Arsaalkenes R−As=C(NMe$_2$)$_2$ [R = PhC(O), 4-EtC$_6$H$_4$C(O), 2,4,6-Me$_3$C$_6$H$_2$C(O), *t*BuC(O), Me$_3$Si]: Versatile Reagents in the Chemistry of Heterocumulenes

Lothar Weber,* Philipp Bayer, Thomas Braun, Hans-Georg Stammler, and Beate Neumann

Fakultät für Chemie der Universität Bielefeld, Universitätsstrasse 25, D-33615 Bielefeld, Germany

Received December 21, 2005

Reaction of [Cp(CO)$_2$M=P=C(SiMe$_3$)$_2$] (where M = Mo (**3a**), W (**3b**)] with 2 equiv of the arsaalkene PhC(O)As=C(NMe$_2$)$_2$ afforded the metalloarsaalkenes Cp(CO)$_2$M-As=C(Ph)−O−P−O−C(Ph)=As−C(SiMe$_3$)$_2$ [where M= Mo (**6a**), W (**6b**)]. Small amounts of [{η^3:η^3-(Me$_3$Si)$_2$CPAs−AsPC(SiMe$_3$)$_2$}{Mo(CO)$_2$Cp}$_2$] (**7**) were formed as a minor product. Similarly, **3b** and 2 equiv of 4-EtC$_6$H$_4$C(O)As=C(NMe$_2$)$_2$ gave rise to the formation of [Cp(CO)$_2$W−As=C(4-EtC$_6$H$_4$)−O−P−O−C(4-EtC$_6$H$_4$)=As−C(SiMe$_3$)$_2$] (**8**). However, treatment of **3a** and **3b** with an excess of *t*BuC(O)As=C(NMe$_2$)$_2$ yielded cocrystals of the η^3-2-phospha-1,3-diarsaallyl complexes [Cp(CO)$_2$M{η^3-*t*BuC(O)AsPAsC(O)*t*Bu}] [where M = Mo (**13a**), W (**13b**)] and the η^3-1,2,3-triarsaallyl complexes [Cp(CO)$_2$M{η^3-*t*BuC(O)AsAsAsC(O)*t*Bu}] [where M = Mo (**14a**), W (**14b**)] in varying ratios. Reaction of **3a** with Me$_3$SiAs=C(NMe$_2$)$_2$ afforded the dinuclear 1,2-diphosphapropene complex [{η^2:η^2-(Me$_3$Si)$_2$C=P−P(H)−C(H)(SiMe$_3$)$_2$}{Mo(CO)$_2$Cp}$_2$] (**15**). The novel compounds **6a**,**b**, **8**, **13a**,**b**, **14a**,**b**, and **15** were characterized by means of spectroscopy (IR and ^{1}H, ^{13}C{^{1}H}, ^{31}P NMR). Moreover the molecular structures of **7**, **8**, **13a**, **14a**, **13b**, **14b**, and **15** were determined by X-ray diffraction analyses.

Introduction

During the course of our studies on arsaalkenes[1] R−As=C(NMe$_2$)$_2$ [R = Cp*(CO)$_2$Fe, HB(3,5-Me$_2$HC$_3$N$_2$)$_3$(CO)$_2$M≡C; M = Mo, W] we observed a facile metal-assisted cleavage of the AsC multiple bond and the generation of η^2-diarsene complexes **1**[2] or cyclotriarsanes **2**[3] as the result of a formal dimerization or trimerization of arsanediyls (RAs) (Scheme 1).

Recently, we described the generation of η^3-2-phospha-1-arsaallyl complexes **4a**−**d** by the formal transfer of arsanediyl units from arsaalkenes onto the organophosphorus ligand of phosphavinylidene complexes **3a**,**b** (Scheme 2).[4]

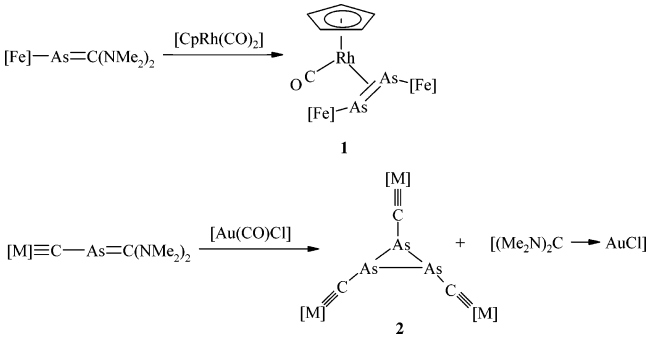
In contrast to the reactivity of the pivaloylarsaalkene the employment of the related *p*-ethylbenzoylarsaalkene 4-EtC$_6$H$_4$C(O)−As=C(NMe$_2$)$_2$ gave rise to the formation of the cyclic phosphenium complex **5** (Scheme 3).[4]

Considering these unexpected results, it was obvious to study the reactivity of organocarbonyl-functionalized arsaalkenes toward metallo-heterocumulenes **3a** and **3b** in more detail.

Results and Discussions

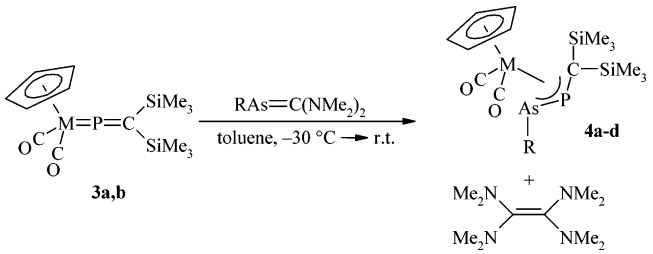
Treatment of complexes [Cp(CO)$_2$M=P=C(SiMe$_3$)$_2$] (**3a**, M = Mo; **3b**, M = W)[5] with 2 equiv of freshly prepared arsaalkene PhC(O)As=C(NMe$_2$)$_2$ in diethyl ether solution over a temperature range of −30 to 20 °C afforded the yellow microcrystalline metalloarsaalkenes **6a** (80%) and **6b** (75%) (Scheme 4).

Scheme 1. Metal-Assisted Cleavage of the As=C Bond of Arsaalkenes[a]



[a] [Fe] = Cp*(CO)$_2$Fe; [M] = [HB(3,5-Me$_3$HC$_3$N$_2$)$_3$M(CO)$_2$], M = Mo, W.

Scheme 2. Formation of 2-Phospha-1-arsaallyl Complexes 4[a]

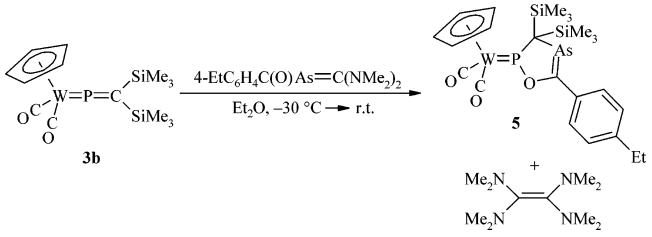


[a] R = *t*BuC(O), M = Mo (a), W (b); R = Cp*(CO)$_2$Fe, M = Mo (c), W (d).

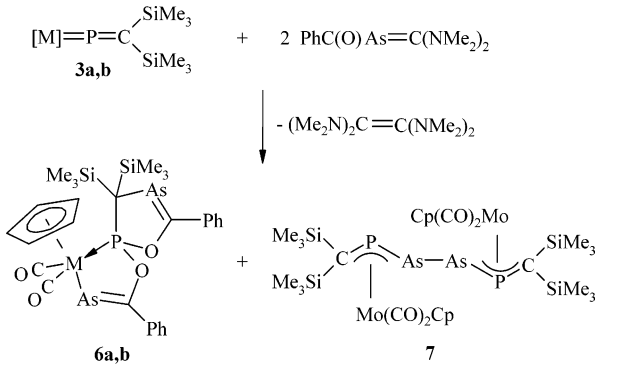
10.1021/om051084t CCC: $33.50
Publication on Web 02/18/2006

(1) Review: Weber, L. *Chem. Ber.* **1996**, *129*, 367.
(2) Weber, L.; Scheffer, M.-H.; Stammler, H.-G., Neumann, B. *Inorg. Chim. Acta* **1999**, *291*, 311.
(3) Weber, L.; Dembeck, G.; Lönnecke, P.; Stammler, H.-G.; Neumann, B. *Organometallics* **2001**, *20*, 2288.
(4) Weber, L.; Bayer, P.; Uthmann, S.; Braun, T.; Stammler, H.-G.; Neumann, B. *Eur. J. Inorg. Chem.* **2006**, 137.

Scheme 3. Formation of Complex 5



Scheme 4. Reaction of Phosphavinylidene Complexes 3a,b with PhC(O)As═C(NMe$_2$)$_2$



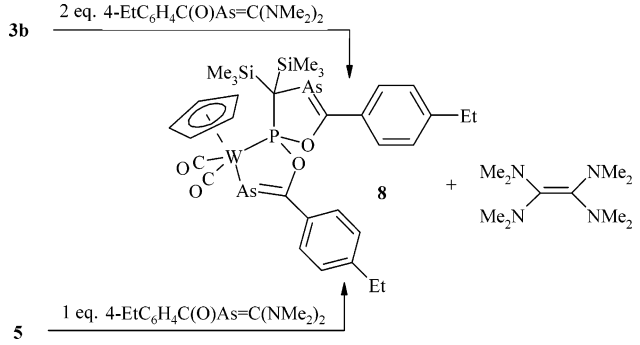
Isolation of the products was effected by column chromatography on Florisil with a 1:1 mixture of pentane/diethyl ether as eluent. Subsequent crystallization furnished analytically pure compounds. In the case of the reaction of the molybdenum complex **3a** with PhC(O)As═C(NMe$_2$)$_2$ a few crystals of a second product, **7**, were isolated from the mother liquor (Scheme 4).

