# Novel Approach to Intermediates Containing a Tungsten−Arsenic Triple Bond†

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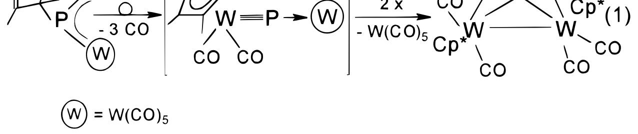
Thermolysis of the arsenidene complex [Cp*As{W(CO)$_5$}$_2$] (**1**) gave [Cp*(CO)$_2$W($\eta^3$-As$_3$)] (**2**), [{W(CO)$_3$Cp*W}$_2$($\mu_3$-As)$_4$] (**3**), and [{W(CO)$_3$Cp*W}$_2$($\mu_3$-As)$_3${$\mu_3$-AsW(CO)$_5$}] (**4**). The products show that **1** has undergone a Cp* migration from the $\sigma$-bound state at the As atom to $\eta^5$ coordination at the transition metal, presumably via an intermediate of the type [Cp*(CO)$_2$W≡As→W(CO)$_5$]. In a second transformation pathway removal of the Cp* group of the arsenidene complex **1** occurs to form an unsaturated species of the type [As{W(CO)$_5$}$_2$]. Compound **2** exhibits the unusual formation of a *cyclo*-As$_3$ ligand, while the tetrahedral tungsten clusters **3** and **4** represent possible tetramers of the intermediates formed in both pathways. Furthermore, photolysis of arsenidene complex **1** results in [As$_2${W(CO)$_5$}$_3$] (**5**), which shows that the second pathway prevails under these conditions.

## Introduction

Complexes with a metal triply bonded to a heavier group 15 element are a novel class of compounds[1] existing in two principal coordination modes: [L$_n$M≡E] (**A**) and [L$_n$M≡E→ML$_m$] (**B**). For phosphorus, both types have been established recently,[2] and investigations of their reaction behavior have been reported.[3] However, examples of the heavier group 15 congeners are still sparse. In 1996, the first arsenido complexes of the type **A** were synthesized in the complexes [N(CH$_2$CH$_2$NSiMe$_3$)$_3$M≡As] (M = Mo,[4] W[5]). Ziegler et al. had previously speculated that a [Cp(CO)$_2$M≡As] (M = Mo, W) intermediate formed in the thermolysis and cophotolysis of the trinuclear cluster [{CpM(CO)$_2$}$_3$($\mu_3$-As)].[6] For antimony, one possible intermediate of that type had been postulated in a complex of the composition [(CO)$_n$M≡Sb]$^-$ ($n$ = 4, M = Cr, Mo, W; $n$ = 3, M = Fe).[7]

Our current interest is focused on the synthesis and reactivity of pnicogenido complexes of type **A** and **B** as either isolable compounds[8] or reactive intermediates. Recently we developed a synthetic concept for the generation of intermediates of type **B** by thermolysis of the phosphinidene complex [Cp*P{W(CO)$_5$}$_2$].[9] By Cp* migration from the $\sigma$-bonded phosphorus atom to the tungsten atom, the phosphido complex intermediate [Cp*(CO)$_2$W≡P→W(CO)$_5$] was formed (eq 1). Thus, we



(1)

obtained the tetrahedral complex [{Cp*W(CO)$_2$}$_2${($\mu$,$\eta^2$-P$_2$)W(CO)$_5$}] as the major product of this reaction formed by dimerization of the phosphido complex intermediate.

This concept is extended in this report to the arsenic analogues in an attempt to produce intermediates containing a W≡As triple bond.

## Results and Discussion

**Synthesis of the Arsenidene Complex [Cp*As{W(CO)$_5$}$_2$] (1).** By a modified procedure described by Jutzi and Kroos,[10] the reaction of Cp*AsCl$_2$ with Na$_2$[W$_2$(CO)$_{10}$] resulted in dark blue platelets of **1**, which were isolated in 28% yield. In the solid state **1** is stable under argon, but its solutions start to deteriorate after only a few hours upon exposure to light. An X-ray structural analysis of **1** was undertaken, revealing two independent molecules in the unit cell, which are similar

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† Dedicated to Professor G. Wilke on the occasion of his 75th birthday.

