

Triple-Bond Reactivity of an AsP Complex Intermediate:
Synthesis Stemming from Molecular Arsenic, As₄

Heather A. Spinney, Nicholas A. Piro, and Christopher C. Cummins*

Department of Chemistry, Massachusetts Institute of Technology,
Cambridge, Massachusetts 02139-4307

Received August 3, 2009; E-mail: ccummins@mit.edu

Abstract: While P₄ is the stable molecular form of phosphorus, a recent study illustrated the possibility of P₂ generation for reactions in organic media under mild conditions. The heavier group 15 element arsenic can exist as As₄ molecules, but As₄ cannot be stored as a pure substance because it is both light-sensitive and reverts thermally to its stable, metallic gray form. Herein we report As₄ activation giving rise to a μ -As₂ diniohium complex, serving in turn as precursor to a terminal arsenide anion complex of niobium. Functionalization of the latter provides the new AsPNMes* ligand, which when complexed with tungsten pentacarbonyl elicits extrusion of the (AsP)W(CO)₅ molecule as a reactive intermediate. Trapping reactions of the latter with organic dienes are found to furnish double Diels-Alder adducts in which the AsP unit is embedded in a polycyclic organic framework. Thermal generation of (AsP)W(CO)₅ in the presence of the neutral terminal phosphide complex P≡Mo(N[Pr]Ar)₃ leads to the *cyclo*-AsP₂ complex (OC)₅W(*cyclo*-AsP₂)Mo(N[Pr]Ar)₃. The (AsP)W(CO)₅ trapping products were crystallized and characterized by X-ray diffraction methods, and computational methods were applied for analysis of the As–As and As–P bonds in the complexes.

Introduction

Yellow arsenic (As₄) is attractive as a soluble, molecular source of this element for chemical synthesis in solution, but its use is complicated because it readily polymerizes to the metallic gray allotrope;¹ As₄ is photosensitive and thermally unstable as a solid, but exhibits good thermal stability in solution and in the gas phase. Bettendorff² has been credited as the first to report yellow arsenic,¹ and an early discussion of arsenic allotropes was provided by Linck.³ Stock and Siebert reported a method of As₄ generation using an electric arc,⁴ while Erdmann and von Unruh diagrammed an As₄ synthesis using what is essentially a simple tube furnace.⁵ Scherer et al. have utilized As₄ solutions prepared in that manner⁶ in xylene or decalin at reflux (140 or 170 °C, respectively) for reactions with transition-metal carbonyls in syntheses of *cyclo*-As_n ligands (*n*

= 3–6,8)⁷ and metal-arsenic clusters.⁸ Having prepared the first complexes containing ligated *cyclo*-P₃, Sacconi et al. reported generation of As₄ by the tube furnace method and its transformation to provide *cyclo*-As₃ as a bridging ligand.⁹ West et al. also described As₄ activation by the disilene system Mes₂Si=SiMes₂ in toluene solution.¹⁰ The foregoing is nearly an exhaustive summary of the known solution-phase reaction chemistry of the As₄ molecule. Herein we add to this body of knowledge that is derived from the tube furnace method of As₄ generation.⁵

In prior work we showed that the niobaziridine-hydride complex HNb(η^2 -*t*-BuHC=NAr)(N[Np]Ar)₂ (**1**, where Np = CH₂*t*-Bu and Ar = 3,5-C₆H₃Me₂; Figure 1) activates P₄ in organic solvents at 20 °C, and that the product of this activation is a μ -P₂ diniohium complex.¹¹ We went on to show that 2e reduction of the μ -P₂ diniohium complex elicited P–P bond cleavage with formation of a terminal phosphide anion complex, [P≡Nb(N[Np]Ar)₃][–].¹² The latter has proven to be quite versatile for transfer of the phosphide phosphorus atom to

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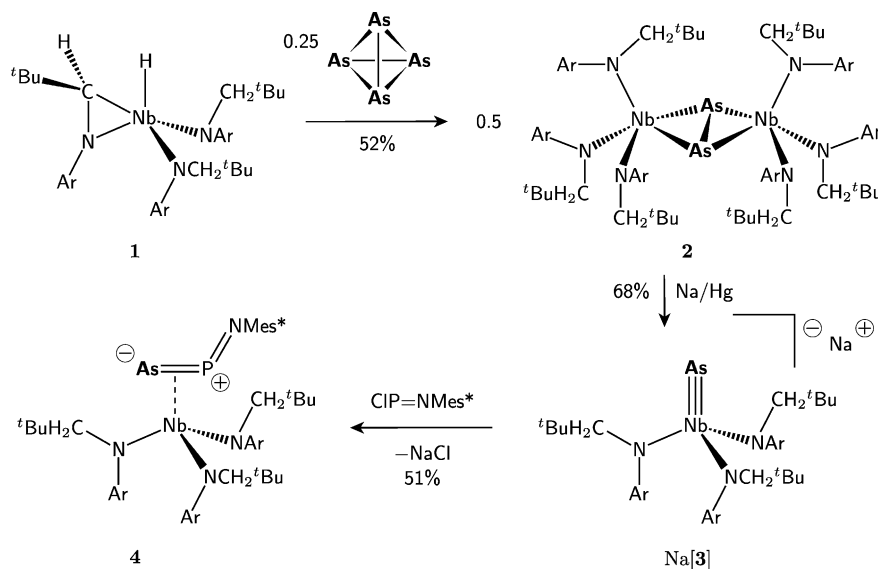


Figure 1. Three-step synthesis of the η^2 -AsPNMes* complex **4** in a sequence encompassing As₄ activation, μ -As₂ ligand reductive cleavage, and terminal arsenide functionalization with the [PNMes*]⁺ electrophile.

various electrophiles, resulting in interesting bound ligands or free main-group species.¹³ Of particular note is the functionalization of $[\text{P}=\text{Nb}(\text{N}[\text{Np}]\text{Ar})_3]^-$ with Niecke's chloroimino-phosphane, CIP=NMes* (Mes* = 2,4,6-C₆H₂tBu₃),¹⁴ leading to the synthesis of a diphosphaazide complex of niobium, (η^2 -PPNMes*)Nb(N[Np]Ar)₃, which upon thermolysis rearranges to the niobium(V) imido, (Mes*N)Nb(N[Np]Ar)₃, with loss of the P₂ molecule.¹⁵ As represented in a series of papers, we have gathered convincing evidence for the intermediacy of the free P₂ molecule as a reactive transient engaging in Diels-Alder reactions with organic dienes and undergoing addition to terminal phosphide M≡P triple bonds to yield *cyclo*-P₃ complexes.^{15,16} Similar triple-bond reactivity has likewise been exhibited by the tungsten pentacarbonyl complex of P₂, having the formula (P₂)W(CO)₅, a species also proposed to be accessible as a reactive transient intermediate.^{15–17} Accordingly, a primary aim of the present work was to investigate the As₄ activation chemistry of **1** in search of parallels with the prior line of inquiry based on P₄ activation.

A second aim of the present work was to discover if our established scheme for P₂ generation/transfer could be extended to provide access to the diatomic molecule AsP, either in free form or else stabilized as its tungsten pentacarbonyl complex. In the gas-phase phosphorus-arsenic system at 600–850 °C, it has been shown that the major species present are the tetrahedral molecules As_nP_{4–n} ($n = 0 - 4$; a selective, low-temperature route to AsP₃ was reported recently),¹⁸ but that the diatomic molecule AsP is also present as a significant percentage of the mixture

and plays an important role in the system.¹⁹ In contrast, the homonuclear diatomic molecules P₂ and As₂ have negligible concentration at these temperatures. An AsP solid solution phase has also been described for the arsenic-phosphorus system under the high-pressure conditions needed to suppress sublimation of the elements near 600 °C.²⁰ Vibrational signatures for the AsP molecule were first observed using a microwave discharge through a flowing mixture of AsCl₃ and PCl₃,²¹ and the molecule has been generated more recently by laser ablation of arsenic in the presence of PH₃.²² AsP has a measured dissociation energy of $429.7 \pm 12.6 \text{ kJ mol}^{-1}$,²³ and an equilibrium bond distance of 1.9995440(2) Å.²² Bimetallic complexes containing bridging AsP ligands have been synthesized by treating the salts [Li][M₂Cp₂(CO)₄(μ -PH₂)] (M = Mo, W) with an equivalent of AsCl₃,²⁴ however, no investigations of AsP triple-bond reactivity under preferred conditions for solution-phase organic reactions (25 °C, 1 atm) have been described.

Results and Discussion

Reaction of Niobaziridine Hydride with As₄. To a cold (–30 °C) solution of As₄ in toluene was added niobaziridine-hydride complex **1** via a solid addition tube, and then the reaction mixture was allowed to warm to room temperature in the dark (Figure 1). After stirring for 16 h, it was observed that the reaction mixture had attained a dark green color, indicative of μ -As₂ complex (μ_2 : η^2 , η^2 -As₂)[Nb(N[Np]Ar)₃]₂, **2**. Diarsenide complex **2** was then isolated as a bright green powder in 52% yield. A single-crystal X-ray diffraction study of complex **2** has not yet resulted in a high quality structure solution, but one

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Table 1. Topological Properties of Selected As–As and As–P Bonds

molecule ^a	distance ^b	ρ_b^c	n^d	$\nabla^2\rho^e$	ε^f	q_{As}^g	q_P^g
As ₂	2.108	0.134	3.00	−0.042	0.00	0.00	
E-HAs=AsH	2.255	0.110	2.00	−0.056	0.33	+0.31	
H ₂ AsAsH ₂	2.482	0.081	1.00	−0.043	0.00	+0.51	
As ₄	2.437	0.079	1.03	−0.003	0.07	+0.00	
AsP	2.006	0.153	3.00	−0.139	0.00	+0.10	−0.10
E-HAs=PH	2.155	0.125	2.00	−0.110	0.33	+0.35	+0.37
H ₂ AsPH ₂	2.366	0.094	1.00	−0.071	0.03	+0.55	+0.86
AsP ₃	2.324	0.091	1.04	−0.015	0.11	+0.17	−0.06
(μ -As ₂)[Nb(N[Me]Ph) ₃] ₂	2.364	0.084	1.14	+0.009	0.36	−0.53	
(η^2 -AsPNMes)Nb(N[Me]Ph) ₃	2.138	0.120	1.72	−0.048	0.06	−0.25	+0.67
(AsP[PW(CO) ₅])Mo(N[Me]Ph) ₃ ^h	2.328	0.090	1.03	−0.013	0.14	−0.00	−0.21
	2.244	0.103	1.28	−0.041	0.02	−0.00	−0.37
(As[PW(CO) ₅])(C ₆ H ₅) ₂	2.297	0.106	1.35	−0.088	0.04	+0.52	+0.36

^a All molecules geometry-optimized without symmetry constraints at the spin-restricted all-electron OLYP ZORA level of theory with QZ4P basis for As, P, Nb, TZ2P basis for C, N, W, and O and DZP basis for H atoms. ^b Distances given in Å. ^c Electron density in el/a_0^3 at the (3, −1) As–As or As–P bond critical point. ^d Bond order n according to the definition $n = \exp(A \times (\rho_b - B))$. For As–As bonds, $A = 19.7363$ and $B = 0.0774921$ as determined by least-squares fitting using As₂, E-HAs=AsH, and H₂AsAsH₂ as reference compounds for triple, double, and single bonds, respectively. For As–P bonds, $A = 17.23$ and $B = 0.088469$ using AsP, E-HAs=PH, and H₂AsPH₂ as reference systems. ^e The value of the Laplacian of the electron density at the (3, −1) As–As or As–P bond critical point in el/a_0^3 . ^f Ellipticity at the (3, −1) As–As or As–P bond critical point. ^g Atomic charge obtained by integration of the electron density over the respective As or P atomic basin. ^h First line of data refers to the As–P bond involving the P atom that is *not* ligated by W(CO)₅.

study did confirm the connectivity proposed for the molecule as drawn (Figure 1).

