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. Examples of molecules that contain one of these pnictogens as a terminal ligand are currently limited to complexes of Mo, Nb and W.\textsuperscript{3–6} Surprisingly versatile with regard to formation of terminal multiple bonds is the three-coordinate compound, \(\text{Mo}(\text{N}^3\text{Bu})\text{Ar})_3\), \(\text{I}\), which has been used as a precursor to stable compounds containing bonds to both heavy and light atomic ligands: \(\text{E}\equiv\text{Mo}(\text{N}^3\text{Bu})\text{Ar})_3\) where \(\text{E} = \text{C}^−\), N, P, O, S, Se, Te.\textsuperscript{7–12} Moreover, this \(\text{Mo}^1\text{As}^3\) transition-metal fragment is isovalent to those free atoms belonging to group 15,\textsuperscript{13} providing an ideal platform for the formation of triple bonds to these elements when they are presented to \(\text{I}\), as demonstrated for \(\text{N}^3\text{As}^4\) and \(\text{P}^4\). While metallic arsenic is unreactive towards \(\text{I}\), molecular \(\text{As}^4\) serves as a reactive and soluble source of arsenic.\textsuperscript{6,15–18} Here we report the synthesis of \(\text{As}≡\text{Mo}(\text{N}^3\text{Bu})\text{Ar})_3\), \(\text{I}\)-\(\text{As}^4\), via the activation of \(\text{As}^4\) by \(\text{I}\).

Heating grey arsenic metal to ca. 650 °C provided a source of \(\text{As}^4\) vapors that were trapped by passage through toluene cooled to −40 °C. This protocol afforded a slurry of \(\text{As}^4\) in toluene that was amenable to use as a source of zero-valent arsenic.\textsuperscript{6} Addition of \(\text{I}\) 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 \(\text{I}\)-\(\text{As}^4\) (Scheme 1). This compound was isolated as a yellow powder in 67% yield following extraction and precipitation from \(\text{Et}_2\text{O}\) solution at −35 °C. An X-ray diffraction study was carried out on a yellow single crystal grown from \(\text{Et}_2\text{O}\) that lacked these signals while reproducing the \(\text{Mo}^1\text{As}^3\) 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, \((\text{Me}_3\text{Si})\text{NCH}_3\text{CH}_2\text{N})\text{N}\), and contain a donor trans to the triple bond.\textsuperscript{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).\textsuperscript{19}

**Scheme 1.** Synthesis of \(\text{I}\)-\(\text{As}^4\)

\[
\begin{align*}
\text{Mo}\left(\begin{array}{c}
\text{N} \\
\text{N} \\
\text{N}
\end{array}\right)_3 & \quad \text{As}^4 \quad \text{toluene} \quad \text{As}^4 \quad \text{Mo}\left(\begin{array}{c}
\text{N} \\
\text{N} \\
\text{N}
\end{array}\right)_3
\end{align*}
\]

To further characterize the uncommon Mo–As bonding pair presented by \(\text{I}\)-\(\text{As}^4\), vibrational spectroscopy was employed because it is a valuable tool for studying metal-ligand multiple bonds.\textsuperscript{20} Initially, we sought to identify the resonant frequency of the Mo–As oscillator present in \(\text{I}\)-\(\text{As}^4\). Vibrational data were acquired on \(\text{P}=\text{Mo}(\text{N}^3\text{Bu})\text{Ar})_3\) (I-P) and \(\text{I}\)-\(\text{As}^4\) by both infrared (IR) and Raman spectroscopies. In the far-IR (600 – 200 cm\(^{-1}\)), CsI pellet, the 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 \(\text{I}\)-\(\text{As}^4\), whereas the band at 538 cm\(^{-1}\) was assigned to \(\text{I}\)-\(\text{P}\). These frequencies matched the Stokes shifts measured by Raman spectroscopy on powder samples of \(\text{I}\)-\(\text{As}^4\) and \(\text{I}\)-\(\text{P}\). 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 \(\text{N}=\text{Mo}(\text{N}^3\text{Bu})\text{Ar})_3\) lacked these signals while reproducing other features observed in spectra of \(\text{I}\)-\(\text{E}^1\) (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.\textsuperscript{21} Using the harmonic oscillator approximation, we found a force constant of 3.87 mdyne Å\(^{-1}\) for \(\text{I}\)-\(\text{As}^4\) and 4.02 mdyne Å\(^{-1}\) for \(\text{I}\)-\(\text{P}\). These values are approximately half of the 7.86 mdyne Å\(^{-1}\) found for \(\text{N}=\text{Mo}(\text{N}^3\text{Bu})\text{Ar})_3\), I-N.\textsuperscript{14} The series of compounds defined by \(\text{I}\)-\(\text{E}\) compares well to the pnictogens reported by Schrock, \(\text{E}=\text{Mo}(\text{Me}_3\text{Si})\text{NCH}_3\text{CH}_2\text{N}\), \(k_{\text{MoAs}} = 3.47\) mdyne Å\(^{-1}\), \(k_{\text{MoP}} = 3.74\) mdyne Å\(^{-1}\), and \(k_{\text{MoN}} = 7.26\) mdyne Å\(^{-1}\).\textsuperscript{3,22} These force constants were interpreted to correspond to a M–E bond order of 3 for each pnictogen.\textsuperscript{22} The slightly larger force constants for the series \(\text{I}\)-\(\text{E}\) 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 \(\text{I}\)-\(\text{E}\).