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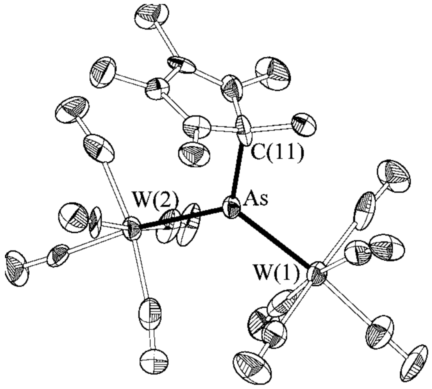


**Figure 1.** Molecular structure of $[Cp^*As\{W(CO)_5\}_2]$ (**1**) (molecule **A**, showing 50% probability ellipsoids; hydrogen atoms are omitted for clarity). Selected bond distances (Å) and angles (deg): W(1)−As = 2.5390(16), W(2)−As = 2.5562(16), As−C(11) = 2.040(18); W(1)−As−W(2) = 124.35, C(11)−As−W(1) = 117.5(5), C(11)−As−W(2) =118.1(5).

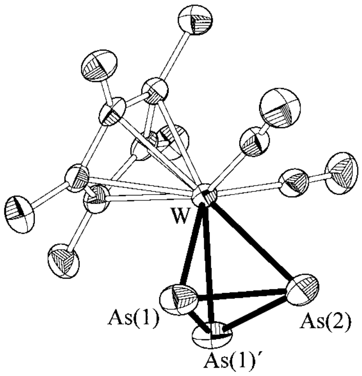
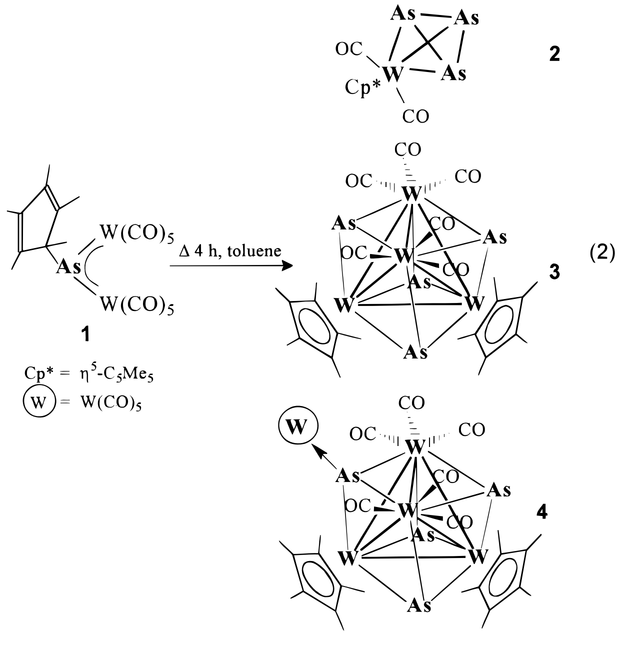


**Figure 2.** Molecular structure of $[Cp^*(CO)_2W(\eta^3\text{-}As_3)]$ (**2**) (showing 50% probability ellipsoids; hydrogen atoms are omitted for clarity). Selected bond distances (Å) and angles (deg): W−As(1) = 2.6301(7), W−As(2) = 2.7017(10), As(1)−As(1)′ = 2.3936(13), As(1)−As(2) = 2.3770(11); As(1)−W−As(1)′ = 54.13(3), As(1)−W−As(2) = 52.93(2), As(1)−As(2)−As(1)′ = 60.46(4), As(2)−As(1)−As(1)′ = 59.77(2).

in their structural parameters. In both, the arsenic atom is in a trigonal-planar environment surrounded by two nearly identical $[W(CO)_5]$ moieties and one $\sigma$-bonded Cp* group (Figure 1 for molecule **A**). A slight deviation exists between the As(1)−W(1) and As(1)−W(2) bond distances (2.5390(16) and 2.5562(16) Å) as well as between the As(2)−W(3) and As(2)−W(4) bond lengths (2.5377(16) and 2.5499(16) Å). Such a deviation also is observed in the P−W bond lengths of the analogous phosphinidene complex $[Cp^*P\{W(CO)_5\}_2]$ (2.428(2) and 2.445(2) Å)[9] and can be explained as a result of the steric repulsion of the Cp* ring toward one of the $[W(CO)_5]$ groups. The $^1H$ NMR spectrum of **1** at room temperature reveals a singlet due to the methyl groups, signifying a fast fluxional series of 1,2-shifts of the Cp* ring. The mass spectrum exhibits as the highest peak a fragment due to the loss of the Cp* group and a subsequent CO fragmentation pattern.

**Thermolysis of $[Cp^*As\{W(CO)_5\}_2]$.** The thermolysis of **1** in refluxing toluene led after 4 h to a color change from the blue of the starting material to dark brown, indicating the completed transformation of **1** (eq 2). In contrast, the thermolysis of the corresponding P analogue of **1**, $[Cp^*P\{W(CO)_5\}_2]$, requires only 1.5 h. Column chromatographic workup of the products of reaction 2 led to the isolation of complexes **2**−**4**.



