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Transition-Metal-Substituted Arsaalkenes. 7.[1] Coupling of Transition Metal Carbynes with a Methylene Arsane Moiety: Structure of $Tp'(CO)_2W{\equiv}C{-}As{=}C(NMe_2)_2$ [$Tp' = HB(3,5\text{-}Me_2HC_3N_2)_3$]

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Condensation of $Tp'(CO)_2M{\equiv}CCl$ [**1a**, M = Mo; **1b**, W; $Tp' = HB(3,5\text{-}Me_2HC_3N_2)_3$] with the arsaalkene $Me_3SiAs{=}C(NMe_2)_2$ afforded the novel arsaalkenyl carbyne complexes $Tp'(CO)_2M{\equiv}C{-}As{=}C(NMe_2)_2$ (**2a**) (M = Mo) and **2b** (M = W). Methylation of **2a** and **2b** occurred at the arsenic atom to give the complexes $[Tp'(CO)_2M{\equiv}CAs(Me)C(NMe_2)_2](SO_3CF_3)$ **3a** (M = Mo) and **3b** (M = W). Compounds **2a**,**b** and **3a**,**b** have been characterized by IR and ^1H and ^{13}C NMR spectroscopy. In addition, the molecular structure of **2b** has been determined by a single-crystal X-ray structural analysis.

Introduction

Recently we reported on the unprecedent coupling of the chlorocarbyne complexes $Tp'(CO)_2M{\equiv}CCl$ **1a** (M = Mo) and **1b** (M = W)[2] with the phosphaalkenes $Me_3SiP{=}C(NR_2)_2$[3] (R = Me, Et) to yield the phosphaalkenyl carbyne complexes $Tp'(CO)_2M{\equiv}C{-}P{=}C(NR_2)_2$ (M = Mo, W; R = Me, Et).[4] These compounds were easily oxidized by gaseous dioxygen to the phosphinatocarbyne complexes $Tp'(CO)_2M{\equiv}C{-}P(O)_2C(NR_2)_2$.[5] Reaction with methyl trifluoromethanesulfonate furnished the salts $[Tp'(CO)_2M{\equiv}C{-}P(Me){=}C(NR_2)_2]SO_3CF_3$, whereas protonation of the tungsten derivative with trifluoromethanesulfonic acid resulted in the formation of a cyclic phosphinocarbene complex $[Tp'(CO)_2\overline{W{=}CHP}C(NMe_2)_2](SO_3CF_3)$ (Scheme 1).[6]

In extension of our studies into the chemistry of arsenic, we were interested in investigating the reactivity of chlorocarbyne complexes **1** toward $Me_3SiAs{=}C(NMe_2)_2$. In particular we wish to establish whether the properties of arsaalkenes just mirror the chemistry of phosphaalkenes or not.[7−9]

Results and Discussion

Reaction of the carbyne complexes **1a** and **1b** with equimolar amounts of arsaalkene $Me_3SiAs{=}C(NMe_2)_2$[7] in diethyl ether in the temperature range 0−20 °C in the absence of daylight led to a color change from yellow to orange (M = Mo) or red (M = W) and to the precipitation of orange **2a** and red-orange **2b** (Scheme 2).

Purification of the products was effected by continuous extraction with boiling diethyl ether. The pseudo-C_s-symmetry of **2a** and **2b** is reflected in their NMR spectra. Thus, the ^1H NMR spectrum of **2a** features a singlet at δ 3.06 for the 12 protons of the dimethylamino groups. The protons of the six methyl groups of the Tp′-ligand are observed as four singlets at δ 2.29, 2.30, 2.36, and 2.63 in a ratio of 3:3:6:6. Two singlets at δ 5.71 and 5.85 in a ratio 1:2 account for the ring protons of the Tp′-ligand. The $^{13}C\{^1H\}$ NMR spectra of **2a** and **2b** are especially interesting in the low-field region, where singlets at δ 349.7 (M = Mo) and δ 329.1 (M = W) appeared for the metal-bound carbon atoms of the novel organoarsenic ligand.

