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Pnictogenium Ions as a Powerful Tool for the Synthesis of Three- and Five-Membered Interpnictogen Chains

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The synthesis and characterization of novel three- and five-membered interpnictogen chain compounds are presented. In a systematic study, the heterodipnictogen complexes $[\{CpMo(CO)_2\}_2(\mu,\eta^{2:2}\text{-}EE')]$ (**Mo_2PAs**: E = P, E′ = As; **Mo_2PSb**: E = P, E′ = Sb; **Mo_2AsSb**: E = As, E′ = Sb) are reacted with *in situ* generated pnictogenium ions of a third pnictogen. Phosphenium ions insert into the As—Sb bond of **Mo_2AsSb** to give $[\{CpMo(CO)_2\}_2(\mu,\eta^{1:1:1:1}\text{-}AsPPh_2Sb)][TEF]$ (**1**) ($[TEF]^-$ = $[Al\{OC(CF_3)_3\}_4]^-$). In contrast, arsenium, stibenium, and bismuthenium ions, respectively, coordinate to the phosphorus atom of **Mo_2PAs** and **Mo_2PSb**. The obtained complexes $[\{CpMo(CO)_2\}_2(\mu,\eta^{2:2}\text{-}SbPAsCy_2)][BArF_{24}]$ (**2**), $[\{CpMo(CO)_2\}_2(\mu,\eta^{2:2}\text{-}AsPSbPh_2)][BArF_{24}]$ (**3**), and $[\{CpMo(CO)_2\}_2(\mu,\eta^{2:2}\text{-}EPBiPh_2)][BArF_{24}]$ (E = As (**5**), E = Sb (**6**)) all contain three different pnictogen atoms in a chain. To even elongate these chains, the stibenium substituted tetrahedranes **3** and $[\{CpMo(CO)_2\}_2(\mu,\eta^{2:2}\text{-}SbPSbPh_2)][BArF_{24}]$ (**4**) are reacted with an additional equivalent of **Mo_2PAs** or **Mo_2PSb** yielding novel five-membered chains of the type E-P-SbPh$_2$-P-E′ (E = E′ = As (**7**); E = E′ = Sb (**8**); E = As, E = Sb (**9**)), with alternating pnictogen sequences. **7–9** are found to be only stable in the solid state whereas a rapid equilibration with their respective starting materials **3** or **4** and **Mo_2PAs** or **Mo_2PSb** is observed in solution.

1. Introduction

Carbon's capability to form new bonds represents the basis for the outstanding structural variety observed in organic molecules.[1] Their manifold utilization ranges from natural nucleotides in DNA or RNA over synthetic pharmaceuticals and food additives to products of daily live, for example, detergents.[1] The diagonal relationship between carbon and phosphorus in the periodic table, in line with comparably high homodiatomic P—P bond energies (205 kJ mol^{-1}),[2] suggests that phosphorus is as well able to form extended (molecular) aggregates.[3,4] This was expressively shown very early on by *Baudler* and coworker, who prepared a plethora of catenated polyphosphorus compounds.[5,6] In contrast, little is known about chains that are built from several different group 15 elements. The main reason for this is the decreasing covalent E—E bond energies going from P to Bi that make such compounds labile and harder to access.[7] However, understanding the bonding within catenated interpnictogen compounds would display a step forward in the development of the structural chemistry of group 15 elements, similar to the one of carbon. The group of *von Hänisch* has put intense efforts into synthesizing the first ternary interpnictogen compound of P, As, and Sb (**Scheme 1**a,**I**) by metalating the arsaphosphine $^tBu_2As\text{-}P(H)^tBu$ with ^nBuLi, followed by addition of $^tBu_2SbCl$ in a salt metathesis reaction.[8] The same group expanded the series of all-^{t}Bu substituted three-membered interpnictogen compounds and succeeded in the synthesis of, for example, $^tBu_2Sb\text{-}P^tBu\text{-}Bi^tBu_2$.[9] Moreover, they were able to synthesize several permutations, in which the order of the pnictogen atoms changed.[10] In addition, they could even introduce terminal -BiAr$_2$ (Ar = C_6H_5 or 2,4,6-$C_6H_2Me_3$) fragments in their chains (Scheme 1a, **II**).[11] Moreover, the groups of *Schulz* and *von Hänisch* reported about molecular compounds containing four[12] or five[13] different pnictogen atoms. Very recently, a PMe$_3$-stabilized stibanylarsinidene was reported by Ni and Wu, which formally contains a substituted P—As—Sb chain (Scheme 1a, **III**).[14] All these examples however require the presence of sterically demanding organic substituents for their stabilization. In contrast, polypnictogen (E_n) ligand complexes bear unsubstituted pnictogen ligands only stabilized by coordination to transition metals. The first E_n ligand complexes bearing two different pnictogen atoms were reported by *Mays* in 1998 by reacting $[\{CpMo(CO)_2(\mu\text{-}H)(\mu\text{-}PH_2)]^-$ with ECl_3 (E = As, Sb) yielding the hetero dipnictogen complexes $[\{CpMo(CO)_2\}_2(\mu,\eta^{2:2}\text{-}PE)]$ (E = P, As (**Mo_2PAs**), Sb (**Mo_2PSb**)).[15] Later, our group developed an improved one-pot synthesis for the same complexes in higher yields, now also allowing for the stabilization of before unknown AsSb (**Mo_2AsSb**), AsBi, and SbBi ligands (Scheme 1b, **IV** to **VI**).[16] Due to the presence of two different pnictogen atoms, these