(2)

The thermolysis products **2**−**4** are yellow, green, and red crystalline compounds, respectively, which are only sparingly soluble in either *n*-hexane or toluene while being readily soluble in THF or $CH_2Cl_2$. The crystal structure of **2** (Figure 2) shows the $WAs_3$ tetrahedral compound in which the $\eta^3$-$As_3$ ligand is capped by a $[Cp^*W(CO)_2]$ unit. In the nearly equilateral triangle *cyclo*-$As_3$ ring the average As−As bond distance is 2.383 Å. These distances are shorter than the As−As bond lengths of $As_4$ (2.44 Å)[11] and $[(triphos)Co(\mu,\eta^3\text{-}As_3)Co(triphos)]^{2+}$ (2.42(2) Å)[12] but correspond with those of the *cyclo*-$As_3$ ligand in $[Co(CO)_3(\eta^3\text{-}As_3)]$ (2.372(5) Å).[13] The data of **2** are in good agreement with those of its isostructural Cr and Mo analogues. $[Cp^*(CO)_2Cr(\eta^3\text{-}As_3)]$ was obtained by Scherer et al.[14] by thermolysis of $[Cp^*(CO)_2Cr]_2$ in the presence of yellow arsenic, while $[Cp^*(CO)_2Mo(\eta^3\text{-}As_3)]$ was obtained by Wachter[15] as a product of the reaction of $[Cp^*(CO)_2Mo]_2$ with $As_4S_4$. Worthy of note is the increase of the average As−As bond distance within the *cyclo*-$As_3$ ring from the Cr (2.352(2) Å) to the Mo (2.375(2) Å) and to the W derivative **2** (2.383(1) Å).

The major products **3** and **4** were isolated as dark green and dark red platelets, respectively. The crystal structures of **3** and **4** (Figures 3 and 4, respectively) depict $W_4$ tetrahedral clusters of $W(CO)_3$ and Cp*W units capped on each face by an As atom. In an alternative view, the structures of **3** and **4** can also be regarded as distorted heterocubanes possessing 58 valence electrons, the vertexes of which are alternately occupied by As or W atoms. The $W_4$ tetrahedral descrip-

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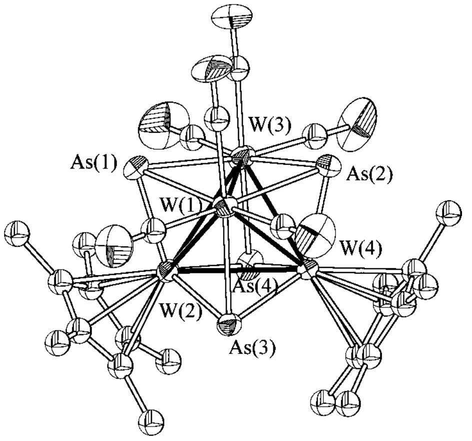


**Figure 3.** Molecular structure of [{W(CO)$_3$Cp*W}$_2$($\mu_3$-As)$_4$] (**3**) (showing 50% probability ellipsoids; hydrogen atoms are omitted for clarity). Selected bond distances (Å) and angles (deg): W(1)−W(2) = 2.8512(9), W(1)−W(3) = 2.9001(9), W(1)−W(4) = 2.8643(10), W(2)−W(3) = 3.0397(9), W(2)−W(4) = 3.122(1), W(3)−W(4) = 3.0285(9), W(1)−As(1) = 2.6117(14), W(1)−As(2) = 2.6078(14), W(1)−As(3) = 2.6512(13), W(2)−As(1) = 2.4622(13), W(2)−As(3) = 2.4975(13), W(2)−As(4) = 2.4846(13), W(3)−As(1) = 2.6262(14), W(3)−As(2) = 2.6139(15), W(3)−As(4) = 2.6458(15), W(4)−As(2) = 2.4664(13), W(4)−As(3) = 2.4841(12), W(4)−As(4) = 2.4844(15); W(1)−W(3)−W(4) = 57.73(2), W(1)−W(3)−W(2) = 57.316(19), W(4)−W(3)−W(2) = 61.887(15), W(2)−As(1)−W(1) = 68.31(4), W(2)−As(1)−W(3) = 73.28(4), W(1)−As(1)−W(3) = 67.24(3), W(1)−As(2)−W(3) = 67.48(3), W(2)−As(4)−W(3) = 72.59(4).

tion corresponds to the Wade−Mingos Rules to give $n + 1$ skeletal electron pairs ($n = 4$). Thus, these complexes are similar in their basic structural framework to [{Cp*W(CO)$_3$}$_2$($\mu_3$-P)$_2${$\mu_3$-PW(CO)$_5$}$_2$] (**6**), which was the minor product (3%) obtained in the thermolysis of the phosphorus analogue [Cp*P{W(CO)$_5$}$_2$].[9] The difference lies in the additional coordination behavior of the capping pnicogenido atoms. In **6**, two of the P atoms coordinate to [W(CO)$_5$] units, whereas in **4** only one and in **3** none of the As atoms coordinate to such a moiety. This indicates the weaker ability of the As lone pair to coordinate to a Lewis-acidic fragment.

