

Reactivity of the Inversely Polarized Arsaalkenes $R\text{--As}=\text{C}(\text{NMe}_2)_2$ $\{\text{R} = [(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_2\text{Fe}], t\text{BuC}(\text{O}), 4\text{-Et-C}_6\text{H}_4\text{C}(\text{O})\}$ towards Phosphavinylidene Complexes $[\eta^5\text{-(C}_5\text{H}_5)(\text{CO})_2\text{M}=\text{P}=\text{C}(\text{SiMe}_3)_2]$ ($\text{M} = \text{Mo}, \text{W}$)

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The reaction of the phosphavinylidene complexes $[\text{Cp}(\text{CO})_2\text{M}=\text{P}=\text{C}(\text{SiMe}_3)_2]$ [$\text{Cp} = \text{C}_5\text{H}_5$, $\text{M} = \text{Mo}$ (**2**), W (**3**)] with the ferrioarsaalkene $[\text{Cp}^*(\text{CO})_2\text{Fe}=\text{As}=\text{C}(\text{NMe}_2)_2]$ (**1a**) ($\text{Cp}^* = \text{C}_5\text{Me}_5$) afforded the novel η^3 -2-phospha-1-arsaallyl complexes $[\eta^3\text{-}\{\text{[Fe]}\text{--As--P--C}(\text{SiMe}_3)_2\}\text{M}(\text{CO})_2\text{Cp}]$ [$\text{M} = \text{Mo}$, $[\text{Fe}] = [\text{Cp}^*(\text{CO})_2\text{Fe}]$ (**4a**); W (**5a**)]. Similarly, treatment of equimolar amounts of **3** with arsaalkene $t\text{BuC}(\text{O})\text{--As}=\text{C}(\text{NMe}_2)_2$ (**1b**) gave rise to the formation of $[\eta^3\text{-}\{t\text{BuC}(\text{O})\text{--As--P--C}(\text{SiMe}_3)_2\}\text{W}(\text{CO})_2\text{Cp}]$ (**5b**) by an arsinidene transfer process. In contrast to this, the more reactive arsaalkene $4\text{-Et-C}_6\text{H}_4\text{C}(\text{O})\text{--}$

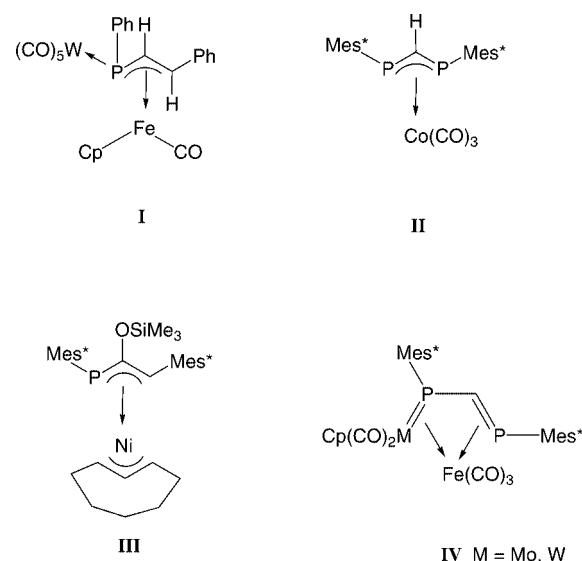
$\text{As}=\text{C}(\text{NMe}_2)_2$ (**1c**) and complex **3** underwent reaction to give the cyclic phosphonium complex $[\text{Cp}(\text{CO})_2\text{W}=\text{P}=\text{O}\text{--C}^a(4\text{-Et-C}_6\text{H}_4)=\text{As-C}^b(\text{SiMe}_3)_2(\text{P-C}^b)]$ (**6**). The novel compounds **4a**, **5a**, **5b**, and **6** were characterized by elemental analyses and by means of spectroscopy (IR, ^1H , ^{13}C , ^{31}P NMR). Moreover, the molecular structures of **4a**, **5b**, and **6** were elucidated by X-ray diffraction analyses.

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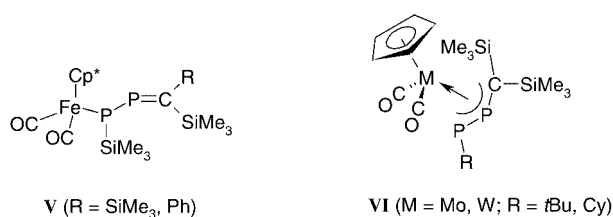
Introduction

The search for novel ligand systems remains an important target for both academic and industrial reasons. Prominent examples are N-heterocyclic carbenes, which, as ancillary ligands in transition-metal complexes, have significantly improved the efficiency of a number of catalyzed processes.^[1] Other remarkable examples concern phosphalkenes, phospholyl compounds, and phosphinines, which have recently emerged from the status of laboratory curiosities to become valuable ligands in complex catalysis.^[2] Compared to a plethora of synthetically useful η^3 -allyl complexes^[3,4] only a few coordination compounds with η^3 -1-phosphaallyl ligands such as **I**^[5] or η^3 -1,3-diphosphaallyl ligands such as **II**^[6] and **III**^[7] have been described. In the dinuclear complexes of type **IV** the 1,3-diphosphaallyl unit is incorporated in a 2,4-phospha-1-metallabutadiene ligand (Scheme 1).^[8]

Complex **III** exhibits catalytic activity in ethylene polymerization.^[7] Whereas 1,2-diphosphaallyllithium compounds^[9] and η^1 -complexes of the isomeric 1,2-diphosphaallyl ligand **V** have been known for some years,^[10] a paper concerning η^3 -complex **VI** was only recently published.^[11]



Scheme 1. (Heteroallyl)transition-metal complexes.