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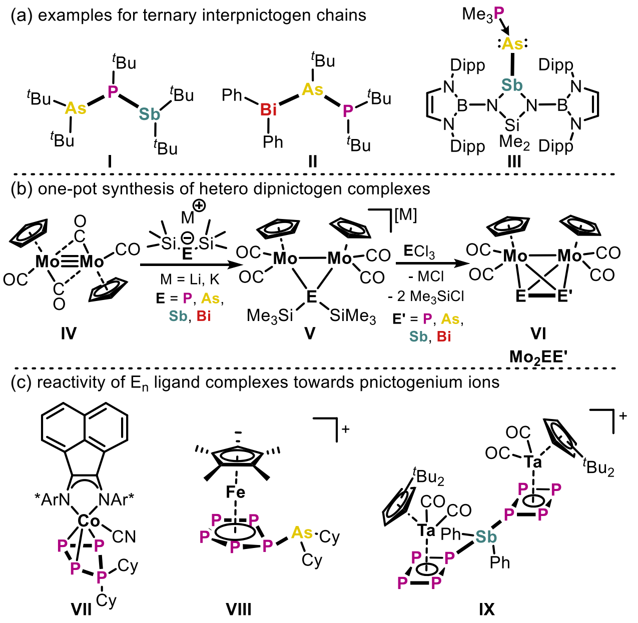


Scheme 1. a) Rare examples for compounds featuring three different pnictogen atoms in a chain; b) one-pot synthesis toward heterodipnictogen complexes of the type [{CpMo(CO)$_2$}$_2$(μ,η$^{2:2}$-EE′)] (E ≠ E′ = P, As, Sb. Bi); c) selected examples of E$_n$ ligand complexes that have been functionalized with pnictogenium ions; Dipp = 2,6-C$_6$H$_3$^{i}Pr$_2$, Ar* = 2,6-dibenzhydryl-4-isopropylphenyl.

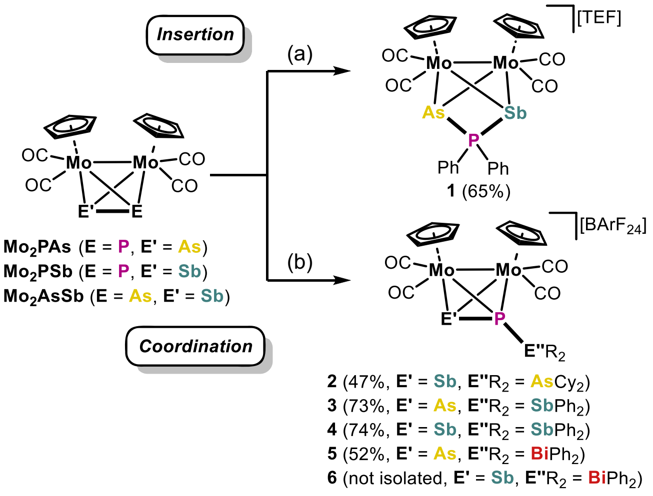
$\mathbf{Mo_2EE'}$ tetrahedranes display ideal starting materials for the introduction of another pnictogen moiety to obtain novel catenated interpnictogen species. Since the pnictogen atoms in these tetrahedranes still have a reactive lone pair of electrons, cationic catenation displays a suitable reaction pathway. Notably, catenation of $\mathbf{Mo_2PE}$ (E = P, As, Sb) with simple group 14 cations was already shown.[17] In contrast, the introduction of cationic group 15 building blocks, namely pnictogenium ions [ER$_2$]$^+$ (E = P-Bi), remains unexplored. In the past, Burford,[18–21] Weigand,[20–22] and Krossing[23,24] already showed that phosphenium ions can insert into P—P bonds, due to their carbene-like character.[25] In contrast, the increased s-p energy separation of the heavier pnictogenium ions should lead to addition compared to insertion.[26] Over the past years, this reactivity was transferred to P$_n$ ligand complexes. Phosphenium ions were found to insert into *cyclo*-P$_3$ (Scheme 1, **VII**),[27–29] *cyclo*-P$_4$,[30–32] and *cyclo*-P$_6$[33] ligands. In contrast, arsenium ions add to the respective phosphorus atoms of [Cp*Fe(η^5-P$_5$)] (Scheme 1c, **VIII**),[34] [{Cp′′′Ta}$_2$(μ,η$^{2:2:2\ 2:1:1}$-P$_8$)],[35] or [Cp″Ta(CO)$_2$(η^4-P$_4$)].[30] Finally, stibenium cations were as well shown to add to the polyphosphorus ligands in [Cp*Fe(η^5-P$_5$)][34] or [Cp″Ta(CO)$_2$(η^4-P$_4$)].[30] In the latter, depending on the sterics of the stibenium ion, a second equivalent of the *cyclo*-P$_4$ complex is necessary to stabilize such a reactive cation (Scheme 1c, **IX**). Reports on the reactivity of bismuthenium ions toward E$_n$ ligand complexes remain unknown until now.