The deshielding of these carbon atoms is more pronounced than in the corresponding phosphaalkenyl−carbyne complexes **I** (M = Mo, δ 337.5 d, $^1J_{PC}$ = 111.3 Hz; M = W, δ 318.3 d, $^1J_{PC}$ = 101.2 Hz)[4] or in the starting materials **1a** (δ 208.70) and **1b** (δ 205.58).[2] Singlets at δ 214.0 (**2a**) and 213.1 (**2b**) are assigned to the methylene carbon atoms of the As=C moiety in the products. In $Me_3SiAs{=}C(NMe_2)_2$ the singlet of the respective carbon atom was observed at δ 213.5.[7] The carbonyl groups of the condensation products give rise to singlets at lower field (**2a**, δ 229.1; **2b**, 227.6) than

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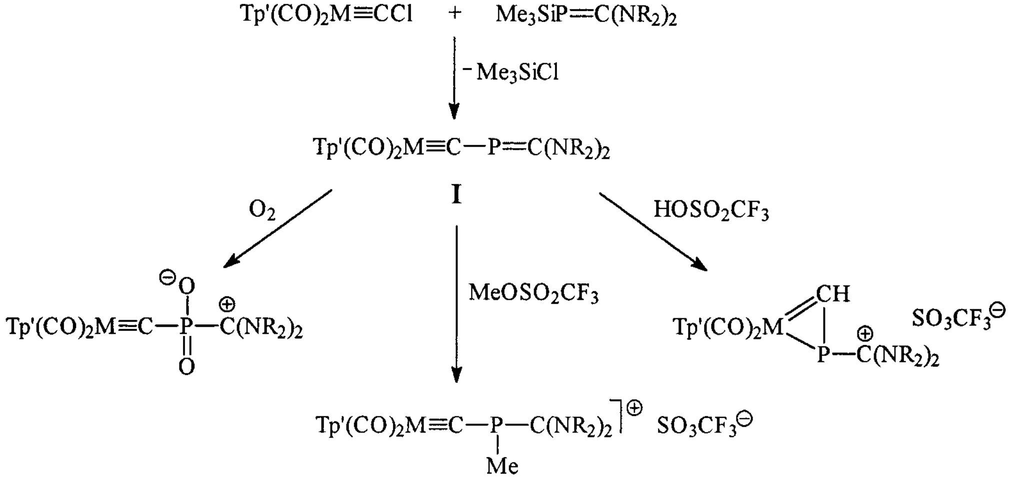
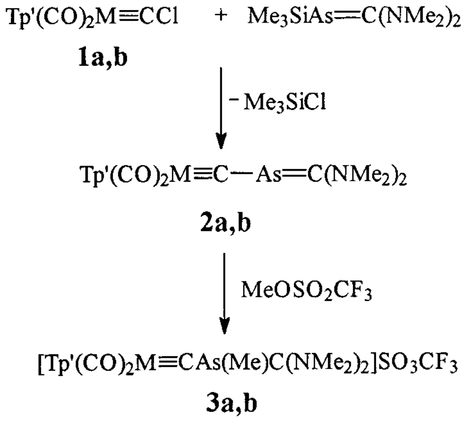
Scheme 1



M = Mo, W; Tp' = HB(3,5-Me$_2$HC$_3$N$_2$)$_3$; R = Me, Et

Scheme 2



M = Mo: **1-3a**; M = W: **1-3b**

those in the precursors $\mathrm{Tp'(CO)_2Mo{\equiv}CCl}$ (δ 224.02) and $\mathrm{Tp'(CO)_2W{\equiv}CCl}$ (δ 221.95).[2]

The strong donor capacity of the novel organoarsenic ligand is also reflected in the ν(CO) region of the IR spectra of compounds **2a** and **2b**. Two intense bands at 1947, 1863 (**2a**) and 1936, 1848 cm^{-1} (**2b**) are considerably shifted to lower wavenumbers in comparison with precursors **1a** ($\nu = 2005$, 1921 cm^{-1}) and **1b** ($\nu = 1991$, 1902 cm^{-1}).[2] They, however, compare well with the carbonyl stretching vibrations in the corresponding phosphaalkenyl–carbyne complexes **I** (Mo, 1946, 1864 cm^{-1}; W, 1935, 1848 cm^{-1}).[4]

On the basis of spectroscopic evidence three mesomeric structures are necessary for the description of the bonding in **2a,b** (Scheme 3).

An X-ray structure analysis was desirable for the unambigious understanding of the bonding situation in arsaalkenyl–carbyne complexes.

X-ray Structural Analysis of 2b. An ORTEP drawing of **2b** is shown in Figure 1; selected bond lengths and angles are given in Table 1.

