of thf-d₈]; 29.3 [iPr-CH]; 29.6 [iPr-CH]; 57.4 [CH₂]; 124.7 [Ar-C]; 125.5 [Ar-C]; 126.4 [Ar-C]; 128.0 [Ar-C]; 128.9 [Ar-C]; 129.6 [Ar-C]; 133.4 [Ar-C]; 140.8 [Ar-C]; 141.4 [Ar-C]; 142.2 [Ar-C]; 142.7 [Ar-C]; 143.1 [Ar-C]; 146.6 [Ar-C]; 163.2 [Ar-C]; 171.3 [CH=N]. ¹²⁵Te{¹H} NMR (125.76 MHz, thf-d₈) δ (ppm): −422.4. IR (cm^{−1}): 3249w-br, 3225w-br (ν_{NH}).

Theoretical Studies. All of the geometry optimizations have been computed with the Gaussian 16 suite of programs.³³ All structures were optimized using the ωB97XD functional combined with the def2-TZVP basis set (which contains Effective Core Potentials for the heavy elements: Sb, Bi, Te); for obtaining the molecular electrostatic potential maps in the case of the anionic compounds, ωB97XD/def2-TZVPD level was applied.³⁴ Stationary points located on the potential energy hypersurface were characterized by harmonic vibrational frequency calculations to check that the stationary point located is a minimum (no imaginary frequencies were obtained). For Wiberg Bond Indexes and NPA charges, NBO analysis was carried out with the NBO 5.9 program.³⁵ The plotting of the molecular orbitals was carried out with the Avogadro program.³⁶ For the atoms in molecules analysis, the Multiwfn program was employed.³⁷

Crystallography. Diffraction data for all compounds were collected using a Bruker Venture D8 diffractometer at 150 K with graphite-monochromated Mo Kα (0.7107 Å) radiation. The frames were integrated with the Bruker SAINT software package using a narrow frame algorithm. Data were corrected for absorption effects using the Multi-Scan method (SADABS). Obtained data were treated by XT-version 2014/5 and SHELXL-2017/1 software implemented in

APEX3 v2016.5-0 (Bruker AXS) system.³⁸ All nonhydrogen atoms were refined using anisotropic displacement parameters. Hydrogen atoms attached to carbon atoms were included in geometrically calculated positions using a riding model. In the structure of (2-As-Dipp)Cl₂, four of six toluene molecules per unit cell are highly disordered. These disordered molecules have been masked by PLATON/SQUEZZE program,³⁹ which resulted in 227 electrons per unit cell. The so-called bell-clappers phenomenon⁷ is present within the structure of 2-As-Dipp, the arsenic atom is present in two rather equivalent positions—treated as a static disorder. The positions (minor disorder) of the carbon and hydrogen atoms of the central phenyl ring remain untreated.

Crystallographic data (excluding structure factors) for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 2097225 (2-As-Dipp)Cl₂; 2097218 (2-Bi-Dipp)Cl₂; 2097220 1-As-tBu; 2097222 2-Sb-Ad; 2097219 1-As-Dipp; 2097224 2-As-Dipp; 2097221 (1'-Sb-Dipp)₂O; 2124017 (1-Sb-Dipp)Se; 2124016 (1-Sb-Dipp)Te; and 2149908 2-Bi-Dipp. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.organomet.2c00236>.

XYZ coordinates (XYZ)

Description of relevant experiments leading to starting compounds, all NMR, IR, Raman, UV–vis, and CV spectra, details of theoretical studies, and crystal and refinement data (PDF)

Accession Codes

CCDC 2097218–2097222, 2097224–2097225, 2124016–2124017, and 2149908 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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