If a 1:1 stoichiometry was used in the reaction of **3a** and the arsaalkene, only compound **6a** was formed as a product and half of the precursor **3a** remained unaffected. This is in contrast to the reaction of **3b** with an equimolar amount of arsaalkene 4-EtC$_6$H$_4$C(O)As═C(NMe$_2$)$_2$, where phosphenium complex **5** was formed as red crystals in 41% yield (Scheme 3).[4]

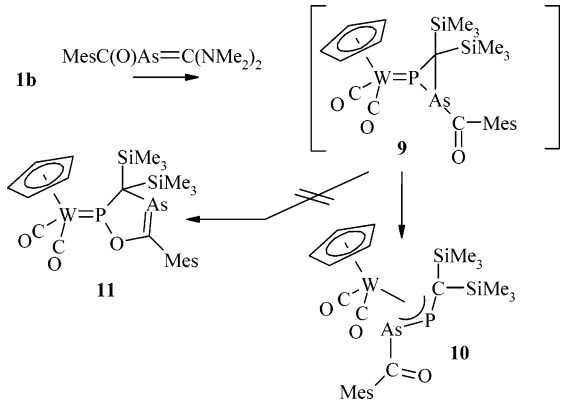
Analogously to the synthesis of spiro compound **6b**, treatment of **3b** with 2 equiv of 4-EtC$_6$H$_4$C(O)As═C(NMe$_2$)$_2$ under comparable conditions led to the formation of spiro compound **8** as yellow crystals in 71% yield. In a control reaction equimolar amounts of **5** and 4-EtC$_6$H$_4$C(O)As═C(NMe$_2$)$_2$ were combined. After 12 h of stirring at 20 °C the ^{31}P NMR spectrum of the reaction mixture showed only the singlet resonance for compound **8** (Scheme 5).

The outcome of the reaction between phosphavinylidenes **3a**,**b** and inversely polarized arsaalkenes is sensitively governed by the nature of the substituent at the arsenic atom. Thus an increase of the steric demand of this substituent on going from benzoyl and 4-ethylbenzoyl derivatives to MesC(O)As═C(NMe$_2$)$_2$ provides a situation where heterocyclic ligands are no longer formed by CO incorporation. Instead treatment of **3b** with 1 equiv of the arsaalkene generated the labile phosphenium complex **9**, which in solution rearranged during a few hours to the 2-phospha-1-arsaallyl complex **10**. Rearrangement was also achieved during column chromatography of freshly prepared **9** on Florisil, whereby pure **10** was obtained as orange crystals in 54% yield (Scheme 6). Phosphenium complex **11**, analogous to **5**, was not observed in this process.

Scheme 5. Formation of Spiro Compound 8



Scheme 6. Formation of 2-Phospha-1-arsaallyl Complex 10



The ^{31}P{^{1}H} NMR spectra of **6a**, **6b**, and **8** shows singlets at δ 258.0, 219.4, and 218.5 ppm, the latter with ^{183}W satellites (J_{PW} = 411 and 414 Hz, respectively), indicating the presence of a coordinative W−P bond. The silyl groups in **6a**, **6b**, and **8** are chemically and magnetically nonequivalent, giving rise to two discrete singlets in the ^{1}H NMR spectra at δ 0.36 s, 0.51 s (**6a**); 0.36 s, 0.54 s (**6b**); and 0.40 s, 0.57 s (**8**) and to two singlets in the ^{13}C{^{1}H} NMR spectra at δ 3.0 s, 4.3 s (**6a**); 2.7 s, 4.0 s (**6b**); and 3.1 s, 4.4 s (**8**) ppm. Low-intensity doublets at δ 44.5 ($^1J_{PC}$ = 22.1 Hz) (**6a**), 43.1 ($^1J_{PC}$ = 13.8 Hz) (**6b**), and 42.9 ($^1J_{PC}$ = 13.5 Hz) (**8**) are due to the quarternary carbon atom adjacent to the P atom. The two chemically and magnetically nonequivalent carbonyl ligands give rise to doublets at δ 229.5 ($^2J_{PC}$ = 5.8 Hz), 242.5 ($^2J_{PC}$ = 23.0 Hz) (**6a**); 218.8 ($^2J_{PC}$ = 9.2 Hz), 231.7 ($^2J_{PC}$ = 15.2 Hz) (**6b**); and 219.4 ($^2J_{PC}$ = 10.8 Hz), 232.4 ($^2J_{PC}$ = 14.8 Hz) (**8**).

The resonances are shifted to lower fields relative to those of precursors **3a** (δ 230.4 ppm) and **3b** (δ 218.9 ppm), indicating the improved donor capacity of the κ(As,P) arsaalkenylphosphine chelating ligands over the phosphavinylidene system.

Doublets at δ 204.6 (d, $^2J_{PC}$ = 14.9 Hz), 217.9 (d, $^2J_{PC}$ = 8.0 Hz) (**6a**); 203.4 (d, $^2J_{PC}$ = 15.2 Hz), 218.0 (d, $^2J_{PC}$ = 9.7 Hz) (**6b**); and 204.2 (d, $^2J_{PC}$ = 16.2 Hz), 218.5 (d, $^2J_{PC}$ = 6.8 Hz) (**8**) are attributed to the tricoordinate carbon atoms of the two different As═C double bonds of the spiro compounds. These values fall in the typical range for δ(As═C) of δ 200.6 ppm in MesAs═C(H)NMe$_2$ to δ 241.5 ppm in Me$_3$SiAs═C(OSiMe$_3$)*t*Bu.[1] The IR spectra of **6a**, **6b**, and **8** in the region of the CO stretching modes are dominated by two intense bands at $\tilde{\nu}$ 1941, 1885 cm^{-1} (**6a**); 1938, 1874 cm^{-1} (**6b**); and 1941, 1874 cm^{-1} (**8**). The absence of bands for the ν(CO) mode of an acylarsane (ca. 1650 cm^{-1}) agrees with the incorporation of this function into the spiro ligand of **6a**, **6b**, and **8**.

Identification of intermediate **9** was limited to the observation of a ^{31}P NMR resonance at δ 264 ppm ($^1J_{PW}$ = 565 Hz).

(5) (a) Arif, A. M.; Cowley, A. H.; Nunn, C. M.; Quashie, S.; Norman, N. C.; Orpen, A. G. *Organometallics* **1989**, *8*, 1878. (b) Niecke, E.; Metternich, H.-J.; Nieger, M.; Gudat, D.; Wenderoth, P.; Malisch, W.; Hahner, C.; Reich, W. *Chem. Ber.* **1993**, *126*, 1299.

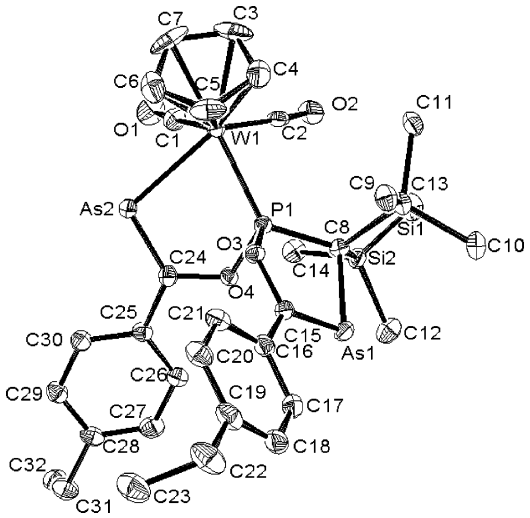
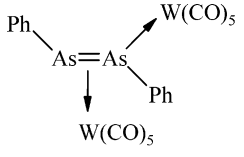


Figure 1. Molecular structure of **8** in the crystal. Selected bond lengths [Å] and angles [deg]: W(1)−C(1) 1.966(3), W(1)−C(2) 1.962(3), W(1)−C(3−7) 2.323(3) − 2.352(3), W(1)−P(1) 2.3790(8), W(1)−As(2) 2.6547(3), As(2)−C(24) 1.825(3), O(4)−C(24) 1.383(3), C(24)−C(25) 1.466(4), P(1)−O(4) 1.649(2), P(1)−O(3) 1.671(2), P(1)−C(8) 1.804(3), As(1)−C(8) 2.035(3), As(1)−C(15) 1.820(3), C(15)−O(3) 1.374(4), C(8)−Si(1) 1.945(3), C(8)−Si(2) 1.919(3), C(15)−C(16) 1.474(4); C(1)−W(1)−C(2) 75.6(1), C(1)−W(1)−As(2) 70.7(1), P(1)−W(1)−As(2) 74.24(2), P(1)−W(1)−C(2) 81.0(1), W(1)−As(2)−C(24) 102.8(1), As(2)−C(24)−O(4) 120.6(2), As(2)−C(24)−C(25) 127.4(2), O(4)−C(24)−C(25) 112.1(3), W(1)−P(1)−O(4) 114.9(1), W(1)−P(1)−O(3) 108.6(1), O(3)−P(1)−O(4) 99.5(1), P(1)−O(3)−C(15) 114.9(2), P(1)−O(4)−C(24) 114.4(2), O(3)−P(1)−C(8) 99.2(1), W(1)−P(1)−C(8) 131.8(1), P(1)−C(8)−As(1) 101.9(1), C(8)−As(1)−C(15) 90.9(1), As(1)−C(15)−O(3) 118.5(2), As(1)−C(15)−C(16) 127.5(2), O(3)−C(15)−C(16) 113.9(3), W(1)−C(1)−O(1) 175.9(3), W(1)−C(2)−O(2) 176.0(3).

Compound **10** features a ^{31}P NMR absorption at δ −18.2, which is similar to that in η^3-2-phospha-1,3-diarsaallyl complex **4b** (δ −18.7 ppm). The carbon atom of the heteroallylic ligand was observed as a doublet at δ 29.1 ppm ($^1J_{PC}$ = 103.7 Hz) in the ^{13}C{^{1}H} NMR spectrum of **10**. Singlet resonances at δ 221.9, 223.2 ppm and a doublet at δ 235.9 ppm ($^2J_{PC}$ = 3.8 Hz) are due to carbonyl ligands and the CO unit of the mesitoyl substituent. In the region of the carbonyl stretching vibrations of the IR spectrum of **10** intense bands at $\tilde{\nu}$ = 1937, 1860, and 1654 cm^{-1} are assigned to these groups.