The W−W bond distances in **3** and **4** are within the known range of W−W single bonds[16] and agree well with compound **6** but are longer than those of similar sulfur−tungsten-containing pseudo-heterocubanes.[17] In both complexes **3** and **4**, the longest distance is found to be between W(2) and W(4) (3.122(1) and 3.1286(9) Å, respectively), due to the bulky Cp* ligands, whereas the others are in the range from 2.8512(9) to 3.0285(9) Å. The W−As bond distances in complexes **3** and **4** lie between 2.4621(14) and 2.6350(18) Å and are similar to those found, for example, in [{Cp(CO)$_2$W}$_2$($\mu$,$\eta^2$-As$_2$)] (2.571(3)−2.682(3) Å).[18] In general, the W−W and W−As bond distances in complexes **3** and **4** are similar.

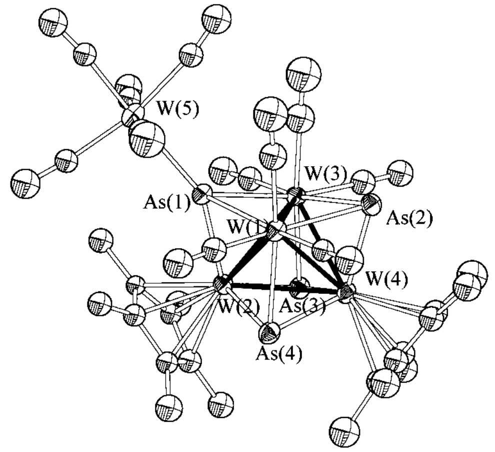
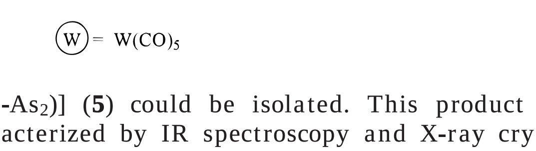


**Figure 4.** Molecular structure of [{W(CO)$_3$Cp*W}$_2$($\mu_3$-As)$_3$-{$\mu_3$-AsW(CO)$_5$}] (**4**) (showing 50% probability ellipsoids; hydrogen atoms are omitted for clarity). Selected bond distances (Å) and angles (deg): W(1)−W(2) = 3.0407(10), W(1)−W(3) = 2.9158(12), W(1)−W(4) = 2.9700(9), W(2)−W(3) = 2.8847(11), W(2)−W(4) = 3.1286(9), W(3)−W(4) = 2.8870(13), W(1)−As(1) = 2.5920(16), W(1)−As(2) = 2.6174(16), W(1)−As(4) = 2.6350(18), W(2)−As(1) = 2.4673(16), W(2)−As(3) = 2.5032(16), W(2)−As(4) = 2.4828(18), W(3)−As(1) = 2.6114(14), W(3)−As(2) = 2.6190(16), W(3)−As(3) = 2.6317(17), W(4)−As(2) = 2.4691(18), W(4)−As(3) = 2.4822(17), W(4)−As(4) = 2.4978(18), W(5)−As(1) = 2.6766(15); W(3)−W(1)−W(2) = 57.89(3), W(3)−W(1)−W(4) = 58.74(2), W(4)−W(1)−W(2) = 62.719(19), W(3)−W(2)−W(1) = 58.89(3), W(3)−W(2)−W(4) = 57.21(2), W(1)−W(2)−W(4) = 57.534(19), W(2)−W(3)−W(4) = 65.65(3), W(4)−W(3)−W(1) = 61.57(3), W(2)−W(3)−W(1) = 63.23(3), W(3)−W(4)−W(2) 57.14(2), W(1)−W(4)−W(2) = 59.75(2), W(3)−W(4)−W(1) = 59.69(2), W(2)−As(1)−W(1) = 73.84(5), W(2)−As(1)−W(3) = 69.16(4), W(1)−As(1)−W(3) = 68.16(4), W(1)−As(2)−W(3) = 67.68(4), W(2)−As(4)−W(4) = 77.83(6).

They only differ in the region close to the atom As(1) due to its coordination to a W(CO)$_5$ group in the case of complex **4**. The bond distances As(1)−W(1) and As(1)−W(3) in **4** are about 0.02 Å shorter than in complex **3**, whereas the bond As(1)−W(2) does not change. Furthermore, in **4**, the W(1)−W(3) bond distance is slightly lengthened (**3**, 2.9001(9) Å; **4**, 2.9158(12) Å) and the bond angles W(2)−As(1)−W(1) and W(1)−As(1)−W(3) are larger than the corresponding angles in **3**.