Therefore, the question arises, if the heterodipnictogen complexes [{CpMo(CO)$_2$}$_2$(μ,η$^{2:2}$-EE′)] ($\mathbf{Mo_2EE'}$) that already contain two different pnictogen atoms can be combined with in situ generated pnictogenium ions of a third pnictogen to access low-valent interpnictogen chain compounds. Herein, we report the synthesis and characterization of novel three-membered heteropnictogen chain compounds as well as unprecedented five-membered interpnictogen chains, stabilized within the coordination sphere of transition metals and organic substituents at one pnictogen atom.

2. Results and Discussion

2.1. Synthesis of Three-Membered Interpnictogen Chains

Instead of reacting $\mathbf{Mo_2PAs}$, $\mathbf{Mo_2PSb}$, and $\mathbf{Mo_2AsSb}$ with all pnictogenium ions [R$_2$E]$^+$ (E = P-Bi, R = Ph, Cy), only those pnictogenium ions were chosen, by which the resulting compounds would have three different pnictogen atoms in a chain (except for **4**). For the generation of the pnictogenium ions [R$_2$E]$^+$ (E = P-Bi, R = Ph, Cy), halide abstraction[36] from the respective halopnictines R$_2$EX (X = Br, Cl) with Tl^I salts of the weakly coordinating anions [TEF]$^-$ ([TEF]$^-$ = [Al{OC(CF$_3$)$_3$}$_4$]$^-$)[37] and [BArF$_{24}$]$^-$ ([BArF$_{24}$]$^-$ = [B(3,5-C$_6$H$_3$(CF$_3$)$_2$)$_4$]$^-$)[38] was performed *in situ* in the presence of the respective tetrahedranes $\mathbf{Mo_2PAs}$, $\mathbf{Mo_2PSb}$, or $\mathbf{Mo_2AsSb}$. The aryl substituted [Ph$_2$P]$^+$ cleanly inserts into the As—Sb bond of $\mathbf{Mo_2AsSb}$ to afford [{CpMo(CO)$_2$}$_2$(μ,η$^{1:1:1:1}$-AsP(Ph)$_2$Sb)][TEF] (**1**) in good yields (65%) (**Scheme 2**). In general, phosphenium ions are known to insert into homo- and heterodiatomic bonds,[36] although this has not been observed for As—Sb bonds so far. In contrast, $\mathbf{Mo_2PSb}$ reacts with the heavier [Cy$_2$As]$^+$ to yield [{CpMo(CO)$_2$}$_2$(μ,η$^{2:2}$-SbPAsCy$_2$)][BArF$_{24}$] (**2**) in 47% isolated yield. In **2**, the arsenium ion coordinates to the lone pair of the P atom of $\mathbf{Mo_2PSb}$. This reaction behavior is in line with the reported reactivity of other polyphosphorus ligand complexes such as [Cp*Fe(η^5-P$_5$)], [Cp″Ta(CO)$_2$(η^4-P$_4$)], or [{Cp′′′Ta}$_2$(μ,η$^{2:2:2\ 2:1:1}$-P$_8$)]. Moreover, the even heavier [Ph$_2$Sb]$^+$ adds to the lone-pair of the phosphorus atom in $\mathbf{Mo_2PAs}$ or $\mathbf{Mo_2PSb}$ to give [{CpMo(CO)$_2$}$_2$(μ,η$^{2:2}$-EPSbPh$_2$)][BArF$_{24}$] (E = As (**3**), E = Sb (**4**)) in



Scheme 2. Synthesis of **1**–**6** from $\mathbf{Mo_2PAs}$, $\mathbf{Mo_2PSb}$, or $\mathbf{Mo_2AsSb}$ via: a) phosphenium ion insertion into the As—Sb bond of $\mathbf{Mo_2AsSb}$ or b) arsenium, stibenium, or bismuthenium ion addition to the phosphorus lone-pair. Reaction conditions: a) Ph$_2$PCl, Tl[TEF], r.t. 16 h in *o*-DFB; b) Cy$_2$AsBr, Ph$_2$SbCl, or Ph$_2$BiCl, Tl[BArF$_{24}$], r.t. 16 h in *o*-DFB.