The most important structural parameter for complex **2** is the As–As interatomic distance, so the model system (μ_2 : η^2 : η^2 -As₂)[Nb(N[Me]Ph)₃]₂ was constructed and subjected to geometry optimization using density functional theory (DFT) methods to obtain r_{As-As} (calcd) = 2.365 Å. In the activation of As₄ by niobaziridine-hydride complex **1**, a rare example is generated of a molecule containing an M₂As₂ butterfly core. The only structurally characterized prior examples of such a molecule are (μ -As₂)[Mn(CO)₂Cp*]₂²⁵ and (μ -As₂)[Pd(PPh₃)₂]₂,²⁶ which have interarsenic distances of 2.225(1) and 2.274(1) Å, respectively. A related structural unit is represented by the complex [AsMoCp'(CO)₂]₂ (Cp' = ⁱPrC₅H₄),²⁷ in which there exists a Mo–Mo bond and the central As₂Mo₂ unit is an approximate tetrahedron with $r_{As-As} = 2.302(1)$ Å. The single-bond covalent radius for As is 1.21 Å,²⁸ while the double-bond covalent radius is 1.14 Å.²⁹ As such, As–As bonds are expected to be ca. 2.42 Å long, while As=As bonds are expected to be ca. 2.28 Å long, and based on the crystallographic data for the diarsane (Mes)₂-As–As(Mes)₂ (2.472(3) Å)³⁰ and the diarsene Mes*As=AsMes* (2.2634(3) Å),³¹ these are indeed acceptable values. By these criteria, our complex **2** (calculated $r_{As-As} = 2.365$ Å) might be assigned some As–As double bond character. To assess this in more detail, we turned to a topological analysis of the calculated electron density; calculated properties for several molecules from the present work as well as for some reference molecules are collected in Table 1. Consideration of the electron density ρ_b at the As–As bond critical point for our model system representing **2** gives a bond order $n = 1.14$ (Table 1). This is consistent with the representation of **2** as drawn in Figure 1 with an

interarsenic single bond. These values compare well with those calculated similarly for the spherical-aromatic³² As₄ molecule: $r_{As-As} = 2.4372$ Å (exp. = 2.44 Å).³³

Terminal Arsenide Anion Synthesis. Two-electron reduction of diarsenide **2** was achieved by treatment with an excess of 1% Na/Hg in tetrahydrofuran (THF) solvent. This led to the isolation in 68% yield of the [Na(THF)]⁺ salt of the arsenide complex anion [As=Nb(N[Np]Ar)₃][−], **3**, which was found to crystallize as a close-contact ion-paired dimer by X-ray diffraction analysis ($r_{As-Nb} = 2.3106(3)$ Å).³⁴ Also isolated and structurally characterized was the [Na(12-crown-4)₂]⁺ salt of anion **3**, and in this case there are no close contacts involving the one-coordinate As atom of the terminal arsenide anion ($r_{As-Nb} = 2.3078(5)$ Å, see Figure 2).

Terminal arsenide complexes—characterized by one-coordinate As that is triply bonded to a metal atom—are rare, but known examples include the triamidoamine-supported complexes As=Mo[(Me₃SiNCH₂CH₂)₃N] ($r_{As-Mo} = 2.252(3)$ Å)³⁵ and As=W[(Me₃SiNCH₂CH₂)₃N] ($r_{As-W} = 2.2903(11)$ Å).³⁶ Unlike the niobium arsenide **3**, the latter two complexes were not prepared *via* As₄ activation chemistry, but by treatment of the corresponding metal chloride compounds with lithium organoarsenide salts. A series of transition-metal Zintl phases containing one-coordinate As atoms (e.g., [Cs₇][As(InAs)₃-Nb≡As], $r_{As-Nb} = 2.390(2)$ Å) have also been reported,³⁷ and these represent the only instances other than our new complex **3** in which a metal terminal arsenide is also a component of an anion. For our purposes, this feature is expected to facilitate functionalization of the terminal arsenide unit.

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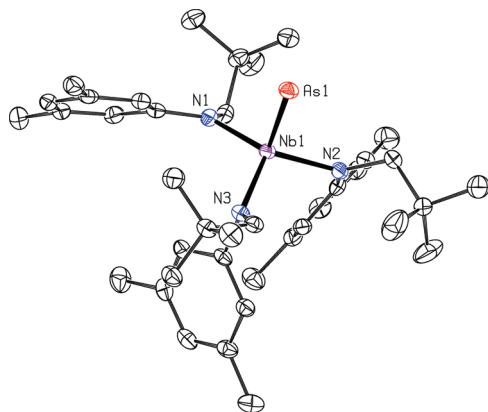


Figure 2. Molecular structure of anion **3** as found in crystals of the salt $[\text{Na}(12\text{-crown-4})][\text{As}=\text{Nb}(\text{N}[\text{Np}]\text{Ar})_3]$ shown with 50% probability thermal ellipsoids. Selected interatomic distances (Å) and angles (deg): Nb1–As1, 2.3078(5); Nb1–N1, 2.107(2); Nb1–N2, 2.058(2); Nb1–N3, 2.051(2); As1–Nb1–N1, 108.10(7); As1–Nb1–N2, 103.48(7); As1–Nb1–N3, 100.89(7).

To model the structure and bonding in anion **3**, the structure of anion $[\text{As}=\text{Nb}(\text{N}[\text{Me}]\text{Ph})_3]^-$ was geometry optimized with no counterion giving rise to a calculated $r_{\text{As-Nb}} = 2.295$ Å. This agrees well with the values observed in both the $[\text{Na}(12\text{-crown-4})_2]^+$ salt of anion **3** ($r_{\text{As-Nb}} = 2.3078(5)$ Å) and the close-contact ion-paired dimer ($r_{\text{As-Nb}} = 2.3106(3)$ Å) and suggests that cation-anion interactions do little to perturb the strong Nb–As bond. Addition of the triple-bond covalent radii for Nb (1.16 Å) and As (1.06 Å) gives a predicted value for a Nb≡As bond of 2.24 Å,³⁸ while similar addition of the double-bond covalent radii gives a predicted value for a Nb=As bond of 2.39 Å.²⁹ Thus we can conclude that the Nb–As bond in $[\text{As}=\text{Nb}(\text{N}[\text{Np}]\text{Ar})_3]^-$, **3**, contains significant triple bond character.

Preparation of the As=P=NMe₃* Complex. Functionalization of the terminal As atom in **3** was achieved by treatment of its $[\text{Na}(\text{THF})]^+$ salt with the phosphorus electrophile¹⁴ $\text{ClP}=\text{NMe}_3^*$ (Figure 1). This provided the desired complex, formulated as $(\eta^2\text{-AsPNMe}_3^*)\text{Nb}(\text{N}[\text{Np}]\text{Ar})_3$, **4**. After separation from NaCl, complex **4** was isolated in 51% yield as an orange-red solid. A spectroscopic signature of complex **4** is a ^{31}P NMR singlet at $\delta = 348$ ppm (benzene-*d*₆, 20 °C). For comparison, the corresponding central phosphorus atom in diphosphaazide complex $(\eta^2\text{-PPNMe}_3^*)\text{Nb}(\text{N}[\text{Np}]\text{Ar})_3$ resonates at $\delta = 335$ ppm.¹⁵ X-ray diffraction analysis (Figure 3) revealed arsaphosphaazide complex **4** to be nearly isostructural with the diphosphaazide complex reported previously, with the AsPNMe₃* ligand coordinated in an η^2 fashion to niobium *via* its terminal AsP moiety. The As–P and P–N bond distances in **4** ($r_{\text{As-P}} = 2.1296(6)$ Å, $r_{\text{P-N}} = 1.564(2)$ Å) are essentially identical in length to those reported in the phospharsene $(\text{Me}_3\text{Si})_2\text{-HCAs}=\text{PMes}^*$ ($r_{\text{As-P}} = 2.124(2)$ Å)³⁹ and the iminophosphane $(\text{Me}_3\text{Si})_3\text{CP}=\text{NMe}_3^*$ ($r_{\text{P-N}} = 1.566(3)$ Å),⁴⁰ and as such the AsPNMe₃* ligand is best represented as a heterocumulene containing As–P and P–N double bonds. A geometry optimization performed on the model compound $(\eta^2\text{-AsPNMe}_3^*)\text{Nb}(\text{N}[\text{Me}]\text{Ph})_3$ gave a calculated $r_{\text{As-P}} = 2.138$ Å and a topological

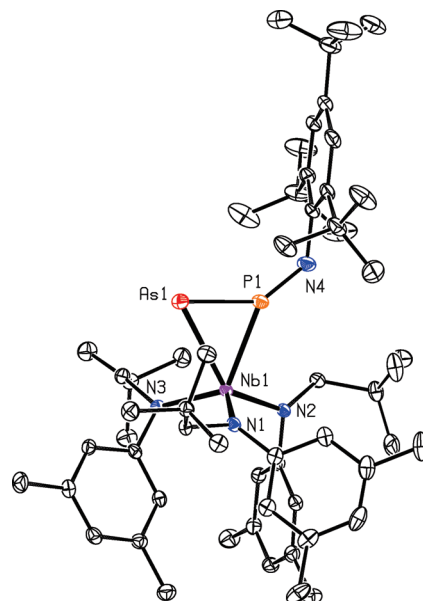


Figure 3. Molecular structure of complex **4** shown with 50% probability thermal ellipsoids. Selected interatomic distances (Å) and angles (deg): As1–P1, 2.1296(6); P1–N4, 1.564(2); Nb1–As1, 2.6704(3); Nb1–P1, 2.4799(6); As1–P1–N4, 140.56(8); As1–P1–Nb1, 70.335(19); Nb1–As1–P1, 60.989(17).

