Synthesis and Characterization of Unsymmetrical (*cis*-(Phosphino−arsino)ethene)tetracarbonylmolybdenum Complexes: Hydroarsination Reactions of ($H_3CC{\equiv}CPPh_2$)Mo(CO)$_5$ and [$H_2C{=}C{=}CH$(DBP)]Mo(CO)$_5$ and Hydrophosphination Reactions of ($Ph_2AsCH_2C{\equiv}CH$)Mo(CO)$_5$

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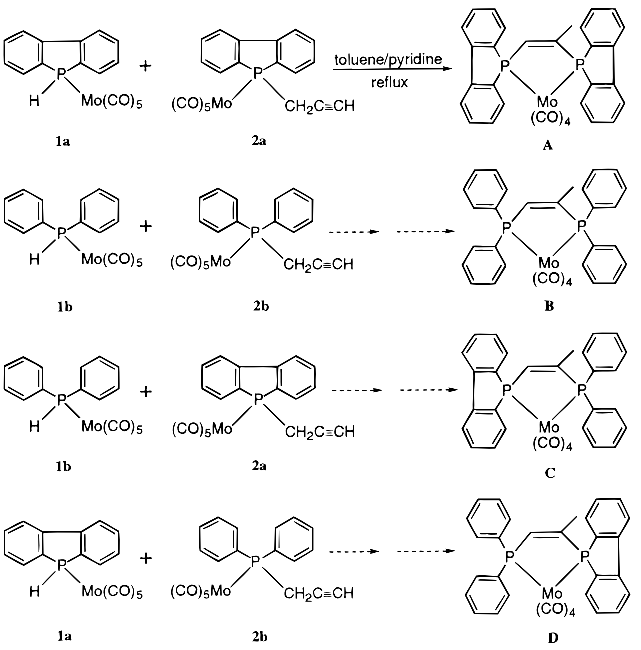
The base-catalyzed hydroarsination reactions of ($H_3CC{\equiv}CPPh_2$)Mo(CO)$_5$ and [$H_2C{=}C{=}CH$(DBP)]Mo(CO)$_5$ (DBP = dibenzophosphole) give several different products as a function of reaction conditions. These products have been characterized by elemental analyses, physical properties, ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectroscopy, and, in two cases, X-ray crystallography.

Introduction

Secondary phosphines are well-known to undergo Michael type additions (hydrophosphination) to coordinated phosphinoalkenes and -alkynes to produce *cis*-diphosphine complexes stereospecifically.[1] Such addition reactions may provide an efficient route for the syntheses of unsymmetrical, rigid, chelating diphosphine ligands which have potential applications in the area of asymmetric catalysis.[2] Previously, as part of extensive studies into reactions of this type, we reported the base-catalyzed additions of the coordinated secondary phosphine/phosphole (**1a**,**b**) to tertiary phosphinoalkyne complexes (**2a**,**b**) that resulted in the formation of mixed unsymmetrical rigid chelate *cis*-diphosphinoethene ligands of the types **A**,[3] **B**,[4] **C**,[5] and **D**[5] (Scheme 1).

To further explore the scope of these reactions we have studied the base-promoted additions of the activated alkene and alkyne complexes **2a′** and **2b″** toward hydroarsination with diphenylarsine to form the unsymmetrical rigid mixed-arsino−phosphino/phospholyl ligands analogous to **B** and **D**. We also studied the aptitude of the (diphenylarsino)alkyne complex ($Ph_2AsCH_2C{\equiv}CH$)Mo(CO)$_5$, **G**, to undergo hydrophosphination with a free and coordinated secondary phosphine and a coordinated secondary phosphole, and the results are reported herein.

Scheme 1



Results and Discussion

We have earlier reported[4] the isomerization of the phosphinoalkyne complex **2b** in the presence of base to produce a mixture of the three isomers **2b**, **2b′**, and **2b″** (propargyl, allenyl, and propynyl), respectively, in solution (Scheme 2). These isomers were separated by column chromatography on silica gel. In a similar manner we were able to obtain the analogous DBP allenyl complex **2a′** (DBP = dibenzophosphole). Complexes **2a′** and **2b″** were separately reacted with free diphenyl arsine (Schemes 3 and 4, respectively) under the same reaction conditions.

The hydroarsination reaction of **2b″** with Ph_2AsH, in the presence of potassium *tert*-butoxide in refluxing diglyme

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(1) Carty, A. J.; Johnson, D. K.; Jacobson, S. E. *J. Am. Chem. Soc.* **1979**, *101*, 5612.

(2) See for example: (a) Kagan, H. B.; Dang, T. P. *J. Am. Chem. Soc.* **1972**, *94*, 4, 6429. (b) Achiwa, K. *J. Am. Chem. Soc.* **1976**, *98*, 8265. (c) Wilson, M. E.; Nuzzo, R. G.; Whitesides, G. M. *J. Am. Chem. Soc.* **1978**, *100*, 2269. (d) Treichel, P. M.; Wong, W. L.; Calabrese, J. C. *J. Organomet. Chem.* **1978**, *159*, C20. (e) Brunie, S.; Mazan, J.; Langlois, N.; Kagan, H. B. *J. Organomet. Chem.* **1976**, *114*, 225. (f) Brown, J. M.; Chaloner, P. A. *J. Chem. Soc., Chem. Commun.* **1978**, 321. (g) Sanger, A. R.; Tan, K. G. *Inorg. Chim. Acta* **1978**, *31*, L439. (h) Brunner, H., Zettlmeier, W., Eds. *Handbook Of Enantioselective Catalysis*; VCH: Weinheim, Germany, 1993; Vol. II.

(3) Wilson, W. L.; Alcock, N. W.; Alyea, E. C.; Song, S.; Nelson, J. H. *Bull. Soc. Chim. Fr.* **1993**, *130*, 673.

(4) Maitra, K.; Catalano, V. J.; Nelson, J. H. *J. Organomet. Chem.* **1997**, *529*, 409.

