Synthesis and Structure of the First η^3-1,2-Diphosphaallyl Complexes $[(\eta^5\text{-}C_5H_5)(CO)_2M\{\eta^3\text{-}RPPC(SiMe_3)_2\}]$ (M = Mo, R = *t*Bu, Cy; M = W, R = *t*Bu) from $[(\eta^5\text{-}C_5H_5)(CO)_2M{=}P{=}C(SiMe_3)_2]$ (M = Mo, W) and Inversely Polarized Phosphaalkenes $RP{=}C(NMe_2)_2$ (R = *t*Bu, Cy)

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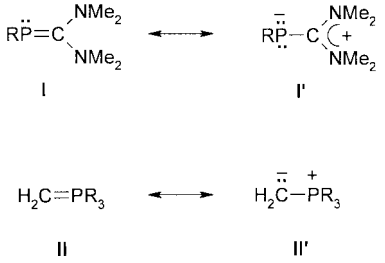
Keywords: Phosphavinylidene complexes / 1,2-Diphosphaallyl complexes / Phosphaalkenes / Molybdenum / Tungsten

Reaction of $[(\eta^5\text{-}C_5H_5)(CO)_2M{=}P{=}C(SiMe_3)_2]$ [where M = Mo (**2**), W (**5**)] with the phosphaalkene *t*BuP=C(NMe$_2$)$_2$ (**1a**) afforded the η^3-1,2-diphosphaallyl complexes $[(\eta^5\text{-}C_5H_5)(CO)_2M\{\eta^3\text{-}t\text{BuPPC}(SiMe_3)_2\}]$, [where M = Mo (**3a**); M = W (**6**)]. Similarly, **2** and CyP=C(NMe$_2$)$_2$ (**1b**; where Cy = cyclohexyl) gave rise to the formation of $[(\eta^5\text{-}C_5H_5)(CO)_2Mo\{CyPPC(SiMe_3)_2\}]$ (**3b**) by a phosphinidene transfer process. Small amounts of $[\{\eta^5\text{-}C_5H_5)(CO)_2Mo\}_2\{\eta^2{:}\eta^2\text{-}Cy_3P_5\}]$ (**4**) were formed as a minor product. However, treatment of **2** and **5** with HP=C(NMe$_2$)$_2$ (**1c**) yielded the complexes $[(\eta^5\text{-}C_5H_5)(CO)_2M\{\eta^2\text{-}(Me_3Si)_2CH\text{–}P{=}P\text{–}C(NMe_2)_2\}]$ [where M = Mo (**9**), W (**10**)]. The novel compounds **3a**, **3b**, **9** and **10** were characterized by means of spectroscopy (IR, ^{1}H, ^{13}C{^{1}H}, ^{31}P{^{1}H} NMR, MS). Moreover, the molecular structures of **3a**, **3b**, **4**, **6** and **10** were determined by X-ray diffraction analysis.

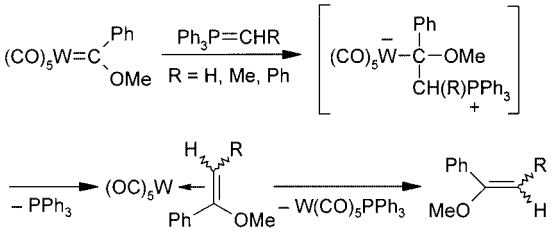
Introduction

Inversely polarized phosphaalkenes R–P=C(NMe$_2$)$_2$ (**I**) with an electron distribution $P^{\delta-}C^{\delta+}$ about the P=C double bond may be described by two canonical formulae (**I** and **I′**).[1] This situation may well be compared with the bonding in phosphorus ylides **II** (see Scheme 1).[2]



Scheme 1. Mesomeric structures of inversely polarized phosphaalkenes (**I**) and phosphorus ylides (**II**).

The chemical behavior of both classes of compounds (e.g. protonation, alkylation, complexation) can only be rationalized by using the zwitterionic structures **I′** and **II′**. Phosphorus ylides are prominent transfer reagents of alkylidene groups onto electrophilic functionalities (e.g. Wittig reaction). Phosphorus ylides undergo reaction with aryl(alkoxy)carbene complexes of the Fischer type to form enol ethers (see Scheme 2).[3]



Scheme 2.: Reaction of Fischer carbene complexes with Wittig reagents.

