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A Terminal Molybdenum Arsenide Complex Synthesized from Yellow Arsenic

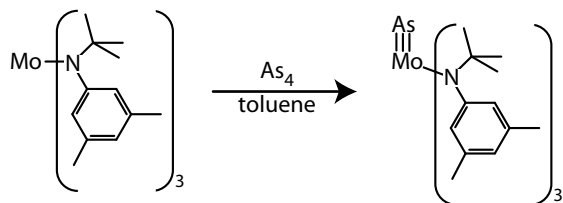
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The atomic ligands of the heaviest group 15 elements (As, Sb, and Bi) remain rarely encountered in transition metal chemistry.^{1,2} Examples of molecules that contain one of these pnictogens as a terminal ligand are currently limited to complexes of Mo, Nb and W.^{3–6} Surprisingly versatile with regard to formation of terminal multiple bonds is the three-coordinate compound, Mo[N(^{*i*}Bu)Ar]₃, **1**, which has been used as a precursor to stable compounds containing bonds to both heavy and light atomic ligands: E≡Mo[N(^{*i*}Bu)Ar]₃ where E = C[–], N, P, O, S, Se, Te.^{7–12} Moreover, this *d*³, C_{3v} transition-metal fragment is isolobal to those free atoms belonging to group 15,¹³ providing an ideal platform for the formation of triple bonds to these elements when they are presented to **1**, as demonstrated for N₂ and P₄.^{8,10,14} While metallic arsenic is unreactive towards **1**, molecular As₄ serves as a reactive and soluble source of arsenic.^{6,15–18} Here we report the synthesis of As≡Mo[N(^{*i*}Bu)Ar]₃, **1-As**, via the activation of As₄ by **1**.

Heating grey arsenic metal to ca. 650 °C provided a source of As₄ vapors that were trapped by passage through toluene cooled to –40 °C. This protocol afforded a slurry of As₄ in toluene that was amenable to use as a source of zero-valent arsenic.⁶ Addition of **1** to this slurry at –40 °C followed by warming to 20 °C led to direct formation of the triple bond between Mo and As yielding **1-As** (Scheme 1). This compound was isolated as a yellow powder in 67% yield following extraction and precipitation from Et₂O/*n*-pentane at –35 °C. An X-ray diffraction study was carried out on a yellow single crystal grown from Et₂O solution at –35 °C. The molecule **1-As** crystallizes in the chiral space group *P*2₁, with chirality induced by the propeller orientation of the three anilide ligands about the Mo–As core (Figure 1). This structure revealed a short Mo–As distance of 2.2248(5) Å. This is comparable to, but slightly shorter than, the known terminal arsenide complexes of molybdenum (2.252(3) Å) and tungsten (2.2903(11) Å) that bear a trisamidoamine ligand, (Me₃SiNCH₂CH₂)₃N, and contain a donor *trans* to the triple bond.^{3,4} The value also agrees well with the sum of the triple-bond covalent radii for As (1.06 Å) and Mo (1.13 Å).¹⁹

Scheme 1. Synthesis of **1-As**



To further characterize the uncommon Mo–As bonding pair presented by **1-As**, vibrational spectroscopy was employed because it is a valuable tool for studying metal-ligand multiple bonds.²⁰ Initially, we sought to identify the resonant frequency of the Mo–As oscillator present in **1-As**. Vibrational data were acquired on P≡Mo[N(^{*i*}Bu)Ar]₃ (**1-P**) and **1-As** by both infrared (IR) and Raman spectroscopies. In the far-IR (600 – 200 cm^{–1}; CsI pellet), the

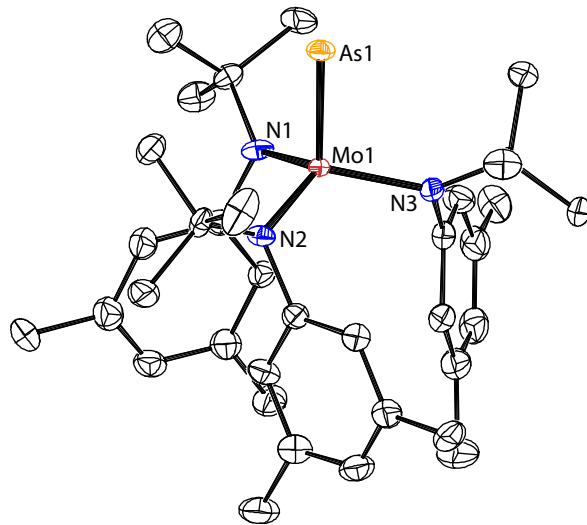


Figure 1. Thermal ellipsoid plot (50% probability) of **1-As** with hydrogen atoms omitted for clarity.

