Synthesis of Tetrahedranes Containing the Unique Bridging Hetero-Dipnictogen Ligand E£ (E ≠ E' = P, As, Sb, Bi)

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Dedicated to Christian Bruneau.

In order to improve and extend the rare class of tetrahedral mixed main group transition metal compounds, a new synthetic route for the complexes [[CpMo(CO)]$_2$(μ$_2$μ$_2$E£)] (E = As (1), Sb (2)) is described leading to higher yields and a decrease in reaction steps. Via this route, also the so far unknown heavier analogues containing AsSb (3a), AsBi (4) and SbBi (5) ligands, respectively, are accessible. Single crystal X-ray diffraction experiments and DFT calculations reveal that they represent very rare examples of compounds comprising covalent bonds between two different heavy pnictogen atoms, which show multiple bond character and are stabilised without any organic substituents. A simple one-pot reaction of [CpMo(CO)]$_2$ with ME(SiMe$_3$)$_2$ (M = Li, K; E = P, As, Sb, Bi) and the subsequent addition of PCl$_3$, AsCl$_3$, SbCl$_3$ or BiCl$_3$, respectively, give the complexes 1-5. This synthesis is also transferable to the already known homo-dipnictogen complexes [[CpMo(CO)]$_2$(μ$_2$μ$_2$E£)] (E = P, As, Sb, Bi) resulting in higher yields comparable to those in the literature reported procedures and allows the introduction of the bulkier and better soluble Cp*(Cp* = tert butylcyclopentadienyl) ligand.

Introduction

Tetrahedral molecules such as the most simple organic representative, the parent tetrahedrane (tricyclo[1.1.0.0$^2$]butane), have always been of great scientific interest, not only due to their aesthetical attraction as a chemical equivalent of a platonic body, but also because of their unusual bonding situation, high ring strain and reactivity.[1] These properties point already to their mostly challenging syntheses and low stability.[2] The probably most prominent inorganic example of this class of compounds is white phosphorus (P$_4$), which can be prepared by sublimation of red phosphorus and is stable under exclusion of air. In contrast, its heavier counterpart, yellow arsenic (As$_4$), is highly unstable and undergoes rapid autolysis degradation under light exposure already.[3] Furthermore, the heavier homologue Sb$_4$ has been observed in the solid state only within thin antimony films received by the evaporation of Sb$_4$ molecules in ultra-high vacuum,[4] while Bi$_4$ is only known in the gas phase.[4] Heteroatomic tetrahedranes built from p-block elements are extremely scarce. Only three examples, namely AsP$_2$(I) and the tetrahedrane derivatives P(CBu$_3$)$_2$(II) and P$_2$(CBu$_3$)$_2$(III), have been reported to date (Scheme 1b).[5] They are, however, highly sensitive to air. While I and III are pyrophoric, compound II degrades after 30 mins at room temperature.

By formal substitution of one or two atoms of the E$_4$ (E = P, As, Sb, Bi) tetrahedra with isolobal 15-valence-electron transition metal fragments, such as [CpMo(CO)]$_2$, stable tetrahedra such as the air-stable (in the solid state) polypnicogen ligand complexes [[CpMo(CO)]$_2$(μ$_2$μ$_2$E£)] ("MoE£") (E = P, As, Sb)[6] and [[CpMo(CO)]$_2$(μ$_2$μ$_2$E£)] ("MoE£") (E = P, As, Sb, Bi) [Scheme 1b] are received (Scheme 1). They can easily be synthesised, characterised and handled and are therefore well-suited starting materials for further investigations and have already proved to be excellent precursors for the formation of extended polypnicogen frameworks upon reduction,[6][9] coordination[9] and oxidation.[10] While for Mo$_2$E$_3$ complexes all representatives of E (E = P, As, Sb, Bi; except E = N) are known, the respective