Recently, we discovered that inversely polarized phosphaalkenes R–P=C(NMe$_2$)$_2$ [where R = *t*Bu (**1a**), Me$_3$Si (**1b**)] react with aryl(alkoxy)carbene complexes affording novel phosphaalkene complexes by a formal transfer of the phosphinidene unit onto the carbene ligand (see Scheme 3).[4]

In contrast with this behavior, reaction of the carbene complex **III** (where Aryl = 2-MeOC$_6$H$_4$) with H–P=C(NMe$_2$)$_2$ (**1c**) yielded the phosphaalkene complex **IX** as a mixture of two isomers (see Scheme 4).[4]

In the present contribution we describe the smooth transfer of phosphinidene units from phosphaalkenes **1** to the electrophilic ligand in the phosphavinylidene complexes **2** and **5**.

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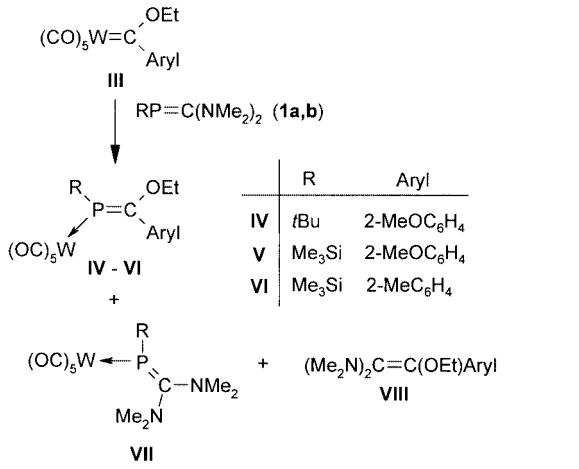
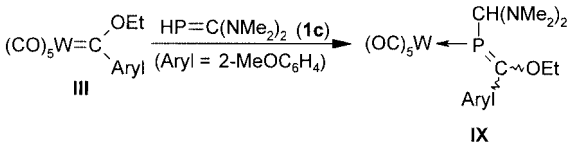


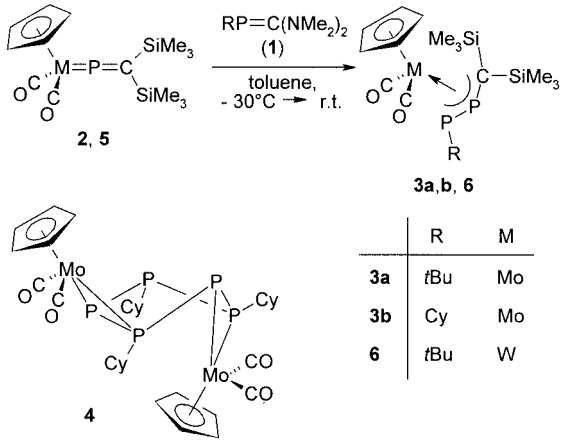
Scheme 3.: Reaction of Fischer carbene complexes with inversely polarized phosphaalkenes.



Scheme 4.: Formation of **IX**.

Results and Discussion

Reaction of the phosphavinylidene complex [(η⁵-C_5H_5)$(CO)_2$Mo=P=C$(SiMe_3)_2$] (**2**)[5] with an equimolar amount of phosphaalkene *t*BuP=C$(NMe_2)_2$ (**1a**)[4b] in toluene in the range of –30 °C to room temperature afforded the yellow complex **3a**, which was purified by column chromatography on silica (31% yield). The air- and moisture-sensitive compound is soluble in saturated hydrocarbons, ethereal and aromatic solvents (see Scheme 5). Similarly, compound **2** was converted into the orange product **3b** by treatment with CyP=C$(NMe_2)_2$ (**1b**) (49% yield). Reaction of (η⁵-C_5H_5)$(CO)_2$W=P=C$(SiMe_3)_2$ (**5**) with **1a** under comparable conditions led to the formation of complex **6** (18%yield).



Scheme 5.: Reaction of **2**, **5** with RP=C$(NMe_2)_2$ (R = *t*Bu, Cy).