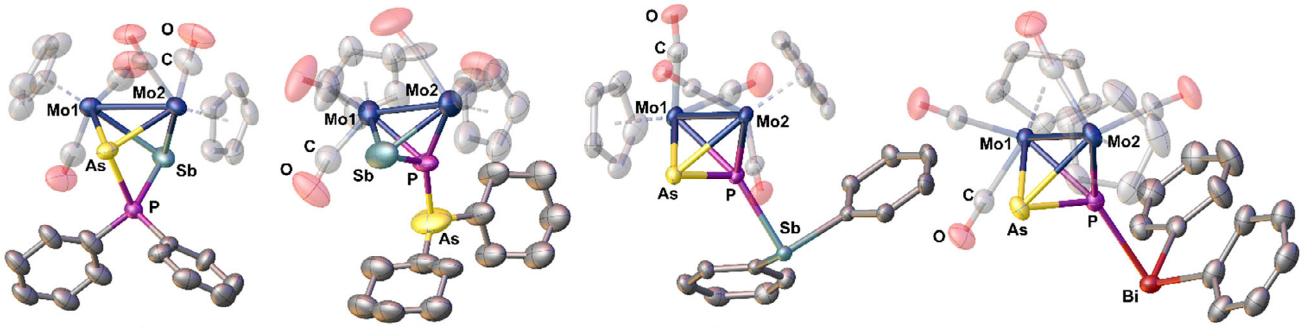
good yields of 73% and 74%, respectively. This displays only the third example of a stibenium ion coordinating to a polypnictogen ligand complex.[30,34] Please note that **4** only contains two different pnictogen atoms; its synthesis is nevertheless mentioned since it serves as starting material for subsequent reactions (*vide infra*). Notably, **1**, **2**, and **3** all consist of a substituted As—P—Sb chain which is coordinated by two $\{CpMo(CO)_2\}$ units. Thereby, the choice of the tetrahedrane and the corresponding pnictogenium ion still allows to control at which pnictogen atom the organic substituents are attached. Next, both **Mo_2PAs** and **Mo_2PSb** were reacted with $[Ph_2Bi]^+$. In both cases, the bismuthenium ion behaves in an identical manner to arsenium and stibenium ions und thus coordinates to the phosphorus lone-pair to form $[\{CpMo(CO)_2\}_2(\mu,\eta^{2:2}\text{-}EPBiPh_2)][BArF_{24}]$ (E = As (**5**, 52%), E = Sb (**6**, *not isolated*)). **6** is extremely sensitive toward light and air and could thus not be isolated in pure form. Nevertheless, the initial formation of **6** in solution could undoubtedly be proven by ^{31}P NMR spectroscopy and mass spectrometry (see Supporting Information). Compounds **5** and **6** are the first reported examples of bismuthenium ions being coordinated by polypnictogen ligand complexes. Lastly, **Mo_2AsSb** was reacted with *in situ* generated $[Ph_2Bi]^+$ to possibly obtain a chain containing the elements As, Sb, and Bi. However, the ^1H NMR spectra obtained from these reaction solutions contain at least eight different signals in the Cp region hinting toward decomposition. Furthermore, elemental bismuth is formed during these reactions indicating ongoing redox processes. The solid-state structures of **1**, **2**, **3**, and **5** are depicted in **Figure 1**. In **1**, the P—As (2.392(3) Å) as well as the P—Sb (2.491(3) Å) bond lengths correspond to single bonds (P—As: 2.32 Å and P—Sb: 2.41 Å).[39,40] Moreover, the As—Sb distance in **1** (3.361(1) Å) is considerably longer than the respective As—Sb bond length in **Mo_2AsSb** (2.515(1) Å)[16] confirming the As—Sb bond scission. In contrast, the P—E bond length of the tetrahedrane scaffold in **2** (P—Sb: 2.314(2) Å), **3** (P—As: 2.212(2) Å), **4** (P—Sb: 2.404(1) Å), and **5** (P—As: 2.199(2) Å) are indeed slightly shortened compared the respective P—E bond lengths in **Mo_2PAs** (2.232(2) Å) and in **Mo_2PSb** (2.470(2) Å).[15] This indicates that the coordination occurs exclusively via the lone pair of phosphorus. The newly formed P—E bonds of **2** (P—As: 2.296(15) Å), **3** (P—Sb: 2.535(1) Å), **4** (P—Sb: 2.540(1) Å), and **5** (P—Bi: 2.656(2) Å) are slightly longer than P—E single bonds (P—As: 2.32 Å, P—Sb: 2.41 Å, P—Bi: 2.62 Å) hinting toward the coordinative nature of these bonds.[39,40] All compounds **1**–**6** are well soluble in CH_2Cl_2 and *ortho*-difluorobenzene (*o*-DFB) and stable under inert gas (except for **6**). Their ^1H NMR spectrum shows a sharp singlet for the Cp ligand at 5.31–5.32 ppm which is in accordance with rotationally unhindered Cp ligands. Furthermore, the room temperature $^{31}P\{^1H\}$ NMR spectra exhibit singlets at −76.7 ppm (**1**), −27.7 ppm (**2**), −119.4 ppm (**3**), −60.0 ppm (**4**), −117.2 ppm (**5**), and −56.5 ppm (**6**). The product signals are on average almost 150 ppm high-field shifted compared to the free tetrahedranes **Mo_2PAs** (30.1 ppm) and **Mo_2PSb** (90.7 ppm), respectively.[15]