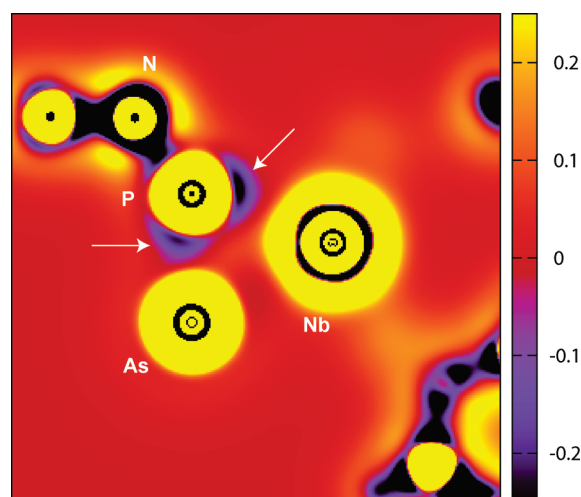


Figure 4. Plot of the Laplacian of the electron density in units of $el a_0^{-3}$ for the model system of **4**, $(\eta^2\text{-AsPNMe}_3^*)\text{Nb}(\text{N}[\text{Me}]\text{Ph})_3$; the plot is in a plane defined by the Nb, As, and P nuclei. Two small arrows indicate areas of valence-shell charge concentration in the P–Nb and P–As bonding regions.

analysis performed on the same molecule gave an As–P bond order $n = 1.72$ (Table 1). A plot of the Laplacian of the electron density for the model system for **4** is shown in Figure 4. The plot is in a plane defined by the Nb, As, and P nuclei and accumulation of valence-shell charge between P and As, as well as P and Nb, is clearly visible. The arsaphosphaazide ligand, AsPNMe₃*, is a new addition to a small group of heavy azide analogues,^{41,42} which also includes the diphosphaazide ligand, PPNMe₃*.

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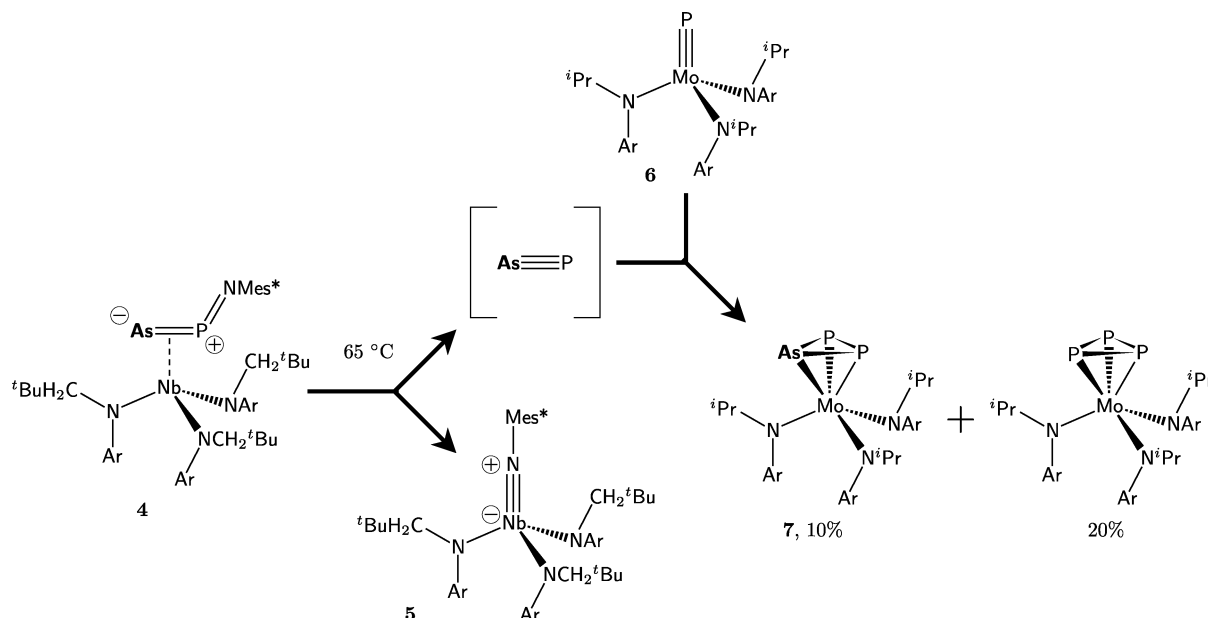


Figure 5. Thermolysis of the As=P=NMe^s* complex **4** results in fragmentation to the niobium imido **5** and the putative As≡P molecule. The latter fragment is absorbed by molybdenum terminal phosphide **6** to yield the new *cyclo*-AsP₂ complex **7**.

Thermolysis of the As=P=NMe^s* Complex with Conversion to a Niobium Imido Complex. Thermolysis of complex **4** was carried out under various conditions. Simple thermolysis in benzene-*d*₆ solution (60 °C, 3 h) gave near quantitative conversion to the known imido complex (Mes^s*N)Nb(N[Ar]₃), **5**, a molecule differing in its chemical formula from that of precursor **4** by only the AsP diatomic unit. An observed kinetic parameter for the first-order disappearance of **4** (benzene-*d*₆, 60 °C) is the rate constant $k = 2.9(1) \times 10^{-4} \text{ s}^{-1}$. Under these conditions, the ³¹P NMR signal for starting **4** was observed to decay away, while no new ³¹P NMR resonances were observed to grow in.

Thermolysis of **4** (65 °C, 3 h) in neat 1,3-cyclohexadiene or neat 2,3-dimethyl-1,3-butadiene did not lead to efficient AsP trapping. The ³¹P NMR spectra of the reaction mixtures showed disappearance of starting material and formation of a multitude of phosphorus-containing products. Attempts to isolate individual compounds from the mixtures were unsuccessful. Resonances at $\delta = -79$ ppm (1,3-cyclohexadiene) and $\delta = -52$ ppm (2,3-dimethyl-1,3-butadiene) were tentatively assigned to the double Diels-Alder adducts of AsP with the respective dienes based on the corresponding shifts for the P₂ adducts, P₂(C₆H₈)₂ ($\delta = -80$ ppm) and P₂(C₆H₁₀)₂ ($\delta = -52$ ppm).¹⁵ Integration of these ³¹P NMR resonances versus an internal standard (PPh₃) revealed that the proposed AsP trapping products, AsP(C₆H₈)₂ and AsP(C₆H₁₀)₂, were formed in 16% and 19% yields, respectively.⁴³

We have discovered previously that M≡P bonds are more effective traps for the P₂ molecule than are organic dienes, and react with P₂ in a one-to-one fashion to form *cyclo*-P₃ metal complexes.¹⁶ As such, **4** was also thermolyzed in benzene in the presence of P≡Mo(N[ⁱPr]Ar)₃, **6**,⁴⁴ with the goal of trapping AsP to form a *cyclo*-AsP₂ molybdenum complex (Figure 5).

The As=P=NMe^s* complex **4** and the molybdenum phosphide **6** do not react upon mixing at room temperature; however, following completion of thermolysis (70 °C, 3 h) two new singlets appeared in the ³¹P NMR spectrum at $\delta = -137$ and $\delta = -185$ ppm. The former is assigned to the new complex (*cyclo*-AsP₂)Mo(N[ⁱPr]Ar)₃, **7**, while the latter is assigned to the previously reported complex (*cyclo*-P₃)Mo(N[ⁱPr]Ar)₃, which has been prepared both *via* thermolysis of the diphosphaazide complex (η^2 -PPNMe^s*)Nb(N[Ar]₃) in the presence of **6**¹⁶ and *via* P₄ activation by Mo(H)(η^2 -Me₂C=NAr)(N[ⁱPr]Ar)₂.⁴⁵ Monitoring formation of **7** by ³¹P NMR (PPh₃ as internal standard) gave an overall yield of 10% for the *cyclo*-AsP₂ compound, compared to 20% for the *cyclo*-P₃ compound. The mixture of (*cyclo*-E₃)Mo(N[ⁱPr]Ar)₃ complexes was separated from the (Mes^s*N)Nb(N[Ar]₃) coproduct, **5**, by dissolving the crude solids from the reaction mixture in Et₂O and cooling the solution to -35 °C, whereupon white, fibrous crystals of the (*cyclo*-E₃)Mo(N[ⁱPr]Ar)₃ complexes precipitated. The (*cyclo*-AsP₂)Mo(N[ⁱPr]Ar)₃, **7**, and (*cyclo*-P₃)Mo(N[ⁱPr]Ar)₃ compounds are indistinguishable by ¹H and ¹³C NMR spectroscopy; only one set of resonances for the anilide ligands was observed when the mixture of the two compounds was dissolved in THF-*d*₈. Further attempts to separate **7** and (*cyclo*-P₃)Mo(N[ⁱPr]Ar)₃ by fractional crystallization were unsuccessful.

The only reported example of a *cyclo*-AsP₂ complex in the literature, (*cyclo*-AsP₂)CrCp(CO)₂, was also formed concomitantly with its *cyclo*-P₃ analogue.⁴⁶ The pair was synthesized by treating the tetrahedral complex [CrCp(CO)₂]₂(μ , η^2 -P₂) with one equivalent of AsCl₃, and the *cyclo*-AsP₂ complex ($\delta = -242$ ppm) appeared 43 ppm downfield from the *cyclo*-P₃ complex ($\delta = -285$ ppm) in the ³¹P NMR spectrum. Crystals of (*cyclo*-AsP₂)CrCp(CO)₂ were obtained in 10% yield *via* fractional crystallization of the reaction mixture. The formation of (*cyclo*-AsP₂)Mo(N[ⁱPr]Ar)₃, **7**, can be explained by a suprafacial [2 +

(43) As commented by a reviewer, the trapping of the AsP fragment with the dienes is somewhat tenuous, since it is based solely on the NMR shift obtained in a mixture of compounds.