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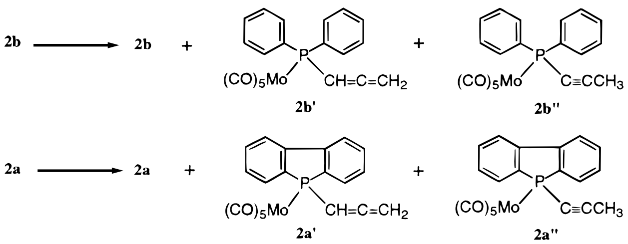
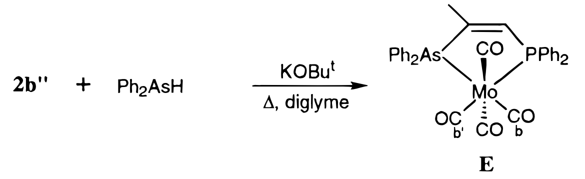
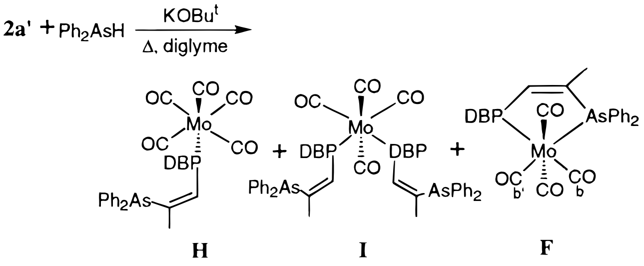
Scheme 2



Scheme 3



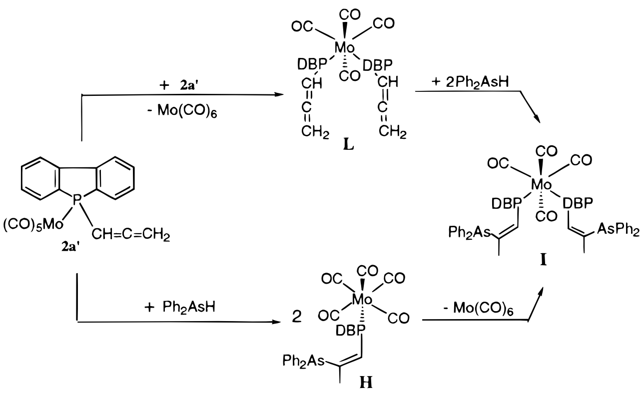
Scheme 4



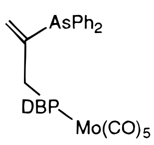
produced the chelate complex **E** as the major isolated product along with the formation of the red bridged arsenide complex $[Ph_2AsMo(CO)_4]_2$. Purification by flash chromatography on silica gel followed by recrystallization from a 1:1 mixture of dichloromethane and methanol produced yellow orange crystals of **E** in 46% yield. Base-promoted addition of the As−H bond across the C≡C triple bond in **2b″** concomitant with the formation of the five-membered chelate ring following the elimination of a CO unit results in the formation of **E**. Hydroarsinations of activated alkenes and alkynes have been reported by others.[6]

Similarly, the reaction of **2a′** with Ph_2AsH produces the chelate complex **F** as the major product along with the formation of complexes **H** and **I** in minor amounts (Scheme 4). The mixed *cis*-As−P complex **H** is the result of the direct addition of the As−H bond (such that the As and P units are *cis* oriented) across the terminal vinyl function of complex **2a′** in a Markovnikov sense. Addition at the same position may also occur in the same manner with the P and As units being oriented *trans* to each other and form the *trans* geometrical isomer. The rigid *cis* isomer **H** having the dangling arsine arm has the favorable geometry as opposed to the *trans* product and can therefore spontaneously eliminate a molecule of CO to form the five-membered chelate ring complex **F**. So far we have not been able to identify or detect the *trans* mixed arsine−phospholyl geometrical isomer of **H** in the product mixture. Analogous dimolybdenum *trans*-diphosphine and mixed phosphole−phosphine complexes have been reported earlier.[4,5] In a similar way, the addition of the As−H bond in the Markovnikov sense across

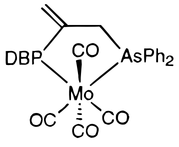
Scheme 5



the internal vinyl fuctional group of **2a′** will produce the dangling arsine complex **J**, which may undergo base promoted



J



K

[1,3] hydrogen migration to produce any of the geometrical isomers of **H**. Alternatively, the driving force of chelation may also cause the intermediate **J** to form the five-membered chelate ring following the elimination of a CO molecule to produce the *exo* methylene complex **K**. The latter may subsequently undergo the [1,3] hydrogen shift to form the thermodynamically more stable complex **F**. Although we have not been able to identify the intermediates **J** and **K** for this particular reaction, we have earlier reported the formation of analogous dimolybdenum diphosphine, diphosphole, and mixed phosphine−phosphole complexes obtained as products of similar hydrophosphination reactions.[4,5] The formation of the *cis*-diphosphole complex **I** in a minor amount indicates that some ligand dissociation followed by the substitution of a CO unit may occur to form the *cis*-bis(phosphole) intermediate **L**, which then rapidly undergoes the hydroarsination reaction at the terminal vinyl group in the Markovnikov sense to give the resultant *cis*-bis(*cis*-DBP−As) complex **I**. It may also be argued that the hydrophosphination reaction precedes the formation of the *cis*-bis(phosphole) intermediate, in which case **H** is formed first, and then two such molecules of **H** condense to form **I** following the elimination of a unit of $Mo(CO)_6$. The latter is more likely as we have isolated **H** from the product mixture. A suggested mechanistic pathway for the formation of **I** is shown in Scheme 5.

From our several attempts to synthesize the secondary arsine complex $Ph_2AsHMo(CO)_5$ by the literature procedure designed to prepare analogous secondary phosphine complexes,[7] we found the former to be highly unstable. In contrast, we were able to synthesize the stable diphenyl tertiary arsinoalkyne complex **G** $[(Ph_2AsCH_2C{\equiv}CH)Mo(CO)_5]$ in 57% yield (see Experimental Section) by following the same synthetic route.[7] We therefore attempted the hydrophoshination reactions of **G** separately with the free secondary phosphine (Ph_2PH) and the coordinated phosphine in complex **1b**. It was observed that, for both of these reaction systems, ligand displacement occurred resulting

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(6) (a) Märkl, G.; Baier, H.; Liebl, R. *Synthesis* **1997**, 842. (b) Chi, P. B.; Kober, F. *Z. Anorg. Allg. Chem.* **1983**, *501*, 89. (c) Berger, H.-O.; Nöth, H. *J. Organomet. Chem.* **1983**, *250*, 33.

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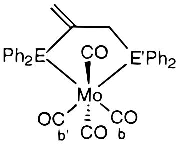
in the formation of a variety of products which made complete separation and characterization of all the complexes in the reaction mixture a difficult and complicated process. From the reaction of **G** with Ph_2PH we isolated the chelate diphosphine complex **B**[4] as the major product. This indicates that the propargyl unit of **G** somehow underwent complete dissociation following its reaction with Ph_2PH present in solution to produce complex **2b**. Complex **2b** subsequently underwent the hydrophosphination reaction with Ph_2PH to produce **B**. Similarly, the reaction of **G** with **1b** produced the expected mixed-arsine−phosphine *exo* methylene chelate complex **M** along with the



M : E = P, E' = As;
N : E, E' = As;
O : E, E' = P;
R : E, E' = DBP;

analogous diarsino *exo* methylene complex **N** and a minor amount of **O**,[4] as evidenced from the $^{31}P\{^1H\}$, ^1H, and $^{13}C\{^1H\}$ NMR spectroscopic data. As seen in the ^1H NMR spectra, these three complexes were present in the ratio **M**:**N**:**O** = 5:3.1:1. All three complexes were eluted in the same fractions during the purification process by column chromatography, and we were able to fractionally crystallize out **M** and **N** as a mixture from a 1:1 dichloromethane/methanol solution. Although several attempts to separate **M** and **N** by further chromatography or crystallization remained unsuccessful, we were able to completely characterize and establish the structures of both of these complexes from the ^1H (**M**, 61.5%; **N**, 38.5%; as seen in the ^1H NMR spectrum) and $^{13}C\{^1H\}$ NMR spectroscopic data. The formation of **N** and **B** further confirms the fact that ligand displacement reactions are a prominent feature of these systems.