Purification of **3b** was achieved by column chromatography and crystallization of the crude yellow product from *n*-pentane. A few crystals of the dinuclear complex **4** were obtained from the concentrated mother liquors by cooling. The $^{31}P\{^1H\}$ NMR spectra of **3a**, **3b** and **6** show doublets at δ = 18.1, 2.4 and –10.7 ppm for the terminal phosphorus atoms of the ligand whereas the central ones give rise to doublets at δ = –6.8, –32.9 and –61,6 ppm. The coupling constants $^1J_{PP}$ were determined as 407.0, 382.2 and 378.8 Hz, respectively. Only in the case of **3b**, the $^{13}C\{^1H\}$ NMR spectra displayed a doublet of doublets at δ = 43.8 ($^1J_{PC}$ = 94.4; $^2J_{PC}$ = 6.9 Hz), which we assigned to the carbon atom of the diphosphaallyl ligand. Two discrete doublets for the *ortho*- and *meta*-carbon atoms of the cyclohexyl substituent agree with a centre of chirality at the central P atom. The ^{13}C NMR resonances of the carbonyl ligands were observed as two singlets in **3a** (δ = 234.3, 235.5 ppm), as a doublet and a singlet at δ = 234.1 ($^2J_{PC}$ = 47.1 Hz) and δ = 235.6 ppm in **3b** and as a singlet and a multiplet at δ = 224.4 and 227.7 ppm in **6**. These resonances are shifted to lower field than those for precursors **2** (δ = 230.4 ppm)[5b] and **5** (δ = 218.9 ppm),[5b] indicating the improved donor capacity of the diphosphaallyl ligands. This is also mirrored by the carbonyl stretching frequencies in the IR spectra of **3a**, **3b** and **6**, which are observed as intense bands at $\tilde{\nu}$ = 1943, 1877 (**3a**); 1930, 1859 (**3b**) and 1938, 1851 cm^{-1} (**6**). The corresponding bands in the precursors **2** and **5** appear at $\tilde{\nu}$ = 1944, 1882 cm^{-1} (KBr) and 1952, 1880 cm^{-1} (*n*-hexane).[5b]

Single crystals of **3a** suitable for an X-ray diffraction study were grown from a diethyl ether/pentane mixture (1:9) at –30 °C (see Figure 1). Compound **6** is isostructural to **3a**, and only the latter will be discussed in detail.[21]

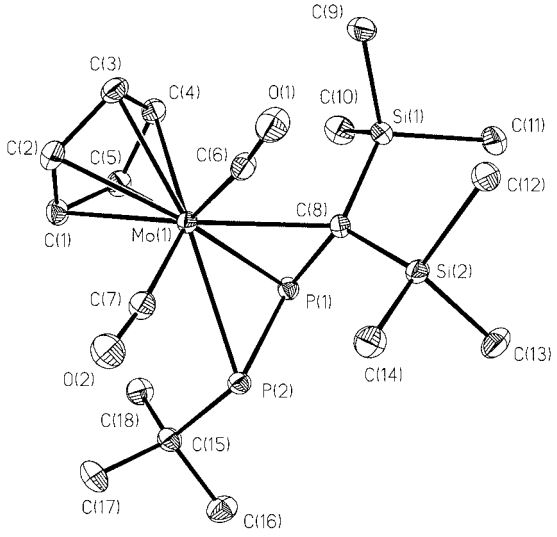
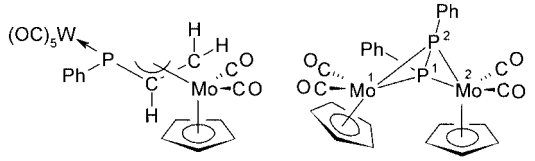


Figure 1. Molecular structure of **3a** in the crystal. Selected bond lengths [Å] and angles [°]: Mo(1)–C(6) 1.9595(12), Mo(1)–C(7) 1.9686(11), Mo(1)–C(8) 2.4372(11), Mo(1)–P(1) 2.4960(3), Mo(1)–P(2) 2.6756(3), P(1)–C(8) 1.7875(12), P(1)–P(2) 2.1234(4), P(2)–C(15) 1.8977(12), C(8)–Si(1) 1.9032(12), C(8)–Si(2) 1.9013(12), C(6)–Mo(1)–C(7) 80.84(5), C(6)–Mo(1)–C(8) 70.91(4), C(7)–Mo(1)–P(2) 64.05(4), C(8)–P(1)–P(2) 97.68(4), P(1)–P(2)–C(15) 103.75(4), P(1)–C(8)–Si(1) 108.09, P(1)–C(8)–Si(2) 123.52(6).