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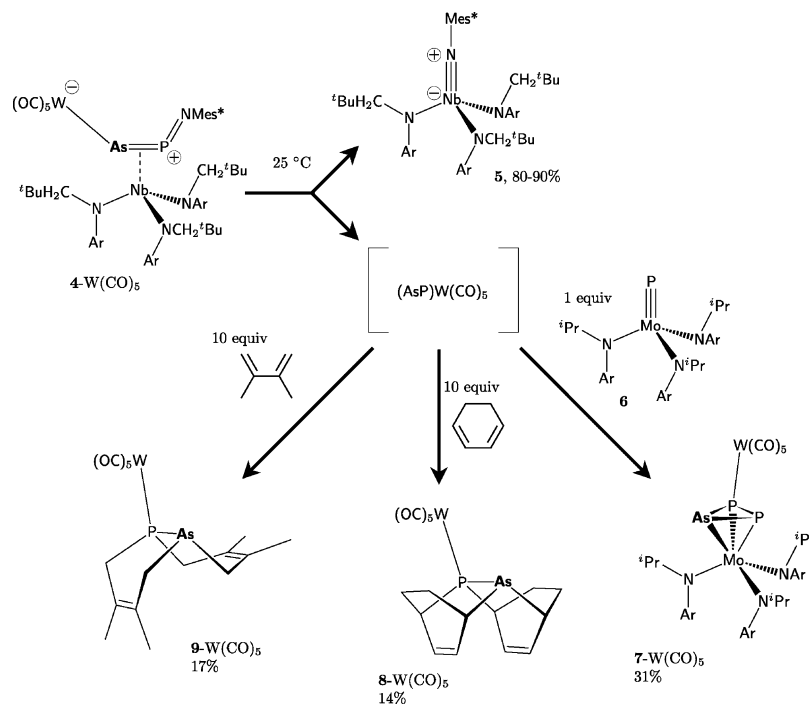


Figure 6. Thermal fragmentation of complex **4-W(CO)₅** in the presence of various trapping agents. Yields shown for the ostensible products of (AsP)W(CO)₅ trapping are isolated yields of pure material after separation from coproduct imido **5**.

2] cycloaddition reaction between $\text{As}\equiv\text{P}$ and $\text{P}\equiv\text{Mo}(\text{N}[\text{Pr}]\text{Ar})_3$, followed by rapid intramolecular isomerization to the molybdenum *cyclo*-AsP₂ complex.¹⁶ The mechanism for As/P exchange to form (cyclo-P₃)Mo(N[Pr]Ar)₃ has not been elucidated.

Synthesis of the (AsP)W(CO)₅ Synthon. In an effort to stabilize AsP in solution after its extrusion from the Nb(N[Np]Ar)₃ platform, we investigated the possibility of its generation as a tungsten pentacarbonyl complex. We have observed previously that coordination of the W(CO)₅ fragment to the terminal P atom of (η^2 -PPNMe⁺)Nb(N[Np]Ar)₃ results in room temperature fragmentation of the complex to the (P₂)W(CO)₅ molecule and the niobium imido **5**.¹⁵ Binding of W(CO)₅ sufficiently stabilizes the P₂ molecule to extend its lifetime in solution, but does not shut down the triple bond reactivity of the diphosphorus moiety. Higher yields of trapping products are generally observed for (P₂)W(CO)₅ than for the unsupported P₂ molecule.^{15–17}

Treatment of [Na(THF)][As=Nb(N[Np]Ar)₃], [Na(THF)][**3**], with a solution of W(CO)₅(THF) resulted in conversion to the W(CO)₅-capped arsenide salt [Na(THF)][(OC)₅WAs=Nb(N[Np]Ar)₃], [Na(THF)][**3-W(CO)₅**], which can be isolated as a red solid in 55% yield. Addition of one equivalent of ClP=NMe⁺ to a solution of [Na(THF)][**3-W(CO)₅**] in thawing Et₂O resulted in formation of (OC)₅W(η^2 -AsPNMe⁺)Nb(N[Np]Ar)₃, **4-W(CO)₅**, via an NaCl elimination reaction. Complex **4-W(CO)₅** is thermally unstable and readily fragments to (Mes⁺N)Nb(N[Np]Ar)₃, **5**, and the (AsP)W(CO)₅ unit, even at temperatures below 0 °C. At 10 °C in toluene-*d*₈ solution, **4-W(CO)₅** is observed to decay following clean first-order kinetics with a rate constant $k = 5.5(3) \times 10^{-4} \text{ s}^{-1}$. The free (AsP)W(CO)₅ molecule was not directly observed by ³¹P NMR spectroscopy.

Trapping of the (AsP)W(CO)₅ Molecule. Having already obtained a measure of success in trapping unsupported AsP with $\text{P}\equiv\text{Mo}(\text{N}[\text{Pr}]\text{Ar})_3$, **6**, we turned our attention to trapping (AsP)W(CO)₅ with the same molybdenum complex. Addition

of one equivalent of **6** to a thawing Et₂O solution of **4-W(CO)₅** yielded a mixture of (Mes⁺N)Nb(N[Np]Ar)₃, **5**, and (OC)₅W(*cyclo*-AsP₂)Mo(N[Pr]Ar)₃, **7-W(CO)₅** (Figure 6). Although **7-W(CO)₅** was observed to form in 70% yield by ¹H NMR spectroscopy, the required separation from **5** resulted in a much lower isolated yield for the red, crystalline solid of 31%. At 20 °C in benzene-*d*₆, **7-W(CO)₅** appears as a broad resonance at $\delta = -169$ ppm in the ³¹P NMR spectrum, presumably resulting from circumambulation of the W(CO)₅ fragment about the *cyclo*-AsP₂ ring. For comparison, the related *cyclo*-P₃ complex, (OC)₅W(*cyclo*-P₃)Mo(N[Pr]Ar)₃, formed by the trapping of (P₂)W(CO)₅ by **6**, resonates at $\delta = -212$ ppm (20 °C, benzene-*d*₆).¹⁶ A small amount of (*cyclo*-AsP₂)Mo(N[Pr]Ar)₃ missing the W(CO)₅ cap ($\delta = -137$ ppm) is always observable in the baseline of ³¹P NMR spectra of **7-W(CO)₅**, despite the established purity of the sample by elemental analysis.

A solution of **7-W(CO)₅** in toluene-*d*₈ was analyzed by variable-temperature ³¹P NMR spectroscopy. At 50 °C, the resonance at $\delta = -169$ ppm sharpened significantly, revealing other small peaks in the baseline at $\delta = -185$ and $\delta = -212$ ppm, which have been assigned as (*cyclo*-P₃)Mo(N[Pr]Ar)₃ and (OC)₅W(*cyclo*-P₃)Mo(N[Pr]Ar)₃, respectively. This demonstrated that As/P exchange may also be occurring in the (AsP)W(CO)₅ trapping reaction with **6**, but to a much lesser extent than with the unsupported AsP molecule. Locking out of the different phosphorus environments in **7-W(CO)₅** did not occur until the temperature of the sample was lowered to -80 °C. At this temperature, a complex pattern of sharp doublets ($J_{\text{PP}} = \text{ca. } 300 \text{ Hz}$) emerged.³⁴ At low temperature, a propeller-like C₃ conformation of the anilide ligands is locked out as well as the migration of the W(CO)₅ about the AsP₂ ring. This makes **7-W(CO)₅** a chiral molecule with two inequivalent phosphorus nuclei. Locking out of the W(CO)₅ fragment on each of As, P1, and P2 gives rise to three distinct isomers of **7-W(CO)₅** with six expected ³¹P NMR resonances. The additional resonances observed are most likely a consequence of

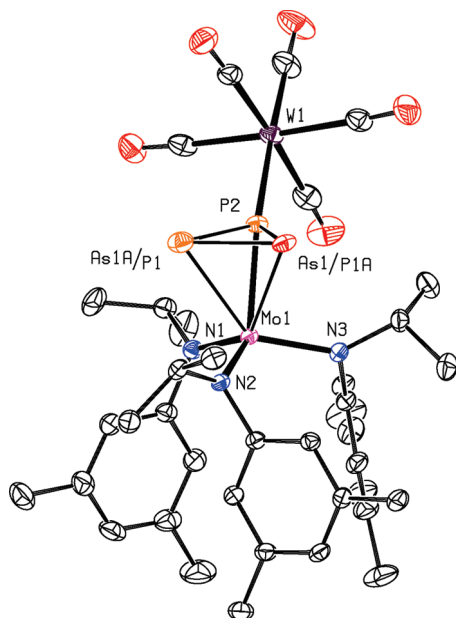


Figure 7. Molecular structure of complex **7-W(CO)₅** shown with 50% probability thermal ellipsoids. The atoms As1 and P1 are site disordered in the solid state structure with the major contributor (57%) shown. Selected interatomic distances (Å) and angles (deg): As1–P1, 2.284(9); As1–P2, 2.227(3); P1–P2, 2.223(12); P2–W1, 2.5463(7); Mo1–As1, 2.611(2); Mo1–P1, 2.636(12); Mo1–P2, 2.4759(7); P2–P1–As1, 59.2(3); P1–P2–As1, 61.8(3); P1–P2–W1, 130.6(3); P2–As1–P1, 59.0(3).

the small amounts of (*cyclo*-AsP₂)Mo(N[ⁱPr]Ar)₃, (*cyclo*-P₃)Mo(N[ⁱPr]Ar)₃, and (OC)₅W(*cyclo*-P₃)Mo(N[ⁱPr]Ar)₃ also present in solution.

The solid state structure of **7-W(CO)₅** exhibits the expected geometry, with the *cyclo*-AsP₂ ring η^3 -coordinated to the molybdenum trisanilide platform (Figure 7). Of note, the W(CO)₅ fragment is η^1 -coordinated to phosphorus and not to the arsenic atom to which it was bound in [3-W(CO)₅][−]. This is not surprising considering the relative nucleophilicities of phosphorus and arsenic, and the established ability of the W(CO)₅ fragment to circumambulate the *cyclo*-AsP₂ ring in solution. Atoms P1 and As1 are site disordered in the crystal structure of **7-W(CO)₅**, with the major contributor (57%) being shown in Figure 7. As/P site disorder is also observed in the solid state structure of the *cyclo*-AsP₂ complex (*cyclo*-AsP₂)CrCp(CO)₂; however, in this case the arsenic atom is disordered over all three positions in the ring.⁴⁶ The bonds about the *cyclo*-AsP₂ ring in the solid state structure of **7-W(CO)₅** are all essentially equal in length ($r_{\text{As-P1}} = 2.284(9)$ Å, $r_{\text{As-P2}} = 2.227(3)$ Å, $r_{\text{P1-P2}} = 2.223(12)$ Å), which is likely a consequence of the site disorder and not a true reflection of the bonding situation in the complex. A geometry optimization performed on the model complex (OC)₅W(*cyclo*-AsP₂)Mo(N[Me]Ph)₃ predicted two different As–P bond lengths in this structure ($r_{\text{As-P}} = 2.328$ Å, $r_{\text{As-P}} = 2.244$ Å), with the shorter distance involving the phosphorus atom bound to W(CO)₅ (Table 1).