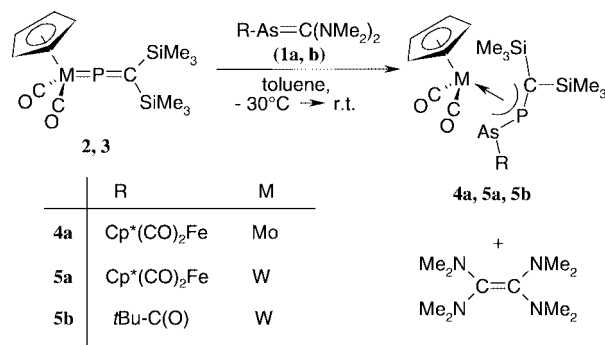


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In this paper we report on the reactivity of inversely polarized arsaalkenes $R-As=C(NMe_2)_2$ [**1**: **a**: $R = Cp^*(CO)_2Fe$, **b**: $tBuC(O)$, **c**: $4-Et-C_6H_4C(O)$] with phosphavinylidene complexes $[Cp(CO)_2M=P=C(SiMe_3)_2]$ (**2**: $M = Mo$; **3**: $M = W$),^[12] whereby the first complexes with η^3 -2-phospha-1-arsaallyl ligands are formed. Part of this work has previously been published in a short communication.^[13]

Results and Discussion

Treatment of complexes $[Cp(CO)_2M=P=C(SiMe_3)_2]$ (**2**: $M = Mo$; **3**: $M = W$) with an equimolar amount of ferriar-saalkene $[Cp^*(CO)_2Fe-As=C(NMe_2)_2]$ (**1a**)^[14] in toluene solution over a temperature range of $-30^\circ C$ to ambient temperature afforded the deep red crystalline η^3 -2-phospha-1-arsaallyl complexes **4a** (35% yield) and **5a** (52% yield). Purification of the products was effected by column chromatography on Florisil with a mixture of hexane/diethyl ether (2:1, v/v) (**4a**) or pentane/diethyl ether (5:1, v/v) (**5a**) as eluents. The air- and moisture-sensitive complexes are well soluble in saturated hydrocarbons, ethereal and aromatic solvents. Analogously, reaction of compound **1b** with an equimolar amount of **3** gives rise to the formation of heteroallyl complex **5b** as an orange solid in 63% yield (Scheme 2). Tetrakis(dimethylamino)ethene is formed as a by-product. After removal of toluene from the reaction mixture, a few drops of the alkene were distilled off and identified by comparison of the 1H and ^{13}C NMR spectra with those of an authentic sample.



Scheme 2. Formation of the 2-phospha-1-arsaallyl complexes **4a**, **5a**, **5b**.

A singlet at $\delta = 4.1$ ppm in the $^{31}P\{^1H\}$ NMR spectrum of **4a**, a doublet in the $^{13}C\{^1H\}$ NMR spectrum at $\delta = 49.9$ ppm ($J_{PC} = 105$ Hz), and singlets in the 1H NMR spectrum for two different trimethylsilyl groups ($\delta = 0.26, 0.61$ ppm), the pentamethylcyclopentadienyl ($\delta = 1.46$ ppm) and the cyclopentadienyl ligands ($\delta = 5.10$ ppm) as well as the absence of resonances due to the $C(NMe_2)_2$ fragment indicate the combination of the phosphavinylidene unit of **2** and the arsanediyl group of **1a** to a novel ligand system in complex **4a**. Accordingly, the tungsten analogue **5a** and the (pivaloylphosphaarsaallyl)tungsten complex **5b** display singlets at $\delta = -18.7$ and -8.9 ppm in the $^{31}P\{^1H\}$ NMR

spectrum. This high-field position is typical for $^{31}P\{^1H\}$ resonances of η^3 -phosphaallyl complexes of tungsten as evident from $[\eta^3-(2,4,6-tBu_3C_6H_2PCHCH_2)W(CO)_2Cp]$ ($\delta = -48.9$ and -28.0 ppm for both isomers).^[15] In the η^3 -1,2-diphosphaallyl complex **VI** the resonances for the central P atom were observed at $\delta = -6.8$ ppm ($M = Mo$, $R = tBu$) and $\delta = -61.6$ ppm ($M = W$, $R = tBu$).^[11] In the $^{13}C\{^1H\}$ NMR spectra of **4a**, **5a**, and **5b** the carbon atoms of the 2-phospha-1-arsaallyl ligands appear as doublets at $\delta = 49.9$ ppm ($J_{PC} = 105.0$ Hz), 35.7 ($J_{PC} = 101.2$ Hz), and 31.8 ($J_{PC} = 98.5$ Hz) ppm. The ^{13}C NMR resonances of the carbonyl ligands were observed at $\delta = 234.0$ (s), 236.0 (s) ($Mo-CO$); 216.7 (s), 218.65 (d, $J_{PC} = 11.5$ Hz) ($Fe-CO$) for **4a**, at $\delta = 222.7$ (s), 224.6 (s) ($W-CO$); 217.1 (s), 219.0 (s) ($Fe-CO$) for **5a**, and at $\delta = 222.8$ (s), 223.9 (s) for **5b**. A ^{13}C NMR doublet at $\delta = 233.5$ ($J_{PC} = 4.1$ Hz) ppm in the spectrum of **5b** was attributed to the acyclic carbonyl group. These resonances are shifted to a lower field relative to those of precursors **2** ($\delta = 230.4$ ppm)^[12b] and **3** ($\delta = 218.9$ ppm)^[12b] indicating the improved donor capacity of the η^3 -2-phospha-1-arsaallyl ligands over the phosphavinylidene system. Similar observations were made with the η^3 -1,2-diphosphaallyl complexes of type **VI** [e.g., $M = Mo$, $R = tBu$; $\delta^{13}CO = 234.3$ (s), 235.5 (s) ppm]. This is also mirrored by the carbonyl stretching frequencies in the IR spectra of **4a**, **5a**, and **5b**, which are observed as intense bands at $\tilde{\nu} = 1929, 1850$ cm^{-1} (**4a**), at $\tilde{\nu} = 1923, 1843$ cm^{-1} (**5a**), and at $\tilde{\nu} = 1941, 1874$ cm^{-1} (**5b**). The differences between the $\nu(CO)$ absorptions of **5a** and **5b** are due to the electron-donating iron substituent in **5a** and the electron-withdrawing pivaloyl group in **5b**. The corresponding bands in the precursors **2** and **3** appear at $\tilde{\nu} = 1944, 1882$ cm^{-1} (KBr) and $1952, 1880$ cm^{-1} (*n*-hexane).^[12b] In the IR spectrum of 1,2-diphosphaallyl complexes **VI** $\nu(CO)$ bands were registered at $\tilde{\nu} = 1943, 1877$ cm^{-1} ($M = Mo$; $R = tBu$) and at $\tilde{\nu} = 1938, 1851$ cm^{-1} ($M = W$; $R = tBu$).^[11]

Single crystals of **4a** and **5a** suitable for an X-ray diffraction analysis were grown from a 1:9 mixture of diethyl ether/*n*-pentane at $-30^\circ C$. Compound **5a** is isostructural to **4a**, and only the latter will be discussed in detail.