Scheme 1. a) Rare examples of compounds featuring covalent As–Bi and Sb–Bi bonds (left), as well as a covalent As–Sb bond, which is in equilibrium with its respective homo-dipnictogen complexes (right); b) heteroatomic main-group tetrahedranes. This work: tetrahedral [[CpMo(CO)]$_2$(μ$_2$μ$_2$P,Sb,As,Bi)] compounds containing scarce covalent hetero-dipnictogen bonds.
hetero-dipnictogen complexes $\text{Mo}_2\text{E}_2$ have been far less investigated. Until now, only two compounds of this class, $[\text{CpMo(CO)}_3]\{\mu_1^1\eta^1\text{PE}^1\}$ (E = As (1), Sb (2)), could be synthesised by Mays et al. in 1998 (Scheme 2). Their approach based on the deprotonation of $[\text{CpMo(CO)}_3]\{\mu_1^1\eta^1\text{H}_2\text{PE}^1\}$ (C), which yields the lithium salt of the anion $[\text{CpMo(CO)}_3]\{\mu_1^1\eta^1\text{H}_2\text{PE}^1\}$ (D). Further reaction with AsCl$_3$ or SbCl$_5$, respectively, gives access to 1 and 2 by elimination of one equivalent of LiCl and two equivalents of HCl. However, the latter can also protonate the anion D back to C, which leads to just moderate yields of 33% (1) and 39% (2), respectively. Another disadvantage of this synthetic route is the elaborate preparation of C, where first $\text{Mo}_{3}\text{PE}_6$ (B) is generated by thermolysis of $[\text{CpMo(CO)}_3]\{\eta^3\text{PE}^1\}$ (A) with white phosphorus to be further hydrolysed with NaOH in THF/H$_2$O. Following this route, C can only be obtained in a yield of just 15%, which leads to an overall yield of 5.0% for 1 and 5.9% for 2, when starting from A. Moreover, a direct route affording C from A was developed by our group in 2003. Additionally, only recently, we were able to show that $[\text{CpMo(CO)}_3]\{\mu^1\eta^1\text{P}^1\text{Sb}^1\}$ (3a) and $[\text{CpMo(CO)}_3]\{\mu^1\eta^1\text{P}^1\text{Sb}^1\}$ (3b) can be synthesised by reacting NaPH with tert-PH$_3$, respectively, after chromatographic work-up. In the last step, these compounds starting directly from A (Scheme 2), which is a derivative of $\text{Mo}_2\text{Pe}_2$ complexes with different Cp$^2$ ligands such as the tert-butyl substituted cyclopentadienyl ligand (Cp$^2$ = $\eta^1$-C$_5$H$_5$(Bu)) and gives access to the so far unknown heavier hetero-dipnictogen derivatives of 1 and 2 such as $[\text{CpMo(CO)}_3]\{\mu^1\eta^1\text{P}^1\text{Sb}^1\}$ (3a) and $[\text{CpMo(CO)}_3]\{\mu^1\eta^1\text{P}^1\text{Sb}^1\}$ (3b) in higher yields. The latter represent the first examples of compounds containing covalent bonds between mixed heavier group 15 elements that do not bear any bulky organic substituents and are only stabilised by transition metal moieties.

### Results and Discussion

When A is reacted with a solution of Li[P(SiMe$_3$)$_3$] (E1) in THF, an immediate colour change from orange-brown to greenish red occurs suggesting the formation of the immediate Li[P(SiMe$_3$)$_3$] (E2) and $[\text{CpMo(CO)}_3]\{\mu^1\eta^1\text{PE}^1\}$ (E = As (1), Sb (2)) in 69% and 59% isolated yields (Scheme 3). Compound 6a is a derivative of D in which the P-bound hydrogen atoms are replaced by SiMe$_3$ groups. Further addition of AsCl$_3$ or SbCl$_5$, respectively, leads to the generation of the tetrahedral molybdenum pnictogen complexes $[\text{CpMo(CO)}_3]\{\mu^1\eta^1\text{PE}^1\}$ (E = As (1), Sb (2)) in 69% and 59% isolated yields (Scheme 3), respectively, after chromatographic work-up. In the last step, two equivalents of Me$_3$SiCl are released avoiding the disadvantageous elimination of HCl. This method not only avoids elaborate reaction steps, but also increases the yield of the compounds 1 and 2 dramatically, compared to the literature (5.0% and 5.9%; Table 1).

The purity of 1 and 2 was proven by $^3$P and $^1$H NMR spectroscopy as well as by elemental analysis and mass spectrometry. It has to be mentioned that compound 1 can also be synthesised by reacting A with NaPH$_3$ (yielding the anion D immediately in solution) and the subsequent addition of AsCl$_3$. But, here again, HCI evolves in the second reaction step leading to side reactions and a relatively low yield of 16%, which, however, still exceeds three times the yield reported by Mays et al.