Trapping of the (AsP)W(CO)₅ molecule can also be achieved by addition of 10 equivalents of either 1,3-cyclohexadiene (C₆H₈) or 2,3-dimethyl-1,3-butadiene (C₆H₁₀) to a thawing Et₂O solution of **4-W(CO)₅** (Figure 6) and allowing the reaction mixture to warm slowly to room temperature. Following separation from (Mes^{*}N)Nb(N[Np]Ar)₃ (**5**), the W(CO)₅-complexed double Diels–Alder adducts of AsP, (OC)₅W(AsP)(C₆H₈)₂ (**8-W(CO)₅**) and (OC)₅W(AsP)(C₆H₁₀)₂ (**9-W(CO)₅**) were isolated as white crystalline solids in 14% and 17% yields,

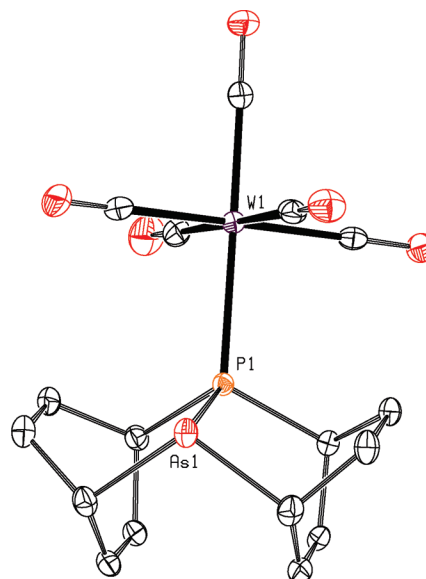


Figure 8. Molecular structure of complex **8-W(CO)₅** shown with 50% probability thermal ellipsoids. Selected interatomic distances (Å) and angles (deg): As1–P1, 2.3010(6); P1–W1, 2.5405(5); As1–P1–W1, 116.22(2).

respectively. Monitoring formation of **8-W(CO)₅** and **9-W(CO)₅** in solution by ³¹P NMR spectroscopy (PPh₃ as internal standard) gave much higher yields of 46% and 52%, indicating that (AsP)W(CO)₅ is trapped much more efficiently by organic dienes than AsP. The formulations of **8-W(CO)₅** and **9-W(CO)₅** were confirmed by high-resolution electron impact mass spectrometry; the molecular ions of both species were located and matched the predicted isotope patterns for (OC)₅W(AsP)(C₆H₈)₂ and (OC)₅W(AsP)(C₆H₁₀)₂. Of note, the (AsP)W(CO)₅ radical cation was also observed in the mass spectrum of both **8-W(CO)₅** and **9-W(CO)₅**.

The ³¹P NMR spectra of compounds **8-W(CO)₅** ($\delta = -23$ ppm, $J_{\text{WP}} = 219$ Hz) and **9-W(CO)₅** ($\delta = -12$ ppm, $J_{\text{WP}} = 225$ Hz) exhibit singlets flanked by ¹⁸³W satellites, indicating that migration of the W(CO)₅ fragment from arsenic to phosphorus has occurred during the course of the reaction. Indeed, the solid-state structures of the double Diels–Alder adducts **8-W(CO)₅** (Figure 8) and **9-W(CO)₅** (Figure 9) confirm that W(CO)₅ is bound to phosphorus in the final products. The (P₂)W(CO)₅ and (As₂)W(CO)₅ molecules have been the subject of a theoretical study concluding that, in contrast to N₂, the P₂ and As₂ ligands preferentially bind side-on to the W center.⁴⁷ If the same is assumed to be true for (AsP)W(CO)₅, it is easy to envision migration of the W(CO)₅ fragment along the As–P bond to the more nucleophilic phosphorus atom during the trapping reactions.

Compounds **8-W(CO)₅** and **9-W(CO)₅** are isostructural to the related (P₂)W(CO)₅ double Diels–Alder adducts of 1,3-cyclohexadiene and 2,3-dimethyl-1,3-butadiene,¹⁵ with the exception of the slightly longer As–P bond distances (**8-W(CO)₅**, $r_{\text{As-P}} = 2.3010(6)$ Å; **9-W(CO)₅**, $r_{\text{As-P}} = 2.3195(11)$ Å). The double 1,3-cyclohexadiene adduct, **8-W(CO)₅**, exhibits a tetracyclic structure with a cofacial pair of C=C π bonds, while the double 2,3-dimethyl-1,3-butadiene adduct, **9-W(CO)₅**, exhibits a more open bicyclic framework. The structure of **8-W(CO)₅** was geometry optimized using DFT calculations (Table 1), giving a calculated $r_{\text{As-P}} = 2.297$ Å, which agrees well with the As–P

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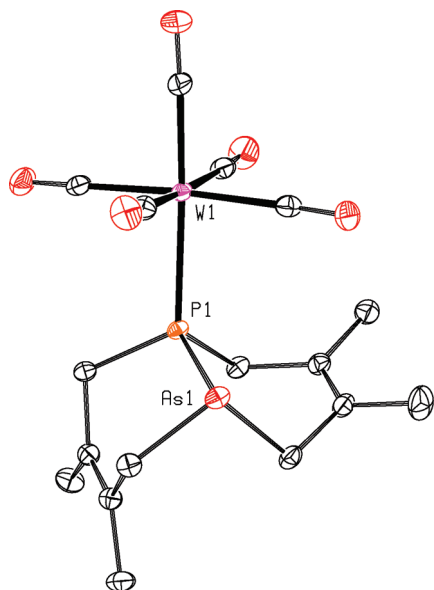


Figure 9. Molecular structure of complex **9**-W(CO)₅ shown with 50% probability thermal ellipsoids. Selected interatomic distances (Å) and angles (deg): As1–P1, 2.3195(11); P1–W1, 2.5191(11); As1–P1–W1, 112.64(4).

bond lengths observed in the solid state structures of **8**-W(CO)₅ and **9**-W(CO)₅ and the predicted As–P bond length from single bond covalent radii (2.32 Å).²⁸

Conclusions

In conclusion, we have used the niobium-mediated activation chemistry of As₄ to access the unsaturated intermediate (AsP)-W(CO)₅ in solution. Despite being bound by tungsten pentacarbonyl, the AsP moiety retains its triple bond reactivity, as witnessed by its ability to react with two equivalents of organic diene in Diels–Alder reactions. The (AsP)W(CO)₅ molecule also reacts in a one-to-one fashion with P≡Mo(N[Pr]Ar)₃ (**6**) to generate the new *cyclo*-AsP₂ molybdenum complex, (OC)₅W(*cyclo*-AsP₂)Mo(N[Pr]Ar)₃ (**7**-W(CO)₅), which has been structurally characterized. In addition to accessing triple-bond reactivity of the proposed (AsP)W(CO)₅ intermediate, this work has yielded a simple mononuclear niobium terminal arsenide anion, [As≡Nb(N[Pr]Ar)₃][−] (**3**), which contains a Nb–As triple bond. The negative charge in **3** facilitates functionalization of the terminal arsenide unit, allowing for the synthesis of the new As≡P=NMe₃⁺ ligand atop the niobium trisilanide framework. Thermolysis of the arsaphosphaazide complex (η²-AsPNMe₃⁺)Nb(N[Pr]Ar)₃ (**4**) results in near quantitative conversion to the niobium imido (Me₃N)Nb(N[Pr]Ar)₃ (**5**), with concomitant loss of the AsP diatomic unit. Trapping reactions involving the As≡P molecule gave very low yields or complex mixtures of products, suggesting that this molecule is less tractable in terms of trapping or transfer than was the case for P≡P when accessed using similar methodology. The synthetic explorations reported herein represent a dual effort to discover triple-bond reactivity for low-coordinate arsenic while defining methods for arsenic incorporation that stem from the element itself.

Experimental Section

General Procedures. All manipulations were performed in a Vacuum Atmospheres model MO-40 M glovebox under an atmosphere of purified N₂. Solvents were obtained anhydrous and oxygen-free from a Contour Glass Solvent Purification System.

Deuterated solvents for NMR spectroscopy were purchased from Cambridge Isotope Laboratories. Benzene-*d*₆ and toluene-*d*₈ were degassed and stored over molecular sieves for at least 2 days prior to use. THF-*d*₈ was distilled from sodium/benzophenone and stored over molecular sieves at −35 °C. Celite 435 (EM Science), 4 Å molecular sieves (Aldrich), and alumina (EM Science) were dried by heating at 200 °C under dynamic vacuum for at least 24 h prior to use. 1,3-Cyclohexadiene and 2,3-dimethyl-1,3-butadiene were purchased from Aldrich, distilled from NaBH₄, and stored over molecular sieves at −35 °C prior to use. Tungsten hexacarbonyl was purchased from Strem and used without further purification. The compounds HNb(η²-BuHC=NAr)(N[Np]Ar)₂ (**1**),¹¹ Mes⁺-NPCI,¹⁴ and P≡Mo(N[Pr]Ar)₃ (**6**)⁴⁴ were prepared according to literature procedures. All glassware was oven-dried at temperatures greater than 170 °C prior to use. NMR spectra were obtained on Bruker Avance 400, Varian Mercury 300, or Varian Inova 500 spectrometers. ¹H NMR spectra were referenced to residual solvent resonances (C₆D₅H, 7.16 ppm, C₄D₇HO, 3.58 ppm, C₇D₇H, 2.09 ppm); ¹³C NMR spectra were referenced to C₆D₆ (128.39 ppm) and C₄D₈O (67.57 ppm); and ³¹P NMR spectra were referenced externally to 85% H₃PO₄ (0 ppm). Elemental analyses were performed by Midwest Microlab, LLC, Indianapolis, Indiana.