Yellow crystals of **8** suitable for an X-ray diffraction analysis were grown from a 2:1 mixture of diethyl ether/pentane at −30 °C. The analysis (Figure 1, Table 1) displays a molecule with a distorted four-legged piano-stool geometry [C(1)−W(1)−C(2) 75.6(1)°, C(1)−W(1)−As(2) 70.7(1)°, P(1)−W(1)−C(2) 81.0(1)°, P(1)−W(1)−As(2) 74.24(2)°] with two nearly linear carbonyl ligands [W(1)−C(1)−O(1) 175.9(3)°, W(1)−C(2)−O(2) 176.6(3)°]. The remaining two legs are represented by a 2-[3′-arsavin-diyl-oxy]-1,2,4-oxaphosphaarsolene, which is chelating the metal atom through bonds W(1)−As(2) [2.6547(3) Å] and W(1)−P(1) [2.3790(8) Å]. The W−As bond is slightly



12

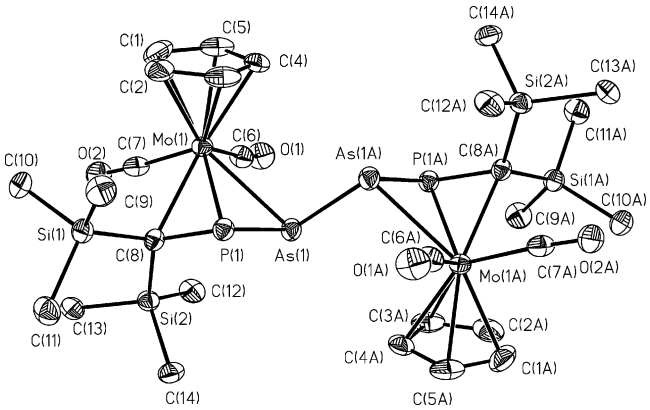


Figure 2. Molecular structure of **7** in the crystal. Selected bond lengths [Å] and angles [deg]: Mo(1)−C(6) 1.943(5), Mo(1)−C(7) 1.969(6), Mo(1)−C(8) 2.444(5), Mo(1)−P(1) 2.491(1), Mo(1)−As(1) 2.755(1), P(1)−As(1) 2.260(1), P(1)−C(8) 1.784(5), As(1)−As(1A) 2.468(1), C(8)−Si(1) 1.908(5), C(8)−Si(2) 1.902(5); C(6)−Mo(1)−C(7) 80.4(2), C(7)−Mo(1)−C(8) 69.2(2), C(6)−Mo(1)−As(1) 65.24(17), As(1)−P(1)−C(8) 101.80(17), P(1)−As(1)−As(1A) 90.51(4), P(1)−C(8)−Si(1) 108.3(2), P(1)−C(8)−Si(2) 121.3(3).

elongated relative to the W−As σ-bond in complex **12** [2.622(4) Å].[6]

Repulsion between the lone pair of electrons at As(2) and the electron-rich W atom may be responsible for the bond lengthening in **8**. The W−P bond length corresponds to values typical for the coordinative W−P bonds[7−9] [e.g., 2.385(2) Å in $Cp(CO)_2\overline{WCH_2P(Ph)N(SiMe_3)_2}$].[7] This novel chelating ligand features the double bond As(2)−C(24) [1.820(3) Å] of a metalloarsaalkene unit and a second double bond As(1)−C(15) [1.821(3) Å] within the 1,2,4-oxaphosphaarsolene ring. These values are well comparable to the AsC separation in complex **5** [1.832(2) Å][4] or in the ferrioarsaalkene $Cp(CO)_2Fe-As{=}C(OSiMe_3)tBu$ [1.821(2) Å].[10] The bond lengths C(15)−O(3) [1.374(4) Å] and C(24)−O(4) [1.383(3) Å] are similar to that in **5** [1.372(3) Å] or in the ferrioarsaalkene [1.356(3) Å], all of them being shorter with respect to an sp^2 C−O single bond (ca. 1.41 Å).[11] The contacts P(1)−O(3) [1.671(2) Å], P(1)−O(4) [1.649(2) Å], and P(1)−C(8) [1.804(3) Å] are markedly shorter than the sum of the covalent radii (1.76 and 1.87 Å)[12] but still reflect bond orders of unity. The five-membered ring is slightly puckered (sum of endocyclic angles 525.3°). The same is true for the metallaheterocycle (sum of endocyclic angles 526.8°). The plane defined by the atoms P(1), O(3), and C(8) and the plane defined by the atoms W(1), P(1), and O(4) are oriented nearly perpendicularly to each other (ψ = 94.3°).

A few yellow crystals of **7** were isolated from the mother liquor after removal of **6a** and subjected to an X-ray diffraction analysis (Figure 2, Table 1).

(6) Lang, H.; Huttner, G.; Sigwarth, B.; Weber, U.; Zsolnai, L.; Jibril, I.; Orama, O. *Z. Naturforsch.* **1986**, *B41*, 191.
(7) Reisacher, H. U.; Duesler, E. N.; Paine, R. T. *J. Organomet. Chem.* **1997**, *539*, 37.
(8) Malisch, W.; Grün, K.; Hirth, U.-A.; Noltemeyer, M. *J. Organomet. Chem.* **1996**, *513*, 31.
(9) Malisch, W.; Grün, K.; Fried, A.; Reich, W.; Schmeusser, M.; Weis, U.; Abd El Baky, C.; Krüger, C. *Z. Naturforsch.* **1998**, *B53*, 1506.
(10) Weber, L.; Meine, G.; Boese, R.; Bungardt, D. *Z. Anorg. Allg. Chem.* **1987**, *549*, 73.
(11) Schubert, U. In *Transition Metal Carbene Complexes*; Verlag Chemie: Weinheim, 1983; p 77.
(12) Holleman-Wiberg. *Lehrbuch der Anorganischen Chemie*, 91st−100th ed.; Berlin, 1985; p 133.

Table 1. Crystallographic Data and Data Collection Parameters

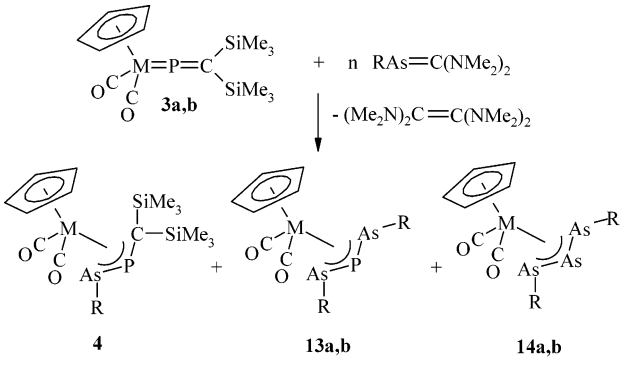
	7	8	13a/14a	13b/14b	15
empirical formula	$C_{28}H_{46}As_2Mo_2O_4P_2Si_4$	$C_{32}H_{41}As_2O_4PSi_2W$	$C_{17}H_{23}As_{2.60}MoO_4P_{0.4}$ + $C_{17}H_{23}As_{2.63}MoO_4P_{0.37}$	$C_{17}H_{23}As_{2.19}O_4P_{0.81}W$ + $C_4H_{10}O$	$C_{28}H_{48}Mo_2O_4P_2Si_4$
M [g mol^{-1}]	962.67	910.49	595.13	738.48	814.84
cryst dimens [mm^3]	0.22 × 0.14 × 0.02	0.56 × 0.11 × 0.10	0.30 × 0.16 × 0.10	0.26 × 0.23 × 0.10	0.28 × 0.24 × 0.24
cryst syst	monoclinic	triclinic	monoclinic	triclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a [Å]	16.5420(11)	10.2900(10)	15.8980(2)	12.0100(1)	10.6460(12)
b [Å]	8.0480(5)	13.5890(2)	21.8910(3)	14.6750(2)	11.9980(12)
c [Å]	16.5900(9)	14.1740(2)	12.3770(2)	15.4320(3)	15.5100(11)
α [deg]	90	96.8760(8)	90	105.7670(7)	76.572(8)
β [deg]	119.130(3)	111.0810(8)	96.3930(8)	91.9150(10)	84.597(6)
γ [deg]	90	104.9750(9)	90	95.0430(9)	71.855(9)
V [Å^3]	1929.3(2)	1736.08(4)	4280.70(11)	2602.71(7)	1830.6(3)
Z	2	2	8	4	2
d_{calcd} [g cm^{-3}]	1.657	1.742	1.847	1.885	1.478
μ [mm^{-1}]	2.590	5.368	4.671	7.278	0.933
F(000)	964	896	2329	1430	836
θ [deg]	3.51−27.47	3.05−25.00	3.05−25.00	2.96−30.00	2.01−30.00
no. reflns collected	27 392	50 109	14 891	64 083	92 096
no. reflns unique	4359	6096	7515	14 709	10 661
R(int)	0.111	0.040	0.117	0.050	0.0324
no, reflns [(I) > 2σ(I)]	3108	5728	6539	12183	9155
refined params	190	387	459	565	553
GOF	1.023	1.034	1.023	1.017	1.072
R1 [I > 2σ(I)]	0.0478	0.0209	0.0227	0.0308	0.0206
wR2 [all data]	0.1100	0.0510	0.0516	0.0758	0.0428
Δρ max./min. [e Å^{-3}]	0.999/−0.678	1.539/−0.778	0.437/−0.460	2.299/−1.948	0.481/−0.453
remarks			2 molecules in the asymmetric unit, which differ in the occupation factor of As/P disorder (60:40; 63:37)	2 molecules in the asymmetric unit, which differ in the occupation factor of As/P disorder (89:11; 73:27)	

The structure determination of **7** revealed a dinuclear complex featuring an η^3:η^3-2,5-diphospha-3,4-diarsa-diallyl ligand with an inversion center in the middle of single bond As(1)−As(1A) [2.468(1) Å]. Both phosphaarsaallyl halves are oriented in parallel planes, which are separated by 0.8189 Å. Bond lengths As(1)−P(1) [2.260(1) Å], P(1)−C(8) [1.784(5) Å], Mo(1)−As(1) [2.755(1) Å], Mo(1)−P(1) [2.491(1) Å], and Mo(1)−C(8) [2.444(5) Å] are in excellent agreement with the corresponding data in mononuclear **4c** [2.2507(7), 1.791(2), 2.7644(3), 2.4940(6), and 2.420(2) Å].[4] The fragment [CpMo(1)(CO)$_2$] is located above the plane defined by the atoms As(1)−P(1)−C(8), whereas unit [CpMo(1A)(CO)$_2$] is placed underneath the plane formed by the atoms As(1A)−P(1A)−C(8A). The valence angles As(1)−P(1)−C(8) [101.80(17)°] and P(1)−C(8)−Si(1) [108.3(2)°] are also similar to those in **4c** [99.15(7)°, 108.67(11)°]. The angle at the arsenic atom in **7** [90.51(4)°] is much smaller than in **4c** [106.59(2)°], where the arsenic atom is ligated to iron.