The analysis displays a molecule with a distorted pianostool geometry [P(2)–Mo(1)–C(7) 64.05(4)°, C(6)–Mo(1)–C(7) 80.84(5)°, C(6)–Mo(1)–C(8) 70.91(4)°] and two nearly linear carbonyl ligands [Mo(1)–C(6)–O(1) 173.84(10)°, Mo(1)–C(7)–O(2) 173.09(11)°]. The most interesting part of the molecule is the 1,2-diphosphaallyl ligand which is unsymmetrically linked to the metal atom in an η^3-fashion via bonds Mo(1)–P(1) [2.4960(3) Å], Mo(1)–P(2) [2.6756(3) Å] and Mo(1)–C(8) [2.4372(11) Å]. The latter bond length significantly exceeds the Mo(1)–C distances displayed by the [C_5H_5Mo] part of the molecule [2.3216(12)–2.3859(12) Å]. In the η^3-1-phosphaallyl complex **7** the observed bond lengths are Mo–C(1) 2.251(3) Å and Mo–C(2) 2.357(3) Å.[6] In complex **7** the Mo–C contact to the central C atom of the phosphaallyl ligand is markedly shorter than the corresponding bond to the terminal C atom. Similarly, in complex **3a** the bond length between the metal and the terminal phosphorus atom of the ligand Mo(1)–P(2) is strongly lengthened [2.6756(3) Å] relative to the Mo(1)–P(1) bond length [2.4960(3) Å]. In complex **7** a metal–phosphorus distance of 2.5343(8) Å was measured.[6] A comparable nonsymmetric ligation of the two phosphorus atoms is present in the "butterfly complex" **8**, 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].[7]



7 **8**

The distance P(1)–P(2) in **3a** [2.1234(4) Å] is intermediate between a double (ca. 2.00 Å)[8] and a single bond (ca. 2.22 Å).[9] In $Cp_2Mo(\eta^2\text{-}P_2H_2)$[10] and **8**, the P–P bond lengths amount to 2.146(3) Å and 2.136 Å, respectively. The bond length P(1)–C(8) in **3a** [1.7875(12) Å] exceeds that of a localized and unsupported P–C double bond (1.65–1.72 Å)[11] but is clearly shorter than a P–C single bond (av. 1.85 Å).[12] In **7** the corresponding bond length was determined as 1.755(3) Å. The η^3-1,2-diphosphaallyl ligand in **3a** is oriented in a fashion in which the terminal atoms P(2) and C(8) are directed towards the two carbonyl ligands. Moreover, the *tert*-butyl substituent at P(2) is located in a *syn* disposition with respect to P(1). The same is found for the atom Si(1). Atoms C(15) and Si(1) are nearly coplanar with the plane defined by the atoms P(2), P(1) and C(8) [torsion angles C(8)–P(1)–P(2)–C(15) = 170.3°; P(2)–P(1)–C(8)–Si(1) = –175.5°]. The substituent $Si(2)Me_3$ at C(8) is directed in an opposite way to the metal atom with a torsion angle P(2)–P(1)–C(8)–Si(2) = 47.1°.

Single crystals of **3b** were grown from pentane at +4 °C (see Figure 2). The analysis shows a molecule, the core of which is comparable to that of **3a** with the cyclohexyl substituent and the group $Si(2)Me_3$ directed towards the central atom P(2) of the η^3-diphosphaallyl ligand. All bond parameters are similar to those in **3a** and do not merit a detailed discussion.

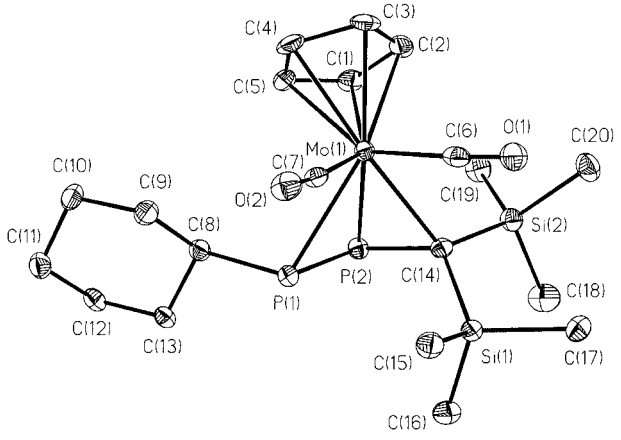


Figure 2. Molecular structure of **3b** in the crystal. Selected bond lengths [Å] and angles [°]: Mo(1)–C(6) 1.964(3), Mo(1)–C(7) 1.954(3), Mo(1)–C(14) 2.428(2), Mo(1)–P(1) 2.6538(6), Mo(1)–P(2) 2.4828(6), P(2)–C(14) 1.784(2), P(1)–C(8) 1.873(2), P(1)–P(2) 2.136(1), C(14)–Si(1) 1.907(2), C(14)–Si(2) 1.907(2); C(6)–Mo(1)–C(7) 79.51(9), C(6)–Mo(1)–C(14) 70.05(8), C(7)–Mo(1)–P(1) 64.63(7), C(14)–P(2)–P(1) 97.95(8), P(2)–P(1)–C(8) 101.18(8), P(2)–C(14)–Si(2) 110.28(12), P(2)–C(14)–Si(1) 120.21(12).