As₄ Generation and Trapping. Yellow arsenic (As₄) is generated by subliming gray arsenic in the apparatus shown in Supporting Information Figure S1. In a typical run, approximately 5 g of gray arsenic is loaded into the middle of the inner horizontal steel tube and heated to a temperature of 515–550 °C for a period of three hours. A stream of argon gas (flow rate: 1 L/min) carries the As₄ vapors into the T-joint, where they meet another stream of room temperature argon (flow rate: 1 L/min). The argon/As₄ mixture is bubbled through a flask containing 500 mL of chilled toluene (−30 °C, bath: 50/50 water/ethylene glycol + liquid N₂), where the As₄ vapors condense in solution. The argon stream leaves the flask and passes through a series of three bleach-filled bubblers to scrub out any escaping arsenic vapors. The entire procedure is performed in the dark to prevent conversion of As₄ to gray arsenic. The saturated solution of As₄ in toluene is then used in the subsequent synthesis of **2**, without the isolation of solid As₄. It is apparent that not all the As₄ remains in solution, as gram quantities of gray arsenic are always observed in the flask after sublimation.

Synthesis of (μ₂:η²,η²-As₂)[Nb(N[Pr]Ar)₃]₂, **2.** In the dark, HNb(η²-BuHC=NAr)(N[Np]Ar)₂ (**1**, 1.81 g, 2.73 mmol), was added under an argon stream to a cold solution of As₄ in toluene (−30 °C; generated as described above) by means of a solid addition funnel. The reaction mixture was kept in the dark, allowed to warm to room temperature, and stirred for 16 h, during which time the color of the solution changed from orange to dark green. The product of the reaction is not light-sensitive, and no further precautions to exclude light were taken during the subsequent workup. The toluene was removed under vacuum, and the resulting green-black residue was taken up in *n*-hexane (400 mL) and filtered through Celite to remove solid arsenic and other insoluble materials. The dark green solution was then evaporated to dryness and the solids obtained thereby were slurried in *n*-pentane (60 mL). The pentane slurry was placed in the freezer for 16 h at −35 °C to induce further precipitation. A bright-green powder was isolated by filtration and washed with cold *n*-pentane. The filtrate was concentrated, placed back in the freezer and a second crop of the green powder was isolated. Total yield: 1.04 g, 0.704 mmol, 52%. Elem. Anal. Calcd for C₇₈H₁₂₀N₆As₂Nb₂: C, 63.41; H, 8.19; N, 5.69. Found: C, 62.61; H, 8.07; N, 5.72. ¹H NMR (benzene-*d*₆, 20 °C, 500 MHz): δ = 6.95 (bs, 12H, *o*-Ar), 6.58 (s, 6H, *p*-Ar), 4.26 (bs, 12H, N-CH₂), 2.23 (s, 36H, Ar-CH₃), 0.99 (s, 54H, C(CH₃)₃) ppm. ¹³C{¹H} NMR (benzene-*d*₆, 20 °C, 125.8 MHz): δ = 154.2 (bs, aryl *ipso*), 138.2 (s, *m*-Ar), 126.6 (s, *p*-Ar), 124.2 (bs, *o*-Ar), 73.5 (bs, N-CH₂), 37.3 (bs, C(CH₃)₃), 30.7 (s, C(CH₃)₃), 22.1 (s, Ar-CH₃) ppm. FTIR (KBr windows, thin film): 2945(s), 1585(s), 1473(s), 1394(m), 1363(m), 1286(m), 1154(m), 1064(m), 999(s), 842(s), 683(s) cm^{−1}.

Synthesis of [Na(THF)][As≡Nb(N[Np]Ar)₃], [Na(THF)][3].

Freshly prepared 1% sodium amalgam (Na: 0.25 g, 11 mmol, 15 equiv/Nb) was added to a dark-green THF (30 mL) solution of (μ_2 : η^2 , η^2 -As₂)[Nb(N[Np]Ar)₃]₂ (**2**, 1.09 g, 0.740 mmol). The mixture was stirred vigorously for 2 h, during which time the color gradually changed from green to bright red. The supernatant solution was decanted from the amalgam and evaporated to dryness, leaving behind a red residue. The red residue was extracted with 50 mL of *n*-pentane and filtered through Celite. The filtrate was concentrated to a volume of 3 mL and placed in the freezer for 16 h at -35°C , during which time a bright orange microcrystalline precipitate deposited. The orange precipitate was isolated by filtration and washed with 1 mL of cold *n*-pentane. The filtrate was concentrated, placed back in the freezer and a second crop of orange powder was isolated. Total yield: 0.836 g, 1.00 mmol, 68%. Crystals suitable for X-ray diffraction were grown over a period of 16 h from a concentrated pentane solution kept at -35°C . Elem. Anal. Calcd for C₄₃H₆₈N₃O₅NaAsNb: C, 61.94; H, 8.22; N, 5.04. Found: C, 61.98; H, 8.33; N, 4.96. ¹H NMR (benzene-*d*₆, 20 $^\circ\text{C}$, 400 MHz): δ = 6.99 (s, 6H, *o*-Ar), 6.48 (s, 3H, *p*-Ar), 4.37 (s, 6H, N-CH₂), 3.67 (m, 4H, THF), 2.24 (s, 18H, Ar-CH₃), 1.56 (m, 4H, THF), 1.13 (s, 27H, C(CH₃)₃) ppm. ¹³C{¹H} NMR (benzene-*d*₆, 20 $^\circ\text{C}$, 100.6 MHz): δ = 158.8 (s, aryl *ipso*), 138.7 (s, *m*-Ar), 123.3 (s, *p*-Ar), 122.0 (s, *o*-Ar), 75.2 (bs, N-CH₂), 68.8 (s, THF), 36.6 (s, C(CH₃)₃), 30.2 (s, C(CH₃)₃), 26.1 (s, THF), 22.2 (s, Ar-CH₃) ppm. FTIR (KBr windows, nujol mull): 1585(s), 1573(m), 1363(m), 1292(m), 1152(m), 994(m), 840(m), 680(s), 675(s) cm⁻¹.

Synthesis of [Na(12-crown-4)][As≡Nb(N[Np]Ar)₃], [Na(12-c-4)][3]. A solution of 0.084 g of 12-crown-4 (0.48 mmol, 2.7 equivalents) in 3 mL of *n*-pentane was added dropwise with stirring to a solution of [Na(THF)][As≡Nb(N[Np]Ar)₃] ([Na(THF)][3], 0.150 g, 0.180 mmol) in *n*-pentane (3 mL). The red color of the solution faded and a yellow precipitate formed. The reaction mixture was allowed to stir for 30 min and then placed in the freezer for 16 h at -35°C to induce further precipitation. The yellow powder was isolated by filtration and washed with cold *n*-pentane (3 mL). Total yield: 0.153 g, 0.137 mmol, 76%. Crystals suitable for X-ray diffraction were grown by adding 3 mL of *n*-pentane to the yellow powder, followed by the dropwise addition of Et₂O until all the material dissolved. The *n*-pentane/Et₂O mixture was placed in the freezer for one week at -35°C , during which time crystals deposited. Elem. Anal. Calcd for C₅₅H₉₂N₃O₈NaAsNb: C, 59.29; H, 8.32; N, 3.77. Found: C, 58.84; H, 8.10; N, 3.80. ¹H NMR (benzene-*d*₆, 20 $^\circ\text{C}$, 500 MHz): δ = 7.02 (s, 6H, *o*-Ar), 6.42 (s, 3H, *p*-Ar), 4.98 (bs, 6H, N-CH₂), 3.20 (s, 24H, crown), 2.25 (s, 18H, Ar-CH₃), 1.46 (s, 27H, C(CH₃)₃) ppm. ¹³C{¹H} NMR (benzene-*d*₆, 20 $^\circ\text{C}$, 125.8 MHz): δ = 157.6 (s, aryl *ipso*), 137.4 (s, *m*-Ar), 121.3 (s, *p*-Ar), 120.9 (s, *o*-Ar), 76.9 (bs, N-CH₂), 66.0 (s, crown), 36.9 (s, C(CH₃)₃), 31.0 (s, C(CH₃)₃), 22.4 (s, Ar-CH₃) ppm. FTIR (KBr windows, nujol mull): 1582(m), 1365(m), 1289(m), 1135(s), 1095(s), 1021(s), 916(m), 674(m) cm⁻¹.

Synthesis of [Na]((OC)₅WAs≡Nb(N[Np]Ar)₃), [Na][3-W(CO)₅].

A 0.015 M yellow solution of W(CO)₅(THF) was prepared by irradiating a solution of W(CO)₆ (0.650 g, 1.85 mmol) in 50 mL of THF in a Rayonet photoreactor equipped with six RPR-4190 (emission maximum at 419 nm) and ten RPR-2540 (emission maximum at 254 nm) lamps for 24 h, with periodic degassing to remove CO. To this solution (42 mL, 0.630 mmol of W(CO)₅(THF)) was added 0.525 g of [Na(THF)][As≡Nb(N[Np]Ar)₃] ([Na(THF)][3], 0.630 mmol), and the dark-red reaction mixture was stirred for 2 h and then pumped down to dryness to yield a dark-red residue. The residue was taken up in 50 mL of *n*-pentane and filtered through Celite to remove excess W(CO)₆. The red filtrate was pumped down to dryness and a ¹H NMR spectrum of the crude material showed quantitative conversion of [Na(THF)][3] to the W(CO)₅-capped analogue [Na(THF)][3-W(CO)₅]. To obtain analytically pure material, the red residue was taken up in 8 mL of Et₂O and placed in the freezer for 16 h at -35°C . During this time, white crystals of W(CO)₆ deposited. The red supernatant

solution was filtered, concentrated to a volume of 4 mL, and placed back in the freezer. More W(CO)₆ was removed by filtration and the red supernatant solution was pumped down to dryness to yield an oily red solid. The red solid was slurried in 2 mL of *n*-pentane and placed in the freezer for 16 h at -35°C . A fine red powder precipitated and was isolated by filtration and washed with a further 2 mL of cold *n*-pentane. Total yield: 0.373 g, 0.344 mmol, 55%. The red powder was further purified by heating for 2 h at 70 $^\circ\text{C}$ in a sublimation apparatus under dynamic vacuum. A few additional mg of W(CO)₆ contaminant was collected on the coldfinger. Elem. Anal. Calcd for C₄₄H₆₀N₃O₅NaAsNbW: C, 48.68; H, 5.57; N, 3.87. Found: C, 48.88; H, 5.66; N, 3.25. ¹H NMR (benzene-*d*₆, 20 $^\circ\text{C}$, 500 MHz): δ = 6.98 (s, 6H, *o*-Ar), 6.46 (s, 3H, *p*-Ar), 4.09 (s, 6H, N-CH₂), 2.18 (s, 18H, Ar-CH₃), 1.10 (s, 27H, C(CH₃)₃) ppm. ¹³C{¹H} NMR (benzene-*d*₆, 20 $^\circ\text{C}$, 125.8 MHz): δ = 208.3 (s, *trans* CO), 202.3 (s, *cis* CO, *J*_{CW} = 125 Hz), 157.7 (s, aryl *ipso*), 139.2 (s, *m*-Ar), 124.3 (s, *p*-Ar), 122.0 (s, *o*-Ar), 73.8 (bs, N-CH₂), 36.4 (s, C(CH₃)₃), 30.0 (s, C(CH₃)₃), 21.9 (s, Ar-CH₃) ppm. FTIR (KBr windows, nujol mull): 2349(m), 2052(s), 1968(s), 1928(vs), 1809(vs), 1584(s), 1365(s), 1155(s), 995(s), 844(s), 687(s), 581(s) cm⁻¹.