### Table 1. All possible combinations of the intermediates 6a-d with EC$_3$. (E = P, As, Sb, Bi) and the resulting products $[\text{CpMo(CO)}_3]\{\mu^1\eta^1\text{E}^1\}$ (EE). Yield improvements compared to the literature syntheses are given subjacent (referred to A).

|   | 6a ("P") | 6b ("As") | 6c ("Sb") | 6d ("Bi") |
|---|---|---|---|---|
| PC$_3$ | P$_2$ | P$_2$ | P$_2$ | unsuccessful |
| 20% | 5% | 5% | 6% | 18% |
| AsCl$_3$ | P$_2$ | P$_2$ | P$_2$ | unsuccessful |
| 20% | 5% | 5% | 6% | 18% |
| SbCl$_3$ | P$_2$ | P$_2$ | P$_2$ | unsuccessful |
| 20% | 5% | 5% | 6% | 18% |
| BiCl$_3$ | P$_2$ | P$_2$ | P$_2$ | unsuccessful |
| 20% | 5% | 5% | 6% | 18% |
Compound Mo₆P₂ (8) can be obtained in the same manner by reacting the solution of the intermediate 6a with PCl₅. Here, the yield can be increased from 20% to 57% (Table 1). However, the synthesis of an analogous complex with a PBi ligand by adding BiCl₃ to 6a was not successful, as it was also reported by them in the article of Mays et al. Only small traces of Mo₆P₂ could be detected by NMR spectroscopy and mass spectrometry, which might suggest that the P–Bi bond is too unstable and the tetrahedral product is either not formed or decomposes rapidly.

Our synthetic route clearly shows that the number of reaction steps could be reduced and that the yield is considerably increased by an easy one-pot reaction, especially for the hetero-dipnictogen complexes 1 and 2. But the more challenging question arises whether the yet unknown hetero-dipnictogen ligands, which only contain the heavier elements As, Sb and Bi, are also accessible. The reaction of A with either Li[As(SiMe₃)₂]₂ (E2), K[Si(SiMe₃)₂] (E3) or K[Bi(SiMe₃)₂] (E4) in THF leads to an immediate colour change from orange-brown to greenish brown (E2), greenish brown (E3) or bronze-coloured (E4) suggesting the formation of the respective intermediates M[[CpMo(CO)₂]₂{μ-η²:η¹-As(SiMe₃)₂}] (M = Li, K; E = As (6b), Sb (6c), Bi (6d)) in solution. The subsequent addition of AsCl₃, SbCl₃ or BiCl₃ respectively, and easy purification by column chromatography lead to the unprecedented complexes [[CpMo(CO)₂]₂{μ-η²:η¹-AsSb}₃] (3a), [[CpMo(CO)₂]₂{μ-η²:η¹-AsBi}₂] (4) and [[CpMo(CO)₂]₂{μ-η²:η¹-SbBi}²] (5) in remarkable isolated yields of 63%, 58% and 46% (Scheme 3, Table 1).

Thus, all combinations of dipnictogen ligands can be synthesised by reacting the respective intermediate 6a-6d with the appropriate pnictogen-trihalide ECl₅ (except Mo₆PBi). While compound 3a can be obtained in two ways, either by combining 6b with SbCl₅ or 6c with AsCl₅, 4 and 5 are only formed by the reaction of 6b or 6c, respectively, with BiCl₅, not by reacting 6d with AsCl₅ or SbCl₅ (Table 1 or Scheme 3). This suggests that either the formation of 6d is less favoured or that 6d is less stable than its lighter counterparts.

The incorporated EE ligands feature very rare bonds between different heavier pnictogen atoms, especially within the compounds 3a, 4 and 5. Compound 3a represents the fourth, 4 and 5 only the third example of compounds with covalent As–Sb [16] or As–Bi [17a, 17b] bonds, respectively. Moreover, they are the first examples of such covalent E–E bonds that are only stabilised by transition metals and do not bear any organic substituents. Therefore, these compounds can be regarded as complexes of the exotic diatomic AsSb, AsBi and SbBi molecules, respectively, which are the heaviest hetero-pnictogen congeners of N₂.