From the view-point of the rules according to Wade and Mingos, **3a** and **3b** display four skeleton atoms with 14 skeleton electrons and thus have to be regarded as *arachno* clusters.

A few crystals of compound **4** were collected from the concentrated *n*-pentane mother liquor at +4 °C (see Figure 3). The complex contains a nearly planar central 2,4,5-tri-cyclohexylcyclopentaphosphane-1,3-diyl ligand, which is

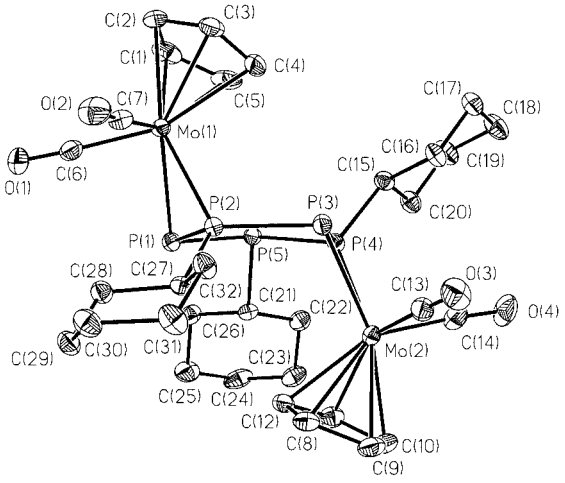
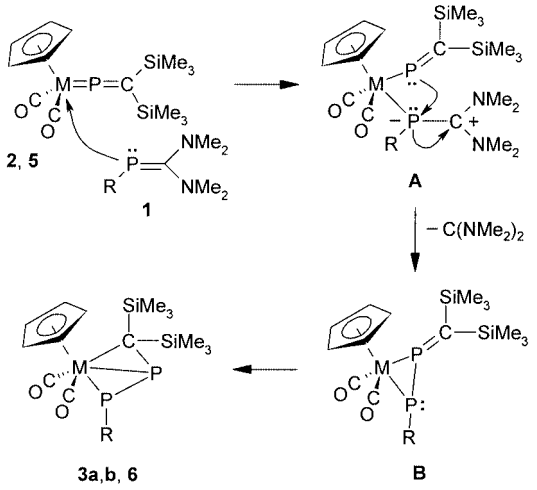


Figure 3. Molecular structure of **4** in the crystal. Selected bond lengths [Å] and angles [°]: Mo(1)–C(6) 1.958(3), Mo(1)–C(7) 1.959(3), Mo(1)–C(1–5) 2.295(2)–2.382(2), Mo(1)–P(1) 2.6204(6), Mo(1)–P(2) 2.4272(6), Mo(2)–C(13) 1.961(3), Mo(2)–C(14) 1.958(2), Mo(2)–C(8–12) 2.344(2)–2.352(2), Mo(2)–P(3) 2.5964(6), Mo(2)–P(4) 2.4480(6), P(1)–P(2) 2.1224(8), P(2)–P(3) 2.1948(8), P(3)–P(4) 2.1281(8), P(4)–P(5) 2.2214(7), P(1)–P(5) 2.2320(8), P(2)–C(27) 1.848(2), P(4)–C(15) 1.860(2), P(5)–C(21), 1.882(2), C(6)–Mo(1)–C(7) 80.67(10), C(6)–Mo(1)–P(1) 77.03(7), C(7)–Mo(1)–P(2) 83.80(7), C(13)–Mo(2)–C(14) 79.48(10), C(13)–Mo(2)–P(3) 71.83(1), C(14)–Mo(2)–P(4) 85.82(7), P(1)–P(2)–P(3) 118.98(3), P(2)–P(3)–P(4) 97.47(3), P(3)–P(4)–P(5) 115.08(3), P(1)–P(5)–P(4) 104.00(3), P(2)–P(1)–P(5) 101.95(3).