Synthesis of (η^2 -AsPNMes*)Nb(N[Np]Ar)₃, **4.** To a stirring, thawing Et₂O solution (30 mL) of [Na(THF)][As≡Nb(N[Np]Ar)₃] ([Na(THF)][3], 0.496 g, 0.595 mmol) was added dropwise a thawing solution of Mes*NPCL (0.212 g, 0.651 mmol, 1.1 equiv) in Et₂O (3 mL). The dark red reaction mixture was allowed to stir while warming to room temperature over 30 min and was then pumped down to dryness. The remaining red residue was taken up in 25 mL of *n*-pentane and filtered through Celite to remove NaCl. A ³¹P{¹H} NMR spectrum of the filtrate showed quantitative conversion to the arsaphosphaazide complex (η^2 -AsPNMes*)-Nb(N[Np]Ar)₃, **4**. The *n*-pentane filtrate was concentrated to a volume of 2 mL and placed in the freezer for 16 h at -35°C , during which time a dark red-orange powder precipitated. The powder was collected by filtration and washed with an additional 1 mL of cold *n*-pentane. Total yield: 0.313 g, 0.304 mmol, 51%. Crystals suitable for X-ray diffraction were obtained by dissolving the powder in a 50/50 Et₂O/(Me₃Si)₂O mixture and placing the resulting solution in the freezer for 16 h at -35°C . Elem. Anal. Calcd for C₅₇H₈₉N₄PAsNb: C, 66.52; H, 8.72; N, 5.44. Found: C, 66.49; H, 8.68; N, 5.43. ¹H NMR (benzene-*d*₆, 20 $^\circ\text{C}$, 500 MHz): δ = 7.76 (s, 2H, *m*-Mes*), 6.63 (s, 6H, *o*-Ar), 6.58 (s, 3H, *p*-Ar), 4.11 (s, 6H, N-CH₂), 2.12 (s, 18H, Ar-CH₃), 1.93 (s, 18H, *o*-C(CH₃)₃ Mes*), 1.48 (s, 9H, *p*-C(CH₃)₃ Mes*), 0.82 (s, 27H, CH₂-C(CH₃)₃) ppm. ¹³C{¹H} NMR (benzene-*d*₆, 20 $^\circ\text{C}$, 125.8 MHz): δ = 152.2 (s, aryl *ipso*), 151.3 (d, *J*_{CP} = 36 Hz, Mes* *ipso*), 142.8 (d, *J*_{CP} = 5 Hz, *m*-Mes*), 139.4 (d, *J*_{CP} = 12 Hz, *o*-Mes*), 138.6 (s, *m*-Ar), 127.6 (s, *p*-Ar), 124.3 (s, *o*-Ar), 122.7 (d, *J*_{CP} = 5 Hz, *p*-Mes*), 73.1 (d, *J*_{CP} = 7 Hz, N-CH₂), 37.3 (d, *J*_{CP} = 2 Hz, *o*-C(CH₃)₃ Mes*), 37.1 (s, CH₂-C(CH₃)₃), 35.2 (d, *J*_{CP} = 1 Hz, *p*-C(CH₃)₃ Mes*), 33.6 (s, *o*-C(CH₃)₃ Mes*), 32.5 (s, *p*-C(CH₃)₃ Mes*), 30.2 (s, CH₂-C(CH₃)₃), 21.9 (s, Ar-CH₃) ppm. ³¹P{¹H} NMR (benzene-*d*₆, 20 $^\circ\text{C}$, 121.5 MHz): δ = 349 (s) ppm. FTIR (KBr windows, nujol mull): 1602(m), 1587(s), 1416(s), 1365(s), 1311(s), 1293(s), 996(m), 848(m), 692(m), 684(m) cm⁻¹.

Synthesis of (OC)₅W(cyclo-AsP₂)Mo(N[Pr]Ar)₃, 7-W(CO)₅.

To a thawing solution of [Na(THF)][(OC)₅WAs≡Nb(N[Np]Ar)₃] ([Na(THF)][3-W(CO)₅], 0.300 g, 0.259 mmol) in Et₂O (10 mL) was added a thawing Et₂O (3 mL) solution of Mes*NPCL (0.085 g, 0.261 mmol, 1 equiv) dropwise. After 30 s of stirring, a yellow Et₂O (4 mL) solution of P≡Mo(N[Pr]Ar)₃ (**6**, 0.159 g, 0.259 mmol, 1 equiv) was quickly added. There was no apparent color change to the dark red reaction mixture. After 3 h of stirring, the reaction mixture was pumped down to dryness, taken up in 30 mL of toluene and filtered through Celite to remove NaCl. The red filtrate was evaporated to dryness, leaving behind a red solid. The solid was slurried in 15 mL of *n*-hexane, and this mixture was placed in the freezer for 16 h at -35°C . The red precipitate (0.285 g) was isolated by filtration and washed with 3 mL of *n*-hexane. Analysis by ¹H NMR spectroscopy of this material revealed that it was

composed of $(OC)_5W(cyclo-AsP_2)Mo(N[Pr]Ar)_3$ (**7-W(CO)₅**, 68%) and $(Mes^*N)Nb(N[Np]Ar)_3$ (**5**, 32%). The red solid was slurried in 5 mL of *n*-pentane and toluene was added dropwise until all the solids dissolved. The toluene/pentane mixture was placed in the freezer for 16 h at $-35^\circ C$, during which time dark-red, block-shaped, X-ray quality crystals of **7-W(CO)₅** grew. The red crystals were isolated by filtration and washed with 15 mL of cold *n*-pentane to remove small, yellow cocrystals of **5**. Total yield: 0.082 g, 0.079 mmol, 31%. Elem. Anal. Calcd for $C_{38}H_{48}N_3O_5P_2AsMoW$: C, 43.74; H, 4.64; N, 4.03. Found: C, 43.91; H, 4.81; N, 4.02. 1H NMR (benzene-*d*₆, $20^\circ C$, 500 MHz): δ = 6.68 (s, 3H, *p*-Ar), 6.27 (bs, 6H, *o*-Ar), 4.90 (bs, 3H, $CH(CH_3)_2$), 2.10 (s, 18H, Ar- CH_3), 0.91 (bs, 18H, $CH(CH_3)_2$) ppm. $^{13}C\{^1H\}$ NMR (benzene-*d*₆, $20^\circ C$, 125.8 MHz): δ = 197.9 (s, *cis* CO), 148.6 (bs, aryl *ipso*), 137.9 (s, *p*-Ar), 137.5 (s, *m*-Ar), 129.4 (s, *o*-Ar), 64.8 (bs, *N*- $CH(CH_3)_2$), 22.6 (bs, $CH(CH_3)_2$), 21.7 (s, Ar- CH_3) ppm. Note: The *trans* CO resonance was not located in the $^{13}C\{^1H\}$ spectrum. $^{31}P\{^1H\}$ NMR (benzene-*d*₆, $20^\circ C$, 121.5 MHz): δ = -169 (bs) ppm. A small peak at δ = -139 ppm is also always observed and has been attributed to a small amount of $(cyclo-AsP_2)Mo(N[Pr]Ar)_3$ (**7**) without the $W(CO)_5$ unit appended. FTIR (KBr windows, nujol mull): 2214(w), 2067(vs), 1980(vs), 1940(vs), 1599(s), 1583(m), 1357(s), 1152(s), 1107(s), 987(s), 933(s), 859(s), 687(vs), 593(vs), 573(vs) cm^{-1} .

Synthesis of $(OC)_5W(AsP)(C_6H_8)_2$, **8-W(CO)₅.** To a thawing solution of $[Na(THF)][(OC)_5WAs\equiv Nb(N[Np]Ar)_3]$ ($[Na(THF)][3-W(CO)_5]$, 0.200 g, 0.173 mmol) in Et₂O (7 mL) was added dropwise a thawing Et₂O (5 mL) solution of Mes^*NPCl (0.057 g, 0.175 mmol, 1 equiv). After 30 s of stirring, 175 μL (1.78 mmol, 10.3 equiv) of 1,3-cyclohexadiene was added *via* syringe. The dark red reaction mixture was stirred for 1 h and then pumped down to dryness, leaving behind a brown residue. The residue was extracted with 10 mL of toluene and filtered through Celite to remove NaCl. The red filtrate was evaporated to dryness and 5 mL of acetonitrile was added, resulting in precipitation of a yellow solid. The yellow solid was isolated by filtration, and characterized as the niobium imido complex, $(Mes^*N)Nb(N[Np]Ar)_3$ (**5**, 0.1324 g, 0.143 mmol, 83% yield). The orange filtrate was evaporated to dryness and slurried in 2 mL of *n*-pentane. Diethyl ether was added dropwise to the slurry until all solids present dissolved and the mixture was placed in the freezer for 48 h at $-35^\circ C$. Colorless, X-ray quality crystals of **8-W(CO)₅** were isolated by filtration and washed with 1 mL of cold *n*-pentane. Total yield: 0.015 g, 0.025 mmol, 14%. Note: Monitoring formation of **8-W(CO)₅** *via* ^{31}P NMR (PPH_3 as internal standard) gave an overall yield of 46%. 1H NMR (benzene-*d*₆, $20^\circ C$, 500 MHz): δ = 5.18 (td, J = 8 and 4 Hz, 2H), 4.75 (td, J = 8 and 3.5 Hz, 2H), 2.55 (m, 4H), 1.70 (q, J = 12 Hz, 2H), 1.23–1.17 (m, 2H), 1.13–1.06 (m, 2H), 0.93–0.78 (m, 2H) ppm. $^{13}C\{^1H\}$ NMR (benzene-*d*₆, $20^\circ C$, 125.8 MHz): δ = 199.2 (d, J_{CP} = 24 Hz, *trans* CO), 197.9 (d, J_{CP} = 6.5 Hz, J_{CW} = 125 Hz, *cis* CO), 125.1 (d, J_{CP} = 8 Hz), 124.5 (d, J_{CP} = 10 Hz), 33.8 (d, J_{CP} = 2 Hz), 32.2 (d, J_{CP} = 4 Hz), 25.4 (d, J_{CP} = 8 Hz), 23.0 (d, J_{CP} = 5 Hz) ppm. $^{31}P\{^1H\}$ NMR (benzene-*d*₆, $20^\circ C$, 161.9 MHz): δ = -22 (s, J_{WP} = 219 Hz) ppm. FTIR (KBr windows, thin film): 2171(w), 2064(s), 1971(m), 1918(vs), 1453(w), 1019(w), 725(w), 644(w), 616(w), 600(m), 573(s) cm^{-1} . HRMS-El: Calcd. for M^+ : 589.946. Found: 589.945. Also present: 509.882 ($W(CO)_5(AsP)-(C_6H_8)^+$), 429.820 ($W(CO)_5(AsP)^+$), 401.825 ($W(CO)_4(AsP)^+$), and others.