The hydrophosphination reaction of **G** with **1a** was also attempted under the same reaction conditions. The $^{31}P\{^1H\}$ NMR spectra of the crude product mixture showed resonances for the two diphosphole chelate complexes **A**[3] and **R**[5] and other decomposition products. Purification by column chromatography using 5% benzene in hexane eluted a 1:1 mixture of **A** and **R** in a few of the fractions. We did not isolate any mixed-arsine−phosphole complexes from this reaction.

The results of the various hydrophosphination reactions of the activated arsinoalkyne complex **G** with secondary phosphines and phospholes led us to conclude that ligand substitution or exchange is a predominant feature for these reaction systems, and therefore, it determines the fate of the Michael addition products formed. There is evidence for some (arsine)pentacarbonylchromium complexes[8] to undergo rapid ligand dissociation followed by substitution with stronger nucleophiles, such as a phosphine. We have encountered such ligand dissociation followed by substitution reactions in the case of mixed-phosphine−phosphole complexes.[5] In contrast, the hydroarsination reactions of the phosphinoalkyne and phospholylalleneyl complexes **2b″** and **2a′**, respectively, with the free secondary arsine gave clean products, and no ligand exchange products were observed in any of these cases. Most likely the free secondary diphenyl arsine molecule acts as a stronger nucleophile toward the unsaturated acetylinic and alleneyl bonds in **2b″** and **2a′**, respectively, resulting in the rapid formation of the Michael addition product followed by chelation.

$^{31}P\{^1H\}$, $^{13}C\{^1H\}$, and ^1H NMR Spectroscopy. The $^{31}P\{^1H\}$ NMR spectra for the rigid chelate complexes **E**, **F**, and **M** each display a single resonance at δ 55.03, 51.95, and 55.34 ppm, respectively, in the region expected for Mo(0) complexes.[4,5] The large downfield shifts for the phosphorus nuclei in each case is consistent with the formation of the five-membered chelate ring.[9] The $^{13}C\{^1H\}$ NMR spectra for these chelate complexes display two distinct sets of resonances for each of the mutually *cis* equatorial carbonyl carbons, and the most downfield resonance corresponds to the carbonyl group *trans* to the arsino unit. The larger $^2J(PC)$ value corresponds to the carbonyl carbon *trans* to the phosphorus atom. The two mutually *trans* carbonyl carbons are chemical shift equivalent and appear most upfield as a doublet due to coupling to the *cis* phosphorus atom. For complex **N** this pattern simplifies and three resonances are observed as singlets, two for each of the equatorial and another upfield one for the pair of axial carbonyls.

The ^1H NMR spectra of **E** and **F** each display the presence of one vinyl proton resonance coupled to the geminal phosphorus and vicinal CH_3 group and as a result is a doublet of quartets in each case. The CH_3 resonance for both molecules, having accidentally the same coupling constant values of $^4J(PH) = {}^4J(HH) = 1.5$ Hz, in both cases appears as an apparent triplet. In the ^1H NMR spectrum for complex **M** the resonances for the two geminal protons are doublets of doublets due to large magnititude coupling to phosphorus and coupling to each other by 0.5 Hz. The methylene proton resonance for **M** appears as a doublet due to coupling to phosphorus with a magnititude of 17.5 Hz. For the analogous diarsine complex **N**, the ^1H NMR spectrum further simplifies and exhibits only three singlets, two in the vinylic region for the two geminal protons and one in the aliphatic region for the two chemically equivalent methylene protons. For this molecule we did not resolve any coupling between the two geminal vinyl protons.

The $^{31}P\{^1H\}$ NMR spectrum for the pentacarbonyl complex **H** displays a singlet at δ 14.27 ppm. The $^{13}C\{^1H\}$ NMR spectrum for this mixed *cis* arsine−phospholyl complex in the carbonyl region displays two sets of resonances of which the more downfield has the higher magnititude coupling constant and corresponds to the CO group *trans* to the phosphorus. The other upfield resonance corresponds to the four carbonyl groups *cis* to phosphorus. The $^{13}C\{^1H\}$ NMR spectrum also shows resonances for the DBP and the phenyl ring carbons in the aromatic region as expected (see Experimental Section). The ^1H NMR spectrum for this complex shows the presence of a vinylic proton coupled to the geminal phosphorus with a magnititude of $^2J(PH) = 35.5$ Hz and also coupled to the *cis* CH_3 protons with a magnitude of 1.5 Hz. These data are in agreement with other reported values for analogous *cis* chelate complexes[3−5] and therefore support the *cis* orientation of the CH_3 and vinyl proton unit with respect to each other and hence the proposed structure.

The $^{31}P\{^1H\}$ NMR spectrum for **I** shows a single resonance at δ 18.29 ppm for the two equivalent phosphorus nuclei present in this molecule. The ^1H and $^{13}C\{^1H\}$ NMR spectra are both second order as expected for an $(R_3P)_2Mo(CO)_4$ complex.[10] The value of $^2J(PP)$ is typical for a *cis*-$(R_3P)_2Mo(CO)_4$ complex.[11] The value of $^4J(PH) \sim 2.0$ Hz suggests that the phosphorus and CH_3 are mutually *trans*.[4,5,7] These data support the proposed structural assignment for **I**.

For the diphenylarsine pentacarbonyl complex **G** the methylene resonance in the ^1H NMR spectrum is a doublet due to

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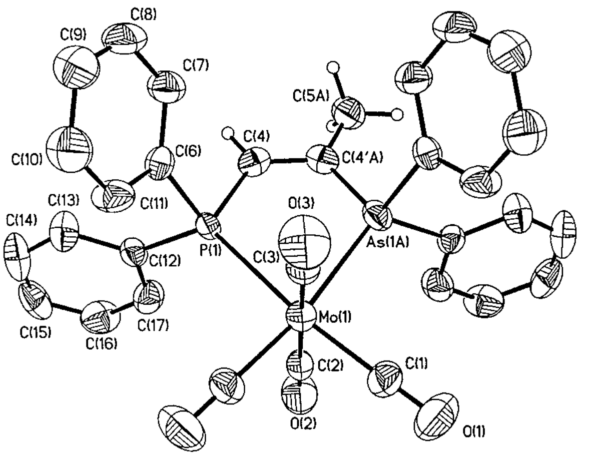

Figure 1. Structural drawing of **E**, showing the atom-numbering scheme (40% probability ellipsoids). Hydrogen atoms have an arbitrary radius of 0.1 Å.