2.2. Calculated Reaction Pathways

To further shed light on the observed addition or insertion reactivities of the pnictogenium ions toward the heterodipnictogen complexes **Mo_2PAs**, **Mo_2PSb**, and **Mo_2AsSb** DFT calculations were performed (ωB97X-D3BJ/def2-TZVP//BP86-D3BJ/def2-TZVP level of theory). In general, two factors need to be considered in order to explain the observed reactivity. First, the calculated orbital energies (**Table 1**) of **Mo_2PAs**, **Mo_2PSb**, and **Mo_2AsSb** suggest that the σ(E—E) bond is more reactive in **Mo_2AsSb** (−7.00 eV) than in **Mo_2PAs** (−8.26 eV) or **Mo_2PSb** (−7.29 eV). On the other hand, the orbital energies of the respective pnictogen lone pairs indicate the phosphorus lone pairs in **Mo_2PAs** (−9.82 eV) or **Mo_2PSb** (−9.87) to be slightly higher in energy than the ones for arsenic or antimony in **Mo_2AsSb** (As: −10.70 eV; Sb: −10.51 eV). The second factor to be considered to explain the reactivities is the tendencies of the respective pnictogenium ions toward insertion or coordination. For $[Ph_2P]^+$, the insertion into the As—Sb bond to form **1** was found to be far more exergonic

Table 1. Calculated energies of selected NBOs for the tetrahedral complexes $[\{CpMo(CO)_2\}_2(\mu,\eta^{2:2}\text{-}EE')]$ (BP86/def2-TZVP).

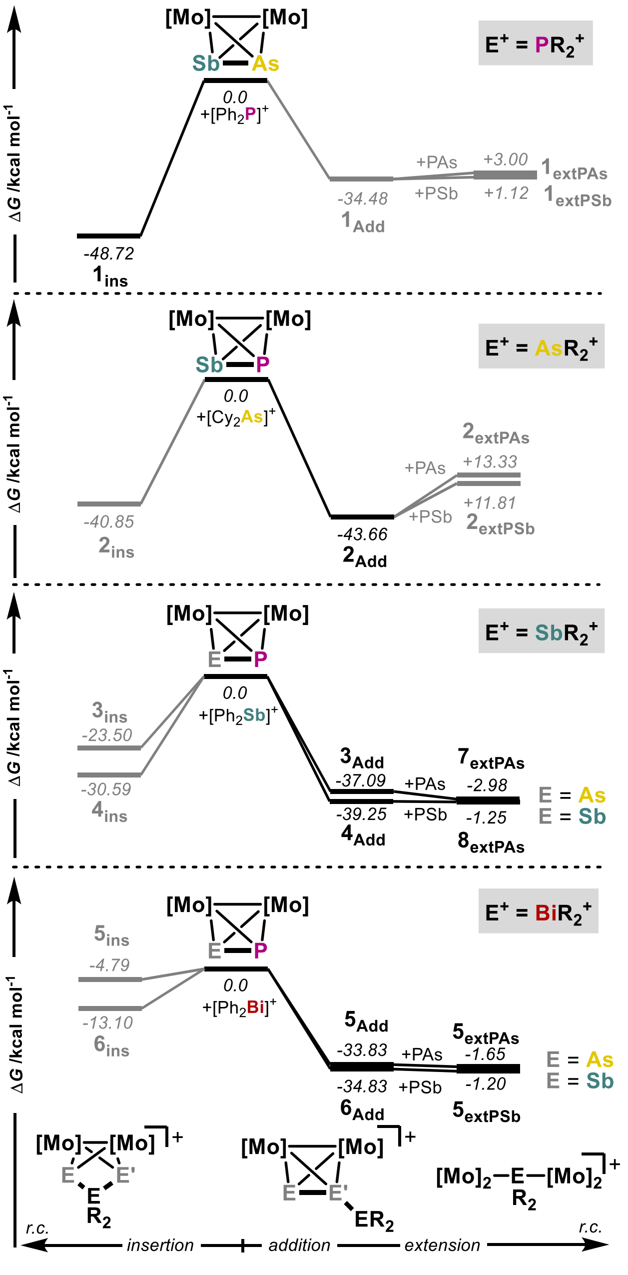
Mo_2EE'	σ(E—E′) [eV]	lp(E) [eV]	lp(E′) [eV]
Mo_2PAs	−8.26	−9.82 (E = P)	−10.64 (E′ = As)
Mo_2PSb	−7.29	−9.87 (E = P)	−10.48 (E′ = Sb)
Mo_2AsSb	−7.00	−10.70 (E = As)	−10.51 (E′ = Sb)