The analysis (see Figure 1) displays a molecule with a distorted piano-stool geometry [$As(1)-Mo(1)-C(20) = 63.87(7)^\circ$, $C(20)-Mo(1)-C(21) = 80.83(11)^\circ$, $C(21)-Mo(1)-C(13) = 69.07(9)^\circ$], with two nearly linear carbonyl ligands [$Mo(1)-C(20)-O(3) = 170.9(2)^\circ$, $Mo(1)-C(21)-O(4) = 175.7(2)^\circ$]. The most interesting part of the molecule is the unprecedented 2-phospha-1-arsaallyl ligand which is unsymmetrically linked to the metal atom in an η^3 -fashion through bonds $Mo(1)-As(1)$ [$2.7644(3)$ Å], $Mo(1)-P(1)$ [$2.4940(6)$ Å], and $Mo(1)-C(13)$ [$2.420(2)$ Å]. The latter bond length significantly exceeds the $Mo(1)-C$ distances of the $[CpMo]$ part of the molecule [$2.316(2)-2.371(2)$ Å]. In the (1,2-diphosphaallyl)molybdenum complex **VI** the corresponding $Mo-C$ bond length was determined to be $2.437(1)$ Å.^[11] The distances between the Mo atom and the terminal carbon atom in **4a** as well as in **VI** clearly exceed the corresponding $Mo-C$ bond lengths in 1-phosphaallyl complex **VII** [$2.357(3)$ Å].^[5c]

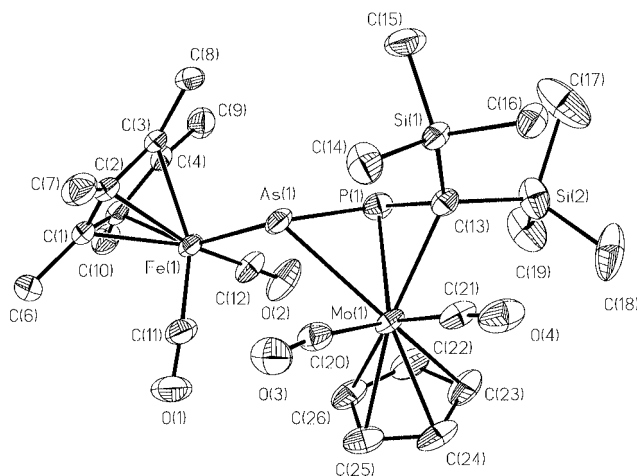
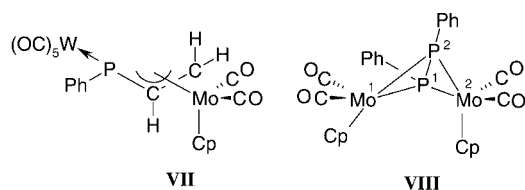
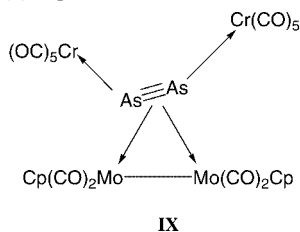


Figure 1. Molecular structure of **4a** in the crystal. Selected bond lengths [Å] and angles [°]: Mo(1)–C(20) 1.953(2), Mo(1)–C(21) 1.959(2), Mo(1)–C(13) 2.420(2), Mo(1)–P(1) 2.4940(6), Mo(1)–As(1) 2.7644(3), P(1)–As(1) 2.2507(7), P(1)–C(13) 1.791(2), As(1)–Fe(1) 2.4098(4), C(13)–Si(1) 1.898(2), C(13)–Si(2) 1.895(2), C(20)–Mo(1)–C(21) 80.83(11), C(21)–Mo(1)–C(13) 69.07(9), C(20)–Mo(1)–As(1) 63.83(7), As(1)–P(1)–C(13) 99.15(7), P(1)–As(1)–Fe(1) 106.59(2), P(1)–C(13)–Si(1) 120.88(12), P(1)–C(13)–Si(2) 108.67(11).



The metal–phosphorus distances in both complexes **4a** [2.4940(6) Å] and **VI** (M = Mo) [2.4960(3) Å] are identical, and intermediate between the Mo–P bond lengths Mo(1,2)–P(1) [2.466, 2.470 Å] and Mo(1,2)–P(2) [2.542, 2.546 Å] in **VIII**.^[16] The Mo(1)–As(1) bond in **4a** is lengthened when compared with the Mo–As contacts in tetrahedrane **IX** [2.531(3), 2.645(3) Å].^[17]



Due to the π -interaction with a metal atom, the As–P distance within the 2-phospha-1-arsaallyl ligand in **4a** [2.2507(7) Å] is longer than the unsupported As=P double bonds in the structurally characterized compounds {(Me₃Si)₂CH}As=P(2,4,6-*t*Bu₃C₆H₂) [2.124 Å]^[18] or [Cp*-(CO)₂FeAs{Cr(CO)₅}=P(2,4,6-*t*Bu₃C₆H₂)] [2.155(1) Å].^[19]

The bond length P(1)–C(13) in **4a** [1.791(2) Å]—as is also found in **VI** (M = Mo) [1.7875(12) Å]—is elongated with respect to a localized and unsupported P=C double bond (1.65–1.72 Å),^[20] but is clearly shorter than a P–C single bond (av. 1.85 Å).^[21] In **VII** the corresponding bond length was determined to be 1.755(3) Å.^[5c] The atoms Fe(1) and

Si(2) in **4a** are directed towards the phosphorus atom enclosing angles Fe(1)–As(1)–P(1) [106.59(2)°], As(1)–P(1)–C(13) [99.15(7)°], and P(1)–C(13)–Si(2) [108.67(11)°]. Substituent Si(1)(CH₃)₃ at C(13) is located above the plane defined by the atoms As(1), P(1), and C(13) with an angle P(1)–C(13)–Si(1) of 120.88(12)°.