η^2-coordinated to the $Cp(CO)_2Mo(1)$ unit via P(1) and P(2) and to the $Cp(CO)_2Mo(2)$ group via atoms P(3) and P(4). Both metal complex fragments are located on opposite sides of the P_5 ring. The bonds Mo(1)–P(1) [2.6204(6) Å] and Mo(2)–P(3) [2.5964(6) Å] between the metal centers and the tricoordinate P atoms are significantly longer than the bonds between the metal centers and the four-coordinate phosphorus atoms [Mo(1)–P(2) 2.4272(6) Å; Mo(2)–P(4) 2.4480(6) Å]. The longer Mo–P contacts may result from repulsion between the lone pair of electrons at P(1) and P(3) and the electron-rich metal atoms.

Interestingly, the η^2-ligated P–P bonds P(1)–P(2) [2.1224(8) Å] and P(3)–P(4) [2.1281(8) Å] are intermediate between double [2.00 Å][8] and single bonds [2.22 Å],[9] thus indicating some multiple bonding. In contrast to this, the endocyclic bonds P(2)–P(3) [2.1948(8) Å], P(4)–P(5) [2.2214(7) Å] and P(1)–P(5) [2.2320(8) Å] may be considered as single bonds. The cyclohexyl substituents at atoms P(2) and P(5) are directed to the face opposite Mo(1) but sterically approaching the $Mo(2)(CO)_2Cp$ moiety. To the best of our knowledge, this mode of coordination of a P_5 ring is without precedence.

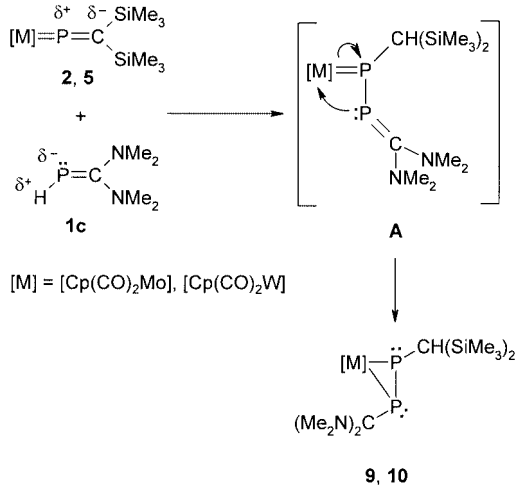
It is conceivable that the formation of complexes **3a**, **3b** and **6** is initiated by a nucleophilic attack of the phosphaalkene by its P atom on the metal centre of precursors **2** or **5** to give adduct **A**. Ring closure and extrusion of $C(NMe_2)_2$ would lead to metallodiphosphiranes **B**. A σ/π-type rearrangement of **B** furnishes the final products **3a**, **3b** and **6** (see Scheme 6). Previously, Mathey et al. observed an equilibrium between a vinylphosphenium tungsten complex and its η^3-phosphaallyl isomer.[6b]



Scheme 6. Proposed mechanism for the formation of **3a**, **3b** and **6**.

Reaction of 2a and 5 with $HP=C(NMe_2)_2$ (1c)

The phosphavinylidene complex **2** was treated with an equimolar amount of phosphaalkene $HP=C(NMe_2)_2$ (**1c**)[13] in diethyl ether in the range of –30 °C to room temperature. Workup by chromatography on a column packed with silica led to the isolation of the light yellow crystalline complex **9** in 21% yield. The corresponding reaction of the tungsten analog $[Cp(CO)_2W=P=C(SiMe_3)_2]$ (**5**) with **1c** was less straightforward and yielded only a few orange crystals of product **10** (see Scheme 7).



Scheme 7. Formation of **9** and **10**.