1 2 3 5

Figure 1. Solid state structures of **1**, **2**, **3**, and **5**; counter anions and H atoms are omitted for clarity, and ellipsoids are drawn at the 50% probability level; Cp and CO ligands are depicted translucent.

(-48.72 kcal mol^{-1}) than the coordination (-34.48 kcal mol^{-1}) to form hypothetical $\mathbf{1}_{\mathbf{Add}}$ (**Scheme 3**, top). For the heavier pnictogenium ions $[R_2E]^+$ (E = As, Sb, Bi; R = Ph, Cy), the exact opposite situation applies. While the insertion of $[R_2E]^+$ into the P—E (E = As, Sb) bond as well as addition to the phosphorus lone pair was found to be exergonic, the addition is energetically more favored (**2**: by -2.81 kcal mol^{-1}, **3**: by -13.59 kcal mol^{-1}, **4**: by -8.66 kcal mol^{-1}, **5**: by -29.04 kcal mol^{-1}, **6**: by -21.73 kcal mol^{-1}) compared to the insertion (Scheme 3). In summary, these results highlight the tendency of the heavier pnictogenium ions toward formation of a coordinated species compared to an insertion. This trend increases drastically going from arsenium ions to bismuthenium ions. This can be attributed to a much higher stability of the coordinating pnictogenium (formally oxidation state +III) compared to the pnictonium center (formally oxidation state +V) that would result from the insertion into a E—E′ bond.[26]



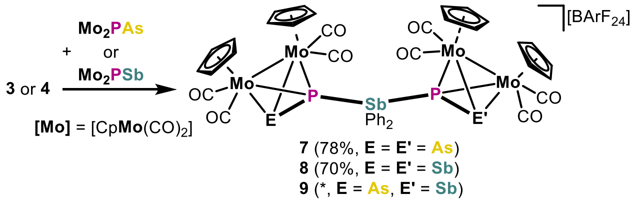
Scheme 3. Calculated reaction pathways for the functionalization of mixed tetrahedrane complexes with pnictogenium cations (ωB97X-D3BJ/def2-TZVP//BP86-D3BJ/def2-TZVP). Experimentally not observed pathways are displayed gray.

In order to estimate the reaction behavior of **1**–**6** toward further elongation of the interpnictogen chain, the reaction energies for the addition of a second equivalent of a tetrahedrane to provide five-membered chain compounds were calculated. They were found to be endergonic for the addition of $\mathbf{Mo_2PAs}$ or $\mathbf{Mo_2PSb}$ to **1** (3.00 and 1.12 kcal mol^{-1}) and **2** (13.33 and 11.81 kcal mol^{-1}), respectively. In contrast, the addition of $\mathbf{Mo_2PAs}$ and $\mathbf{Mo_2PSb}$ to **3**–**6** is slightly exergonic by -1.20 kcal mol^{-1} to -2.98 kcal mol^{-1} (Scheme 3), thus offering a synthetic entry for these five-membered chain structures, which was further explored experimentally.

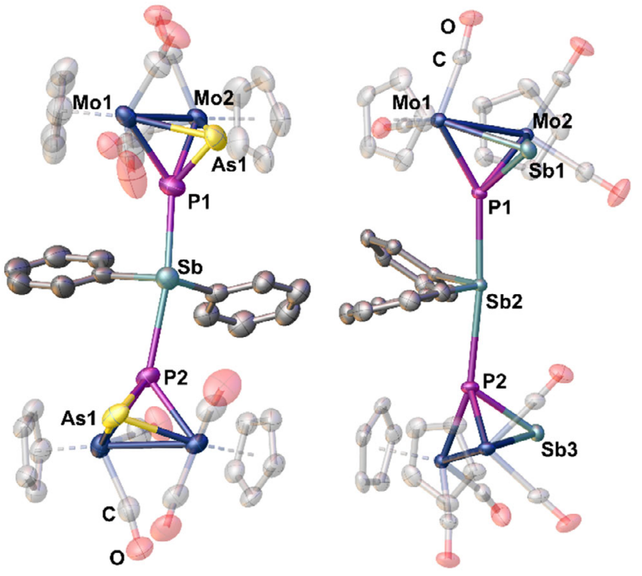
2.3. Synthesis of Five-Membered Interpnictogen Chains