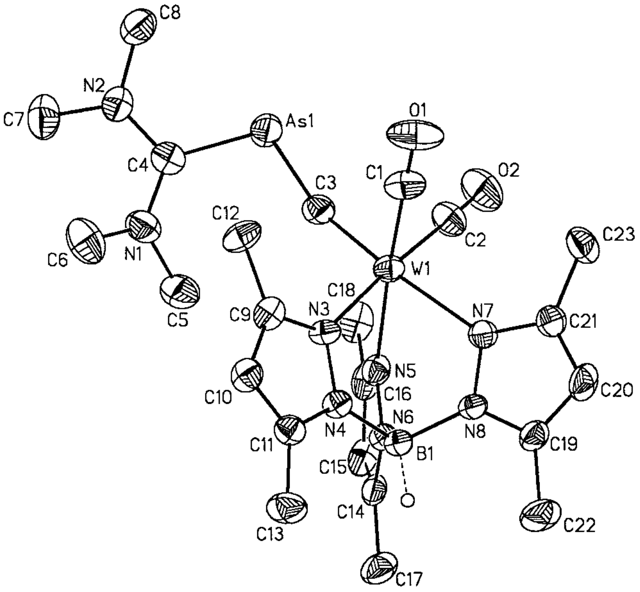
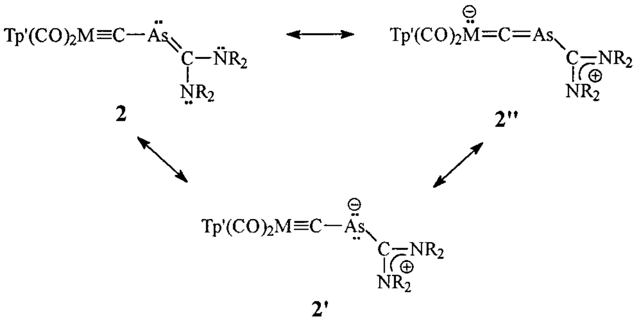


Figure 1. Molecular structure of **2b** in the crystal.

Scheme 3



The complex is a monomeric molecule with distorted octahedral geometry. Three facial positions are occupied by the nitrogen atoms of the tripod ligand. The bond angles between the organoarsenic ligand and the two carbonyls are less than 90° [81.8(4)°; 83.4(3)°], as are those between the nitrogen donor atoms N(3), N(5), and N(7) of the Tp′-ligand [81.4(2)–81.9(2)°]. The most interesting structural feature of the molecule is the geometry of the organoarsenic ligand. The bond length W(1)–C(3) of 1.825(9) Å compares well with the corresponding bond lengths in $\mathrm{Tp'(CO)_2W{\equiv}C{-}P{=}C(NEt_2)_2}$ [1.838(6) Å][4] and $\mathrm{[Tp'(CO)_2W{\equiv}CPMe_2Ph]PF_6}$ [1.821(9) Å][10] and has to be regarded as a metal–carbon triple bond. Accordingly, the ligand in **2b** is rather an arsaalkenyl-functionalized carbyne as depicted in formulas **2** and **2′** than a terminal isoarsaalkyne ligand as

Table 1. Selected Bond Lengths [Å] and Angles [deg] for Compound 2b

W(1)−C(1)	1.969(9)	W(1)−C(2)	1.978(9)
W(1)−C(3)	1.825(9)	As(1)−C(3)	1.900(9)
As(1)−C(4)	1.913(8)	C(4)−N(1)	1.359(9)
C(4)−N(2)	1.354(10)	N(1)−C(5)	1.456(10)
N(1)−C(6)	1.423(10)	N(2)−C(7)	1.461(10)
N(2)−C(8)	1.464(10)	W(1)−N(3)	2.222(5)
W(1)−N(5)	2.231(6)	W(1)−N(7)	2.304(6)
C(3)−W(1)−C(1)	83.4(3)	C(3)−W(1)−C(2)	81.4(4)
C(1)−W(1)−C(2)	88.7(3)	C(3)−W(1)−N(3)	101.9(3)
C(3)−W(1)−N(5)	102.1(3)	C(1)−W(1)−N(3)	94.9(3)
C(1)−W(1)−N(7)	92.9(3)	C(1)−W(1)−C(2)	88.7(3)
C(2)−W(1)−N(7)	95.4(3)	C(2)−W(1)−N(5)	94.3(3)
C(1)−W(1)−N(5)	174.0(3)	C(2)−W(1)−N(3)	175.3(3)
C(3)−W(1)−N(7)	175.2(3)	N(3)−W(1)−N(5)	81.9(2)
N(3)−W(1)−N(7)	81.4(2)	N(5)−W(1)−N(7)	81.7(2)
W(1)−C(3)−As(1)	165.2(4)	C(3)−As(1)−C(4)	101.7(3)
As(1)−C(4)−N(1)	127.0(6)	As(1)−C(4)−N(2)	116.8(6)
N(1)−C(4)−N(2)	116.2(7)	C(5)−N(1)−C(6)	114.3(8)
C(4)−N(1)−C(5)	122.4(7)	C(4)−N(1)−C(6)	122.7(8)
C(4)−N(2)−C(7)	121.5(7)	C(4)−N(2)−C(8)	121.3(7)
C(7)−N(2)−C(8)	113.9(7)	W(1)−C(1)−O(1)	177.8(8)
W(1)−C(2)−O(2)	177.4(8)		