The products are very soluble in ethereal and aromatic solvents, whereas they appear to be nearly insoluble in saturated hydrocarbons. Compounds **9** and **10** are dicarbonyl(cyclopentadienyl) complexes featuring the yet unknown diphosphaallyl anion $[(Me_3Si)_2CH–P–P=C(NMe_2)_2]^-$ as an η^2 ligand. The $^{31}P\{^1H\}$ NMR spectra of **9** and **10** displayed AB spin systems at δ = –70 and –75 ppm ($^1J_{AB}$ = 421.9 Hz) and δ = –105.8 ($^1J_{WP}$ = 46.0 Hz) and –114.5 ppm ($^1J_{AB}$ = 400.0 Hz), respectively. In the ^1H NMR spectrum of **9**, the singlets at δ = 0.29, 0.51, 2.49 and 5.06 ppm are attributed to the CH and the Me_3Si groups of the $CH(SiMe_3)_2$ substituent, to the Me_2N unit and the C_5H_5 ligand, respectively. The ^{13}C NMR resonance of the carbonyl ligands of **9** was observed at δ = 203.7 ppm. In comparison with precursor **2** (δ = 230.4 ppm) this resonance is strongly shifted to high field. It is also obvious from the ν(CO) stretching frequencies in **9** ($\tilde{\nu}$ = 1889 s, 1803 cm^{-1}) and **2** (KBr, $\tilde{\nu}$ = 1944 s, 1882 cm^{-1}) that the novel ligand transfers more electron density onto the $[CpMo(CO)_2]$ unit than the phosphavinylidene ligand in **2**. Orange crystals of **10** suitable for X-ray diffraction analysis were grown from diethyl ether at 4 °C. The results of this study are shown in Figure 4, while selected bond lengths and bond angles are given in the caption. The compound consists of a central tungsten atom linked to a cyclopentadienyl ring, two terminal carbonyl ligands, and the η^2-$(Me_3Si)_2CH–P–P=C(NMe_2)_2$ diphosphaallylic ligand; the geometry around the tungsten atom is that of a "four-legged piano-stool" type. The W–P bond lengths [W(1)–P(1) 2.5352(7) Å, W(1)–P(2) 2.5695(7) Å] are not equivalent.

The longer bond is similar to the corresponding distances found in $[W(CO)_5(\mu,\eta^2{:}\eta^1{:}\eta^1)$-$P_2Cl_2\{W(CO)_5\}_2]$, that is, 2.573(4) and 2.582(4) Å.[14] According to structural work by Huttner et al.[15] or Mathey et al.[16] on $[W(CO)_5$-$(\mu,\eta^2{:}\eta^1{:}\eta^1)$-$P_2Ph_2\{W(CO)_5\}_2]$ the W–P bonds of the W–

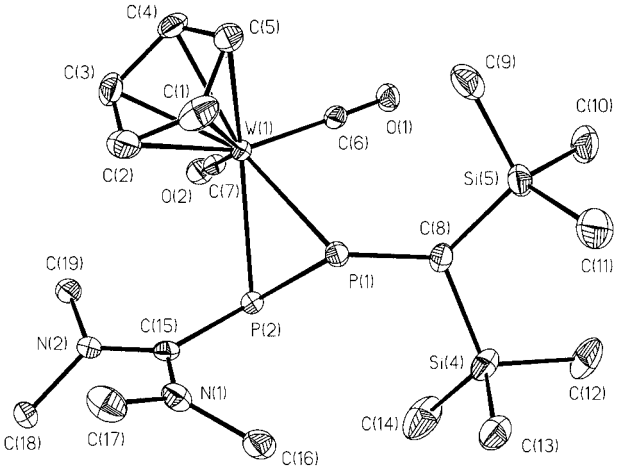


Figure 4. Molecular structure of **10** in the crystal. Selected bond lengths [Å] and angles [°]: W(1)–C(6) 1.946(3), W(1)–C(7) 1.957(3), W(1)–C(1–5) 2.337(3)–2.398(3), W(1)–P(1) 2.5352(7), W(1)–P(2) 2.5695(7), P(1)–P(2) 2.1739(9), P(1)–C(8) 1.889(3), C(8)–Si(4) 1.906(3), C(8)–Si(5) 1.916(3), P(2)–C(15) 1.878(3), N(1)–C(15) 1.342(3), N(2)–C(15) 1.356(3), N(1)–C(16) 1.472(3), N(1)–C(17) 1.477(4), N(2)–C(18) 1.478(3), N(2)–C(19) 1.468(3); C(6)–W(1)–C(7) 77.57(10), C(6)–W(1)–P(1) 84.84(7), C(7)–W(1)–P(2) 77.81(7), C(8)–P(1)–P(2) 107.60(9), P(1)–P(2)–C(15) 102.64(8), P(2)–C(15)–N(1) 123.15(19), P(2)–C(15)–N(2) 119.61(18), N(1)–C(15)–N(2) 117.1(2), C(8)–P(1)–P(2)–C(15) 150.4, P(2)–P(1)–C(8)–Si(4) –72.2, P(2)–P(1)–C(8)–Si(5) 160.0.