**Photolysis of [Cp*As{W(CO)$_5$}$_2$].** Irradiation of a toluene solution of **1** for 2 h at ambient temperatures resulted in a color change from deep blue to red-brown (eq 3). After chromatographic workup, only [{W(CO)$_5$}$_3$-($\mu$,$\eta^2$-As$_2$)] (**5**) could be isolated. This product was characterized by IR spectroscopy and X-ray crystallography. Compound **5** exhibits a diatomic arsenic



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(17) (a) Compare with [α-W$_4$S$_4$($\mu$-dtp)$_3$(dtp)$_3$] (2.742−2.896 Å) and [$\beta$-W$_4$S$_4$($\mu$-dtp)$_2$(dtp)$_4$] (2.756(5)−2.846(3) Å) in: Shao-Fang, L.; Jian-Quan, H.; Hong-Hui, Z.; Jun-Qian, L.; Ding-Ming, W.; Zi-Xiang, H.; Can-Zhong, L.; Jin-Ling, H.; Jia-Xi, L. *Polyhedron* **1991**, *10*, 2203−2215. (b) Compare with W$_4$S$_8$(H$_2$NCH$_2$CH$_2$NH$_2$)$_4$]S (2.801(2)−2.878(2) Å) in: Wood, P. T.; Pennington, W. T.; Kolis, J. W.; Wu, B.; O'Connor, C. J. *Inorg. Chem.* **1993**, *32*, 129−130.

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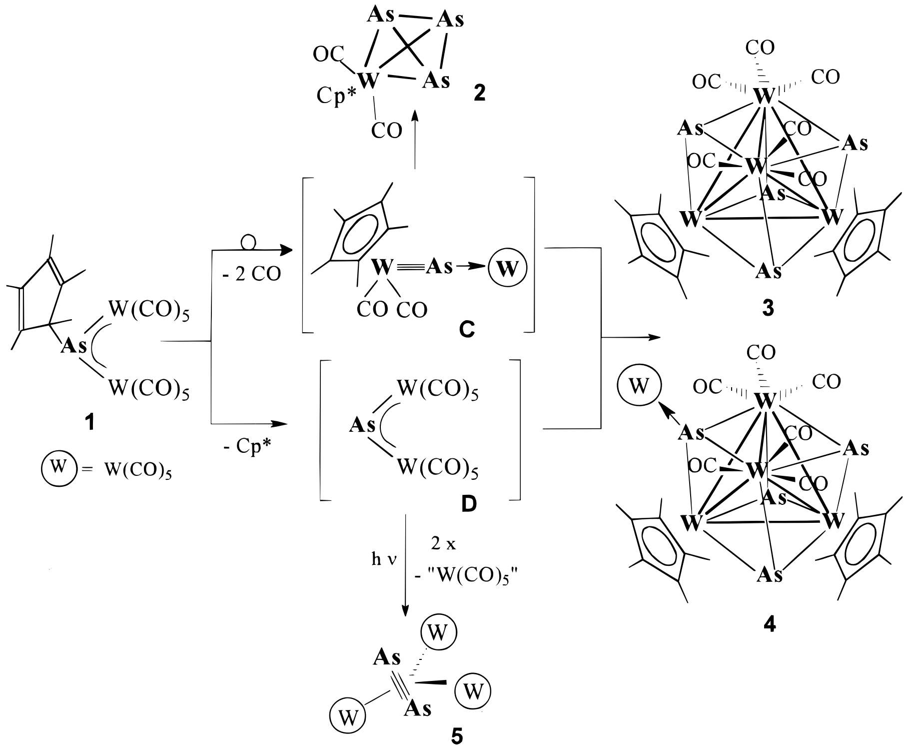
**Scheme 1. Proposed Reaction Pathway of the Transformation of the Arsenidene Complex 1**



ligand supported at the middle of a wheel-type framework of three [W(CO)$_5$] groups. This compound has been reported previously and was structurally characterized by Huttner[19] as the product of the reaction of AsCl$_3$ with either [W(CO)$_5$thf] or Na$_2$[W$_2$(CO)$_{10}$].