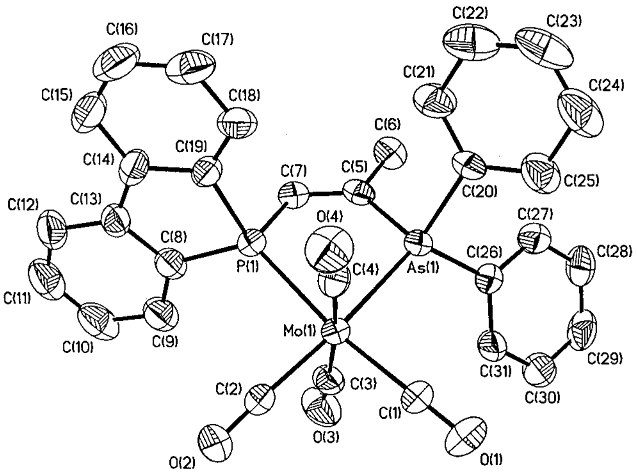

Figure 2. Structural drawing of **F**, showing the atom-numbering scheme (40% probability ellipsoids). Hydrogen atoms have been omitted for clarity.

coupling to the alkyne hydrogen, and the latter in turn is a quartet. The chemical shifts for the other protons in the molecule lie in the expected regions. The ${}^{13}C\{{}^{1}H\}$ NMR spectrum for this complex is simple, as all the resonances are singlets. Two sets of resonances are observed for the five carbonyl groups, and the most downfield one corresponds to the cabonyl carbon *trans* to the arsenic atom, while the other relatively upfield resonance is due to the four *cis* carbonyls. The two alkyne resonances appear in the region typical for sp-hybridized carbons. The NMR spectral data for all complexes are fully consistent with the assigned structures.

Crystal Structure Analysis. X-ray crystal structures of complexes **E**−**G** were obtained to gain conclusive support for their structures. These structures are shown in Figures 1−3, respectively. Selected bond distances and angles are listed in Tables 1 and 2, respectively. All three complexes exist as discrete molecules with no abnormal intermolecular contacts. The molecular structure of **E** is disordered accross a mirror plane that bisects the ethylenic double bond and passes through the two axial carbonyl groups and the metal atom. Both **E** and **F** have a distorted octahedral geometry at the metal center, and this distortion may be attributed largely to the formation of the five-membered chelate ring. The equatorial plane in each case is formed by the two mutually *cis* oriented arsenic and phosphorus atoms and the two carbonyl groups *trans* to them.

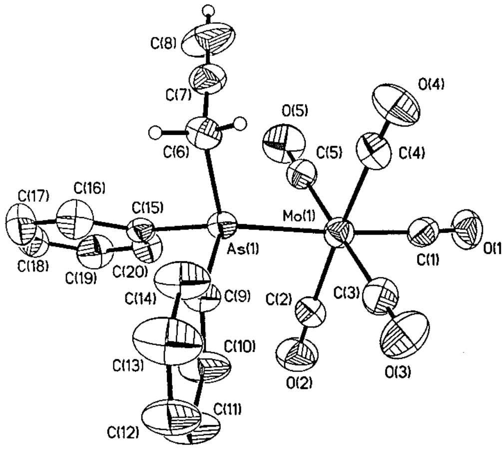

Figure 3. Structural drawing of **G**, showing the atom-numbering scheme (40% probability ellipsoids). Hydrogen atoms have an arbitrary radius of 0.1 Å.

The bond angles C(1)#1−Mo(1)−As(1)#1, C(1)−Mo(1)−P(1) are 171.7(2), 173.2(2)° and C(1)−Mo(1)−P(1), C(2)−Mo(1)−As(1) are 172.6(2), 172.3(2)° for **E** and **F**, respectively, signifying the *trans* orientation of the two equatorial cabonyl groups with respect to the arsenic and phosphorus atoms in both molecules. The bond angles C(2)−Mo(1)−C(3) for **E** and C(3)−Mo(1)−C(4) for **F** are 176.3(4) and 174.9(2)°, respectively, consistent with the mutual *trans* orientation of the two axial carbonyls. The Mo−P bond distances are slightly shorter than the Mo−As distances for both **E** and **F** (see Table 1) as expected[12] and are in very good agreement with those reported for similar Mo(0) complexes.[13] Notably, in both of these molecules the C−O bond lengths of the two mutually *trans* carbonyls are shorter than those of the two carbonyls *trans* to the phosphine and arsine ligands (see Table 1), which may be a result of the better donor ability of the latter groups. In complex **F** the bond distances 1.318(7) and 1.504(7) Å for C(5)−C(7) and C(5)−C(6) signify the presence of a double bond and a single bond, respectively. Moreover, the C(7)−C(5)−C(6) bond angle (124.4(6)°) confirms the presence of sp^2 hybridization at C(15). Similarly, for **E** the bond distances C(4′)−C(5) and C(4′)−C(4)#1 are 1.44(1) and 1.317(2) Å, suggesting the presence of a double and a single bond, respectively. For the pentacarbonyl complex **G** the geometry at the metal center is a slightly distorted octahedron with the angles around the metal atom ranging from 87.9(4) to 92.0(4)°. The metal−carbon bond *trans* to the arsine moiety is slightly shorter than the other metal−carbon bonds, which may be due to the better donor ability of the arsine ligand. The bond distance Mo(1)−As(1) (2.5799(11) Å) lies in close agreement with those reported for similar As−Mo bonds.[13]

Experimental Section

1. Reagents and Physical Measurements. *Caution: Arsenic compounds are potentially hazardous and should be handled with due care!*

Commercially available, reagent grade chemicals were used unless otherwise indicated. All experiments were performed under a dry nitrogen atmosphere using standard Schlenk line techniques. (RPh$_2$P)Mo(CO)$_5$ and (RDBP)Mo(CO)$_5$, where R = H and −CH$_2$C≡CH, were prepared by literature methods.[7] Tetrahydrofuran was distilled under nitrogen from sodium benzophenone ketyl, and diglyme was distilled