Analogously to the synthesis of Mo₆P₂, the homo-dipnictogen complexes Mo₆As₂, Mo₆Sb₂, and Mo₆Bi₂ can be synthesised via this method too, again resulting in a remarkable yield enhancement compared to their hitherto existing preparations (except for the antimony complex; Table 1). Additionally, this synthesis could be scaled-up to a multigram scale, which enables the systematic investigation of the reactivity of this class of compounds. All the tetrahedral complexes are well soluble in dichloromethane and toluene and moderately soluble in ortho-difluorobenzene and nonpolar solvents such as n-hexane or n-pentane. Overall, the heavier the pnictogen atoms are, the more the solubility decreases.

The products 1–5 can be crystallised from saturated CHCl₃ solutions at −30 °C leading to dark red blocks suitable for single crystal X-ray diffraction. Since 1 and 2 are already described in the literature, only the solid-state structures of 3a–5 (Figure 1) will be discussed. They are isostructural with a distorted Mo₆EE’ tetrahedron as the central structural motif and crystallise in the monoclinic space groups P2₁/n (3a), P2₁ (4) or I2/a (5), respectively, with two half molecules (3a), one (4) or one half molecule (5) in the asymmetric unit. The AsSb ligand of 3a exhibits a 50:50 disorder over the two sites with an average
bond length of 2.515(1) Å, which is in between those of the diarsenic (2.311(3) Å)\(^{[24]}\) and the diantimony complexes (2.678(1) Å).\(^{[19]}\) Additionally, it is just slightly longer than the sum of the covalent radii for an As–Sb double bond (2.47 Å).\(^{[20]}\) Therefore, it shows a structural similarity to all other existing complexes of the type [(CpMo(CO))\(n\)\(\mu\)\(\eta^2\)-EE]]\(^{[19]}\). It represents, however, the first example of an As–Sb bond with a multiple bond character. The same accounts for the complexes 4 and 5. The former bears an AsBi ligand with a bond length of 2.64(2) Å,\(^{[18]}\) the latter an SbBi ligand with a bond length of 2.79(2) Å. Both are again disordered over the two sites in a ratio of 50:50 and the diantimony (2.678(1) Å)\(^{[19]}\) and the dibismuth (2.838(1) Å)\(^{[17]}\) complexes. The same behaviour is observed for the Mo–Mo distances of 3a–5, which are slightly elongated in comparison to the respective lighter homopnictogen complex Mo\(\text{E=}=\text{E}\) (the former bears an AsBi ligand with a bond length of 2.55 Å; Sb–Bi: 2.77 Å) covalent radii, while 5 bears a double bond.\(^{[20]}\) Additionally, the bond length of the SbBi ligand in 5 is again between those of the diantimony (2.678(1) Å)\(^{[19]}\) and the dibismuth (2.838(1) Å)\(^{[17]}\) complexes. The same behaviour is observed for the Mo–Mo distances of 3a–5, which are slightly elongated in comparison to the respective lighter homopnictogen complex Mo\(\text{E=}=\text{E}\), but shortened in comparison to the heavier analogue. The Cp ligands in 3a–5 are arranged in an eclipsed manner to each other. Overall, the newly formed complexes 3a–5 can, on the one hand, be described as tetrahedra, isolobal to \(\text{P}=\text{P}\) and As\(\text{Sb}\), and, on the other hand, as EE dumbbells stabilised by an Mo\(\text{E=}=\text{E}\) unit, each featuring a formal triple bond. The rather short E–E distances are nicely reproduced by DFT calculations (c.f. Supporting Information). For example, the As–Sb distance in the optimized geometry of 3a is with 2.515 Å in excellent agreement with the experimental value (vide supra). Moreover, the As–Sb multiple bond character is reflected in the Wiberg bond order with a Löwdin orthogonalized basis (see Supporting Information for details of 1.40). The corresponding Wiberg bond orders of the As–Bi and Sb–Bi bonds in 4 and 5 are 1.35 and 1.36, respectively.

The \(^1\)H NMR spectra of 1–5 all feature one singlet in the characteristic region for Cp ligands.\(^{[21]}\) Likewise, one singlet is observed in the \(^{13}\)C\(\text{(H)}\) NMR spectra as well as characteristic signals for the CO ligands. The phosphorus-containing complexes 1 and 2 were characterised by \(^{31}\)P NMR spectroscopy, revealing the expected signals at \(\delta = 34.55 \text{ ppm} (1 \text{ in C}_{6}D_{6})\)\(^{[22]}\) and 98.8 ppm (2 in C\(_6\)D\(_6\))\(^{[22]}\) as reported in literature.\(^{[21]}\) However, in some cases, both solutions show an additional small signal at \(-44.5 \text{ ppm}\), which can be attributed to trace impurity of Mo\(\text{P}=\text{P}\).