From the view-point of the Wade–Mingos rules molecule **4a** as well as the related compounds **5a** and **5b** possess four skeleton atoms and 14 skeleton electrons and thus have to be regarded as *arachno* clusters.^[22] Orange single crystals of the (η^3 -2-phospha-1-arsaallyl)tungsten complex **5b** were grown from diethyl ether/*n*-pentane (1:5) at –30 °C (see Figure 2). The analysis shows a molecule, the core of which is similar to that of **4a** with the pivaloyl substituent and the group Si(1)Me₃ directed towards the central atom P(1) of the η^3 -heteroallyl ligand. The bonds As(1)–P(1) [2.269(1) Å] and P(1)–C(8) [1.806(2) Å] within the 2-phospha-1-arsaallyl ligand of **5b** are slightly longer than in **4a**. The bond As(1)–C(15) to the carbonyl carbon atom of the pivaloyl substituent [2.063(2) Å] is markedly elongated when compared with the As–C(O) contact in the precursor arsaalkene [1.938(4) Å].^[23] The sum of single bond radii of As and C is 1.98 Å.^[24] The formal As=C double bond of precursor **1b** was elongated to 1.924(5) Å^[23] [in Cp*(CO)₂Fe–As=C(NMe₂)₂: As–C = 1.876(8) Å].^[14] The bond length C(15)–O(3) is that of a localized carbonyl group.^[24] The atoms C(15) and Si(1) are located in the plane defined by the atoms C(8), P(1), and As(1). These atoms are attached to the tungsten center by bonds W(1)–As(1) [2.759(1) Å], W(1)–P(1) [2.498(1) Å], and W(1)–C(8) [2.439(2) Å]. They are all well comparable to those in **5a**: W(1)–As(1) [2.7854(2) Å], W(1)–P(1) [2.4955(5) Å], and W(1)–C(8)

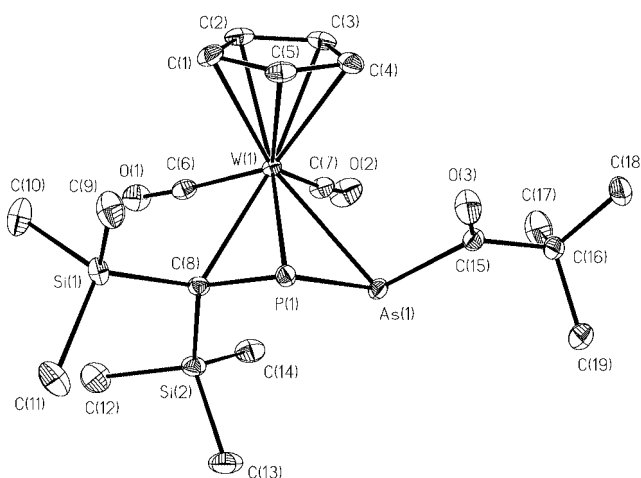
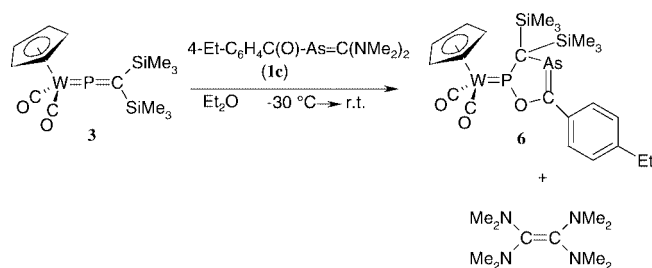


Figure 2. Molecular structure of **5b** in the crystal. Selected bond lengths [Å] and angles [°]: W(1)–C(6) 1.968(2), W(1)–C(7) 1.977(2), W(1)–C(8) 2.439(2), W(1)–P(1) 2.498(1), W(1)–As(1) 2.759(1), P(1)–C(8) 1.806(2), P(1)–As(1) 2.269(1), As(1)–C(15) 2.063(2), C(8)–Si(1) 1.912(2), C(8)–Si(2) 1.922(2), O(3)–C(15) 1.214(2), C(15)–C(16) 1.541(2), C(6)–W(1)–C(7) 80.30(8), C(6)–W(1)–C(8) 67.13(7), C(7)–W(1)–As(1) 67.62(6), C(8)–P(1)–As(1) 97.66(6), P(1)–As(1)–C(15) 93.86(5), As(1)–C(15)–O(3) 122.37(13), O(3)–C(15)–C(16) 122.47(16), As(1)–C(15)–C(16) 115.07(12), P(1)–C(8)–Si(1) 107.49(9), P(1)–C(8)–Si(2) 122.05(10), Si(1)–C(8)–Si(2) 114.60(9).

[2.411(2) Å]. The W–As π -bonds in $[\eta^1:\eta^2\text{-PhAs}=\text{AsPhW}(\text{CO})_5]_2$ [2.728(4) and 2.769(4) Å] are similar to the W–As bond length in **5b**. The W–P π -bond length in $\eta^3\text{-}\{2,4,6\text{-}t\text{Bu}_3\text{C}_6\text{H}_2\text{-P}(\text{O})\text{CHCH}_2\}\text{W}(\text{CO})_2\text{Cp}$ [2.488(1) Å] is also in good agreement with the respective atom distance in **5b**.^[25] The W(1)–C(8) bond in **5b** [2.439(2) Å], however, is markedly lengthened in comparison to those in $\eta^3\text{-}\{2,4,6\text{-}t\text{Bu}_3\text{C}_6\text{H}_2\text{P}(\text{O})\text{CHCH}_2\}\text{W}(\text{CO})_2\text{Cp}$ [2.344(5), 2.335(4) Å].^[25]