Synthesis of $(OC)_5W(AsP)(C_6H_{10})_2$, **9-W(CO)₅.** To a thawing solution of $[Na(THF)][(OC)_5WAs\equiv Nb(N[Np]Ar)_3]$ ($[Na(THF)][3-W(CO)_5]$, 0.200 g, 0.173 mmol) in Et₂O (7 mL) was added dropwise a thawing Et₂O (5 mL) solution of Mes^*NPCl (0.057 g, 0.175 mmol, 1 equiv). After 30 s of stirring, 200 μL (1.77 mmol, 10.2 equiv) of 2,3-dimethyl-1,3-butadiene was added *via* syringe. The dark red reaction mixture was stirred for 1 h and then pumped down to dryness, leaving behind a dark red residue. The residue was extracted with 10 mL of toluene and filtered through Celite to remove NaCl. The red filtrate was evaporated to dryness and 5 mL

of acetonitrile was added, resulting in precipitation of a yellow solid. The yellow solid was isolated by filtration and characterized as the niobium imido complex, $(Mes^*N)Nb(N[Np]Ar)_3$ (**5**, 0.159 g, 0.172 mmol, 99% yield). The red-brown filtrate was evaporated to dryness and slurried in 2 mL of *n*-pentane. Diethyl ether was added dropwise to the slurry until all solids present dissolved and the mixture was placed in the freezer for 48 h at $-35^\circ C$. Colorless, X-ray quality crystals of **9-W(CO)₅** were isolated by filtration and washed with 1 mL of cold *n*-pentane. Total yield: 0.018 g, 0.030 mmol, 17%. Note: Monitoring formation of **9-W(CO)₅** *via* ^{31}P NMR (PPH_3 as internal standard) gave an overall yield of 53%. Elem. Anal. Calcd for $C_{17}H_{20}O_5PAsW$: C, 34.37; H, 3.39. Found: C, 33.92; H 3.32. 1H NMR (benzene-*d*₆, $20^\circ C$, 400 MHz): δ = 2.25 (m, 2H), 2.05 (d, 2H), 1.70–1.57 (m, 4H), 1.55 (bs, 6H, CH_3), 1.38 (dd, J = 5 Hz and 1 Hz, 6H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (benzene-*d*₆, $20^\circ C$, 100.6 MHz): δ = 199.9 (d, J_{CP} = 23 Hz, *trans* CO), 197.7 (d, J_{CP} = 6.5 Hz, J_{CW} = 125 Hz, *cis* CO), 124.3 (d, J_{CP} = 8 Hz, CCH_3), 33.8 (bs), 26.6 (d, J_{CP} = 6 Hz), 21.4 (d, J_{CP} = 2 Hz), 20.8 (d, J_{CP} = 3 Hz) ppm. $^{31}P\{^1H\}$ NMR (benzene-*d*₆, $20^\circ C$, 121.5 MHz): δ = -12 (s, J_{WP} = 225 Hz) ppm. FTIR (KBr windows, thin film): 2916(w), 2857(w), 2354(w), 2065(s), 1975(s), 1950(s), 1898(vs), 1645(w), 1436(w), 1408(w), 1383(w), 1048(w), 1018(w), 830(m), 819(m), 808(w), 780(w), 597(s), 575(vs) cm^{-1} . HRMS-El: Calcd for M^+ : 593.978. Found: 593.980. Also present: 565.984 ($W(CO)_4(AsP)(C_6H_{10})_2^+$), 483.906 ($W(CO)_4(AsP)(C_6H_{10})^+$), 429.822 ($W(CO)_5(AsP)^+$), 401.827 ($W(CO)_4(AsP)^+$), and others.

Kinetics of the Fragmentation of **4.** Stock solutions containing $(\eta^2-AsPNMes^*)Nb(N[Np]Ar)_3$ (**4**, 151 mg) and $ONb(N[Np]Ar)_3$ (46 mg, used as an internal standard) were prepared in C_6D_6 (4.1 g) and stored at $-35^\circ C$ between uses. An aliquot of this solution was transferred to a sealable (J. Young) NMR tube, which was then inserted into a prewarmed NMR probe ($60^\circ C$). The temperature of the probe was verified by an ethylene glycol NMR thermometer before each run. Four-scan 1H NMR spectra (relaxation delay = 16 s) were collected every three minutes over a period of three half-lives. The integral of the methylene residue of **4** as a function of time, corrected versus the internal standard, was fit to the first-order rate equation, $I(t) = Ae^{-kt} + b$, using the automated routine of Origin 6.⁴⁸ The experiment was repeated three times. The average rate constant for the decay of **4** at $60^\circ C$ is $2.9(1) \times 10^{-4} s^{-1}$. As shown in Figure S22 (Supporting Information), conversion of **4** to the niobium imido complex, $(Mes^*N)Nb(N[Np]Ar)_3$ (**5**), is not quantitative and other unidentified anilide-containing products are also formed.

Kinetics of the Fragmentation of **4-W(CO)₅.** A thawing Et₂O solution (1 mL) of Mes^*NPCl (17 mg, 0.052 mmol, 1 equiv) was added to a thawing Et₂O solution (2 mL) of $[Na(THF)][(OC)_5WAs\equiv Nb(N[Np]Ar)_3]$ ($[Na(THF)][3-W(CO)_5]$, 58 mg, 0.050 mmol). This solution was stirred for 30 s before the solvent was removed *in vacuo*. The residue was extracted with a toluene-*d*₈ (1.0 g) solution of ferrocene (7 mg, 0.04 mmol, used as an internal standard). The resulting extract was filtered cold through Celite into a sealable (J. Young) NMR tube, which was then frozen for transport to an NMR probe precooled to $10^\circ C$. The temperature of the probe was verified by an ethylene glycol NMR thermometer before each run. Four-scan 1H NMR spectra (relaxation delay = 16 s) were collected every three minutes over a period of four half-lives. The integral of the methylene residue of **4-W(CO)₅** as a function of time, corrected versus the internal standard, was fit to the first-order rate equation, $I(t) = Ae^{-kt} + b$, using the automated routine of Origin 6.⁴⁸ The experiment was repeated three times.⁴⁹ The average rate constant for the decay of **4-W(CO)₅** at $10^\circ C$ is $5.5(3) \times 10^{-4} s^{-1}$. As shown in Figure S23 (Supporting Informa-

(48) <http://microcal.com>, Microcal(TM) Origin Version 6.0, Copyright 1991–1999, Microcal Software, Inc.

(49) It should be noted that by the time data collection started on the samples, approximately one third of the **4-W(CO)₅** present in solution had already converted to the niobium imido **5**.

tion), conversion of $4\text{-W}(\text{CO})_5$ to the niobium imido complex, $(\text{Mes}^*\text{N})\text{Nb}(\text{N}[\text{Np}]\text{Ar})_3$ (**5**), is nearly quantitative.

Details of X-ray Structure Determinations. Crystals were mounted in hydrocarbon oil on a nylon loop or a glass fiber. Low-temperature (100 K) data were collected on a Siemens Platform three-circle diffractometer coupled to a Bruker-AXS Smart Apex CCD detector with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) performing ϕ - and ω -scans. A semiempirical absorption correction was applied to the diffraction data using SADABS.⁵⁰ All structures were solved by direct or Patterson methods using SHELXS^{51,52} and refined against F^2 on all data by full-matrix least-squares with SHELXL-97.^{52,53} All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are linked (1.5 times for methyl groups). In structures where disorders were present, the disorders were refined within SHELXL with the help of rigid bond restraints as well as similarity restraints on the anisotropic displacement parameters for neighboring atoms and on 1,2- and 1,3-distances throughout the disordered components. The relative occupancies of disordered components were refined freely within SHELXL.⁵⁴ Further details on all structures are provided in Tables S1 and S2, and in the form of cif files available as part of the Supporting Information or from the CCDC under deposition numbers 710856–710861.⁵⁵

Computational Details. Quantum chemical calculations were carried out to probe the electronic structure of the As–As and As–P bonds contained within the new product molecules, to be compared with some reference systems analyzed by the same methods. Geometry optimizations were carried out using the Amsterdam Density Functional (ADF) code version 2006.01,⁵⁶ using the LDA

functional of Vosko, Wilk, and Nusair (VWN)⁵⁷ together with the GGA functional known as OLYP which is a combination of Handry and Cohen's OPTX functional for exchange and Lee, Yang, and Parr's nonlocal correlation functional.⁵⁸ The zero-order regular approximation (ZORA) was used for inclusion of relativistic effects.⁵⁹ The basis sets were QZ4P (quadruple- ζ with four polarization functions) for As, P, Nb, TZ2P for C, N, W, and O and DZP for H atoms as supplied with ADF, and frozen core approximations were made for carbons on the anilide ligands (1s). All molecules were geometry-optimized without symmetry constraints to default convergence criteria and energies are uncorrected for zero-point energies. Bond multiplicities were calculated using the method of Nalewajski and Mrozek within ADF.⁶⁰ Electron density topologies and orbital contours were analyzed using the packages DGrid and Basin by Kohout.⁶¹

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Supporting Information Available: Additional experimental details and figures showing NMR spectra, variable-temperature NMR data, mass spectra, kinetic plots, and X-ray crystallography structures; tables of crystal data; lists of optimized geometry coordinates; and crystallographic information files. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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