Since compounds **5** and **6** were found to be extremely light sensitive, the stibenium-substituted tetrahedranes **3** and **4** were chosen as model substrates for investigating their further reactivity. Frontier molecular orbital analysis of **3** shows its LUMO+8 (see Supporting Information, Figure S 52) having significant p-orbital contribution at the stibenium cation hinting toward a Sb centered reactivity toward nucleophiles such as $\mathbf{Mo_2PAs}$ and $\mathbf{Mo_2PSb}$.

Reaction of **3** with equimolar amounts of $\mathbf{Mo_2PAs}$ afforded $[\{(CpMo(CO)_2)_2(\mu,\eta^{2:2}\text{-}PAs)\}_2SbPh_2][BArF_{24}]$ (**7**) in 78% yield (**Scheme 4**, **Figure 2**). Moreover, $[\{(CpMo(CO)_2)_2(\mu,\eta^{2:2}\text{-}PSb)\}_2SbPh_2][BArF_{24}]$ (**8**, 70%) could be isolated from the reaction of **4** with one equivalent of $\mathbf{Mo_2PSb}$. The P—As or P—Sb bond lengths within the tetrahedrane in **7** (2.205(2) Å, 2.125(2) Å) or **8** (2.406(1) Å, 2.390(1) Å) do not significantly deviate from those in the respective starting materials **3** (2.212(2) Å) and **4** (2.404(1) Å). In contrast, the P—Sb distances from the bridging stibenium cation are within the range of 2.619(1) Å to 2.936(1) Å, which is significantly longer than a P—Sb single bond (2.41 Å).[39,40] However, they still are far below the sum of the respective van der Waals radii (3.86 Å),[41] hinting toward the coordinative nature of these bonds. Moreover, the bond lengths are as well significantly elongated compared with their respective starting materials **3** (P—Sb: 2.535(1) Å) and **4** (P—Sb: 2.540(1) Å). Similar bond elongation was reported by the groups of Wild and Chitnis when they reacted $[(R_3P)SbPh_2]^+$ (R = Ph, Me) with another equivalent of PR_3 (R = Ph, Me) to obtain $[(R_3P)_2SbPh_2]^+$



Scheme 4. Synthesis of **7**–**9** by reacting **3** or **4** with an equivalent Mo_2PAs, Mo_2PSb. Reaction conditions: r.t. 1–3 h in *o*-DFB. *The crystalline yield of **9** could not be determined in percent since the solid-state structure of **9** shows complex mixed occupancies of **7**, **8**, and **9** as well as of **3** and **4**.



7

8

Figure 2. Solid state structures of **7** and **8**; counter anions and H atoms are omitted for clarity and ellipsoids are drawn at the 50% probability level; Cp and CO ligands are depicted translucent.