spectra of these two compounds were nearly identical with the exception of two resonant absorptions located at 538 and 394 cm^{–1}. The lower frequency vibration at 394 cm^{–1} was assigned to the Mo–As stretching mode for **1-As**, whereas the band at 538 cm^{–1} was assigned to **1-P**. These frequencies matched the Stokes shifts measured by Raman spectroscopy on powder samples of **1-As** and **1-P**. Interestingly, both of these vibrational modes had a stronger relative intensity in the Raman spectrum than in the far-IR spectrum. Additional far-IR data and Raman spectroscopy data acquired on ^{14/15}N≡Mo[N(^{*i*}Bu)Ar]₃ lacked these signals while reproducing other features observed in spectra of **1-E** (E = As, P); therefore, these data corroborated the assignment of these vibrations.

Vibrational force constants have a linear correlation with bond order; therefore, these values offer another means of characterizing the Mo–E bond.²¹ Using the harmonic oscillator approximation, we found a force constant of 3.87 mdyne Å^{–1} for **1-As** and 4.02 mdyne Å^{–1} for **1-P**. These values are approximately half of the 7.86 mdyne Å^{–1} found for N≡Mo[N(^{*i*}Bu)Ar]₃, **1-N**.¹⁴ The series of compounds defined by **1-E** compares well to the pnictogens reported by Schrock, E≡Mo(Me₃SiNCH₂CH₂)₃N, *k*_{MoAs} = 3.47 mdyne Å^{–1}, *k*_{MoP} = 3.74 mdyne Å^{–1}, and *k*_{MoN} = 7.26 mdyne Å^{–1}.^{3,22} These force constants were interpreted to correspond to a M–E bond order of 3 for each pnictogen.²² The slightly larger force constants for the series **1-E** relative to those found in the complexes of Schrock are likely a reflection of stronger bonds. The origin of these differences is not entirely straightforward, but could be attributed the lack of a donor in the position *trans* to the triply-bonded ligand in the series **1-E**.

Bonding in **1-As** was further examined by quantum chemical calculations, using the X-ray coordinates as a starting point for geometry optimization.^{23,24} This analysis shows that the HOMO and

HOMO-1 of **1-As** are the π symmetry bonding orbitals between Mo and As. Correspondingly, the LUMO and LUMO+1 orbitals are the antibonding counterparts. These orbitals are separated by a HOMO-LUMO gap of 2.3 eV, which may be taken as a qualitative measure of the bonding interaction.²⁵ In contrast to bonding patterns of the lighter elements (C, N, O), the heavier main group elements are characterized by a stabilized orbital of largely s character sometimes called an “inert pair”.^{26,27} Therefore, we anticipated that the orbital that contained the most arsenic 4s character would be much lower in energy relative to the π symmetry bonding orbitals; this orbital (HOMO-78) was located 8.7 eV below the HOMO.

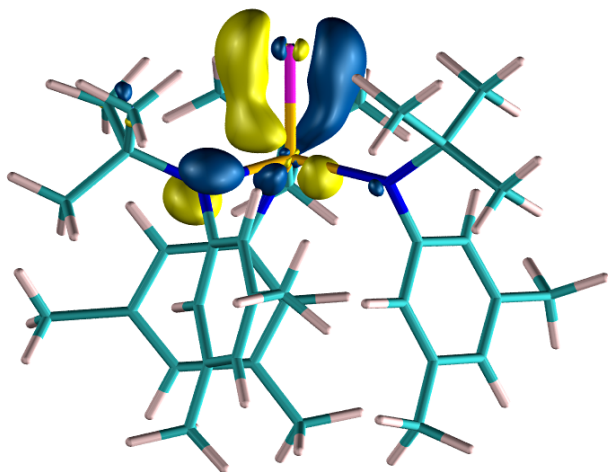


Figure 2. The HOMO of **1-As** appears π bonding with respect to Mo and As. This orbital is shown at an isosurface value 0.07.

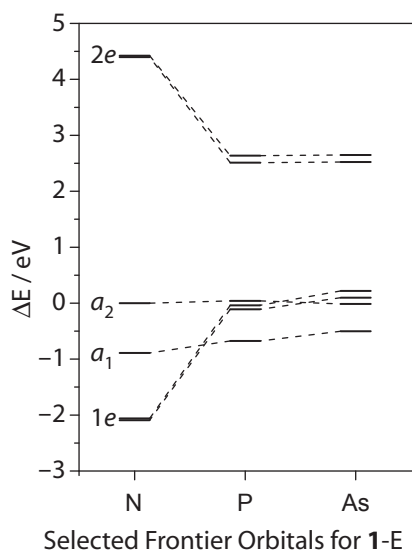


Figure 3. A graph that correlates selected frontier orbitals for the series of compounds $E\equiv Mo(N[{}^tBu]Ar)_3$ ($E = N, P, As$). Here the $1e$ orbital refers to the $E-Mo$ π bond, while $2e$ is the antibond; the a_1 orbital is the highest lying orbital with pseudo- C_{3v} symmetry. The a_2 orbital is a combination of anilide orbitals that finds no symmetry match on Mo in a C_{3v} field.