given in **2″**. Consistent with an sp-hybridized donor carbon atom, the valence angle W(1)−C(3)−As(1) of 165.2(4)° deviates only slightly from linearity. In [Tp′(CO)$_2$W≡CPMe$_2$Ph]$^+$ and in Tp′(CO)$_2$W≡CP=C(NEt$_2$)$_2$ angles W−C−P are 168.1(5)°[11] and 167.9(4)°,[4] respectively. The bonds between the two-coordinate arsenic atom and carbon atoms C(3) and C(4) [1.900(9) and 1.913(8) Å] are of comparable length and not significantly longer than the As=C bond in (η^5-C$_5$Me$_5$)(CO)$_2$FeAs=C(NMe$_2$)$_2$ [1.876(8) Å].[7] It clearly exceeds the corresponding value in (η^5-C$_5$H$_5$)(CO)$_2$FeAs=C(OSiMe$_3$)(*t*Bu) [1.821(2) Å].[11] Theoretical calculations on HAs=CH$_2$ led to a double-bond length of 1.79 Å.[12] As=C bond lengthening in **2b** is readily explained by π-conjugation with the lone pairs of electrons at the nitrogen atoms of the amino substituents. Accordingly, the bond lengths between the nitrogen atoms N(1) and N(2) and the trigonal planar carbon atom C(4) (sum of angles 360.0°) [N(1)−C(4) = 1.359(9) Å and N(2)−C(4) = 1.354(10) Å] are shortened with respect to the calculated value of a $C_{sp^2}-N_{sp^2}$ single bond of 1.450 Å.[13] Considering the different hybridizations at C(3) (sp) and C(4) (sp^2), the bond As(1)−C(3) may be viewed as a single bond. For the arsenic carbon single bonds in the 1,2-dihydroarsete PhAsCH$_2$C(Ph)=C(Ph) 1.989(6) and 1.949(4) Å were determined.[14] A similar argument was presented in the discussion of the PC bonds in Tp′(CO)$_2$W≡C−P=C(NEt$_2$)$_2$ [1.759(7) Å]. The valence angle C(3)−As(1)−C(4) of 101.7(3)° in **2b** is more obtuse than in arsaalkene CF$_3$As=C(F)NEt$_2$ [94.3(4)°].[15] The latter angle is close to the calculated angle H−As−C of 96.7° in HAs=CH$_2$.[12] In contrast to Tp′(CO)$_2$W≡C−P=C(NEt$_2$)$_2$, where the diaminomethylene group is oriented toward the opposite side of the tripod ligand, in **2b** this functionality clearly points toward the tripod ligand. In conclusion, following the X-ray diffraction study, the electronic ground state of **2b** is best described by the formulas **2** and **2′**.