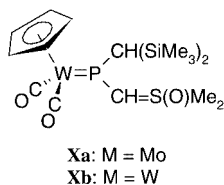
To the best of our knowledge compounds **4a**, **5a**, and **5b** are the first $\eta^3\text{-2-phospha-1-arsaallyl}$ complexes. One $\eta^1\text{-2-phospha-1-arsaallyl}$ complex ($\eta^5\text{-C}_5\text{Me}_5(\text{CO})_2\text{FeAs}(\text{SiMe}_3)\text{-P}=\text{C}(\text{SiMe}_3)_2$) was recently described.^[26] 2-Phospha-1-arsapropenes are rare compounds. To the best of our knowledge there are two accounts in the literature of such species. Thermolabile $\text{Ph}_2\text{As-P}=\text{C}(\text{Ph})\text{SiMe}_3$ ^[27] decomposes within 1 d to Ph_4As_2 and a diphosphabicyclobutane, whereas $t\text{Bu}_2\text{As-P}=\text{C}(\text{SiMe}_3)_2$ is stable at ambient temperature.^[28]

Reaction of phosphavinylidene complex **3** with the more reactive arsaalkene 4-Et-C₆H₄C(O)As=C(NMe₂)₂ (**1c**) in diethyl ether took a completely different course. Here the cyclic phosphonium complex **6** was isolated as red crystals in 41 % yield. (Scheme 3).



Scheme 3. Formation of the phosphonium complex **6**.

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **6** displays a singlet at $\delta = 313.2$ ppm with ^{183}W satellites ($J_{\text{P,W}} = 728$ Hz), which indicates the presence of a W=P double bond. The data are comparable with the ^{31}P NMR spectra of complexes **Xa**, **b** ($\delta = 306.4$ ppm; 244.8 ppm, $J_{\text{P,W}} = 604$ Hz)^[29] and **IV** ($\text{M} = \text{Mo}$: $\delta = 304$ ppm; $\text{M} = \text{W}$: $\delta = 246.8$ ppm, $J_{\text{P,W}} = 638$ Hz).^[8]



Both silyl groups are chemically and magnetically equivalent giving rise to a singlet at $\delta = 0.47$ ppm in the ^1H NMR spectrum and a singlet at $\delta = 1.9$ ppm in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of the compound. A doublet of low intensity at $\delta = 60.1$ ppm ($J_{\text{P,C}} = 50.3$ Hz) is due to a quaternary carbon atom adjacent to the P atom. The two chemically and magnetically equivalent carbonyl ligands give rise to a singlet at $\delta = 226.9$ ppm with ^{183}W satellites ($J_{\text{W,C}} = 183$ Hz). A singlet at $\delta = 222.8$ ppm is assigned to the ^{13}C nucleus of an As=C double bond. This value falls in the range of $\delta =$

200.6 ppm in $\text{MesAs}=\text{CHNMe}_2$ to $\delta = 241.5$ ppm in $\text{Me}_3\text{Si-As}=\text{C}(\text{OSiMe}_3)t\text{Bu}$.^[30] The IR spectrum in the region of the CO stretching modes is characterized by two intense bands at $\tilde{\nu} = 1938, 1859\text{ cm}^{-1}$. No bands are found for the $\tilde{\nu}(\text{CO})$ mode of an acylarsane (e.g., $\tilde{\nu} = 1660\text{ cm}^{-1}$ in **5b**). Yellow single crystals of compound **6** (Figure 3) were obtained from a diethyl ether solution at -30°C . The analysis displays a molecule with a distorted piano-stool geometry [$\text{P}(1)\text{-W}(1)\text{-C}(1)$ $95.1(1)^\circ$, $\text{P}(1)\text{-W}(1)\text{-C}(2)$ $96.2(1)^\circ$, $\text{C}(1)\text{-W}(1)\text{-C}(2)$ $84.6(1)^\circ$] with two nearly linear carbonyl ligands [$\text{W}(1)\text{-C}(1)\text{-O}(1)$ $177.8(3)^\circ$, $\text{W}(1)\text{-C}(2)\text{-O}(2)$ $175.1(2)^\circ$].

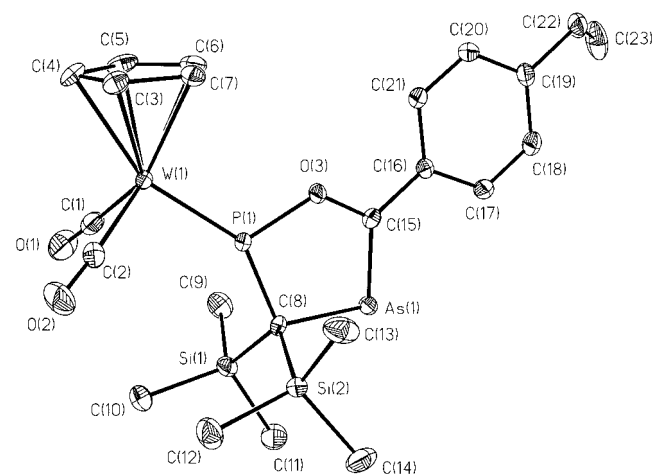
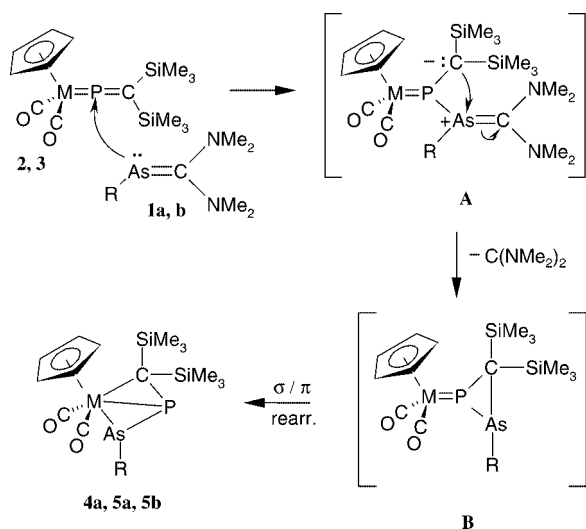


Figure 3. Molecular structure of **6** in the crystal. Selected bond lengths [Å] and angles $^\circ$: W(1)–C(1) 1.976(3), W(1)–C(2) 1.960(3), W(1)–P(1) 2.232(1), P(1)–O(3) 1.698(2), O(1)–C(1) 1.159(3), O(2)–C(2) 1.164(3), O(3)–C(15) 1.372(3), C(15)–C(16) 1.472(3), As(1)–C(15) 1.832(2), As(1)–C(8) 2.023(2), C(8)–Si(1) 1.932(3), C(8)–Si(2) 1.941(3), C(1)–W(1)–C(2) $84.6(1)^\circ$, C(1)–W(1)–P(1) $95.1(1)^\circ$, C(2)–W(1)–P(1) $146.0(1)^\circ$, W(1)–P(1)–O(3) $114.2(1)^\circ$, W(1)–P(1)–C(8) $146.0(1)^\circ$, O(3)–P(1)–C(8) $99.8(1)^\circ$, P(1)–C(8)–As(1) $106.7(1)^\circ$, C(8)–As(1)–C(15) $92.1(1)^\circ$, As(1)–C(15)–O(3) $118.5(2)^\circ$, P(1)–O(3)–C(15) $118.7(1)^\circ$, O(3)–C(15)–C(16) $114.5(2)^\circ$, As(1)–C(15)–C(16) $127.0(2)^\circ$.