Having isolated all the compounds in the series $E\equiv Mo(N[{}^tBu]Ar)_3$ ($E = N, P, As$) prompted us to compare the frontier orbitals among the compounds in this series using quantum chemical methods. For all three compounds, the combination of p orbitals on the anilide nitrogens that is primarily non-bonding with respect to Mo were found to have similar energy (Figure 3, a_2).²⁸ This is consistent

with the notion that the ligand-based non-bonding molecular orbital in a pseudo- C_{3v} -symmetric field is not greatly altered by the atomic ligand triply bound to Mo. We noted that upon moving from N to P and As there is a drastic decrease in the splitting between the π symmetry bonding and antibonding orbitals that is consistent with the notion that heavier elements form less stable π bonds (Figure 3, $1e$ and $2e$).²⁹ In the case for $E = N$, the π bond lies approximately 2 eV below the HOMO. The corresponding orbital is higher in energy for $E = P$ and becomes the HOMO for $E = As$. This trend is what one would expect based on considerations of electronegativity: the triple bond to nitrogen contains significant ionic contributions that serve to stabilize the π bonds by polarizing them toward the electronegative element. Similar trends have been documented for the related chalcogen series $AMo(N[{}^tBu]Ar)_3$ ($A = O, S, Se, Te$).¹¹ The orbital labeled a_1 is the highest filled orbital that is symmetric about the C_3 axis (Figure 3). Upon changing from N to P to As this orbital is only slightly destabilized. For **1-N**, this orbital corresponds to the nitrogen lone pair; however, the nature of this orbital changes upon descending the pnictogen series.^{26,27,30}

Table 1. Bond dissociation energies, stretching force constants, bond lengths, and calculated bond indices for the terminal pnictogen complexes **1-E**

	BDE ^a	k^b	r_{exp}^c	Bond Index ^d
1-As	~74	3.87	2.2248(5)	2.4853
1-P	92.2	4.02	2.119(4)	2.5109
1-N	155.3	7.86	1.651(4)	2.7038

^a Values are in kcal/mol and experimentally determined for **1-P** and **1-N**; ^{31,32} the value is calculated for **1-As** (see Supporting Information).

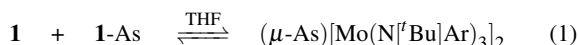
^b Values are in mdyne/Å calculated using the harmonic oscillator approximation. ^c Experimental bond length from X-ray diffraction studies. ^d Nalewajski-Mrozek bond index.

The Nalewajski-Mrozek (N-M) Bond Index is a quantitative measure of bond order that has recently been applied to metal-ligand multiple bonds.³³ This measure was found to correlate well with chemical intuition of bond order and yield bond multiplicities that are relatively independent of the chosen basis set.³³ For these reasons, it seemed worthwhile to compare the quantitative N-M bond index for the Mo-E bond contained in **1-E** ($E = N, P, As$). The computed values for the N-M multiplicities are reported in Table 1, alongside experimental measurements of the Mo-E multiple bond. The values of the N-M bond index support our suggestion that the three complexes, **1-E**, all contain a considerable degree of molybdenum-pnictogen multiple bonding. The bond index was observed to decrease in the order $Mo-N \gg Mo-P > Mo-As$. This behavior parallels our results obtained from both vibrational spectroscopy and qualitative molecular orbital analysis which suggest that the Mo-N bond is considerably stronger in **1-N** than the Mo-E bond in **1-P** and **1-As**. Solution-phase thermochemistry data have been used to estimate the triple bond dissociation energies for **1-N** and **1-P** as 155.3 and 92.2 kcal/mol, respectively.^{31,32} Calculations on this series suggest that the Mo-As triple bond is nearly 18 kcal/mol weaker than the M-P triple bond, in contrast to the dramatic 60 kcal/mol weakening observed upon going from N to P.

The reactivity of **1-As** was briefly explored to provide a comparison to the related molecules **1-N** and **1-P**. In general, the reactivity of **1-As** was found to be quite limited. For example, **1-As** was not found to engage in a reaction with MeOTf under the mild conditions that afford methylation of **1-N**.³⁴ Nor was **1-As** found to abstract a sulfur atom from $SSbPh_3$, a reagent which readily transfers its chalcogen to **1-P**.¹² Similarly, the potent O-atom transfer reagent dimethyldioxirane (DMDO) will afford $OPMo(N[{}^tBu]Ar)_3$ from **1-P**,³⁵ but we were unable to obtain $OAsMo(N[{}^tBu]Ar)_3$ us-

ing this methodology; only unreacted **1**-As was recovered from the reaction mixture.