We previously described the reaction between equimolar amounts of **3b** and of the pivaloylarsaalkene *t*BuC(O)As═C(NMe$_2$)$_2$, where the 2-phospha-1-arsaallyl complex [Cp(CO)$_2$W{η^3-*t*BuC(O)AsPC(SiMe$_3$)$_2$}] (**4b**) was isolated in 63% yield.[4] The situation changes significantly when the experiment was conducted with twice the molar amount of arsaalkene under otherwise comparable conditions. Here complex **4b** was isolated in only 22% yield from the first orange-red zone of the Florisil-loaded column. From the second deep-red zone we isolated dark red crystals, which—according to an X-ray analysis—were disclosed as an inseparable 81:19 mixture of the η^3-2-phospha-1,3-diarsaallyl complex **13b** and η^3-1,2,3-triarsaallyl complex **14b**. Assuming that an even greater excess of the arsaalkene would furnish the η^3-triarsaallyl complex as the sole product, phosphavinylidene complex **3b** was treated with a 10-fold amount of the arsaalkene. In this case the heteroallyl complex [Cp(CO)$_2$W{η^3-*t*BuC(O)AsPC(SiMe$_3$)$_2$}] (**4b**) was no longer formed. Purification by column chromatography afforded dark red crystals of a 35:65 mixture of [Cp(CO)$_2$W{η^3-*t*BuC(O)AsPAsC(O)*t*Bu}] (**13b**) and [Cp(CO)$_2$W{η^3-*t*BuC(O)AsAsAsC(O)*t*Bu}] (**14b**) (Scheme 7).

Analogously, reaction of **3a** with a 10-fold excess of arsaalkene gave a 38:62 mixture of [Cp(CO)$_2$Mo{η^3-*t*BuC(O)AsPAsC(O)*t*Bu}] (**13a**) and [Cp(CO)$_2$Mo{η^3-*t*BuC(O)AsAsAsC(O)*t*Bu}] (**14a**). Medium-intense bands in the IR spectra of the mixed crystals **13a**/**14a** and **13b**/**14b** at 1660 and 1690 cm^{-1} are due to the ν(CO) vibration of the pivaloyl functions at the arsenic atoms. The CO-stretching modes of the terminal carbonyls in **13a**/**14a** and **13b**/**14b** are observed at 1953 and 1997 cm^{-1} as broad intense bands. In the $^{13}C\{^1H\}$ spectra of **13a**/**14a**, doublets at δ 231.2 ($^2J_{PC}$ = 4.6 Hz), 231.4 ($^2J_{PC}$ = 5.8 Hz), and 235.9 ppm (d, $^2J_{PC}$ = 5.8 Hz) are assigned to the two different carbonyl ligands and the acyl function at arsenic of **13a**. In the triarsaallyl complex the CO ligands give rise to singlets at δ = 226.9 and 233.6 ppm, whereas a singlet at 235.7 ppm is due to the acyl groups. In the $^{13}C\{^1H\}$ NMR spectrum of cocrystallizing **13b** and **14b** a similar situation is observed. The $^{31}P\{^1H\}$ NMR spectra of **13a** and **13b** show singlets at δ 5.8 and 9.4 ppm or δ −54.4 and −61.6 ppm.

Scheme 7. Reaction of 3a,b with $RAs{=}C(NMe_2)_2$ (R = *t*BuCO)



n	4	13a : 14a		13b : 14b	
1	66			–	–
2	22			81	19
10	–	38	62	35	65

The most reliable information on the nature of the novel heteroallyl complexes was provided by the X-ray structural investigation of the mixed crystals of **13a**/**14a** (M = Mo) and **13b**/**14b** (M = W).

The X-ray analysis of the dark red crystals **13b**/**14b** shows two molecules in the asymmetric unit, which differ in the occupation factor of the P/As disorder (89:11; 73:27) (Figure 3, Table 1).

The complexes consist of dicarbonyl cyclopentadienyl tungsten units, to which a 2-phospha-1,3-diarsaallyl ligand is coordinated in the η^3-mode. There is a disorder about the central phosphorus atoms P(1) and P(2) by the arsenic atoms As(5B) and As(6B). As a result, bonding parameters involving these atoms are of minor accuracy. As the bonding data in both molecules are not significantly different, only the complex with atom W(1) will be discussed in more detail. The cyclopentadienyl ring is unsymmetrically coodinated to the metal atom with W−C distances ranging from 2.279(4) Å [W(1)−C(3)] to 2.372(4) Å [W(1)−C(5)]. The geometry about the metal is that of a distorted piano-stool [C(6)−W(1)−As(1) = 82.6(1)°, C(7)−W(1)−As(2) 86.3(1)°, C(6)−W(1)−C(7) 83.6(2)°] with two nearly linear carbonyl ligands [W(1)−C(6)−O(1) = 176.3(3)°, W(1)−C(7)−O(2) = 173.9(3)°]. The most interesting parts of the molecules are the unprecedented 2-phospha-1,3-diarsaallyl and 1,2,3-triarsaallyl ligands, which are nearly symmetrically linked to the metal in an η^3-fashion through bonds W(1)−As(1) [2.6623(4) Å], W(1)−As(2) [2.6662(4) Å], and W(1)−P(1) [2.59(2) Å] or W(1)−As(5B) [2.65(5) Å]. The W−As π-bonds are shorter than in complex $[Cp(CO)_2W\{\eta^3$-*t*BuC(O)AsPC$(SiMe_3)_2\}]$ (**4b**) [2.759(1) Å], whereas the W−P contact in **4b** is markedly shorter [2.498(1) Å] than in **13b**. Bonding to the pivaloyl substituents is similar to **4b** [As−C(CO) 2.063(2) Å]. Both pivaloyl groups are directed toward the central heteroatom of the allylic ligand.

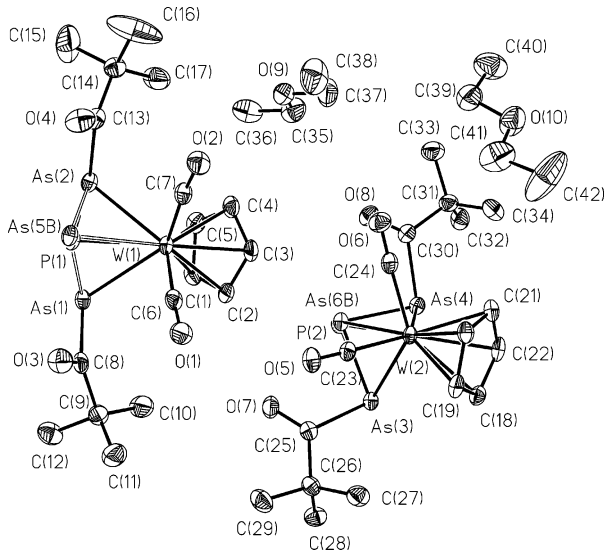


Figure 3. Molecular structure of **13b**/**14b** in the crystal. Selected bond lengths [Å] and angles [deg]: W(1)−C(6) 2.002(4), W(1)−C(7) 1.996(4), W(1)−As(1) 2.6623(4), W(1)−As(2) 2.6662(4), W(1)−P(1) 2.59(2), W(1)−As(5B) 2.65(5), As(1)−P(1) 2.27(2), As(2)−P(1) 2.30(2), As(1)−As(5B) 2.34(6), As(2)−As(5B) 2.23(6), As(1)−C(8) 2.044(4), As(2)−C(13) 2.046(4), C(8)−O(3) 1.212(5), C(13)−O(4) 1.207(5). C(6)−W(1)−C(7) 83.6(2), C(6)−W(1)−As(1) 82.6(1), C(7)−W(1)−As(2) 86.3(1), As(1)−W(1)−As(2) 70.45(1), C(8)−As(1)−P(1) 93.4(4), C(13)−As(2)−P(1) 92.6(5), As(1)−P(1)−As(2) 84.7(6), C(13)−As(2)−As(5B) 90.8(16), C(8)−As(1)−As(5B) 95.4(13), As(1)−As(5B)−As(2) 84(2).

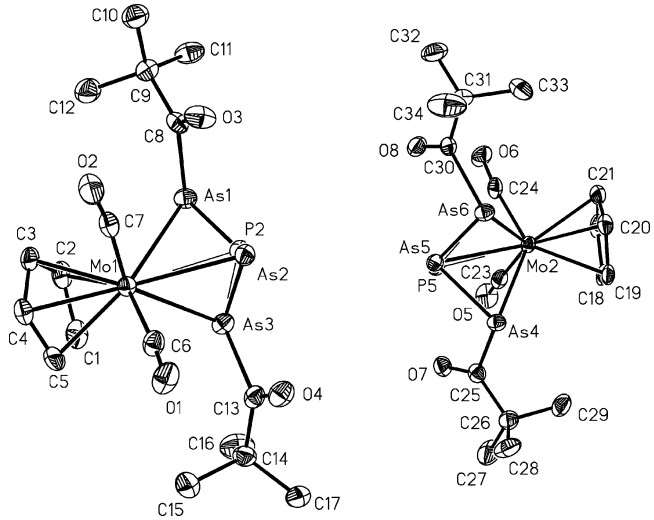


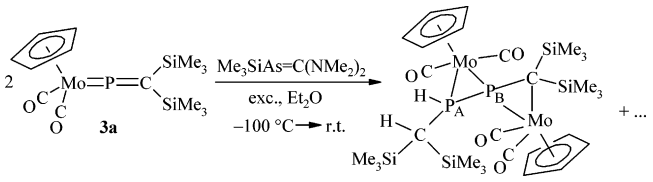
Figure 4. Molecular structure of **13a**/**14a** in the crystal. Selected bond lengths [Å] and angles [deg]: Mo(1)−C(6) 2.011(3), Mo(1)−C(7) 2.004(3), Mo(1)−As(1) 2.6586(4), Mo(1)−As(2) 2.682(7), Mo(1)−As(3) 2.6848(4), As(1)−C(8) 2.030(3), As(3)−C(13) 2.028(3), C(8)−O(3) 1.206(3), C(13)−O(4) 1.211(3), As(1)−As(2) 2.382(6), As(2)−As(3) 2.337(8), Mo(1)−P(2) 2.60(3), As(1)−P(2) 2.24(3), As(3)−P(2) 2.35(3). C(6)−Mo(1)−C(7) 84.4(1), C(6)−Mo(1)−As(3) 86.9(1), C(7)−Mo(1)−As(1) 85.4(1), As(1)−Mo(1)−As(3) 67.94(1), C(8)−As(1)−P(2) 95.3(9), C(13)−As(3)−As(2) 95.8(2), As(1)−P(2)−As(3) 81.1(10), As(1)−As(2)−As(3) 78.5(2), Mo(1)−C(6)−O(1) 175.5(3), Mo(1)−C(7)−O(2) 172.2(2).

