Inorganic Chemistry
Communication

Inorg. Chem. **2009**, *48*, 9599–9601 **9599**
DOI: 10.1021/ic9016068

A Terminal Molybdenum Arsenide Complex Synthesized from Yellow Arsenic

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Received August 25, 2009

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.

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 molybdenum, niobium, and tungsten.[3−6] Impressively versatile with regard to the formation of terminal multiple bonds is the three-coordinate compound Mo(N[^{t}Bu]Ar)$_3$ (**1**), which has been used as a precursor to stable compounds containing bonds to both heavy and light atomic ligands: EMo(N[^{t}Bu]Ar)$_3$, where E = C^-, N, P, O, S, Se, and 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 molybdenum, as demonstrated for N_2 and P_4.[8,10,14] While metallic arsenic is unreactive toward **1**, molecular As_4 serves as a reactive and soluble source of arsenic.[6,15−18]

Heating gray arsenic metal to ca. 650 °C provided a source of As_4 vapors, which were trapped by passage through toluene cooled to −40 °C.[6] The addition of **1** to this slurry at −40 °C followed by warming to 20 °C led to the 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 Et_2O/n-pentane at −35 °C. The molecule **1**-As crystallizes in the chiral space group $P2_1$, 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 triamidoamine ligand, $(Me_3SiNCH_2CH_2)_3N$, 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]

We sought to identify the resonant frequency of the Mo−As oscillator present in **1**-As.[20] Vibrational data were acquired on P≡Mo(N[^{t}Bu]Ar)$_3$ (**1**-P) and **1**-As by both 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 **1**-As, whereas the band at 538 cm^{-1} was assigned to the phosphide mode for **1**-P. These frequencies matched the

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Published on Web 09/18/2009

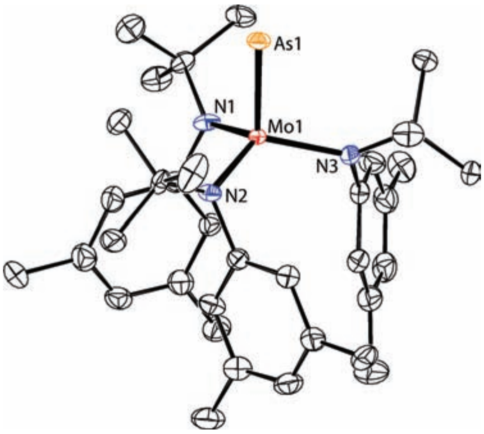
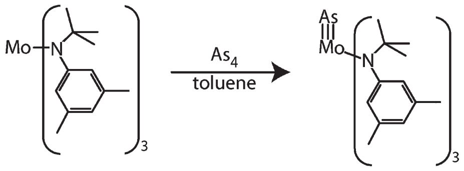


Figure 1. Thermal ellipsoid plot (50% probability) of **1**-As with hydrogen atoms omitted for clarity.

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



Stokes shifts measured by Raman spectroscopy on powder samples of **1**-As and **1**-P. Additional far-IR data and Raman spectroscopy data acquired on $^{14/15}$N≡Mo(N[^{t}Bu]Ar)$_3$ lacked these signals while reproducing other features observed in spectra of **1**-E (E = As and P).

Vibrational force constants have a linear correlation with the 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 mdyn/Å for **1**-As and 4.02 mdyn/Å for **1**-P. These values are approximately half of the 7.86 mdyn/Å value found for NMo(N[^{t}Bu]Ar)$_3$ (**1**-N).[14] The series of compounds defined by **1**-E compares well to the pnictogens reported by Schrock, EMo(Me$_3$SiNCH$_2$CH$_2$)$_3$N, k_{MoAs} = 3.47 mdyn/Å, k_{MoP} = 3.74 mdyn/Å, and k_{MoN} = 7.26 mdyn/Å.[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 highest occupied molecular orbital (HOMO) and HOMO−1 of **1**-As are the π-symmetry bonding orbitals between Mo and As. Correspondingly, the lowest unoccupied molecular orbital (LUMO) and LUMO+1 orbitals are the antibonding counterparts. These orbitals are separated by a HOMO−LUMO gap of 2.3 eV, a qualitative measure of the bonding interaction.[25] In contrast to bonding patterns of the lighter elements (C, N, and 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 4*s* 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.