This finding clearly shows that the arsenic atom in the molecule should exhibit a pronounced nucleophilicity. To experimentally prove this idea, compounds **2a** and **2b** were subjected to the reaction with equimolar amounts of methyl triflate in ethereal solution at −100 °C. The vessel was well protected from daylight. The saltlike methylation products **3a**,**b** were obtained as orange solids, which were purified by continuous extraction into boiling ether (Scheme 2). The alkylation of **2a** and **2b** is accompanied by a strong shielding of the carbyne atoms, which are observed in **3a** and **3b** at δ 299.7 and δ 283.2, respectively. A similar situation is found for the resonances of the amino-substituted tricoordinate carbon atoms (**3a**, δ 181.7; **3b**, δ 182.0), which are upfield shifted by 31.1−32.3 ppm, when compared with the starting materials. Singlet resonances at δ 11.7 (**3a**) and 11.2 (**3b**) were attributed to the methyl group at the arsenic atom. The chirality of **3a** and **3b**, which is due to an asymmetrically substituted arsenic atom, is reflected by the presence of two discrete singlet resonances for the chemically and magnetically different carbonyls at δ 226.7 and 226.9 (**3a**) and δ = 225.1 and 225.3 (**3b**). The high-field shifts of 2.3 and 2.4 ppm for these signals on going from neutral **2a**,**b** to cationic **3a**,**b** agree with a decreased transfer of electron density from the organoarsenic ligand in the cations onto the carbonyls. This is underlined by the IR spectra, where the ν(CO) bands in the alkylation products are registered at higher wavenumbers [**3a**, 1997, 1911 cm^{-1}; **3b**, 1981, 1888 cm^{-1}) than in the IR spectra of the precursors **2a** (1947, 1863 cm^{-1}) and **2b** (1936, 1848 cm^{-1}). The ^{1}H NMR spectrum of **3a** features a singlet at δ 1.85 for the methyl group at the arsenic atom. At room temperature a singlet at δ 3.45 accounting for the 12 protons of the dimethylamino groups was observed. At −70 °C this resonance is split into two singlets at δ 3.23 and 3.52 of equal intensity. The six chemically and magnetically different ring methyl groups give rise to five singlets in the ratio of 3:3:6:3:3 at both temperatures. In the ^{13}C NMR spectrum (22 °C) one singlet is registered for the four carbon atoms of the dimethylamino groups (δ 45.3). At −70 °C this is replaced by two singlets of equal intensity at δ 44.2 and 44.6. All six different ring carbon atoms of the tripod ligand, which are connected with a methyl group, are registered as discrete singlets at 22 °C as well as at −70 °C. The methyl groups give rise to four singlets at δ 12.7−16.3 in the ratio 2:1:1:2 at ambient temperature, the low-field resonance of which is split into two singlets at −70 °C (δ 15.7, 15.9). In contrast with the behavior of their phosphorus analogues, the protonation of **2a** and **2b** did not lead to tractable products.

Experimental Section

All operations were performed under dry, oxygen-free dinitrogen using standard Schlenk techniques. Solvents were dried by standard methods and freshly distilled under argon prior

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to use. Infrared spectra were recorded on a Bruker FT-IR IFS66 spectrometer. ^{1}H and ^{13}C NMR spectra were recorded at 22 °C using Bruker AC 100 (^{1}H, 100.13 MHz) and Bruker Avance DRX 500 (^{1}H, 500.13 MHz; ^{13}C, 125.75 MHz). Standards: $SiMe_4$ (^{1}H, ^{13}C). Elemental analyses were performed at the microanalytical laboratory of the University of Bielefeld and at Mikroanalytisches Laboratorium H. Kolbe, Mülheim/Ruhr. The chlorocarbyne complexes [Tp′(CO)$_2$M≡CCl] [M = Mo (**1a**), W (**1b**)][2] as well as the arsaalkene $Me_3SiAs{=}C(NMe_2)_2$[7] were synthesized according to literature procedures. Methyl trifluoromethanesulfonate (Aldrich) was purchased commercially.

Preparation of Compounds. Tp′(CO)$_2$Mo≡C−As=C(NMe$_2$)$_2$ (2a). A solution of $Me_3SiAs{=}C(NMe_2)_2$ (0.55 g, 2.2 mmol) in 10 mL of diethyl ether was added dropwise to the solution of **1a** (1.00 g, 2.01 mmol) in 150 mL of diethyl ether at 0 °C. The device was protected from light throughout the reaction. The color of the solution changed from yellow to orange. The mixture was then stirred at room temperature for 3 h, during which an orange precipitate separated. It was filtered in the dark, and the filter-cake was washed with diethyl ether (1 × 50 mL) and *n*-pentane (1 × 50 mL). The solid residue was extracted into 100 mL of boiling diethyl ether. Storing at room temperature for 72 h yielded microcrystalline orange **2a** (0.90 g, 71%). IR (KBr, cm^{-1}) ν: 2551 w (BH), 1947 vs (CO), 1863 vs (CO). ^{1}H NMR (CD_2Cl_2) δ: 2.29, 2.30 (s, each 3H, Tp′CH$_3$), 2.36, 2.63 (s, each 6H, Tp′CH$_3$), 3.06 (s, 12H, NCH$_3$), 5.71 (s, 1H, Tp′H), 5.85 (s, 2H, Tp′H). ^{13}C{^{1}H} NMR (CD_2Cl_2) δ: 12.6 (s, 1C, Tp′*C*H$_3$), 12.9 (s, 2C, Tp′*C*H$_3$), 14.5 (s, 1C, Tp′*C*H$_3$), 15.9 (s, 2C, Tp′*C*H$_3$), 44.2 (s, 4C, NCH$_3$), 106.1 (s, 3C, Tp′*C*H), 144.8 (s, 2C, Tp′*C*CH$_3$), 145.5 (s, 1C, Tp′*C*CH$_3$), 151.5 (s, 1C, Tp′*C*CH$_3$), 151.9 (s, 2C, Tp′*C*CH$_3$), 214.0 (s, 1C, As=C), 229.1 (s, 2C, CO), 349.7 (s, 1C, Mo≡C). MS/EI, *m*/*z*: 636 [M^{+}]. Anal. Calcd for $C_{23}H_{34}AsBMoN_8O_2$ (636.25): C, 43.41; H, 5.38; N, 17.61. Found: C, 43.37; H, 5.54; N, 17.22.