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Table 1. Bond Distances (Å) for Complexes **E**−**G**

complex **E**[a]		complex **F**		complex **G**	
Mo(1)−C(1)#1	1.938(8)	Mo(1)−C(2)	1.974(6)	Mo(1)−C(1)	1.977(10)
Mo(1)−C(1)	1.939(8)	Mo(1)−C(1)	1.992(7)	Mo(1)−C(5)	2.014(9)
Mo(1)−C(3)	1.990(10)	Mo(1)−C(3)	2.015(7)	Mo(1)−C(3)	2.015(10)
Mo(1)−C(2)	1.996(11)	Mo(1)−C(4)	2.043(7)	Mo(1)−C(2)	2.024(10)
Mo(1)−P(1)#1	2.4840(13)	Mo(1)−P(1)	2.468(2)	Mo(1)−C(4)	2.030(10)
Mo(1)−P(1)	2.4841(13)	Mo(1)−As(1)	2.6003(9)	Mo(1)−As(1)	2.5799(11)
Mo(1)−As(1)	2.5349(14)	As(1)−C(20)	1.947(5)	As(1)−C(9)	1.949(7)
Mo(1)−As(1)#1	2.5349(13)	As(1)−C(26)	1.952(6)	As(1)−C(15)	1.951(8)
O(1)−C(1)	1.139(8)	As(1)−C(5)	1.968(6)	As(1)−C(6)	1.963(8)
O(2)−C(2)	1.136(11)	P(1)−C(7)	1.816(6)	O(1)−C(1)	1.114(11)
O(3)−C(3)	1.131(10)	P(1)−C(8)	1.815(6)	O(2)−C(2)	1.120(10)
As(1)−C(4′)	1.81(1)	P(1)−C(19)	1.830(6)	O(3)−C(3)	1.132(11)
C(4′)−C(4′)#1	1.317(2)	O(1)−C(1)	1.153(7)	O(4)−C(4)	1.105(11)
C(4′)−C(5)	1.44(1)	O(2)−C(2)	1.153(6)	O(5)−C(5)	1.119(10)
P(1)−C(4)	1.89(1)	O(3)−C(3)	1.142(7)	C(6)−C(7)	1.435(12)
		O(4)−C(4)	1.141(7)	C(7)−C(8)	1.186(14)
		C(5)−C(7)	1.318(7)		
		C(5)−C(6)	1.504(7)		

[a] Atoms marked with a number symbol are related to their symmetry-equivalent atoms by the transformation x, $-y + {}^{3}/_{2}$, z.

Table 2. Bond Angles (deg) for Complexes **E**−**G**

complex **E**[a]		complex **F**		complex **G**	
C(1)#1−Mo(1)−C(1)	92.3(4)	C(2)−Mo(1)−C(1)	92.0(2)	C(1)−Mo(1)−C(5)	88.0(3)
C(1)#1−Mo(1)−C(3)	87.8(3)	C(2)−Mo(1)−C(3)	86.1(2)	C(1)−Mo(1)−C(3)	92.0(4)
C(1)−Mo(1)−C(3)	87.8(3)	C(1)−Mo(1)−C(3)	92.7(3)	C(5)−Mo(1)−C(3)	179.5(4)
C(1)#1−Mo(1)−C(2)	89.7(3)	C(2)−Mo(1)−C(4)	89.2(2)	C(1)−Mo(1)−C(2)	90.6(4)
C(1)−Mo(1)−C(2)	89.7(3)	C(1)−Mo(1)−C(4)	89.3(3)	C(5)−Mo(1)−C(2)	91.6(3)
C(3)−Mo(1)−C(2)	176.3(4)	C(3)−Mo(1)−C(4)	174.9(2)	C(3)−Mo(1)−C(2)	88.9(4)
C(1)#1−Mo(1)−P(1)	93.9(2)	C(2)−Mo(1)−P(1)	95.3(2)	C(1)−Mo(1)−C(4)	88.8(4)
C(1)−Mo(1)−P(1)	173.2(2)	C(1)−Mo(1)−P(1)	172.6(2)	C(5)−Mo(1)−C(4)	91.6(3)
C(3)−Mo(1)−P(1)	89.7(2)	C(3)−Mo(1)−P(1)	88.7(2)	C(3)−Mo(1)−C(4)	87.9(4)
C(2)−Mo(1)−P(1)	93.1(2)	C(4)−Mo(1)−P(1)	90.0(2)	C(2)−Mo(1)−C(4)	176.7(4)
C(1)−Mo(1)−As(1)#1	95.5(2)	C(2)−Mo(1)−As(1)	172.3(2)	C(1)−Mo(1)−As(1)	176.3(2)
C(1)#1−Mo(1)−As(1)#1	171.7(2)	C(1)−Mo(1)−As(1)	94.1(2)	C(5)−Mo(1)−As(1)	89.8(2)
C(3)−Mo(1)−As(1)#1	89.9(2)	C(3)−Mo(1)−As(1)	89.0(2)	C(3)−Mo(1)−As(1)	90.2(3)
C(2)−Mo(1)−As(1)#1	93.0(2)	C(4)−Mo(1)−As(1)	95.5(2)	C(2)−Mo(1)−As(1)	92.3(3)
O(1)−C(1)−Mo(1)	177.4(7)	P(1)−Mo(1)−As(1)	78.64(4)	O(1)−C(1)−Mo(1)	176.4(8)
O(2)−C(2)−Mo(1)	176.4(9)	C(7)−C(5)−C(6)	124.4(6)	O(2)−C(2)−Mo(1)	177.4(8)
O(3)−C(3)−Mo(1)	174.6(9)			O(3)−C(3)−Mo(1)	178.9(9)
C(4)#1−C(4)−P(1)	119.6(2)			O(4)−C(4)−Mo(1)	177.3(9)
C(4′)#1−C(4′)−As(1)	120.2(2)			O(5)−C(5)−Mo(1)	178.6(8)
				C(8)−C(7)−C(6)	176.0(12)

[a] See footnote *a* in Table 1.

under nitrogen over sodium. Silica gel for column chromatography (grade 12, 28−200 mesh) was obtained from Aldrich. Melting points were determined on a Mel-Temp apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. Solution infrared spectra were obtained on a Perkin-Elmer Paragon 1000 PC FT spectrometer in sealed CaF$_2$ cells. ^{31}P{^{1}H}, ^{13}C{^{1}H}, and ^{1}H NMR spectra were recorded at 121.66 (202.35), 75 (125.70), and 300 (499.86) MHz, respectively, on either a General Electric GN-300 or Varian Unity Plus−500 spectrometer. Proton and carbon chemical shifts are relative to internal Me$_4$Si, and phosphorus chemical shifts are relative to external PPh$_3$ (δ(^{31}P) = −6.0 ppm); all shifts to low field (high frequency) are positive.