A similar result was obtained when **3a** was reacted with a 10-fold excess of the arsaalkene. Red crystals were grown from a diethyl ether/*n*-pentane mixture at −30 °C. The X-ray analysis shows two molecules in the asymmetric unit (Figure 4, Table 1), which differ in the occupation factor of As/P disorder (60:40, 63:37).

Geometric parameters in both molecules do not differ significantly; thus, only the molecule with Mo(1) will be discussed in more detail. The situation about the $Cp(CO)_2Mo$ fragment is similar to that in **4c**. The unprecedented 2-phospha-1,3-diarsaallyl and 1,2,3-triarsaallyl ligands are attached to the metal atom in a η^3-fashion.

The bonding parameters within the triarsaallyl complex are of sufficient accuracy to allow some discussion. The arsenic−

Scheme 8. Formation of Complex 15



15

arsenic bond lengths As(1)−As(2) [2.382(6) Å] and As(2)−As(3) [2.337(8) Å] are well comparable with the As−As separation in complexes **12** [2.342(4) Å][6] and are between those of an As−As single bond [2.468(1) Å in **7**] and an unsupported As−As double bond [2.246(1) Å in Mes*As═As{Cr(CO)$_5$}-CH(SiMe$_3$)$_2$].[13] The arsenic metal contacts Mo(1)−As(1) [2.6586(4) Å], Mo(1)−As(2) [2.682(7) Å], and Mo(1)−As(3) [2.6848(4) Å] are of similar lengths but considerably shorter than the respective bond in the 2-phospha-1-arsaallyl complex **4c** [2.7644(3) Å]. As in complexes **13b**/**14b** the pivaloyl substituents are directed toward the center atom As(2). As already mentioned, to the best of our knowledge there are no reports on η^3-2-phospha-1,3-diarsaallyl and η^3-1,2,3-triarsaallyl complexes in the literature. In a short communication Jutzi et al. described the formation of lithium derivatives of a triphosphaallyl and of a 1,3-diphospha-2-arsaallyl system. Both anions, which are substituted by supermesityl substituents, were characterized as trans/trans and cis/trans isomers by ^{31}P NMR spectroscopy.[14]

The reaction of arsaalkene Me$_3$SiAs═C(NMe$_2$)$_2$ with molybdenum complex **3a** proceeded with yet a different result. Combination of the reactants in a 2:1 molar ratio in diethyl ether in the range −100 to 20 °C afforded the As-free complex **15** as dark red crystals after chromatographic workup (yield 0.57 g, 64%) (Scheme 8).

The ^{31}P{^{1}H} NMR spectrum of **15** displayed two doublets at δ −120.3 ($^1J_{PP}$ = 583.0 Hz) and 102.6 ppm ($^1J_{PP}$ = 583.0 Hz), which points to the presence of two directly connected different P atoms. In the proton-coupled ^{31}P NMR spectrum the low-field doublet remains unaffected (P_B), whereas the second ^{31}P nucleus (P_A) gives rise to a doublet of doublets. A large J_{PH} coupling of 384.1 Hz agrees with a PH function. The second J_{PH} coupling of 27.3 Hz is caused by the methyne proton of the CH(SiMe$_3$)$_2$ substituent. Consistently, a doublet at δ 4.62 ($^1J_{PH}$ = 386.9 Hz) in the ^{1}H NMR spectrum is attributed to the PH group. A doublet of doublets at δ 2.09 ($^2J_{PH}$ = 25.8 Hz, $^3J_{PH}$ = 4.4 Hz) is due to the hydrogen atom of the CHSi$_2$ unit. The appearance of four carbonyl ^{13}C NMR resonances [δ 240.0 (dd, $^1J_{PC}$ = 34.5, $^2J_{PC}$ = 5.8 Hz), 242.2 (d, $^1J_{PC}$ = 20.7 Hz), 244.5 (dd, $^1J_{PC}$ = 16.0, $^2J_{PC}$ = 6.9 Hz); 249.0 (s) ppm] and four intense ν(CO) bands in the IR spectra point to an unsymmetric combination of two molecules of **3a**, induced by the electron-abundant arsaalkene. The nature of product **15** was unambigiously established by an X-ray structure analysis (Figure 5, Table 1). The analysis reveals the presence of a dinuclear complex in which two [CpMo(CO)$_2$] fragments are linked to the 1,2-diphosphapropene (Me$_3$Si)$_2$CH−P(H)−P═C(SiMe$_3$)$_2$ from opposite faces via bonds Mo(1)−P(1) [2.4699(4) Å], Mo(1)−P(2) [2.5820(4) Å], Mo(2)−P(2) [2.4283(4) Å], and Mo(2)−C(22) [2.458(1) Å]. The separation P(2)−C(22) of 1.788(1) Å is similar to the one in **4c** [1.791(2) Å][4] and typical for an η^2-coordinated phosphaalkene. The PP bond length of

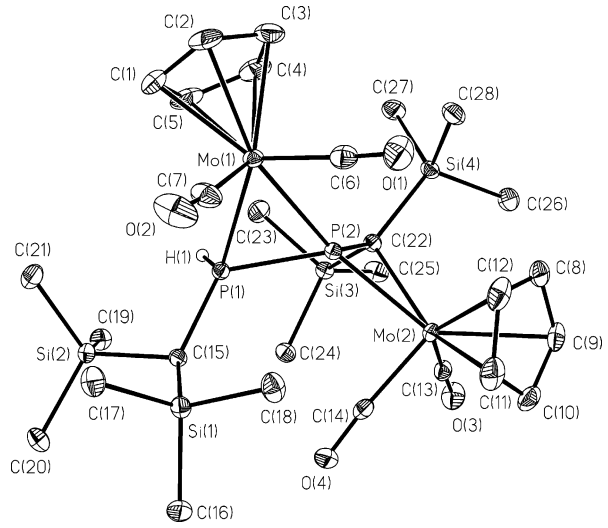
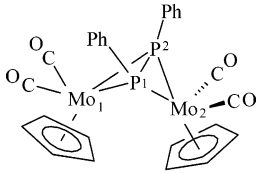


Figure 5. Molecular structure of **15** in the crystal. Selected bond lengths [Å] and angles [deg]: Mo(1)−C(1−5) 2.311(2)−2.390(2), Mo(1)−C(6) 1.983(2), Mo(1)−C(7) 1.964(2), Mo(1)−P(1) 2.4699(4), Mo(1)−P(2) 2.5820(4), P(1)−H(1) 1.28(2), P(1)−P(2) 2.1558(5), P(1)−C(15) 1.833(1), Si(1)−C(15) 1.917(1), Si(2)−C(15) 1.925(1), P(2)−C(22) 1.788(1), Si(3)−C(22) 1.884(1), Si(4)−C(22) 1.886(1), Mo(2)−P(2) 2.4283(4), Mo(2)−C(22) 2.458(1), Mo(2)−C(8−12) 2.312(1)−2.425(2), Mo(2)−C(13) 1.976(1), Mo(2)−C(14) 1.945(2).

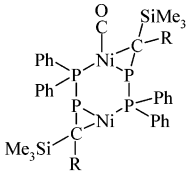
2.1558(5) Å is markedly shorter than a PP single bond (ca. 2.20 Å).[12] The contact of atom Mo(1) to atoms P(1) and P(2) differs by 0.11 Å. A comparable nonsymmetric ligation of two phosphorus atoms is present in the butterfly complex **16**, featuring two short bonds Mo(1,2)−P(1) [2.466, 2.470 Å] and two longer bonds Mo(1,2)−P(2) [2.542, 2.546 Å].[15]



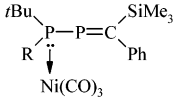
16

The bond length Mo(2)−C(22) [2.4283(4) Å] is similar to the one in **4a** [2.4372(11) Å], and thus the contact of bond P(2)−C(22) to Mo(2) may be regarded as a π-bond. Investigations on the ligating properties of 1,2-diphosphapropenes are not new. R. Appel et al. isolated the dinuclear nickel complexes **17** from the reaction of diphosphapropenes Ph$_2$PP═C(SiMe$_3$)R (R = Ph, Me$_3$Si) with [Ni(CO)$_4$].[16]

In his Ph.D. thesis under the supervision of R. Appel, G. Bruder carefully investigated the complex formation of diphosphapropenes with respect to the substitution pattern at the tricoordinate phosphorus atom and the substituents at the P═C backbone. Stable η^1-complexes of type **18** were obtained with *t*Bu$_2$P and *t*Bu(Me$_3$Si)P substituents at the P atom of the P═C unit.[17]

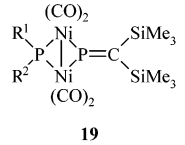


17



18

(R = *t*Bu, Me$_3$Si)



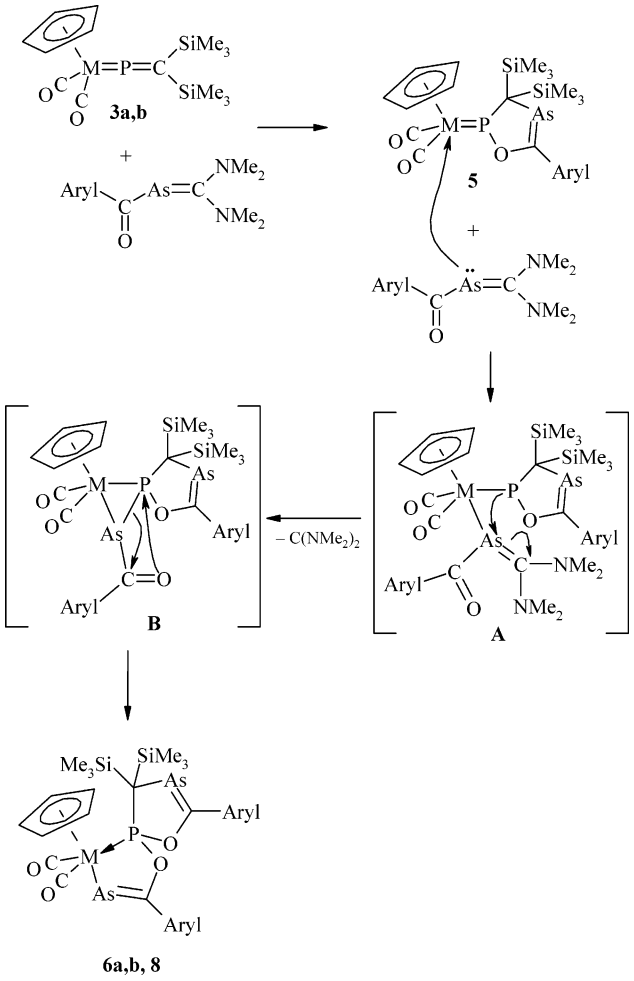
19

R^1 = R^2 = C$_6$H$_{11}$, *t*Bu, Me$_3$Si

(13) Cowley, A. H.; Kilduff, J. E.; Lasch, J. G.; Norman, N. C.; Pakulski, M.; Ando, F.; Wright, T. C. *Organometallics* **1984**, *3*, 1044.