Tp′(CO)$_2$W≡C−As=C(NMe$_2$)$_2$ (2b). A solution of $Me_3SiAs{=}C(NMe_2)_2$ (0.50 g, 2.01 mmol) in 10 mL of diethyl ether was added in the dark dropwise to the cold solution (0 °C) of **1b** (1.17 g, 2.00 mmol) in 200 mL of diethyl ether. The color of the mixture changed from yellow to red. Stirring was continued at room temperature for 12 h, during which time a red solid precipitated. The precipitate was filtered in the dark and washed with 50 mL of diethyl ether and 50 mL of *n*-pentane. The red solid was then continuously extracted for 48 h into 100 mL of boiling diethyl ether to yield 0.88 g (60%) of orange-red **2b**. IR (KBr, cm^{-1}) ν: 2553 w (BH), 1936 vs (CO), 1848 vs (CO). ^{1}H NMR (CD_2Cl_2) δ: 2.31 (s, 3H, Tp′CH$_3$), 2.34 (s, 3H, Tp′CH$_3$), 2.37 (s, 6H, Tp′CH$_3$), 2.65 (s, 6H, Tp′CH$_3$), 3.07 (s, 12H, NCH$_3$), 5.76 (s, 1H. Tp′H), 5.90 (s, 2H, Tp′H). ^{13}C{^{1}H} NMR (CD_2Cl_2) δ: 12.6 (s, 1C, Tp′*C*H$_3$), 12.8 (s, 2C, Tp′*C*H$_3$), 15.2 (s, 1C, Tp′*C*H$_3$), 16.5 (s, 2C, Tp′*C*H$_3$), 44.1 (s, 4C, NCH$_3$), 106.4 (s, 3C, Tp′*C*H), 144.7 (s, 2C, Tp′*C*CH$_3$), 145.7 (s, 1C, Tp′*C*CH$_3$), 152.4 (s, 1C, Tp′*C*CH$_3$), 152.7 (s, 2C, Tp′*C*CH$_3$), 213.1 (s, 1C, As=C), 227.6 (s, $^{1}J_{WC}$ = 183.3 Hz, 2C, CO), 329.1 (s, 1C, W≡C). MS/EI, *m*/*z*: 724 [M^{+}]. Anal. Calcd for $C_{23}H_{34}AsBN_8O_2W$ (724.16): C, 38.14; H, 4.73; N, 15.47. Found: C, 37.71; H, 4.86; N, 15.54.