Bonding in \(\text{I}\)-\(\text{As}^4\) was further examined by quantum chemical calculations, using the X-ray coordinates as a starting point for geometry optimization.\textsuperscript{23,24} This analysis shows that the HOMO and
HOMO–1 of 1-As are the \( \pi \) 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 \( \pi \) symmetry bonding orbitals; this orbital (HOMO–78) was located 8.7 eV below the HOMO.

![Figure 2](image.png)

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

Having isolated all the compounds in the series \( \text{E} = \text{Mo}[\text{N}^3\text{Bu}]\text{Ar}_3 \) (\( \text{E} = \text{N, P, As} \)) we prompted us to compare the frontier orbitals among the compounds in this series using quantum chemical methods. For all three compounds, the combination of \( \rho \) orbitals on the anilide nitrogens that is primarily non-bonding with respect to Mo were found to have similar energy (Figure 3, \( \alpha_2 \)).\(^{28}\) 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 \( \pi \) symmetry bonding and antibonding orbitals that is consistent with the notion that heavier elements form less stable \( \pi \) bonds (Figure 3, 1e and 2e).\(^{29}\) In the case for \( \text{E} = \text{N} \), the \( \pi \) bond lies approximately 2 eV below the HOMO. 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 \( \pi \) bonds by polarizing them toward the electronegative element. Similar trends have been documented for the related chalcogen series \( \text{AMo}[(\text{N}^3\text{Bu})\text{Ar}]_3 \) (A = O, S, Se, Te).\(^{11}\) The orbital labeled \( \alpha_1 \) 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.\(^{26, 27, 30}\)

| \( \text{E} \) | \( \text{BDE}^a \) (kcal/mol) | \( \text{r}_{\text{exp}}^b \) (Å) | Bond Index\(^c\) |
|---|---|---|---|
| 1-As | \( \sim 74 \) | 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.\(^{31, 32}\) \(^b\) The value is calculated for 1-As (see Supporting Information). \(^c\) Bond indices are in \( \text{mdyne/Å} \) calculated using the harmonic oscillator approximation. \(^d\) Experimental bond length from X-ray diffraction studies. \(^e\) Nalewajski-Mrozek bond index.

The Nalewajski-Mrozek (N-M) Bond Index is a quantitative measure of bond order that has recently been applied to metallic 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 (\( \text{E} = \text{N, P, As} \)). The computed values for the N-M multiplicity 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 Mo–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 dimethylidioxirane (DMDO) will afford OPtMo(N\(^3\)Bu)Ar\(_3\) from 1-P,\(^{35}\) but we were unable to obtain OPtMo(N\(^3\)Bu)Ar\(_3\) us-

![Figure 3](image.png)

**Figure 3.** A graph that correlates selected frontier orbitals for the series of compounds \( \text{E} = \text{Mo}[\text{N}^3\text{Bu}]\text{Ar}_3 \) (\( \text{E} = \text{N, P, As} \)). Here the 1e orbital refers to the E–Mo \( \pi \) bond, while 2e is the antibond; the \( \alpha_1 \) orbital is the highest lying orbital with pseudo-\( C_{3v} \) symmetry. The \( \alpha_2 \) orbital is a combination of anilide orbitals that finds no symmetry match on Mo in a \( C_{3v} \) field.
ing this methodology; only unreacted I-As was recovered from the reaction mixture.

One reaction was found to engage in was a reversible capping by 1 to form the complex (µ-As)[Mo(N[N-Bu]Ar)]$_2$ (2, Eq. 1). Upon cooling an equimolar mixture of I-As and 1 to -80°C, the originally yellow-brown solution took on a bright purple hue, indicative of formation of (µ-As)[Mo(N[N-Bu]Ar)]$_2$. 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 $^1$H NMR spectroscopy in 5°C intervals over the temperature range -54 to -96°C. This analysis yielded the parameters $\Delta H = -12.4(1.6)$ kJ/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 $\Delta S$ of -56 e.u. was found for the formation of the related µ-S complex from the terminal sulfide complex Smo(N[N-Bu]Ar) and I.$^1,12$ Both this µ-S complex and the related µ-P complex, (µ-P)[Mo(N[N-Bu]Ph)]$_2$, are observed to form at ~35°C, a temperature at which the µ-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, SSBPh3, 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 I-As, a compound that contains a Mo–As triple bond and is one of very few compounds with a bond 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 Mo–E and discussed in relationship to its congeners Mo–P. The authors thank the United States National Science Foundation for support through grant CHE-7919157 and Prof. Karsten Meyer for his generous contribution of the As$_2$-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.

**Notes and References**

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