2.1. Synthesis of (Ph$_2$AsCH$_2$C≡CH)Mo(CO)$_5$ (G). To a solution of 5.0 g (16.33 mmol) of AsPh$_3$ in 15 mL of freshly distilled tetrahydrofuran was added 1.0 g (144.1 mmol) of lithium (cut into small flat pieces) under a nitrogen atmosphere with stirring. After 15−20 min, when the solution became deep red, 240 mL of freshly distilled THF was added, and the reaction mixture was stirred at ambient temperature for 4 h. During this period, the color of the reaction mixture intensified to a deep orange red. The excess lithium was removed under a N$_2$ purge and disposed of by cautiously reacting it with approximately 300 mL of 95% ethanol. Then 0.73 g (5.44 mmol) of anhydrous AlCl$_3$ was added to the reaction mixture.[14] (*Caution! The reaction of the AlCl$_3$ with phenyllithium is vigorous; white fumes may result.*) The reaction mixture was stirred for 15 min, and then 4.32 g (16.36 mmol) of Mo(CO)$_6$ was added under a N$_2$ purge. Effervescence was detected, and the solution turned bright red-orange. The reaction mixture was stirred at ambient temperature for 1−2 h until the effervescence ceased followed by the addition of 1.5 molar equiv of propargyl chloride. The reaction mixture immediately paled in color. The mixture was allowed to stir at ambient temperature for about 30 min, followed by the addition of 100 mL of 1 M HCl and 100 mL of hexane. The contents of the reaction flask were then transferred to a 1 L separatory funnel, and the aqueous layer was removed and discarded. To the organic phase was added 50 mL of ether, and the solution was washed with two 100 mL portions of 1 M HCl followed by two 100 mL portions of H$_2$O. The organic phase was dried with anhydrous magnesium sulfate and filtered by suction through 80 mL of silica gel covered with 2 cm of Celite in a 200 mL fritted glass funnel. The silica gel was washed with 200 mL of ether, and the combined solvents were removed from the filtrate by rotary evaporation using a water bath that was initially at ambient temperature and gradually heated to 95−100 °C; the flask containing the product was left on the rotary evaporator until the unreacted Mo(CO)$_6$ had sublimed. The flask was allowed to cool and was removed from the rotary evaporator. The crude product was purified by column chro-

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(14) Holland, S.; Mathey, F.; Fischer, J. *Polyhedron* **1986**, *5*, 1413.

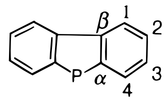
matography on silica gel with hexane as eluant. The first few fractions eluted some ureacted Mo(CO)$_6$ followed by the elution of some ligand oxides. About 4.7 g (9.32 mmol, 57.1%) of the diphenylpropargylarsine complex (**G**) was recovered.

2.2. Base-Catalyzed Reaction of Diphenylarsine with 2b″. To a solution of 0.23 g (0.50 mmol) of **2b″** in 75 mL of freshly distilled diglyme was added an equimolar amount of diphenylarsine (0.2 mL) by means of a syringe under nitrogen, and the mixture was stirred for 3−4 min. A catalytic amount of potassium *tert*-butoxide (0.005 g) was added to this reaction mixture, and it was allowed to reflux for 1 h under an atmosphere of nitrogen with stirring. The solvent was removed by vacuum distillation while warming the reaction vessel on a hot water bath. The resulting yellow orange oil was dissolved in methylene chloride and washed with 2 × 50 mL of 1 M HCl and 50 mL of water. The organic layer was dried with magnesium sulfate and filtered through a 1 cm thick silica bed layered with 0.5 cm of Celite. The Celite−silica bed was further washed with another 20 mL of dichloromethane to wash out all the products. The volume of the combined filtrates was reduced to 15−20 mL on a rotary evaporator. To this was added an equal volume of methanol, and the resulting mixture was allowed to stand at −20 °C for 8 h whereby pale orange yellow crystals of **E** (0.15 g, 0.23 mmol, 46%) separated out.

2.3. Base-Catalyzed Reaction of Diphenylarsine with 2a′. To a solution of 1.24 g (2.70 mmol) of **2a′** in 150 mL of freshly distilled diglyme was added 0.62 g (2.70 mmol) of diphenylarsine by means of a syringe under a nitrogen atmosphere with stirring. This was followed by the addition of 0.02 g of potassium *tert*-butoxide. The resultant solution was refluxed for 4.5 h. The solvent was removed by vacuum distillation while warming the reaction vessel on a hot water bath. The oily brown crude product mixture was purified by column chromatography on silica gel using 10% benzene in hexane as the eluant. The concentration of benzene in the eluant was gradually increased. The first few fractions eluted some ligand oxides followed by the elution of 0.14 g (0.20 mmol, 7.4%) of complex **H**. The next few fractions eluted the chelate product **F** which on recrystallization from 1:1 dicholoromethane/methanol solution gave pale yellow to almost colorless crystals of pure **F** (1.14 g, 1.73 mmol, 64%). Last, 0.15 g of complex **I** (0.13 mmol, 5.0%) was eluted from the column as a bright yellow band.

2.4. Base-Catalyzed Reaction of G with 1b. To a solution of 1.66 g (3.3 mmol) of **G** and 1.39 g (3.3 mmol) of **1b** in 170 mL of freshly distilled diglyme was added a catalytic amount of potassium *tert*-butoxide (0.025 g), and the mixture was refluxed for 3.5 h under an atmosphere of nitrogen with stirring. The color of the solution turned deep reddish brown. The solvent was removed by vacuum distillation. The residue was dissolved in a minimum volume of dichloromethane, and the organic layer was washed with 75 mL of 1 M HCl and 75 mL of water. The organic layer was dried with magnesium sulfate and filtered through a 1 cm thick Celite bed, followed by washing the bed with some dichloromethane. The solvent was removed under vacuum, and the reddish brown oily solid was purified by column chromatography on silica gel using 5% benzene in hexane as the eluant. The concentration of benzene in the eluant was gradually increased. The first few fractions eluted some oxides of the ligands and some unreacted starting material **1b** and **G**. The later fractions eluted a mixture of 0.56 g of **M**, **N**, and **O** in the ratio 5:3.1:1 as determined from the ^{1}H NMR spectrum. Fractional crystallization from a 1:1 mixture of dichloromethane and methanol gave 0.25 g of crystals of a mixture of **M** and **N**. We were unable to further separate this mixture by either column chromatography or fractional crystallization. Consequently, they were only characterized as a mixture.

3.1. Characterization of the Complexes. E: Pale yellow solid. Mp: >186 °C (dec). IR (CH$_2$Cl$_2$): ν_{CO} (cm^{-1}) 2024 (m), 1910 (s), 1888 (sh). ^{31}P{^{1}H} NMR (CDCl$_3$, 202.35 MHz): δ 55.03. ^{1}H NMR (CDCl$_3$, 499.86 MHz): δ 7.60−7.39 (m, 20H, aromatic H's), 7.36 (dq, ^2J(PH) = 5.5 Hz, $^4J_{HH}$ = 1.5 Hz, 1H, CH$_3$C═C*H*), 2.34 (apparent t, ^4J(PH) = ^4J(HH) = 1.5 Hz, 3H, CH$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 125.70 MHz): δ 218.20 (d, ^2J(PC) = 8.6 Hz, CO$_{eq,b'}$), 216.69 (d, ^2J(PC) = 26.0 Hz, CO$_{eq,b}$), 208.69 (d, ^2J(PC) = 8.7 Hz, 2CO$_{ax}$), 159.56 (d, ^2J(PC) = 32.2 Hz, C═*C*CH$_3$), 139.54 (d, ^1J(PC) = 37.5 Hz, C═*C*H), 137.34 (d, ^1J(PC) = 40.0 Hz, C$_i$), 136.27 (d, ^3J(PC) = 3.4 Hz, C$_{i'}$), 132.05 (s, C$_{o'}$), 131.64 (d, ^2J(PC) = 12.7, Hz, C$_o$), 129.81 (s, C$_{p'}$), 129.74 (d, ^4J(PC) = 1.8 Hz, C$_p$), 129.00 (s, C$_{m'}$), 128.60 (d, ^3J(PC) = 9.4 Hz, C$_m$), 21.28 (d, ^3J(PC) = 16.5 Hz, CH$_3$). Anal. Calcd for C$_{31}$H$_{24}$MoAsO$_4$P: C, 56.30; H, 3.62. Found: C, 56.44; H, 3.51