[Tp′(CO)$_2$Mo≡C−As(Me)C(NMe$_2$)$_2$](SO$_3$CF$_3$) (3a). In the absence of light a cold suspension (−100 °C) of **2a** (0.30 g, 0.47 mmol) in 350 mL of diethyl ether was combined with a solution of 0.49 mmol of methyl triflate in 25 mL of diethyl ether. It was warmed to 20 °C, and stirring was continued for 4 h. A light orange-red amorphous precipitate separated, which was filtered off and washed (1 × 50 mL of diethyl ether, 1 × 50 mL of *n*-pentane) to give the crude powder **3a**. Purification was effected by continuous extraction for 72 h with a total of 200 mL of diethyl ether to give 0.25 g (66%) of crystalline orange **3a**. IR (KBr, cm^{-1}) ν: 2553 w (BH), 1997 vs (CO), 1911 vs (CO). ^{1}H NMR (CD_2Cl_2, 22 °C) δ: 1.85 (s, 3H, AsCH$_3$), 2.33 (s, 3H, Tp′CH$_3$), 2.35 (s, 3H, Tp′CH$_3$), 2.40 (s, 6H, Tp′CH$_3$), 2.50 (s, 3H, Tp′CH$_3$), 2.55 (s, 3H, Tp′CH$_3$), 3.45(s, 12H, NCH$_3$), 5.80 (s, 1H. Tp′H), 5.85 (s, 2H, Tp′H). ^{1}H NMR (CD_2Cl_2, −70 °C) δ: 1.75 (s, 3H, AsCH$_3$), 2.25 (s, 3H, Tp′CH$_3$), 2.27 (s, 3H, Tp′CH$_3$), 2.32 (s, 6H, Tp′CH$_3$), 2.42 (s, 3H, Tp′CH$_3$), 2.46 (s, 3H, Tp′CH$_3$), 3.23 (s, 6H, NCH$_3$), 3.52 (s, 6H, NCH$_3$), 5.78 (s, 1H, Tp′H), 5.96 (s, 2H, Tp′H). ^{13}C{^{1}H} NMR (CD_2Cl_2, 22 °C) δ: 11.7 (s, 1C, AsCH$_3$), 12.7 (s, 2C, Tp′*C*H$_3$), 12.8 (s, 1C, Tp′*C*H$_3$), 14.6 (s, 1C, Tp′*C*H$_3$), 16.3 (s, 2C, Tp′*C*H$_3$), 45.3 (s, 4C, NCH$_3$), 106.8 (s, 2C, Tp′*C*H), 107.0 (s, 1C, Tp′*C*H), 121.2 (q, $^{1}J_{CF}$ = 320.7 Hz, 1C, CF$_3$), 145.9 (s, 1C Tp′*C*CH$_3$), 146.0 (s, 1C, Tp′*C*CH$_3$), 146.5 (s, 1C, Tp′*C*CH$_3$), 150.7 (s, 1C, Tp′*C*CH$_3$), 150.8 (s, 1C, Tp′*C*CH$_3$), 152.0 (s, 1C, Tp′*C*CH$_3$), 181.7 (s, 1C, AsCN$_2$), 226.7 (s, 1C, CO), 226.9 (s, 1C, CO), 299.7 (s, 1C, Mo≡C). ^{13}C{^{1}H} NMR (CD_2Cl_2, −70 °C) δ: 10.8 (s, 1C, AsCH$_3$), 12.4 (s, 2C, Tp′*C*H$_3$), 12.5 (s, 1C, Tp′*C*H$_3$), 14.1 (s, 1C, Tp′*C*H$_3$), 15.7 (s, 1C, Tp′*C*H$_3$), 15.9 (s, 1C, Tp′*C*H$_3$), 44.2 (s, 2C, NCH$_3$), 44.6 (s, 2C, NCH$_3$), 106.1 (s, 2C, Tp′*C*H), 106.2 (s, 1C, Tp′*C*H), 119.9 (q, $^{1}J_{CF}$ = 320.3 Hz, 1C, CF$_3$), 145.5 (s, 1C Tp′*C*CH$_3$), 145.6 (s, 1C, Tp′*C*CH$_3$), 146.1 (s, 1C, Tp′*C*CH$_3$), 150.0 (s, 1C, Tp′*C*CH$_3$), 150.2 (s, 1C, Tp′*C*CH$_3$), 151.3 (s, 1C, Tp′*C*CH$_3$), 179.4 (s, 1C, AsCN$_2$), 225.7 (s, 1C, CO), 226.1 (s, 1C, CO), 301.9 (s, 1C, Mo≡C). MS/EI, *m*/*z*: 651 [M^{+}]. Anal. Calcd for $C_{25}H_{37}AsBF_3MoN_8O_5S$ (800.35): C, 37.50; H, 4.66; N, 14.00. Found: C, 37.42; H, 4.64; N, 13.50.