The third leg is represented by a 1,2,4-oxaphospharsolenium ligand which is linked to the metal atom through a W=P double bond of 2.232(1) Å. The bond length lies between those in $[\text{Cp}(\text{CO})_2\text{W}=\text{PO}^a\text{-CMe}_2\text{-CMe}_2\text{-O}^b(\text{P-O}^b)]$ [2.181 Å]^[31] and $\text{Cp}(\text{CO})_2\text{W}=\text{P}(t\text{Bu})_2$ [2.284(4) Å].^[32] This ring ligand without precedent features an As–C(15) double bond of 1.832(2) Å, which is well comparable to the As–C separation in the metalloarsaalkene $[\text{Cp}(\text{CO})_2\text{Fe-As}=\text{C}(\text{O-SiMe}_3)t\text{Bu}]$ [1.821(2) Å].^[33] The bond length C(15)–O(3) [1.372(3) Å] is similar to the one in the metalloarsaalkene [1.356(3) Å], both being shorter with respect to an sp^2 C–O single bond (ca. 1.41 Å).^[34] The contacts P(1)–O(3) [1.698(2) Å] and P(1)–C(8) [1.814(2) Å] are markedly shorter than the sum of the covalent radii (1.76 and 1.87 Å) but still reflect bond orders of unity. The five-membered ring is slightly puckered (sum of endocyclic angles 535°). The plane defined by the atoms P(1), O(3), and C(8) bisects the angle C(1)–W(1)–C(2), enclosing angles of 43° with vector W(1)–C(1) and 41° with vector W(1)–C(2).

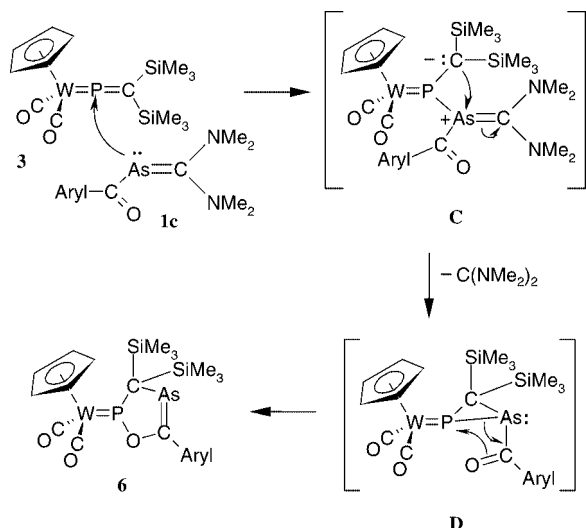
Mechanisms

It is conceivable that the formation of complexes **4a**, **5a**, and **5b** is initiated by the nucleophilic attack of the arsaalkene through its As atom on the phosphorus center of precursors **2** and **3** to give adduct **A**. Extrusion of $\text{C}(\text{NMe}_2)_2$ would lead to intermediate **B**. A σ/π -type rearrangement of **B** affords the final products (see Scheme 4).



Scheme 4. Proposed mechanism for the formation of **4a**, **5a**, and **5b**.

The formation of the functionalized phosphonium complex **6** may be initiated by the nucleophilic attack of arsaalkene **1c** through its electron-abundant arsenic atom at the phosphorus center of **3** affording zwitterion **C**, which collapses to phospharsirenium complex **D**. Incorporation of the carbonyl group into the As–P bond of the strained ring leads to the observed product **6** (Scheme 5).



Scheme 5. Proposed mechanism for the formation of **6**.

Conclusions

Transition-metal-induced cleavages of inversely polarized arsaalkenes to give cyclotriarsanes^[35] or an η^2 -diarsene complex^[36] were observed. Here the smooth generation of η^3 -2-phospha-1-arsaallyl complexes **4a**, **5a**, **5b**, and complex **6** featuring the 1,2,4-oxaphospharsolenium ligand underlines the ability of arsaalkenes to act as convenient sources for arsanediyl (arsinidene) units under mild conditions.

Experimental Section

General: All manipulations were performed under dry, oxygen-free nitrogen using standard Schlenk techniques. Solvents were rigorously dried with an appropriate drying agent and freshly distilled under N_2 before use. The following compounds were prepared according to literature procedures: $[\text{Cp}^*(\text{CO})_2\text{M}=\text{P}=\text{C}(\text{SiMe}_3)_2]$ [$\text{M} = \text{Mo}$ (**2**), W (**3**)],^[12] $[\text{Cp}^*(\text{CO})_2\text{Fe}-\text{As}=\text{C}(\text{NMe}_2)_2]$ (**1a**),^[14] $\text{Me}_3\text{Si}-\text{As}=\text{C}(\text{NMe}_2)_2$,^[14] IR: Bruker FT-IR VECTOR 22. ^1H -, ^{13}C -, and ^{31}P NMR (C_6D_6 , room temp.): Bruker AM Avance DRX 500 (^1H : 500.13 Hz; ^{13}C : 125.75 MHz; ^{31}P : 202.46 MHz); references: SiMe_4 (^1H , ^{13}C , 85% H_3PO_4 (^{31}P)). Florisil (Merck), pivaloyl chloride, and 4-ethylbenzoyl chloride were purchased commercially.