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F: Pale yellow solid. Mp: >190 °C (dec). IR (CH$_2$Cl$_2$): ν_{CO} (cm^{-1}) 2024 (m), 1928 (sh), 1908 (s), 1898 (sh). ^{31}P{^{1}H} NMR (CDCl$_3$, 121.66 MHz): δ 51.95. ^{1}H NMR (CDCl$_3$, 499.86 MHz): δ 7.96−7.38 (m, 18H, aromatic H's), 6.45 (dq, ^2J(PH) = 8.0 Hz, ^4J(HH) = 1.5 Hz, 1H, CH$_3$C═C*H*), 2.17 (apparent t, ^4J(PH) = ^4J(HH) = 1.5 Hz, 3H, CH$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 125.70 MHz): δ 216.45 (d, ^2J(PC) = 7.7 Hz, CO$_{eq,b'}$), 215.86 (d, ^2J(PC) = 24.9 Hz, CO$_{eq,b}$), 209.06 (d, ^2J(PC) = 9.1 Hz, 2CO$_{ax}$), 159.00 (d, ^2J(PC) = 32.3 Hz, C═*C*CH$_3$), 142.69 (d, ^2J(PC) = 7.8 Hz, C$_\beta$), 140.26 (d, ^1J(PC) = 31.4 Hz, C═*C*H), 139.45 (d, ^1J(PC) = 42.2 Hz, C$_\alpha$), 136.70 (d, ^3J(PC) = 3.5 Hz, C$_i$), 132.12 (s, C$_o$), 130.69 (d, ^2J(PC) = 1.4 Hz, C$_2$), 130.27 (d, ^2J(PC) = 16.1 Hz, C$_4$), 129.97 (s, C$_p$), 129.14 (s, C$_m$), 128.56 (d, ^3J(PC) = 10.2 Hz, C$_3$), 121.53 (d, ^3J(PC) = 4.9 Hz, C$_1$), 20.94 (d, ^3J(PC) = 17.5 Hz, CH$_3$). Anal. Calcd for C$_{31}$H$_{22}$MoAsO$_4$P: C, 56.40; H, 3.33. Found: C, 56.53; H, 3.21.

G: Colorless solid. Mp: 56 °C. IR (CH$_2$Cl$_2$): ν_{CO} (cm^{-1}) 2075 (w), 1990 (sh), 1949 (s, br). ^{1}H NMR (CDCl$_3$, 499.86 MHz): δ 7.44−7.55 (m, 10H, Ph), 3.10 (d, ^4J(HH) = 3.0 Hz, 2H, CH$_2$), 2.18 (t, ^4J(HH) = 3.0 Hz, 1H, C≡C*H*). ^{13}C{^{1}H} NMR (CDCl$_3$, 125.70 MHz): δ 210.21 (s, CO$_{trans}$), 205.21 (s, 4CO$_{cis}$), 136.35 (s, C$_i$), 131.50 (s, C$_o$), 130.20 (s, C$_p$), 129.07 (s, C$_m$), 78.10 (s, H$_2$C*C*≡C), 73.79 (s, ≡*C*H), 20.32 (s, CH$_2$). Anal. Calcd for C$_{20}$H$_{13}$MoAsO$_5$: C, 47.66; H, 2.58. Found: C, 47.73; H, 2.49.

H: Pale yellow solid. Mp: 131−132 °C. IR (CH$_2$Cl$_2$): ν_{CO} (cm^{-1}) 2072 (w), 1988 (sh), 1946 (s, br). ^{31}P{^{1}H} NMR (CDCl$_3$, 202.35 MHz): δ 14.27. ^{1}H NMR (CDCl$_3$, 499.86 MHz): δ 7.92−7.26 (m, 18H, aromatic H's), 6.05 (dq, ^2J(PH) = 34.5 Hz, ^4J(HH) = 1.5 Hz, 1H, CH$_3$C═C*H*), 1.60 (apparent t, ^4J(PH) = ^4J(HH) = 1.5 Hz, 3H, CH$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 125.70 MHz): δ 209.56 (d, ^2J(PC) = 21.2 Hz, CO$_{trans}$), 204.96 (d, ^2J(PC) = 8.8 Hz, 4CO$_{cis}$), 159.51 (d, ^2J(PC) = 11.2 Hz, HC═*C*CH$_3$), 141.35 (d, ^2J(PC) = 8.7 Hz, C$_\beta$), 139.93 (d, ^1J(PC) = 41.7 Hz, C$_\alpha$), 137.72 (s, C$_i$), 133.70 (s, C$_o$), 130.44 (d, ^2J(PC) = 1.5 Hz, C$_2$), 129.94 (d, ^2J(PC) = 15.3 Hz, C$_4$), 129.21 (d, ^2J(PC) = 13.5 Hz, H*C*═CCH$_3$), 128.95 (s, C$_p$), 128.88 (s, C$_m$), 128.60 (d, ^3J(PC) = 10.1 Hz, C$_3$), 121.67 (d, ^3J(PC) = 5.0 Hz, C$_1$), 20.50 (d, ^3J(PC) = 10.4 Hz, CH$_3$). Anal. Calcd for C$_{32}$H$_{22}$MoAsO$_5$P: C, 55.84; H, 3.22. Found: C, 55.63; H, 3.13.