(R = Ph, Me).[42,43] As expected, the respective P1-Sb-P2/P1-Sb2-P2 angles in **7** (166.40(4)°) or **8** (174.20(2)°) are close to 180°. When dissolving **7** or **8** in CD_2Cl_2, ^{31}P chemical shifts of -45.8 ppm (**7**) or 19.7 ppm (**8**) are observed. These resonances appear at almost the average of the chemical shifts of the individual building blocks (-44.6 ppm and 15.3 ppm expected for **7** and **8**, respectively). Notably, both signals are significantly broadened (**7**: $\nu_{1/2} = 110$ Hz, **8**: $\nu_{1/2} = 232$ Hz). This suggests that in solution both **7** and **8** dissociate into **3** and **4**, and $\mathbf{Mo_2PE}$, respectively. More precisely, **3** or **4** and the corresponding $\mathbf{Mo_2PE}$ tetrahedrane exchange rapidly on the NMR time scale probably via **7** or **8** as an intermediate. Slight offsets of the chemical shifts compared to the expected ones can be explained by small amounts of the formed starting materials. Finally, it was aimed to synthesize the "mixed" derivative $[\{(CpMo(CO)_2)_2(\mu,\eta^{2:2}\text{-}PAs)\}\{(CpMo(CO)_2)_2(\mu,\eta^{2:2}\text{-}PSb)\}SbPh_2]$ $[BArF_{24}]$ (**9**), which was obtained by two ways: 1) reaction of **3** with one equivalent $\mathbf{Mo_2PSb}$ or 2) reaction of **4** with equimolar amounts of $\mathbf{Mo_2PAs}$. Compounds **7**–**9** are, to the best of our knowledge, the first examples of five-membered chains that are built from three different alternating pnictogen atoms (excluding N). Interestingly, **9** co-crystallizes in a 1:1 ratio with **3**/**4** (mixed occupancy) as well as **7** and **8**, hinting toward the presence of dynamic equilibria also for these species in solution (see Supporting Information, Figure S48 and S49). When dissolving **9** in CD_2Cl_2, the obtained $^{31}P\{^1H\}$ NMR spectrum reveals two broad resonances at -23.3 ppm ($\nu_{1/2} = 177$ Hz) and -9.8 ppm ($\nu_{1/2} = 89$ Hz). Interestingly, these observed chemical shifts originating from the mixed complex **9** significantly deviate from the averaged chemical shifts observed for **7** (-45.2 ppm) and **8** (20.2 ppm). Assuming full dissociation similar to **7** and **8** (*vide supra)*, this indicates that **3**, **4**, $\mathbf{Mo_2PAs}$ and $\mathbf{Mo_2PSb}$ are not equally populated. The significant high field shifts of both signals of **9** can be explained by an increased population of **4**, while the population of **3** decreases (see Supporting Information). Upon cooling, the signals broaden first (until -40 °C), and four new resonances with different line widths are formed upon further cooling to -80 °C indicating that different dynamic processes are present in solution (see Figure S38, Supporting Information). Furthermore, the CEST profiles from a pseudo-2D ^{31}P-CEST[44,45] are extraordinary broad ($\nu_{1/2} = 6$ kHz for -10 ppm and $\nu_{1/2} = 9$ kHz for -23 ppm) (see Figure S36 and S 40, Supporting Information). We interpret that as the contribution of a myriad of structures not detectable with VT-NMR. To further demonstrate the dynamic nature of these compounds, 50 µmol of **9** were dissolved in CD_2Cl_2 and $\mathbf{Mo_2PAs}$ or $\mathbf{Mo_2PSb}$ was added in portions of 9.3 or 6.8 µmol, respectively. When $\mathbf{Mo_2PAs}$ was added stepwise to **9**, a slight downfield shift of both signals to -9.9 ppm and to 0.1 ppm was observed (Figure S41, Supporting Information). Upon addition of in total 105.7 µmol $\mathbf{Mo_2PSb}$, both signals of **9** shifted downfield to end up at 17.42 ppm (close to **8**) and at 32.42 ppm (Figure S42, Supporting Information). In conclusion, all NMR methods indicate a full dissociation of **7**, **8**, and **9** in solution. Only the extremely broad CEST profile hints at the presence of short-lived, associated structures as found in the crystal structures.

3. Conclusion

In summary, this study gives an overview of the addition and insertion behavior of pnictogenium ions toward the complexes $\mathbf{Mo_2PAs}$, $\mathbf{Mo_2PSb}$, and $\mathbf{Mo_2AsSb}$. Phosphenium ions insert into the As—Sb bond of $\mathbf{Mo_2AsSb}$ yielding **1**, which consists of a three-membered As-P(Ph)$_2$-Sb chain stabilized by two $\{CpMo(CO)_2\}$ fragments. In contrast, arsenium, stibenium, and bismuthenium ions add to the phosphorus lone pair in $\mathbf{Mo_2PAs}$ and $\mathbf{Mo_2PSb}$, respectively, affording compounds bearing novel three-membered E-P-E′R$_2$ chains (E = Sb, E′R$_2$ = AsCy$_2$ (**2**); E = As, E′R$_2$ = SbPh$_2$ (**3**); E = Sb, E′R$_2$ = SbPh$_2$ (**4**); E = As, E′R$_2$ = BiPh$_2$ (**5**); E = Sb, E′R$_2$ = BiPh$_2$ (**6**)). DFT calculations give insights into the reaction pathway and explain the observed differences between phosphenium ions and their heavier congeners. Furthermore, a second equivalent of $\mathbf{Mo_2PAs}$ or $\mathbf{Mo_2PSb}$ was added to the stibenium substituted derivatives **3** and **4** to afford the unprecedented five-membered interpnictogen chains of the type E-P-SbPh$_2$-P-E′ (E = E′ = As (**7**); E = E′ = Sb (**8**); E = As, E = Sb (**9**)), which are stabilized by in total four $\{CpMo(CO)_2\}$ units. ^{31}P NMR spectroscopic investigations shed light on the behavior of **7**–**9** in solution. It was found that these five-membered interpnictogen chains only exist in the solid state. In solution, they rapidly dissociate into their respective starting materials **3**, **4**, and $\mathbf{Mo_2PAs}$ or $\mathbf{Mo_2PSb}$. Summing up, the obtained complexes discussed within this work reveal unprecedented three- and five-membered interpnictogen chain compounds. These findings help to understand the bonding within mixed group 15 elements which displays a step forward in the development of the structural chemistry of group 15 elements, similar to the one of carbon.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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