**Discussion of the Reaction Pathway.** The nature of the products shows that the thermolysis of the arsenidene complex **1** undergoes the expected Cp* migration from a $\sigma$-bound state at the arsenic to a $\eta^5$-coordinated mode at one of the tungsten atoms, as seen in all three isolated products, particularly within the *cyclo*-As$_3$ complex **2** (Scheme 1). This suggests the possible W−As triply bound intermediate [Cp*(CO)$_2$W≡As→W(CO)$_5$] (**C**), as was found to be the major route in the thermolysis of the corresponding phosphinidene complex [Cp*P{W(CO)$_5$}$_2$].[9] However, in the case of the arsenic compound, a second pathway occurs via Cp* elimination, leading to the possible intermediate [As{W(CO)$_5$}$_2$] (**D**). The intermediates **C** and **D** could react together to form the tetrahedral clusters of tungsten **3** and **4**, with loss of [W(CO)$_5$] groups, due to the lower coordination ability of the arsenic lone pair in comparison to the phosphorus lone pair. Both pathways seem to be equally probable in the transformation of the arsenidene complex **1** under thermal conditions, since the tungsten clusters **3** and **4** are the major products of the thermolysis. For the corresponding reaction starting from [Cp*P{W(CO)$_5$}$_2$], the tungsten cluster **6** was isolated only in trace amounts.[9] Under photochemical activation the competing pathway of a Cp* elimination dominates, giving the As$_2$ ligand complex **5** as the sole product. The origin of the thermolysis product **2** might be the reaction of intermediate **C** either with two molecules of **D**, with the loss of W(CO)$_5$ groups, or with complex **5**, which is not found to be a product of the thermolysis reaction (2).

## Conclusions

The present work finds a precedent in the recent finding that an intermediate containing a W−P triple bond is formed upon thermolysis of the complex [Cp*P{W(CO)$_5$}$_2$]. Observations that such a W−As triple-bond-containing intermediate might also be accessible by using the As complex **1** open up a new route for generating a series of heavier pnicogenido ligand intermediates. However, two equivalent pathways occur in the thermolysis of [Cp*As{W(CO)$_5$}$_2$], involving the formation of [Cp*(CO)$_2$W≡As→W(CO)$_5$] and [As{W(CO)$_5$}$_2$]. Each opens up a broad perspective for trapping these intermediates with reactive molecules such as, for example, alkynes, phosphaalkynes, and dienes. This initiates as well new possibilities for generating such intermediates and corresponding products of the heavier congeners, Sb and Bi. Furthermore, the use of different pnicogenidene complexes of the type [Cp*E{W(CO)$_5$}$_2$] (E = P, As, Sb, Bi) in cothermolysis and cophotolysis reactions could allow the synthesis of novel mixed EE′ ligand complexes of different group 15 elements, an area where, until now, just a few examples have existed.[20]

## Experimental Section

All reactions were performed under an atmosphere of dry argon with standard vacuum, Schlenk, and glovebox techniques. Solvents were purified and degassed by standard procedures. Photolysis reactions were carried out with a Hanau

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**Table 1. Crystallographic Data for 1−4**

| | **1** | **2** | **3** | **4**·$0.5C_7H_8$ |
|---|---|---|---|---|
| formula | $C_{20}H_{15}AsO_{10}W_2$ | $C_{12}H_{15}As_3O_2W$ | $C_{26}H_{30}As_4O_6W_4$ | $C_{34.5}H_{34}As_4O_{11}W_5$ |
| formula wt | 857.94 | 599.85 | 1473.58 | 1843.55 |
| cryst size, mm | 0.15 × 0.11 × 0.02 | 0.20 × 0.12 × 0.08 | 0.08 × 0.04 × 0.02 | 0.20 × 0.20 × 0.08 |
| *T*, K | 190(1) | 210(2) | 200(1) | 200(1) |
| space group | $P2_1/n$ | *Pnma* | $P2_1/n$ | $P2_1/c$ |
| cryst syst | monoclinic | orthorhombic | monoclinic | monclinic |
| *a*, Å | 15.387(2) | 8.5450(17) | 10.180(2) | 17.402(4) |
| *b*, Å | 18.193(2) | 13.506(3) | 16.340(3) | 14.307(3) |
| *c*, Å | 17.997(2) | 13.253(3) | 19.866(4) | 18.855(4) |
| $\beta$, deg | 103.34(2) | 90.0 | 97.73(3) | 116.15(3) |
| *V*, Å$^3$ | 4902.2(10) | 1529.5(5) | 3274.4(11) | 4213.9(15) |
| *Z* | 8 | 4 | 4 | 4 |
| $d_{calcd}$, g/cm$^3$ | 2.325 | 2.605 | 2.989 | 2.906 |
| $\mu$, mm$^{-1}$ | 10.768 | 13.984 | 18.054 | 16.769 |
| *F*(000) | 3168 | 1104 | 2648 | 3324 |
| radiation ($\lambda$), Å | 0.710 73 | 0.710 73 | 0.710 73 | 0.710 73 |
| diffractometer | STOE IPDS | STOE IPDS | STOE IPDS | STOE IPDS |
| $2\theta$ range, deg | $3.52 \le 2\theta \le 52.06$ | $4.30 \le 2\theta \le 51.82$ | $4.14 \le 2\theta \le 51.82$ | $3.72 \le 2\theta \le 51.76$ |
| *hkl* range | $-18 \le h \le 18$,<br>$-22 \le k \le 13$,<br>$-22 \le l \le 22$ | $-10 \le h \le 9$,<br>$-16 \le k \le 16$,<br>$-16 \le l \le 16$ | $-12 \le h \le 12$,<br>$-20 \le k \le 20$,<br>$-24 \le l \le 24$ | $-21 \le h \le 21$,<br>$-17 \le k \le 17$,<br>$-23 \le l \le 23$ |
| no. of rflns collected | 20 206 | 9427 | 23 390 | 24 888 |
| no. of indep rflns with $I > 2\sigma(I)$ | 5242 ($R_{int} = 0.0837$) | 1417 ($R_{int} = 0.0524$) | 4638 ($R_{int} = 0.0568$) | 6177 ($R_{int} = 0.1409$) |
| no. of data/restraints/params | 8504/0/605 | 1541/0/91 | 6066/0/233 | 7692/0/266 |
| goodness of fit on $F^2$ | 0.886 | 1.102 | 0.964 | 1.039 |
| R1,[a] wR2[b] ($I > 2\sigma(I)$) | 0.0520, 0.1138 | 0.0269, 0.0691 | 0.0389, 0.0945 | 0.0448, 0.1213 |
| R1,[a] wR2[b] (all data) | 0.0917, 0.1251 | 0.0298, 0.0706 | 0.0550, 0.1046 | 0.0573, 0.1339 |
| largest diff peak, hole, e/Å$^3$ | 2.605, −2.256 | 1.209, −0.852 | 2.255, −1.662 | 1.852, −2.770 |