I: Yellow solid. Mp: 82 °C. IR (CH$_2$Cl$_2$): ν_{CO} (cm^{-1}) 2020 (w), 1950 (sh), 1922 (sh), 1906 (s), 1890 (sh). ^{31}P{^{1}H} NMR (CDCl$_3$, 121.66 MHz): δ 18.29. ^{1}H NMR (CDCl$_3$, 499.86 MHz): δ 7.38−6.98 (m, 36H, aromatic H's of Ph, DBP), 5.84 (m, $|^2J$(PH) + ^4J(PH)$|$ = 29.0 Hz, 2H, H$_a$), 1.48 (m, $|^4J$(PH) + ^6J(PH)$|$ = 2.5 Hz, 6H, CH$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 125.70 MHz): δ 213.50 (AXX′, ^2J(PP) = 21.2 Hz, ^2J(PC) = 22.5 Hz, ^2J(P′C) = −7.5 Hz, CO$_{eq}$), 209.28 (t, ^2J(PC) = 9.6 Hz, CO$_{ax}$), 154.08 (AXX′, $|^2J$(PC) + ^4J(PC)$|$ = 9.2 Hz, C$_b$), 141.42 (AXX′, $|^2J$(PC) + ^4J(PC)$|$ = 6.8 Hz, C$_\beta$), 139.02 (AXX′, ^2J(PP) = 21.2 Hz, ^1J(PC) = 36.3 Hz, ^3J(PC) = 1.8 Hz, C$_\alpha$), 138.28 (s, C$_i$), 133.63 (s, C$_o$), 132.70 (AXX′, $|^1J$(PC) + ^3J(PC)$|$ = 18.6 Hz, H*C*═CCH$_3$), 129.68 (AXX′, $|^2J$(PC) + ^4J(PC)$|$ = 15.7 Hz, C$_4$), 129.05 (s, C$_2$), 128.58 (s, C$_m$), 128.52 (s, C$_p$), 127.84 (AXX′, $|^3J$(PC) + ^5J(PC)$|$ = 9.8 Hz, C$_3$), 121.12 (AXX′, $|^3J$(PC) + ^5J(PC)$|$ = 4.1 Hz, C$_1$), 20.13 (AXX′, $|^3J$(PC) + ^5J(PC)$|$ = 9.9 Hz, CH$_3$). Anal. Calcd for C$_{58}$H$_{44}$MoAs$_2$O$_4$P$_2$: C, 62.61; H, 3.99. Found: C, 62.47; H, 3.82.

M: IR (CH$_2$Cl$_2$): ν_{CO} (cm^{-1}) 2020 (w), 2010 (sh), 1911 (s, br), 1882 (sh). ^{31}P{^{1}H} NMR (CDCl$_3$, 121.66 MHz): δ 55.34. ^{1}H NMR (CDCl$_3$, 499.86 MHz): δ 7.3−7.6 (m, 20H, aromatic H's), 5.80 (dd, ^3J(PH) = 24.0 Hz, ^2J(HH) = 0.5 Hz, 1H, H$_b$), 5.03 (dd, ^2J(PH) = 11.5 Hz, ^2J(HH) = 0.5 Hz, 1H, H$_a$), 3.15 (d, ^2J(PH) = 17.5 Hz, 2H, CH$_2$). ^{13}C{^{1}H} NMR (CDCl$_3$, 125.70 MHz): δ 217.24 (d, ^2J(PC) = 8.9 Hz, CO$_{eq,b'}$), 216.68 (d, ^2J(PC) = 24.9 Hz, CO$_{eq,b}$), 209.58 (d, ^2J(PC) =

Table 3. Crystallographic Data for Complexes **E**−**G**

	complex		
	E	**F**	**G**
chem formula	$C_{31}H_{24}AsMoO_4P$	$C_{31}H_{22}AsMoO_4P$	$C_{20}H_{13}AsMoO_5$
fw	662.33	660.32	504.16
cryst system	orthorhombic	triclinic	monoclinic
space group	*Pnma*	$P\bar{1}$	$P2_1/n$
a (Å)	17.192(2)	11.2340(10)	11.848(2)
b (Å)	21.649(4)	11.5840(10)	13.006(3)
c (Å)	7.7420(10)	12.4650(10)	13.506(2)
α (deg)	90	62.770(10)	90
β (deg)	90	86.550(10)	95.191(12)
γ (deg)	90	77.270(10)	90
V (Å^3)	2881.5(7)	1405.4(2)	2072.7(7)
Z	4	2	4
ρ_{calcd} (Mg/m^3)	1.527	1.560	1.616
μ (mm^{-1})	1.684	1.726	2.243
$R_1(F)^a$	0.0544	0.0476	0.0673
$_wR_2(F^2)^b$	0.1215	0.0877	0.1691
GOF	1.040	1.015	1.030

[a] $R_1(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $_wR_2(F^2) = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{0.5}$.

8.5 Hz, 2CO$_{ax}$), 144.64 (d, ^1J(PC) = 28.5 Hz, *C*═CH$_2$), 136.85 (d, ^3J(PC) = 1.9 Hz, C$_{i'}$), 133.49 (d, ^1J(PC) = 35.2 Hz, C$_i$), 133.15 (d, ^2J(PC) = 13.1 Hz, C$_o$), 132.48 (s, C$_{o'}$), 130.20 (d, ^4J(PC) = 1.9, Hz, C$_p$), 130.02 (s, C$_{p'}$), 129.07 (s, C$_{m'}$), 128.65 (d, ^3J(PC) = 9.6 Hz, C$_m$), 126.43 (d, ^2J(PC) = 2.1 Hz, C═*C*H$_2$), 36.71 (d, ^2J(PC) = 31.8 Hz, CH$_2$).

N: IR (CH$_2$Cl$_2$): ν_{CO} (cm^{-1}) 2020 (w), 2010 (sh), 1911 (s, br), 1882 (sh). ^{1}H NMR (CDCl$_3$, 499.86 MHz): δ 7.3−7.6 (m, 20H, aromatic H's), 5.95 (s, 1H, H$_b$), 5.15 (s, 1H, H$_a$), 3.05 (s, 2H, CH$_2$). ^{13}C{^{1}H} NMR (CDCl$_3$, 125.70 MHz): δ 217.22 (s, CO$_{eq,b'}$), 216.92 (s, CO$_{eq,b}$), 209.16 (s, 2CO$_{ax}$), 146.03 (s, *C*═CH$_2$), 136.94 (s, C$_i$), 134.93 (s, C$_i$), 131.69 (s, 2C$_o$), 129.85 (s, C$_p$), 129.82 (s, C$_p$), 128.95 (s, C$_m$), 128.93 (s, C$_m$), 125.35 (s, C═*C*H$_2$), 35.86 (s, CH$_2$).

3.2. X-ray Data Collection and Processing. Pale yellow crystals of **G** and **F** and yellow-orange crystals of **E** were grown by slow diffusion of methanol into saturated solutions of methylene chloride through an ethereal layer at −20 °C. Suitable crystals were mounted on glass fibers and placed on a Siemens P4 diffractometer. Crystal data and details of data collection for complexes **E**−**G** are given in Table 3. Intensity data were taken in the ω-mode at 298 K with Mo Kα graphite-monochromated radiation (λ = 0.710 73 Å). Three check reflections monitored every 100 reflections showed random (<2%) variation during the data collections. The data were corrected for Lorentz, polarization effects, and absorption (using an empirical model derived from azimuthal data collections). Scattering factors and corrections for anomalous dispersion were taken from a standard source.[15] Calculations were performed with the Siemens SHELXTL PLUS version 5.03 software package on a personal computer. The structures were solved by direct methods. Anisotropic thermal parameters were assigned to all non-hydrogen atoms. Hydrogen atoms were refined at calculated positions with a riding model in which the C−H vector was fixed at 0.96 Å.

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Supporting Information Available: An X-ray crystallographic file, in CIF format, for **E**−**G** is available on the Internet only. Access information is given on any current masthead page.

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(15) *International Tables for X-Ray Crystallography*; D. Reidel Publishing: Boston, MA, 1992; Vol. C.