(14) Jutzi, P.; Meyer, U. *Phosphorus Sulfur* **1988**, *40*, 275.

Scheme 9. Proposed Mechanism for the Formation of 6a, 6b, and 8



Reaction of $[Ni(CO)_4]$ with $R^1R^2P-P=C(SiMe_3)_2$ led to the cleavage of the P−P bond under formation of dinuclear complexes **19**.[17] A mode of coordination of a diphosphapropene as given in molecule **15** where the P=C bond spans two different metal atoms and the phosphino as well as the phosphorus atom of the double bond are coordinated to the same metal center is new.

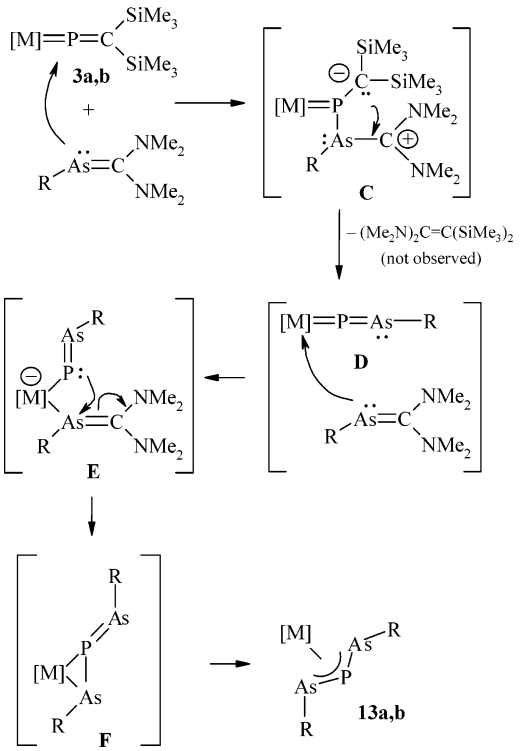
Mechanisms

The formation of the spiro compounds **6a**, **6b**, and **8** involves compounds such as **5** as intermediates. Their formation from equimolar amounts of an aroylarsaalkene and **3b** has been discussed[4] (Scheme 9).

A second molecule of arsaalkene attacks the M=P double bond to give **A**. Extrusion of the carbene $C(NME_2)_2$ and P−As bond formation leads to **B**, which eventually was converted into the products by incorporation of the acyclic carbonyl group into the P−As bond.

The formation of complexes **13a**,**b**/**14a**,**b** from **3a**,**b** and an excess of arsaalkene remains unclear. At the moment we can only say that the treatment of $[Cp(CO)_2M\{\eta^3$-*t*BuC(O)AsPC$(SiMe_3)_2\}]$ (**4a**,**b**) with *t*BuC(O)As=$C(NMe_2)_2$ to give **13a**,**b** and **14a**,**b** failed, indicating that these species are not intermediates.

Scheme 10. Proposed Mechanism for the Formation of Compounds 13a,b



For the formation of the 2-phospha-1,3-diarsaallyl complexes **13a**,**b** we propose an initial attack at the P atom of **3a**,**b** to give **C**, which first cyclizes and then fragments with liberation of the putative alkene $(Me_2N)_2C=C(SiMe_3)_2$ and the formation of metalloarsaphosphene **D**. The latter is attacked at the metal atom to yield **E**. Extrusion of $C(NMe_2)_2$ from **E** and the rearrangement of **F** gave one of the final products (Scheme 10). Unfortunately neither the intermediates nor the alkene was detected by NMR-monitoring.

The mechanism of the formation of **15** is unclear at the moment.

Conclusions

The reactivity of electron-abundant arsaalkenes RAs=$C(NMe_2)_2$ toward phosphavinylidene complexes $[Cp(CO)_2M=P=C(SiMe_3)_2]$ (**3a**,**b**) is sensitively governed by the substitution pattern at the arsenic atom and by the stoichiometry of the reactants employed. Whereas $[Cp^*(CO)_2FeAs=C(NMe_2)_2]$ and **3a**,**b** invariantly led to 2-phospha-1-arsaallyl complexes **4c**,**d**, the results obtained with *t*BuC(O)As=$C(NMe_2)_2$ appeared to be different. A 1:1 stoichiometry afforded 2-phospha-1-arsaallyl complexes **4a**,**b**, whereas a 1:10 stoichiometry gave cocrystals of novel 1,2,3-triarsaallyl and 2-phospha-1,3-diarsaallyl complexes **14** and **13**. The aroyl-substituted arsaalkenes Aryl−C(O)-As=$C(NMe_2)_2$ (Aryl = Ph, 4-EtC_6H_4) and equimolar amounts of **3a**,**b** underwent reaction to yield 1,2,4-oxaphosphaarsolenium complexes **5**, whereas with a 2 M excess of arsaalkene the spiro compounds **6a**,**b** and **8** were formed in high yield. Increasing the steric bulk at the aryl ring as given in MesC(O)As=$C(NMe_2)_2$ prevented the ring closure, and 2-phospha-1-arsaallyl complex **10** was obtained. Arsaalkene $Me_3SiAs=C(NMe_2)_2$ served as a reducing agent toward **3a** to give the dinuclear diphosphapropene complex **15** with a novel mode of coordination.

(15) Fenske, D.; Merzweiler, K. *Angew. Chem.* **1986**, *98*, 357; *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 338.

(16) Appel, R.; Casser, C.; Knoch, F. *J. Organomet. Chem.* **1985**, *297*, 21.

(17) Bruder, G. Ph.D. Thesis, University of Bonn, 1989.

Experimental Section

General Procedures. All operations were performed under dry, oxygen-free nitrogen using standard Schlenk techniques. Solvents were dried by standard techniques and freshly distilled under nitrogen prior to use. Infrared spectra were recorded with a Bruker FT-IR VECTOR 22 spectrometer. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded in C_6D_6 at 22 °C using a Bruker AM Avance DRX 500 (^{1}H, 500.13 MHz; ^{13}C, 125.76 MHz; ^{31}P, 200.46 MHz). References: $SiMe_4$ (^{1}H, ^{13}C), 85% H_3PO_4 (^{31}P). Elemental analyses were performed at the microanalytical laboratory of the University of Bielefeld. Crystal structures were determinated using a Nonius Kappa CCD; all data were collected at 100 K. Programs for solution and refinement were SHELXS-97 and SHELXL-97. Compounds [Cp(CO)$_2$Mo=P=C(SiMe$_3$)$_2$] (**3a**),[5] [Cp(CO)$_2$W=P=C(SiMe$_3$)$_2$] (**3b**),[5] and Me$_3$SiAs=C(NMe$_2$)$_2$[6] were synthesized according to literature procedures. Florisil (Merck), pivaloyl chloride, benzoyl chloride, 4-ethylbenzoyl chloride, and 2,4,6-trimethylbenzoyl chloride were purchased commercially.

Preparation of Compounds: [Cp(CO)$_2$Mo−As=C(Ph)−O−P−O−C(Ph)=As−C(SiMe$_3$)$_2$] (6a) and [{η^3:η^3-(Me$_3$Si)$_2$C−P−As−As−P−C(SiMe$_3$)$_2$}{Mo(CO)$_2$Cp}$_2$] (7). A solution of benzoyl chloride (0.50 g, 3.62 mmol) in 15 mL of diethyl ether was combined with a solution of Me$_3$SiAs=C(NMe$_2$)$_2$ (0.90 g, 3.62 mmol) in 20 mL of *n*-pentane. The mixture was stirred at −30 °C for 30 min to give a slurry of arsaalkene PhC(O)As=C(NMe$_2$)$_2$. The slurry was transferred into a dropping funnel, which was cooled to −30 °C, and then added dropwise to the chilled ethereal solution (−30 °C, 20 mL) of [Cp(CO)$_2$Mo=P=C(SiMe$_3$)$_2$] (**3a**) (0.72 g, 1,81 mmol). After stirring for 4 h at −20 °C it was warmed to ambient temperature. After 12 h of stirring at 20 °C volatile components were removed in vacuo. The black residue was dissolved with diethyl ether (20 mL), then Florisil was added (5 g) and the resulting slurry was concentrated to dryness. The coated Florisil was transferred to the top of a column (d = 1.5 cm, l = 6 cm) charged with Florisil (20 g). A yellow zone was eluted with a 1:1 mixture of diethyl ether/*n*-pentane. Concentration to the beginning of crystallization and storing the solution at −30 °C for 48 h afforded **6a** (1.11 g, 80%) as a yellow microcrystalline solid. IR (KBr, cm^{-1}): ν 1941 (vs, CO), 1885 (vs, CO). ^{1}H NMR: δ 0.36 (s, 9H, SiMe$_3$), 0.51 (s, 9H, SiMe$_3$), 4.87 (s, 5H, Cp), 6.79−6.85 (m, 4H, Ph), 6.89−6.92 (m, 2H, Ph), 7.69−7.71 (m, 2H, Ph), 8.06 − 8.08 (m, 2H, Ph). ^{13}C{^{1}H} NMR: δ 3.0 (s, SiMe$_3$), 4.3 (s, SiMe$_3$), 44.5 (d, $^1J_{PC}$ = 22.1 Hz, PC), 91.2 (s, Cp), 124.4 (s, Ph), 124.7 (s, Ph), 128.3 (s, Ph), 128.9 (s, Ph), 129.2 (s, Ph), 130.3 (s, Ph), 138.0 (d, $^3J_{PC}$ = 5.7 Hz, *i*-C−Ph), 141.7 (d, $^3J_{PC}$ = 12.6 Hz, *i*-C−Ph), 204.6 (d, $^2J_{PC}$ = 14.9 Hz, As=C), 217.9 (d, $^2J_{PC}$ = 8.0 Hz, As=C), 229.5 (d, $^2J_{PC}$ = 5.8 Hz, CO), 242.5 (d, $^2J_{PC}$ = 23.0 Hz, CO). ^{31}P{^{1}H} NMR: δ 258.0 s. Anal. Calcd for $C_{28}H_{33}As_2MoO_4PSi_2$ (766.49): C, 43.87; H, 4.33. Found: C, 43.69; H, 4.22. Concentration of the mother liquor and repeated storage at −30 °C gave a few yellow crystals of the dinuclear complex **7**. The characterization of this compound was limited to an X-ray structural analysis.