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum w(F_o{}^2 - F_c{}^2)^2]/[\sum(F_o{}^2)^2]^{1/2}$.

type TQ150 mercury lamp. NMR spectra were recorded on a Bruker AC 250 ($^1$H, 250.133 MHz; $^{13}$C, 62.896 MHz; standard $Me_4Si$ ($^1$H and $^{13}$C), 85% $H_3PO_4$ ($^{31}$P)). IR spectra were recorded in KBr on a Bruker IFS28 FT-IR spectrometer. Mass spectra were recorded on a Finnigan MAT 711 spectrometer at 70 eV. Elemental analysis was performed by the analytical laboratory of the Institut für Anorganische Chemie.

Unless otherwise noted, commercial grade chemicals were used without further purification. Silica gel was activated by heating under high vacuum ($10^{-3}$ Torr) at 200 °C for 2 days. Cp*$AsCl_2$[21] and $Na_2[W_2(CO)_{10}]$[22] were prepared by literature methods.

**[Cp*As{$W(CO)_5$}$_2$] (1).** $Na_2[W_2(CO)_{10}]$ (1.840 g, 2.65 mmol) was suspended in *n*-pentane (100 mL) and the suspension cooled to 0 °C. Under vigorous stirring, a solution of Cp*$AsCl_2$ (725 mg, 2.58 mmol) in *n*-pentane (30 mL) was added dropwise, and the yellow suspension immediately turned intense blue. The suspension was warmed to room temperature and was then stirred for 4 h. The mixture was filtered and washed with *n*-hexane (4 × 30 mL), and the blue filtrate was reduced in vacuo to 70 mL and stored at −30 °C. The product was isolated as blue platelets with a golden luster (626 mg, 0.730 mmol, 28%). $^1$H NMR ($C_6D_6$, 303 K): $\delta$ 1.727 (s). $^{13}$C{$^1$H} NMR ($C_6D_6$, 301 K): $\delta$ 14.70 ($CH_3$), 133.26 ($Me_5C_5$), 197.32 (CO). EI MS: *m*/*z* (%) 722.8 (13) [$M^+$ − Cp*], 694.9 (8) [$M^+$ − Cp*(CO)], 666.9 (15) [$M^+$ − Cp*$(CO)_2$], 638.8 (11) [$M^+$ − Cp*$(CO)_3$], 610.9 (8) [$M^+$ − Cp*$(CO)_4$], 135 (91) [Cp*]. IR (KBr; $\tilde{\nu}$(CO), cm$^{-1}$): 2058 (m), 2039 (s), 2010 (m), 1957 (br). Anal. Calcd for $C_{20}H_{15}O_{10}AsW_2$: C, 28.00; H, 1.76. Found: C, 28.34; H, 2.23.