This indicates that a slight intermolecular exchange between the pnictogen atoms can take place in these syntheses and, therefore, small amounts of the homo-dipnictogen complexes are generated which cannot be separated by column chromatography. The amount of the produced Mo\(\text{P}=\text{P}\) is very little (ratio of 20:1 or higher in favour of 1 or 2, respectively) though. Small amounts of homo-dipnictogen complexes can also be observed in the \(^1\)H NMR spectra of 3a–5 in some reactions. The identity of 1–5 has been unambiguously proven by mass spectrometry, where the molecular ion peak has been detected. In addition, in some cases, peaks of low intensity corresponding to the homopnictogen species have been also detected. The composition of 1–5 is further supported by the elemental analysis. All the synthesised tetrahedral compounds, including 3b, 7 and 8 (vide infra), are stable in air, in contrast to other heteroatomic tetraedranes.\(^{[5a–c]}\)

It was also possible to isolate crystals of the intermediates 6a–c (regardless of several attempts, no crystals for 6d could be obtained), which were suitable for single-crystal X-ray diffraction by adding the respective crown ethers (12-crown-4 for lithium, 18-crown-6 for potassium) within the first reaction step and layering with \(n\)-hexane at \(-30^\circ\)C (Figure 2). The anions of the intermediates 6a–c are isostructural to each other as well as to D, which is a derivative of 6a where the SiMe\(_3\) groups are substituted by protons. They crystallise in the space groups P2\(_1\)/\(n\) (6a, P2\(_2\)/\(n\) (6b) and P 1(6c), respectively. In the newly formed anions, the pnictogenido \([\text{E(SiMe}_3])_2\] units bridge the Mo–Mo bond with E–Mo distances in the range between a single and a double bond (P–Mo: 2.4304(6) Å; As–Mo: 2.5170(3) Å; Sb–Mo: 2.6897(7) Å). The pnictogen atom features a distorted tetrahedral geometry. The Mo–Mo distances (6a: 3.1890(5) Å; 6b: 3.2445(3) Å; 6c: 3.2598(8) Å) are dramatically increased compared to the starting material A (2.4477(12) Å)\(^{[23]}\) reasoning that the original triple bond is completely degraded and only an elongated single bond between the molybdenum atoms is left. Additionally, the Mo–Mo distances increase from the lighter to the heavier pnictogen elements as expected. Compared to its derivative D, compound 6a shows a similar Mo–Mo distance, but slightly elongated Mo–P bonds (D: 2.3752(2)-2.3782(2) Å). This is caused by the sterically more demanding SiMe\(_3\) groups in contrast to the P-bound hydrogen atoms of D. A similar derivative of the arsenic compound 6b is not known yet, but a related structural motif can be found in the neutral compound.
The complexes 3a–5 were synthesised by using \([\text{Cp}\text{Mo(CO)}]_2\) as starting material exemplifying \([\text{Cp}\text{Mo(CO)}]_2(\mu-H)(\mu-\text{AsH}_2)]\) with a bridging \([\text{AsH}_2]^-\) unit instead of \([\text{As}3\text{SiMe}_3]^-\). Interestingly, 6c is the first crystallographically characterized compound with a dibenzo unit bridging a dimolybdenum fragment. And, although the solid-state structure of the bismuth derivative 6d could not be determined, it probably reveals the same constitution, which is unprecedented for bismuth.

The electronic structures of 6a–d have been investigated by DFT calculations, which are in excellent agreement with the experimentally determined geometric parameters, especially the elongated Mo–Mo distances. Although the Mo–Mo distances in 6a–d are longer than in the corresponding Mo\(_2\)EE' derivatives 1–5, the Wiberg bond orders in Löwdin orthogonalized basis are only slightly lower (for example: Mo–Mo 3.199 Å, WBI 0.53 in 6a vs. Mo–Mo 3.048 Å, WBI 0.53 in 1), indicating the presence of an elongated Mo–Mo single bond. This is also substantiated by the Intrinsic Bonding Orbitals, which show the presence of a Mo–Mo bond, although with additional orbital contribution from the CO groups (see Fig. S34 in the Supporting Information).