$t\text{BuC}(\text{O})\text{As}=\text{C}(\text{NMe}_2)_2$ (1b**):** A solution of pivaloyl chloride (0.18 g, 1.50 mmol) in *n*-pentane (10 mL) was added dropwise to a chilled solution (-30°C) of $\text{Me}_3\text{SiAs}=\text{C}(\text{NMe}_2)_2$ (0.37 g, 1.50 mmol) in *n*-pentane (30 mL). A yellow precipitate separated. Stirring was continued for 30 min, and the solvent was decanted. The precipitate was washed twice with cold *n*-pentane (30 mL, -30°C) and dried in vacuo to afford 0.27 g (69%) of **1b** as a pale yellow solid. IR (Nujol): $\tilde{\nu} = 1584, 1530\text{ cm}^{-1}$. ^1H NMR: $\delta = 1.40$ (s, 9 H, $t\text{Bu}$), 2.65 (s, 12 H, NCH_3) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR: $\delta = 27.9$ [s, $\text{C}(\text{CH}_3)_3$], 43.5 (s, NCH_3), 49.8 [s, $\text{C}(\text{CH}_3)_3$], 210.7 (s, CN_2), 240.1 (s, CO) ppm. Because of the pronounced thermolability of the compound it was not possible to obtain reliable elemental analyses.

$[\text{Cp}(\text{CO})_2\text{Mo}\{\eta^3\text{-}[\text{Cp}^*(\text{CO})_2\text{Fe}]\text{AsPC}(\text{SiMe}_3)_2\}]$ (4a**):** A solution of **1a** (0.76 g, 1.81 mmol) in toluene (20 mL) was added dropwise to a well-stirred chilled solution (-30°C) of **2** (0.72 g, 1.81 mmol) in toluene (25 mL). It was slowly warmed to ambient temperature and stirring was continued for 12 h. The reaction mixture was freed from solvent and volatile components. The black residue was dissolved with diethyl ether (10 mL), then Florisil was added (5 g) and the slurry was concentrated to dryness. The coated Florisil was transferred to the top of a column ($d = 1.5\text{ cm}$, $l = 6\text{ cm}$) charged with Florisil (20 g). A dark red zone was eluted with a 2:1 mixture of diethyl ether/*n*-pentane. Removal of solvents from the eluate afforded 0.46 g (35%) of dark red crystalline **4a**. IR (KBr): $\tilde{\nu} = 1850, 1929, 1977\text{ cm}^{-1}$ ($\text{C}=\text{O}$). ^1H NMR: $\delta = 0.26$ (s, 9 H, SiMe_3), 0.61 (s, 9 H, SiMe_3), 1.46 (s, 15 H, C_5Me_5), 5.10 (s, 5 H, Cp) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR: $\delta = 4.27$ (s, SiCH_3), 4.35 (s, SiCH_3), 9.4 [s, $\text{C}_5(\text{CH}_3)_5$], 49.9 (d, $J_{\text{PC}} = 105\text{ Hz}$, PCSi_2), 91.2 (s, Cp), 95.6 [s, $\text{C}_5(\text{CH}_3)_5$], 216.7 (s, FeCO), 218.65 (d, $J_{\text{PC}} = 11.5\text{ Hz}$, FeCO), 234.3 (s, MoCO), 236.8 (s, MoCO) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR: $\delta = 4.1$ (s) ppm. $\text{C}_{26}\text{H}_{38}\text{AsFeMoO}_4\text{PSi}_2$ (728.44): calcd. C 42.87, H 5.26; found C 43.17, H 5.29.

$[\text{Cp}(\text{CO})_2\text{W}\{\eta^3\text{-}[\text{Cp}^*(\text{CO})_2\text{Fe}]\text{AsPC}(\text{SiMe}_3)_2\}]$ (5a**):** Analogously, the combination of **1a** (0.76 g, 1.81 mmol) in toluene (20 mL) with **3** (0.89 g, 1.81 mmol) in toluene (25 mL) at -30°C and identical workup [Florisil, diethyl ether/*n*-pentane (5:1)] afforded 0.77 g (52%) of dark red crystalline **5a**. IR (KBr): $\tilde{\nu} = 1843, 1923, 1975\text{ cm}^{-1}$ ($\text{C}=\text{O}$). ^1H NMR (C_6D_6): $\delta = 0.25$ (s, 9 H, SiMe_3), 0.66

Table 1. Crystal data and data collection parameters.

Compound	4a	5b	6
Empirical formula	C ₂₆ H ₃₈ AsFeMoO ₄ PSi ₂	C ₁₉ H ₃₂ AsO ₃ PSi ₂ W	C ₂₃ H ₃₂ AsO ₃ PSi ₂ W
<i>M_r</i> [g mol ⁻¹]	728.42	654.37	702.41
Crystal dimensions [mm]	0.25 × 0.25 × 0.24	0.28 × 0.22 × 0.22	0.38 × 0.32 × 0.20
Crystal system	monoclinic	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>C</i> 2/ <i>c</i>
<i>a</i> [Å]	12.9620(1)	12.9170(18)	25.798(4)
<i>b</i> [Å]	18.3280(2)	10.7550(6)	16.597(2)
<i>c</i> [Å]	13.7430(2)	17.904(3)	15.674(3)
β [°]	104.2460(8)	93.036(13)	126.137(8)
<i>V</i> [Å ³]	3164.49(6)	2483.8(6)	5420.0(15)
<i>Z</i>	4	4	8
$\rho_{\text{calcd.}}$ [g cm ⁻³]	1.529	1.750	1.722
μ [mm ⁻¹]	2.047	6.150	5.643
<i>F</i> (000)	1480	1280	2752
θ [°]	2.95–30.00	3.30–30.00	3.02–27.50
No. refl. collected	18141	87578	81627
No. refl. unique	9224	7234	6231
<i>R</i> (int)	0.0186	0.0501	0.0453
No. refl. [<i>I</i> > 2 σ (<i>I</i>)]	7859	6307	5302
Refined parameters	336	253	287
GOF	1.035	1.061	1.141
<i>R_F</i> [<i>I</i> > 2 σ (<i>I</i>)]	0.0318	0.0167	0.0173
<i>wR_{F2}</i> [<i>I</i> > 2 σ (<i>I</i>)]	0.0757	0.0326	0.0364
$\Delta\rho_{\text{max/min}}$ [e·Å ⁻³]	0.970/–0.829	0.652/–0.573	0.979/–0.790