[Cp(CO)$_2$WAs=C(Ph)−O−P−O−C(Ph)=As−C(SiMe$_3$)$_2$] (6b). Analogously to the preparation of **6a** a slurry of in situ-generated PhC(O)As=C(NMe$_2$)$_2$ (3.62 mmol) was combined with [Cp(CO)$_2$W=P=C(SiMe$_3$)$_2$] (**3b**) (0.89 g, 1.81 mmol) in a diethyl ether solution at −30 °C to produce 1.16 g (75%) of yellow solid **6b**. IR (KBr, cm^{-1}): ν 1938 (vs, CO), 1874 (vs, CO). ^{1}H NMR: δ 0.36 (s, 9H, SiMe$_3$), 0.54 (s, 9H, SiMe$_3$), 4.88 (s, 5H, Cp), 6.79−6.84 (m, 4H, Ph), 6.90−6.93 (m, 2H, Ph), 7.66−7.68 (m, 2H, Ph), 8.10−8.12 (m, 2H, Ph). ^{13}C{^{1}H} NMR: δ 2.7 (s, SiMe$_3$), 4.0 (s, SiMe$_3$), 43.1 (d, $^1J_{PC}$ = 13.8 Hz, PC), 89.4 (s, Cp), 124.0 (s, Ph), 124.5 (s, Ph), 128.0 (s, Ph), 128.9 (s, Ph), 129.2 (s, Ph), 130.0 (s, Ph), 137.7 (d, $^3J_{PC}$ = 7.0 Hz, *i*-C-Ph), 140.9 (d, $^3J_{PC}$ = 12.5 Hz, *i*-C-Ph), 203.4 (d, $^2J_{PC}$ = 15.2 Hz, As=C), 218.0 (d, $^2J_{PC}$ = 8.3 Hz, As=C), 218.8 (d, $^2J_{PC}$ = 9.7 Hz, CO), 231.7 (d, $^2J_{PC}$ = 15.2 Hz, CO). ^{31}P{^{1}H} NMR: δ 219.4 (s, $^1J_{WP}$ = 411 Hz). Anal. Calcd for $C_{28}H_{33}As_2O_4PSi_2W$ (854.41): C, 39.56; H, 3.89. Found: C, 39.32; H, 3.78.

[Cp(CO)$_2$WAs=C(4-EtC$_6$H$_4$)−O−P−O−C(4-EtC$_6$H$_4$)=As−C(SiMe$_3$)$_2$] (8). The ethereal solution (10 mL) of 4-ethylbenzoyl chloride (0.61 g, 3.62 mmol) was added dropwise to the chilled solution (−30 °C) of Me$_3$SiAs=C(NMe$_2$)$_2$ (0.89 g, 3.62 mmol) in 15 mL of *n*-pentane. A yellow precipitate of arsaalkene 4-EtC$_6$H$_4$C(O)As=C(NMe$_2$)$_2$ spontaneously separated. The slurry was stirred for 30 min before the solution of complex **3b** (0.89 g, 1.81 mmol) in 20 mL of diethyl ether was slowly added (−30 °C). It was warmed to room temperature and stirred for 12 h. Solvent and volatiles were removed in vacuo, and the dark residue was dissolved with 10 mL of diethyl ether. Florisil (5 g) was added to this solution, and the slurry was freed from solvent. The coated Florisil was loaded on top of a column, filled with Florisil (20 g). A yellow zone was eluted with a 2:1 mixture of diethyl ether/*n*-pentane. Concentration of the elute to the beginning crystallization and storing at −30 °C afforded 1.17 g (71%) of product **8** as yellow rods. IR (KBr, cm^{-1}): ν 1941 (vs, CO), 1874 (vs, CO). ^{1}H NMR: δ 0.40 (s, 9H, SiMe$_3$), 0.57 (s, 9H, SiMe$_3$), 0.85 (t, $^3J_{HH}$ = 7.6 Hz, 3H, C*H*$_3$CH$_2$), 0.88 (t, $^3J_{HH}$ = 7.5 Hz, 3H, C*H*$_3$CH$_2$), 2.07 (q, $^3J_{HH}$ = 7.5 Hz, 2H, CH$_3$C*H*$_2$), 2.15 (q, $^3J_{HH}$ = 7.5 Hz, 2H, CH$_3$C*H*$_2$), 4.93 (s, 5H, Cp), 6.65 (d, $^3J_{HH}$ = 8.2 Hz, 2H, Ph), 6.72 (d, $^3J_{HH}$ = 8.2 Hz, 2H, Ph), 7.68 (d, $^3J_{HH}$ = 8.2 Hz, 2H, Ph), 8.10 (d, $^3J_{HH}$ = 8.2 Hz, 2H, Ph). ^{13}C{^{1}H} NMR: δ 3.1 (s, SiMe$_3$), 4.4 (s, SiMe$_3$), 14.8 (s, *C*H$_3$CH$_2$), 15.1 (s, *C*H$_3$CH$_2$), 29.0 (s, CH$_3$*C*H$_2$), 42.9 [d, $^1J_{PC}$ = 13.5 Hz, *C*(SiMe$_3$)$_2$], 89.7 (s, Cp), 124.6 (s, Ph), 125.1 (s, Ph), 128.6 (s, Ph), 128.8 (s, Ph), 135.8 (d, $^3J_{PC}$ = 6.7 Hz, *i*-C-Ph), 139.2 (d, $^3J_{PC}$ = 13.5 Hz, *i*-C-Ph), 144.2 (s, Ph), 147.0 (s, Ph), 204.2 (d, $^2J_{PC}$ = 16.2 Hz, As=C), 218.5 (d, $^2J_{PC}$ = 6.8 Hz, As=C), 219.4 (d, $^2J_{PC}$ = 10.8 Hz, CO), 232.4 (d, $^2J_{PC}$ = 14.8 Hz, CO). ^{31}P{^{1}H} NMR: δ 218.5 (s, $^1J_{PW}$ = 414 Hz). Anal. Calcd for $C_{32}H_{41}As_2O_4PSi_2W$ (910.49): C, 42.22; H, 4.54. Found: C, 42.17; H, 4.33.

Reaction of [Cp(CO)$_2$W=P−O−C(4-EtC$_6$H$_4$)=As−C(SiMe$_3$)$_2$] (5) with 4-EtC$_6$H$_4$−C(O)As=C(NMe$_2$)$_2$. The arsaalkene was generated from Me$_3$SiAs=C(NMe$_2$)$_2$ (0.15 g, 0.6 mmol) and 0.10 g (0.6 mmol) of 4-EtC$_6$H$_4$C(O)Cl in 10 mL of diethyl ether at −30 °C. To the slurry of 4-EtC$_6$H$_4$C(O)As=C(NMe$_2$)$_2$ was added the ethereal solution (10 mL) of complex **5** (0.42 g, 0.6 mmol). Stirring was continued for 2 h at −30 °C, before it was warmed to 20 °C. A ^{31}P NMR spectrum of the reaction mixture after 12 h of stirring at room temperature displayed only the singlet resonance for **8**.

Preparation of [Cp(CO)$_2$W{η^3-MesC(O)AsPC(SiMe$_3$)$_2$}] (10). Arsaalkene MesC(O)As=C(NMe$_2$)$_2$ was formed as a slurry at −30 °C by slow combination of a solution of MesC(O)Cl (0.33 g, 1.81 mmol) in diethyl ether (15 mL) and a solution of Me$_3$SiAs=C(NMe$_2$)$_2$ (0.45 g, 1.81 mmol) in *n*-pentane (20 mL). Stirring at −30 °C was continued for 30 min, then the slurry was transferred into a chilled dropping funnel and added dropwise to the chilled solution (−30 °C) of **3b** (0.89 g, 1.81 mmol) in diethyl ether (25 mL). After stirring for 4 h at −30 °C and 12 h at ambient temperature the ^{31}P{^{1}H} NMR spectrum of the reaction mixture showed a singlet at δ 264 ppm ($^1J_{PW}$ = 565 Hz) as the only signal. After removal of solvent and volatiles the black residue was coated on 5 g of Florisil and chromatographed on Florisil. An orange-red zone was eluted with a diethyl ether/pentane mixture. Concentration to the beginning crystallization and storage at −30 °C afforded 0.70 g (54%) of **10** as orange crystals. IR (KBr, cm^{-1}): ν 1654 (s, AsCO), 1937 (s, WCO), 1860 (s, WCO). ^{1}H NMR: δ 0.16 (s, 9H, SiMe$_3$), 0.36 (s, 9H, SiMe$_3$), 2.32 (s, 3H, *p*-CH$_3$), 2.50 (s, 6H, *o*-CH$_3$), 5.14 (s, 5H, C$_5$H$_5$), 6.45 (s, 2H, aryl). ^{13}C{^{1}H} NMR: δ

4.0 [s, $Si(CH_3)_3$], 9.1 [s, $Si(CH_3)_3$], 19.3 (s, CH_3), 25.4 (s, CH_3), 29.1 [d, $^1J_{PC}$ = 103.7 Hz, $C(SiMe_3)_2$], 90.4 (s, C_5H_5), 128.0 (s, Ph), 129.1 (s, Ph), 134.8 (s, Ph), 139.4 (s, Ph), 221.9 (s, WCO), 223.2 (s, WCO), 235.9 (d, $^2J_{PC}$ = 3.8 Hz, AsCO). $^{31}P\{^1H\}$ NMR: δ −18.2 s. Anal. Calcd for $C_{24}H_{34}AsO_3PSi_2W$ (716.45): C, 40.24; H, 4.78. Found: C, 40.28; H, 4.63.