One reaction that **1**-As was found to engage in was a reversible capping by **1** to form the complex $(\mu\text{-As})[\text{Mo}(\text{N}^t\text{BuAr})_3]_2$ (**2**, Eq. 1). Upon cooling an equimolar mixture of **1**-As and **1** to -80°C , the originally yellow-brown solution took on a bright purple hue, indicative of formation of $(\mu\text{-As})[\text{Mo}(\text{N}^t\text{BuAr})_3]_2$. This color change was reversible upon repeated cooling and warming cycles. The thermodynamic parameters for this reversible reaction were extracted from a van't Hoff plot of equilibrium constants measured by ^1H NMR spectroscopy in 5°C intervals over the temperature range -54 to -96°C . This analysis yielded the parameters $\Delta H = -12.4(1.6)$ kcal/mol and $\Delta S = -59(8)$ e.u. The very large negative entropy for the reaction to form **2** is consistent with the large decrease in degrees of freedom imposed by the interdigitation of *tert*-butyl groups that is required to accommodate the short, one-atom bridge in **2**. A very similar value for ΔS of -56 e.u. was found for the formation of the related $\mu\text{-S}$ complex from the terminal sulfide complex $\text{SMo}(\text{N}^t\text{BuAr})_3$ and **1**.¹² Both this $\mu\text{-S}$ complex and the related $\mu\text{-P}$ complex, $(\mu\text{-P})[\text{Mo}(\text{N}^t\text{BuPh})_3]_2$, are observed to form at -35°C , a temperature at which the $\mu\text{-As}$ complex is unobserved.^{12,36} This contrast can be attributed to a less negative enthalpy associated with formation of **2**. This in turn can be ascribed to a manifestation of the inert-pair effect. This low energy lone pair is also likely responsible for the lack of reactivity toward the reagents mentioned above (MeOTf , SSbPh_3 , and DMDO) that would seek to engage this electron pair in bonding interactions.



Herein we have reported the preparation and X-ray crystal structure of **1**-As, a compound that contains a Mo–As triple bond and is one of very few compounds with a bone fide one-coordinate As atom in the solid state.³⁷ The molecular structure has been examined by vibrational spectroscopy and quantum chemical methods, and discussed in relationship to its congeners **1**-N and **1**-P. Comparison of the Mo–E multiple bonds within this series, as well as those reported by Schrock and Scheer,^{3,4,22} allows features that are characteristic of multiple bonding to be contrasted between the lighter and heavier elements. The results summarized herein show that the characteristics of Mo–E bonding within **1**-E are largely preserved for E = As or P, and that the most pronounced differences in the Mo–E bond are noted when comparing one of these two molecules to **1**-N. These results agree with the idea that the lighter elements (C, N, O) deviate from “normal” chemical behavior in their unique propensity to form strong multiple bonds.³⁸

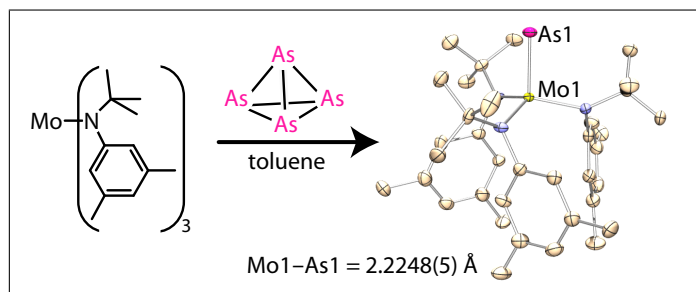
Acknowledgement The authors thank the United States National Science Foundation for support through grant CHE-719157 and Prof. Karsten Meyer for his generous contribution of the As_4 -generating apparatus.

Supporting Information Available: Experimental procedures and characterization data for **1**-As and **2**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- A search of the Cambridge Structural Database on July 20, 2009, revealed four such molecules: $\text{As}\equiv\text{M}(\text{Me}_3\text{SiNCH}_2\text{CH}_2)_3\text{N}$ (M = Mo, W),^{3,4} 2,4,6- $^t\text{Bu}_3\text{C}_6\text{H}_2\text{C}\equiv\text{As}$,³⁹ and $[(\text{F}_3\text{C})_3\text{BC}\equiv\text{As}]^-$.⁴⁰
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Graphical TOC Entry



A terminal molybdenum arsenide complex is synthesized in one step from the reactive As_4 molecule. The properties of this complex with its arsenic atom ligand are discussed in relation to the analogous nitride and phosphide complexes.