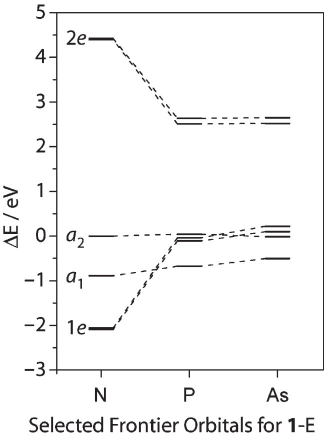


Figure 2. Graph that correlates selected frontier orbitals for the series of compounds E≡Mo(N[^{t}Bu]Ar)$_3$ (E = N, P, and As). Here the 1*e* orbital refers to the E−Mo π bond, while 2*e* is the antibond; the a_1 orbital is the highest-lying orbital with pseudo-C_{3v} symmetry. The a_2 orbital is a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

For all three compounds **1**-E, the combination of *p* orbitals on the anilide nitrogen atoms, which are primarily nonbonding with respect to Mo, was found to have similar energy (Figure 2, a_2).[28] This is consistent with the notion that the ligand-based nonbonding molecular orbital in a pseudo-C_{3v}-symmetric field is not greatly altered by the atomic ligand triply bound to Mo. 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.[29] 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. Similar trends have been documented for the related chalcogen series AMo(N-[^{t}Bu]Ar)$_3$ (A = O, S, Se, and Te).[11] The orbital labeled a_1 is the highest filled orbital that is symmetric about the C_3 axis. Upon changing from N to P to As, this orbital is only slightly destabilized. For **1**-N, this orbital corresponds to the nitrogen

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(30) The five atomic orbitals that contribute most to the highest occupied a_1-like orbital for the species **1**-E are listed: N, 109 A: N(p_z), 10.27%; C21(p_y), 9.09%; C33(p_x), 8.53%; C30(p_x), 7.32%; C18(p_y), 6.86%. P, 109 A: P(p_z), 37.81%; Mo(d_{z^2}), 8.92%; Mo(s), 4.15%; C21(p_x), 3.01%; C9(p_y), 2.85%. As, 180 A: As(p_z), 45.99%; Mo(d_{z^2}), 15.04%; Mo(s), 4.03%; C29(p_x), 2.88%; As(s), 2.68%.

lone pair; however, the nature of this orbital changes upon descending the pnictogen series.[26,27,30]

The Nalewajski–Mrozek (NM) bond index is a quantitative measure of the 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] Our computed values of NM multiplicities are reported in Table 1, alongside experimental measurements of the Mo–E multiple bond. The values of the NM bond index support our suggestion that the three complexes, **1**-E, all contain a considerable degree of Mo–E 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 in **1**-N is considerably stronger 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 (BDEs) 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.

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 that readily transfers its chalcogen to **1**-P.[12] Similarly, the potent oxygen-atom-transfer reagent dimethyldioxirane (DMDO) affords OPMo(N[^{t}Bu]Ar)$_3$ from **1**-P,[35] but we were unable to obtain OAsMo(N[^{t}Bu]Ar)$_3$ using 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 (μ-As)[Mo(N[^{t}Bu]Ar)$_3$]$_2$ (**2**, eq 1). Upon cooling of an equimolar mixture of **1**-As and **1** to −80 °C, the originally yellow-brown solution took on a bright-purple hue, indicative of the formation of (μ-As)[Mo(N[^{t}Bu]Ar)$_3$]$_2$. 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 ^{1}H NMR spectroscopy in 5 °C intervals over the temperature range −54 to −96 °C. This analysis yielded the parameters $\Delta H = -12.4(1.6)$ kcal/mol and $\Delta S = -59(8)$ eu. The very large negative entropy for the reaction to form **2** is consistent with the large decrease in the 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 eu was found for the formation of the related μ-S complex from the terminal sulfide complex SMo(N[^{t}Bu]Ar)$_3$ and **1**.[12] Both this μ-S complex and the related μ-P complex, (μ-P)[Mo(N[^{t}Bu]Ph)$_3$]$_2$, are observed to form at −35 °C, a temperature at which the μ-As complex is not observed.[12,36] This contrast is attributed to a less negative enthalpy associated with the 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.

Table 1. Bond Dissociation Energies (BDEs), 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 the Supporting Information). [b] Values are in mdyn/Å calculated using the harmonic oscillator approximation. [c] Experimental bond length from X-ray diffraction studies. [d] Nalewajski–Mrozek bond index.

$$\mathbf{1} + \mathbf{1}\text{-As} \rightleftharpoons (\mu\text{-As})[\mathrm{Mo(N[^tBu]Ar)_3}]_2 \qquad (1)$$

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 arsenic atom in the solid state.[37] A comparison of the Mo–E multiple bonds within the **1**-E 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 those of **1**-N. These results agree with the idea that the lighter elements (C, N, and O) deviate from "normal" chemical behavior in their unique propensity to form strong multiple bonds.[38]

Acknowledgment. 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: Crystallographic data in CIF format and 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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