Reaction of $[Cp(CO)_2W{=}P{=}C(SiMe_3)_2]$ (3b) with 2 *t*BuC(O)As=C(NMe$_2$)$_2$. The arsaalkene was formed as a yellow slurry by combining the solution of pivaloyl chloride (0.44 g, 3.62 mmol) in 25 mL of diethyl ether with a pentane solution (30 mL) of $Me_3SiAs{=}C(NMe_2)_2$ (0.90 g, 3.62 mmol) at −30 °C during 30 min. The slurry was transferred in a chilled dropping funnel (−30 °C) and then added dropwise at −30 °C to the ethereal solution (20 mL) of complex **3b** (0.89 g, 1.81 mmol). Stirring at −30 °C was continued for 4 h, then the mixture was stirred at room temperature for another 12 h. Volatiles were removed in vacuo, and the residue was chromatographed on a Florisil-loaded column. A first orange-red zone was eluted with a 5:1 mixture of diethyl ether/*n*-pentane. The elute was concentrated to the beginning crystallization and stored at −30 °C to afford 0.26 g (22%) of $[Cp(CO)_2W\{\eta^3$-*t*BuC(O)AsPC(SiMe$_3$)$_2\}]$ (**4b**) as orange irregular crystals. Subsequently a deep-red zone was eluted with a 10:1 mixture of diethyl ether/pentane, from which 0.51 g (42%) of dark red crystals was isolated. According to an X-ray structural analysis, the crystals consist of 81% $[Cp(CO)_2W\{\eta^3$-*t*BuC(O)AsPAsC(O)*t*Bu$\}]$ (**13b**) and 19% $[Cp(CO)_2W\{\eta^3$-*t*BuC(O)AsAsAsC(O)*t*Bu$\}]$ (**14b**). IR (KBr, cm^{-1}): ν 1660 (s, AsCO), 1690 (m, AsCO), 1953 (br, WCO), 1997 (br, WCO). ^1H NMR (**13b**): δ 1.06 (s, 18H, *t*Bu), 4.66 (s, 5H, Cp); (**14b**): δ 1.06 (s, 18H, *t*Bu), 5.05 (s, 5H, Cp). $^{13}C\{^1H\}$ NMR (**13b**): δ 26.6 [s, $C(CH_3)_3$], 33.3 [d, $^3J_{PC}$ = 16.1 Hz, $C(CH_3)_3$], 84.0 (s, Cp), 84.1 (s, Cp), 212.0 (d, $^2J_{PC}$ = 3.4 Hz, CO), 212.1 (d, $^2J_{PC}$ = 4.6 Hz, CO), 234.8 (d, $^2J_{PC}$ = 6.9 Hz, AsCO); (**14b**): δ 26.8 [s, $C(CH_3)_3$], 50.2 [s, $C(CH_3)_3$], 85.5 (s, Cp), 90.6 (s, Cp), 213.1 (s, CO), 218.9 (s, CO), 235.5 (s. AsCO). $^{31}P\{^1H\}$ NMR (**13b**): δ −54.4 s, −61.6 s. Anal. Calcd for $C_{30}H_{23}As_{2.19}O_4P_{0.81}W$ (664.39): C, 30.73; H, 3.50. Found: C, 30.50; H, 3.82.

Reaction of $[Cp(CO)_2Mo{=}P{=}C(SiMe_3)_2]$ (3a) with 10 *t*BuC(O)As=C(NMe$_2$)$_2$. Analogously, the arsaalkene was prepared by combining pivaloyl chloride (2.4 g, 20 mmol) in 50 mL of diethyl ether with the solution of $Me_3SiAs{=}C(NMe_2)_2$ (5.0 g, 20 mmol) in 40 mL of *n*-pentane at −30 °C. A solution of **3a** (0.72 g, 1.8 mmol) in 30 mL of diethyl ether was added dropwise to the resulting slurry. An analogous workup afforded dark red crystals (0.25 g, 23%) of a mixture of 38% $[Cp(CO)_2Mo\{\eta^3$-*t*BuC(O)AsPAsC(O)-*t*Bu$\}]$ (**13a**) and 62% $[Cp(CO)_2Mo\{\eta^3$-*t*BuC(O)AsAsAsC(O)*t*Bu$\}]$ (**14a**). IR (KBr, cm^{-1}): ν 1660 (s, AsCO), 1690 (m, AsCO), 1953 (br, MoCO), 1997 (br, MoCO). ^1H NMR (**13a**): δ 1.05 (s, 18H, *t*Bu), 4.89 (s, 5H, Cp); (**14a**): δ 1.06 (s, 18H, *t*Bu), 4.70 (s, 5H, Cp). $^{13}C\{^1H\}$ NMR (**13a**): δ 26.4 [s, $C(CH_3)_3$], 33.1 [d, $^3J_{PC}$ = 16.1 Hz, $C(CH_3)_3$], 87.5 (s, Cp), 87.6 (s, Cp), 231.2 (d, $^2J_{PC}$ = 4.6 Hz, CO), 231.4 (d, $^2J_{PC}$= 5.8 Hz, CO), 235.9 (d, $^2J_{PC}$ = 5.8 Hz, AsCO); (**14a**): δ 26.8 [s, $C(CH_3)_3$], 50.3 [s, $C(CH_3)_3$], 86.2 (s, Cp), 92.2 (s, Cp), 226.9 (s, CO), 233.6 (s, CO), 235.7 (s, AsCO). $^{31}P\{^1H\}$ NMR (**13a**): δ 5.8 (s), 9.4 (s). Anal. Calcd for $C_{17}H_{23}As_{2.62}MoO_4P_{0.38}$ (595.13): C, 34.40; H, 3.90. Found: C, 34.46; H, 3.89.

Reaction of $[Cp(CO)_2W{=}P{=}C(SiMe_3)_2]$ (3b) with 10 *t*BuC(O)As=C(NMe$_2$)$_2$. As described before, reaction of **3b** (0.89 g, 1.8 mmol) and 20 mmol of the arsaalkene afforded 0.11 g (9%) of dark red crstals, consisting of 35% **13b** and 65% **14b**.

$\{\eta^2$:η^2-(Me$_3$Si)$_2$C=P−P(H)−CH(SiMe$_3$)$_2\}\{$Mo(CO)$_2$Cp$\}_2$] (15). A solution of $Me_3SiAs{=}C(NMe_2)_2$ (0.89 g, 3.62 mL) in *n*-pentane (15 mL) was added dropwise at −100 °C to the solution of **3a** (0.89 g, 2.19 mmol) in diethyl ether (20 mL). The mixture was slowly warmed to room temperature and stirred for 12 h. Solvent was removed in vacuo (10^{-5} bar). Unreacted arsaalkene was recovered by distillation at 10^{-6} bar and 60 °C (0.61 g, 69%). The solid residue was chromatographed on a column filled with Florisil as described before. A dark red zone was eluted with diethyl ether. Concentration to the beginning crystallization and storing at −30 °C gave compound **15** (0.57 g, 64%) as dark red irregular crystals. IR (KBr, cm^{-1}): ν 1828 (s, C≡O), 1874 (s, C≡O), 1923 (s, C≡O), 1945 (s, C≡O). ^1H NMR: δ 0.10 (s, 9H, $SiMe_3$), 0.15 (s, 9H, $SiMe_3$), 0.37 (s, 9H, $SiMe_3$), 0.49 (s, 9H, $SiMe_3$), 2.09 (dd, $^2J_{PH}$ = 25.8 Hz, $^3J_{PH}$ = 4.4 Hz, 1H, $CHSi_2$), 4.62 (d, $^1J_{PH}$ = 386.9 Hz, PH), 4.88 (s, 5H, Cp), 5.40 (s, 5H, Cp). $^{13}C\{^1H\}$ NMR: δ 0.63 (s, $SiMe_3$), 0.65 (s, $SiMe_3$), 1.44 [dd, $^1J_{CP}$ = 26.4, $^2J_{CP}$ = 1.2 Hz, $C(SiMe_3)_2$], 1.99 [dd, $^1J_{CP}$ = 27.0, $^2J_{CP}$ = 9.2 Hz, $CH(SiMe_3)_2$], 2.55 (s, $SiMe_3$), 6.00 (s, $SiMe_3$), 91.1 (s, Cp), 92.0 (s, Cp), 240.0 (dd, $^1J_{CP}$ = 34.5, $^2J_{CP}$ = 5.8 Hz, C≡O), 242.2 (d, $^1J_{CP}$ = 20.7 Hz, C≡O), 244.5 (dd, $^1J_{CP}$ = 16.0, $^2J_{CP}$ = 6.9 Hz, C≡O), 249.0 (s, CO). $^{31}P\{^1H\}$ NMR: δ −120.3 (d, $^1J_{PP}$ = 583.0 Hz), 102.6 (d, $^1J_{PP}$ = 583.0 Hz, PMo_2). ^{31}P NMR: δ −120.3 (ddd, $^1J_{PP}$ = 583.0, $^1J_{PH}$ = 384.1, $^2J_{PH}$ = 27.3 Hz, PH), 102.6 (d, $^1J_{PP}$ = 583.0 Hz). Anal. Calcd for $C_{28}H_{48}Mo_2O_4P_2Si_4$ (814.84): C, 41.31; H, 5.94. Found: C, 41.27; H, 6.00.

Supporting Information Available: Tables of X-ray data, atomic coordinates, thermal parameters, complete bond lengths and angles, and thermal ellipsoid plots for compounds **7**, **8**, **13a**/**14a**, **13b**/ **14b**, and **15**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM051084T