Besides making the novel hetero-dipnictogen complexes 3a–5 accessible, the synthetic strategy reported herein also allows to introduce substituted Cp ligands, such as tert-butylcyclopentadienyl (Cp’), to vary the solubility and the electronic as well as the steric properties of the complexes. This might be crucial for further reactivity studies. The following complexes were synthesised by using \([\text{Cp}\text{Mo(CO)}]_2\) as starting material exemplifying \([\text{Cp}\text{Mo(CO)}]_2(\mu-\eta^2-\text{AsSb}_2)]\) (7), \([\text{Cp}\text{Mo(CO)}]_2(\mu-\eta^2-\text{SB}_2)]\) (8) and \([\text{Cp}\text{Mo(CO)}]_2(\mu-\eta^2-\text{AsSb})\) (3b).

The complexes 7 and 8 had already been synthesised by our group in the past, even though with a remarkably low yield hampering the investigation of further reactivity. Nonetheless, they had already proved to be suitable starting materials for building different anionic pnictogen frameworks upon reduction. This shows the necessity of making these compounds available in a larger scale, which can be achieved via the new synthetic route. That way, the yields of the complexes 7 (5.4%–55%) and 8 (6.0%–29%) can be dramatically increased and also the unprecedented compound 3b can be obtained in a remarkably good yield of 49%.

Interestingly, the \(^1\text{H}\) NMR spectrum of 3b (in contrast to the spectra of 7 and 8) shows three multiplets in a ratio of 1:2:1 for the aromatic protons instead of the expected two triplets, which indicates that the protons in 2,5 and 3,4 position, respectively, are not chemical or magnetical equivalent in 3b. This is confirmed by \(^{13}\text{C}\)\(^{1}\text{H}\) NMR spectroscopy, where four singlets instead of two for the proton bound C atoms of the Cp’ ring are observed.

Furthermore, orange red crystals suitable for X-ray diffraction of the complexes 3b, 7 and 8 could be obtained by cooling saturated CH\(_2\)Cl\(_2\) solutions from room temperature to −30°C. Their solid-state structures (cf. Figure 3 for 3b) show tetrahedral Mo\(_2\)EE' cores, which are almost identical to their Cp congeners.

Conclusions

We developed a new and easy one-pot synthesis of air-stable tetrahedral dimolybdenum dipnictogen complexes, which en-
ables not only an impressive yield improvement (see Table 1) for the already known hetero-dipnictogen complexes [CpMo(CO)_3(μ-E(SiMe_3)N)] (E = As (1), Sb (2)) and the homo-dipnictogen complexes Mo_2E_2 (E = P, As, Sb, Bi), but, more importantly, also gives access to unprecedented complexes containing the heavier hetero-dipnictogen ligands AsSb (3), AsBi (4) and SbBi (5). Now, these syntheses can also be carried out in a multigram scale. The complexes 3–5 extend the very rare class of E_2 ligand complexes of the exotic diatomic AsSb as well as representing the first ever examples in which these covalent bonds between two different heavy pnictogen atoms tetrahedrane analogues, with all of them featuring very rare for the already known hetero-dipnictogen complexes [CpMo(CO)_3(μ-E(SiMe_3)N)] (E = As, Sb, Bi, P), 2061903, 2061904, 2061910, 2061906, 2061907, 2072587 ([CpMo(CO)_3(μ-E(SiMe_3)N)]) contain(s) the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

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**Conflict of Interest**

The authors declare no conflicts of interest.

**Keywords:** pnictogen · bismuth · antimony · molybdenum · mixed main group elements

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New synthetic pathway towards organometallic tetrahedrane derivatives $[[\text{CpMo(CO)}_2]_2(\mu_2: \eta^2_2:\eta^2_{EE'})]$ ($E \neq E' = P$, As, Sb, Bi) involving a hetero-dipnictogen ligand is reported, leading to dramatic yield enhancements for already known compounds, the reduction of reaction steps and access to so far unknown $\text{AsSb}$, $\text{AsBi}$ and $\text{SbBi}$ ligand complexes, which feature unseen covalent bonds between two different heavy group 15 elements without organic substituents.

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Synthesis of Tetrahedranes Containing the Unique Bridging Hetero-Dipnictogen Ligand $EE'$ ($E \neq E' = P$, As, Sb, Bi)