[Tp′(CO)$_2$W≡C−As(Me)C(NMe$_2$)$_2$](SO$_3$CF$_3$) (3b). Analogously a suspension of **2b** (0.30 g, 0.41 mmol) in 200 mL of chilled diethyl ether (−100 °C) was treated in the dark with a solution of 0.46 mmol of methyl triflate in 11 mL of diethyl ether. Warming up to ambient temperature was accompanied by the formation of a red precipitate. Stirring of the suspension was continued overnight. It was filtered, and the orange-red amorphous solid was washed (1 × 10 mL of diethyl ether, 1 × 10 mL of *n*-pentane). Continuous extraction with 150 mL of boiling diethyl ether for 48 h afforded 0.18 g (49% yield) of **3b** as orange crystals. IR (KBr, cm^{-1}) ν: 2553 w (BH), 1981 vs (CO), 1888 vs (CO). ^{1}H NMR (CD_2Cl_2) δ: 1.81 (s, 3H, AsCH$_3$), 2.33 (s, 3H, Tp′CH$_3$), 2.38 (s, 3H, Tp′CH$_3$), 2.40 (s, 6H, Tp′CH$_3$), 2.53 (s, 3H, Tp′CH$_3$), 2.55 (s, 3H, Tp′CH$_3$), 3.44(s, 12H, NCH$_3$), 5.83 (s, 1H. Tp′H), 6.02 (s, 2H, Tp′H). ^{13}C{^{1}H} NMR (CD_2Cl_2) δ: 11.2 (s, 1C, AsCH$_3$), 12.7 (s, 3C, Tp′*C*H$_3$), 15.2 (s, 1C, Tp′*C*H$_3$), 17.0 (s, 1C, Tp′*C*H$_3$), 17.2 (s, 1C, Tp′*C*H$_3$), 45.2 (s, 4C, NCH$_3$), 107.1 (s, 2C, Tp′*C*H), 107.3 (s, 1C, Tp′*C*H), 121.2 (q, $^{1}J_{CF}$ = 320.6 Hz, 1C, CF$_3$), 146.0 (s, 2C, Tp′*C*CH$_3$), 146.7 (s, 1C, Tp′*C*CH$_3$), 151.6 (s, 2C, Tp′*C*CH$_3$), 153.0 (s, 1C, Tp′*C*CH$_3$), 182.0 (s, 1C, AsCN$_2$), 225.1 (s, 1C, CO), 225.3 (s, 1C, CO), 283.2 (s, 1C, W≡C). MS/EI, *m*/*z*: 739 [M^{+}]. Anal. Calcd for $C_{25}H_{37}AsBF_3N_8O_5SW$ (888.26): C, 33.80; H, 4.19; N, 12.61. Found: C, 33.70; H, 4.07; N, 12.44.

X-ray Structural Analysis of 2b. Single crystals of **2b** were grown from diethyl ether. An orange plate with the approximate dimensions of 0.16 × 0.14 × 0.03 mm^{3} was measured on a Siemens SMART CCD area detector system with a three-axis goniometer and with Mo Kα radiation (λ = 0.71073 Å) at 298 K. Crystal data and refinement details: space group $I4_1/a$ (tetragonal), cell dimensions $a = 22.1701(2)$ Å, $c = 23.2316(3)$ Å, $V = 11418.6(2)$ Å^{3} (refined from all reflections with $F > 20\sigma(F)$), $Z = 16$, $d_{calcd} = 1.685$ g cm^{-3}, $\mu = 5.231$ mm^{-1}, data reduction with the SAINT program (V 4.028, Siemens), covering more than 97% of the data: 39450 reflections collected ($2\theta_{max} = 50°$), of which 5032 were unique ($R_{int} = 0.1086$) and 3824 observed [$I > 2\sigma(I)$]. Empirical absorption correction with redundant data (SADABS programm, Siemens), max/min transmission 1.00/0.34, *R*(merg) before/after correction 0.198/0.103. Structure solution and refinement on F^{2} with SHELXTL-PLUS Vers. 5.03/Iris (Siemens), 326 parameters, anisotropic refinement for all heavy atoms, hydrogen atoms treated as riding groups with a 1.2-fold (1.5-fold for methyl groups) isotropic *U* value as the equivalent *U* value of the corresponding C atom. R1 = 0.0502; wR2 = 0.1213 (all data), GooF(F^{2}) = 1.049, $w^{-1} = \sigma^2(F_o^{2}) + (0.0707P)^2$, where

$P = [(\max F_o^2) + (2F_c^2)]/3$, max/min residual electron densities 2.566 and -1.111 e Å^{-3}.

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Supporting Information Available: Tables of X-ray data, atomic coordinates, thermal parameters, complete bond distances and angles, and thermal ellipsoid plots for compound **2b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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