**Thermolysis of [Cp*As{$W(CO)_5$}$_2$], Synthesis of 2−4.** A solution of **1** (245 mg, 0.286 mmol) in toluene (50 mL) was refluxed for 4 h, during which time the solution changed color from deep blue to dark brown. The solvent was completely removed in vacuo, and the resulting brown residue was transferred onto silica gel and separated by column chromatography (30 × 2.5 cm, Merck 60). Elution with *n*-hexane/toluene (5:1) gave a yellow fraction containing **2**, which was recrystallized from *n*-hexane to give yellow rods (11 mg, 0.018 mmol, 19%). This was followed by a dark green fraction (5:1 *n*-hexane/toluene) yielding **3** in the form of dark green platelets after recrystallization from toluene (22 mg, 0.015 mmol, 21%). Elution with *n*-hexane/toluene (3:1) resulted in a red fraction containing **4**, which was recrystallized from toluene and isolated as dark red platelets (40 mg, 0.022 mmol, 31%). Data for **2**: $^1$H NMR ($C_6D_6$, 301 K) $\delta$ 1.69 (s); $^{13}$C{$^1$H} NMR ($C_6D_6$, 301 K) $\delta$ =2.56 ($CH_3$), 96.83 ($Me_5C_5$), 212.94 (CO); EI-MS *m*/*z* (%) 600 (44) [$M^+$], 544 (87) [$M^+$ − 2CO], 409 (3) [$M^+$ − Cp*-$(CO)_2$]; IR (KBr; $\tilde{\nu}$(CO), cm$^{-1}$) 1949 (s), 1884 (s). Anal. Calcd for $C_{12}H_{15}As_3O_2W$: C, 24.03; H, 2.52. Found: C, 24.37; H, 2.92. Data for **3**: $^1$H NMR ($C_6D_6$, 301 K) $\delta$ 2.42 (s); EI MS *m*/*z* (%) 1390 (3) [$M^+$ − 3CO], 1113 (18) [$M^+$ − Cp*$W(CO)_5$], 994 (32) [$M^+$ − Cp*$AsW(CO)_3$], 938 (100) [$M^+$ − Cp*$AsW(CO)_5$]; IR (KBr; $\tilde{\nu}$(CO), cm$^{-1}$) 2004 (s), 1970 (vs), 1960 (sh), 1930 (s), 1905 (m). Anal. Calcd for $C_{26}H_{30}As_4O_6W_4$: C, 21.19; H, 2.05. Found: C, 21.33; H, 2.49. Data for **4**: $^1$H NMR ($C_6D_6$, 301 K) $\delta$ 1.89 (s); EI-MS *m*/*z* (%) 961 (77) [$As_3W_4{}^+$], 946 (41) [Cp*$W_4$-$As^+$]; IR (KBr; $\tilde{\nu}$(CO), cm$^{-1}$) 2066 (vs), 2010 (s), 1992(sh), 1981 (br), 1962 (sh), 1931 (m), 1923 (m), 1920 (m), 1914 (m), 1895 (s).

**Photolysis of [Cp*As{$W(CO)_5$}$_2$], Synthesis of [$As_2${$W(CO)_5$}$_3$] (5).** A solution of **1** (223 mg, 0.260 mmol) in toluene (70 mL) was irradiated with a mercury lamp through quartz glass and stirred for 2 h, during which time the solution changed color from deep blue to red-brown. The solvent was completely removed in vacuo, and the remaining brown residue was transferred onto silica gel and separated by column chromatography. Elution with *n*-hexane/toluene (5:1) gave a light red fraction containing **5**, which was isolated as red rods upon recrystallization from toluene (41 mg, 0.036 mmol, 28%). IR (KBr; $\tilde{\nu}$(CO), cm$^{-1}$) 2062 (s), 2016 (sh), 1947 (vs). X-ray and spectroscopic data are in good agreement with those described in ref 19.

**Crystal Structure Analysis.** Crystal structure analyses of **1**−**4** were performed on a STOE IPDS diffractometer with Mo K$\alpha$ radiation ($\lambda$ = 0.710 73 Å). Machine parameters, crystal

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data, and data collection parameters are summarized in Table 1. The structures were solved by direct methods with the program SHELXS-86,[23a] and full-matrix least-squares refinement on $F^2$ in SHELXL-97[23b] was performed with anisotropic displacements for non-H atoms. Hydrogen atoms were located in idealized positions and refined isotropically according to the riding model. Because of the limited quality of the crystals, only the W, As, and CO atoms for **3** and the W and As atoms of **4** were refined anisotropically. For **3**, the Cp* ligands are disordered: their percentage of occupancy (60/40) and the temperature factors were freely refined.

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**Supporting Information Available:** Complete tables of crystal data, atomic coordinates, H atom parameters, bond distances, and anisotropic displacement parameters and fully labeled figures for **1**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0003436

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(23) (a) Sheldrick, G. M. SHELXS-86; University of Göttingen, Göttingen, Germany, 1986. (b) Sheldrick, G. M. SHELXL-97; University of Göttingen, Göttingen, Germany, 1997.