(s, 9 H, SiMe₃), 1.47 (s, 15 H, C₅Me₅), 5.13 (s, 5 H, Cp) ppm. ¹³C{¹H} NMR (C₆D₆): δ = 4.4 (d, *J*_{PC} = 9.2 Hz, SiCH₃), 9.5 [s, C₅(CH₃)₅], 10.1 (s, SiCH₃), 35.7 (d, *J*_{PC} = 101.2 Hz, PCSi₂), 89.6 (s, Cp), 95.6 [s, C₅(CH₃)₅], 217.1 (s, FeCO), 219.0 (s, FeCO), 222.7 (s, WCO), 224.6 (s, WCO) ppm. ³¹P{¹H} NMR (C₆D₆): δ = –18.7 (s) ppm. C₂₆H₃₈AsFeO₄PSi₂W (816.35): calcd. C 38.26, H 4.49; found C 38.68, H 4.90.

[Cp(CO)₂W{η³-tBuC(O)}AsPC(SiMe₃)₂] (5b): A chilled solution (–30 °C) of arsaalkene **1b** (1.81 mmol) in diethyl ether (20 mL) was added dropwise to a well-stirred cold solution (–30 °C) of complex **3** (0.89 g, 1.81 mmol) in diethyl ether (25 mL). Stirring at –30 °C was continued for 4 h before the reaction mixture was slowly warmed to room temp. After 12 h of stirring, solvent and volatile components were removed in vacuo. The black residue was dissolved in diethyl ether (10 mL). Florisil (5 g) was added and the slurry was concentrated to dryness. As described earlier, the crude material was chromatographed on a Florisil column (*d* = 1.5 cm, *l* = 6 cm) charged with Florisil (20 g). An orange-red zone was eluted with a diethyl ether/pentane mixture (5:1). Removal of solvents from the eluate afforded 0.75 g (63%) of orange crystalline **5b**. IR (KBr): $\tilde{\nu}$ = 1941, 1874 (C=O), 1660 (C=O) cm⁻¹. ¹H NMR: δ = 0.16 (d, *J*_{PH} = 1.6 Hz, 9 H, SiMe₃), 0.45 (s, 9 H, SiMe₃), 1.05 (s, 9 H, *t*Bu), 4.96 (s, 5 H, Cp) ppm. ¹³C{¹H} NMR: δ = 4.0 (d, *J*_{PC} = 9.7 Hz, SiCH₃), 8.5 (s, SiCH₃), 26.2 [s, C(CH₃)₃], 31.8 [d, *J*_{PC} = 98.5 Hz, C(SiMe₃)₂], 50.1 [s, C(CH₃)₃], 90.1 (s, Cp), 222.8 (s, WCO), 223.9 (s, WCO), 233.53 (d, *J*_{PC} = 4.1 Hz, AsCO) ppm. ³¹P{¹H} NMR: δ = –8.9 (s) ppm. C₁₉H₃₂AsO₃PSi₂W (654.38): calcd. C 34.87, H 4.93; found C 34.82, H 4.92.

[Cp(CO)₂W=POC^a(4-Et–C₆H₄)=AsC^b(SiMe₃)₂(P–C^b)] (6): A solution of 4-ethylbenzoyl chloride (0.61 g, 3.62 mmol) in diethyl ether (10 mL) was added dropwise to a chilled solution (–30 °C) of Me₃SiAs=C(NMe₂)₂ (0.89 g, 3.62 mmol). Stirring was continued for 30 min to give **1c**. A solution of complex **3** (0.89 g, 1.81 mmol) in diethyl ether (20 mL) was slowly added with vigorous stirring. It was slowly warmed to room temp. and stirring was continued for 12 h. It was concentrated to dryness and the black residue was

dissolved in diethyl ether (10 mL). Florisil (5 g) was added and the slurry was freed from solvent. The coated Florisil was transferred onto the top of a column (*d* = 1.5 cm, *l* = 6 cm) charged with Florisil (20 g). A red zone was eluted with pentane. Removal of solvents in vacuo afforded 0.52 g (41%) of deep red crystalline **6**. IR (KBr): $\tilde{\nu}$ = 1859, 1938 (C=O) cm⁻¹. ¹H NMR: δ = 0.47 (s, 18 H, SiMe₃), 1.01 (t, *J*_{H,H} = 7.5 Hz, 3 H, CH₃CH₂), 2.30 (q, *J*_{H,H} = 7.5 Hz, 2 H, CH₃CH₂), 5.15 (s, 5 H, Cp), 6.87 (d, *J*_{H,H} = 8.2 Hz, 2 H, Ph), 7.77 (d, *J*_{H,H} = 8.2 Hz, 2 H, Ph) ppm. ¹³C{¹H} NMR: δ = 1.9 (s, SiMe₃), 15.4 (s, CH₃CH₂), 29.2 (s, CH₃CH₂), 60.1 [d, *J*_{PC} = 60.3 Hz, C(SiMe₃)₂], 89.6 (s, Cp), 124.4 (s, Ph), 128.3 (s, Ph), 128.7 (s, Ph), 147.4 (s, Ph), 222.8 (s, As=C), 226.9 (s, *J*_{WC} = 183 Hz, C=O) ppm. ³¹P{¹H} NMR: δ = 313.2 (*J*_{P,W} = 728 Hz) ppm. C₂₃H₃₂AsO₃PSi₂W (702.42): calcd. C 39.33, H 4.59; found C 39.47, H 4.69.

X-ray Crystallography: Crystallographic data were collected with a Nonius Kappa CCD diffractometer with Mo-*K*_α (graphite monochromator, λ = 0.71073 Å) at 100 K. Crystallographic programs used for the structure solution and refinement were SHELXS-97,^[37] SIR-97,^[38] and SHELXL-97.^[37] The structures were solved by direct methods and were refined by using full-matrix least squares on *F*² of all unique reflections with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were included at calculated positions with *U*(H) = 1.2 *U*_{eq} for CH₂ groups, *U*(H) = 1.5 *U*_{eq} for CH₃ groups. Crystal data for the compounds are listed in Table 1. CCDC-250373 (**4a**), -279437 (**5b**), and -279438 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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