η^2-P_2Ph_2 unit are significantly longer [2.604 Å (av)] than in **10**. The elongation of the bond W(1)–P(2) with respect to the bond W(1)–P(1) may be the result of steric repulsion between the C_5H_5 ring and the bis(dimethylamino)carbenium unit. The P–P bond of 2.1739(9) Å is markedly longer than the bonds in complexes $[W(CO)_5(\mu,\eta^2{:}\eta^1{:}\eta^1)$-$P_2Cl_2\{W(CO)_5\}_2]$ [2.1460(6) Å] and $[W(CO)_5(\mu,\eta_2{:}\eta_1{:}\eta_1)$-$P_2Ph_2\{W(CO)_5\}_2]$ [2.140(15) Å[15] and 2.163(3) Å[16]]. It is possible to describe the bonding situation in **9** and **10** as that of a diphosphametallacyclopropane with essentially endocyclic single bonds, well aware of the fact that single bonds in cyclopropane derivatives are usually shorter than C–C bonds in unstrained C–C chains. The bond lengths P(1)–C(8) [1.889(3) Å] and P(2)–C(15) [1.878(3) Å] are as expected for single bonds. Carbon atom C(15) is trigonal planar, the formal positive charge of this carbenium center is stabilized by the planar atoms N(1) and N(2) by π conjugation, which becomes evident by the short C–N contacts [N(1)–C(15) 1.342(3) Å and N(2)–C(15) 1.356(3) Å]. Such a situation is well known from η^1 complexes of inversely polarized phophaalkenes.[1] The substituents at the P(2) unit are in an (*E*) disposition with the carbenium unit directed towards the $M(C_5H_5)$ fragment. The torsion angle C(8)–P(1)–P(2)–C(15) amounts to 150.4°. For a rationalization of the formation of **9** and **10** we postulate the formal addition of the P–H bond of the phosphaalkene **1c** to the P=C double bond of **2** and **5** to yield the intermediate **A**. Coordination of the second P atom to the metal atom with its lone pair gives the observed metalladiphosphiranes (see Scheme 7).

Conclusion

Inversely polarized phosphaalkenes $RP{=}C(NMe_2)_2$ serve as convenient sources of the phosphinidene unit PR, which can be transferred onto carbene ligands to afford η^1-phosphaalkene complexes, as was shown previously. In this paper, this synthetic principle is consistently extended to electrophilic phosphavinylidene complexes, which are cleanly converted into coordination compounds featuring the novel η^3-1,2-diphosphaallylic ligand. It is obvious that the performed synthetic method may easily be generalized with other electrophilic complexes containing vinylidene, phosphinidene, isocyanide and even carbonyl ligands. Moreover, it is tempting to also test this kind of transfer reactions with inversely polarized arsaalkenes.

Experimental Section

General: All manipulations were performed under dry, oxygen-free nitrogen using standard Schlenk techniques. Solvents were vigorously dried with an appropriate drying agent and freshly distilled under N_2 before use. The following compounds were prepared according to literature procedures: $[Cp(CO)_2M{=}P{=}C(SiMe_3)_2]$ M = Mo (**2**); M = W (**5**),[5] *t*BuP=$C(NMe_2)_2$ (**1a**),[4b] HP=$C(NMe_2)_2$ (**1c**);[13] $CyPH(SiMe_3)$,[17] $[(Me_2N)_2CSMe]I$.[18] IR spectra: Bruker FT-IR VECTOR 22. ^{1}H-, ^{13}C- and ^{31}P-NMR spectra: room temp., Bruker AM Avance DRX 500 (^{1}H, 500.13 Hz; ^{13}C, 125.75 MHz; ^{31}P, 202.46 MHz). References: $SiMe_4$ (^{1}H, ^{13}C), 85% H_3PO_4 (^{31}P). MS: Bruker Esquire Ion Trap mass spectrometer. Silica 60 (Merck) was purchased commercially.

CyP=C(NMe$_2$)$_2$ (1b): A solution of cyclohexyltrimethylsilylphosphane (18.8 g, 10.0 mmol) in 100 mL of THF was combined with an equimolar amount of a 1.6 M solution of *n*-butyllithium in *n*-hexane (6.25 mL, 10.0 mmol). The resulting slurry was added dropwise at 20 °C for 2 h to a slurry of *N*,*N*,*N*′,*N*′,*S*-pentamethylthiuronium iodide (27.4 g, 10.0 mmol) in THF (20 mL). Stirring was continued for 15 h. The solvent was removed in vacuo to afford an orange, viscous residue. The latter was triturated with *n*-pentane (150 mL) and filtered. The filter cake was washed with *n*-pentane (2 × 20 mL) and subsequently with diethyl ether until the washings became colorless. The orange-red filtrate was freed from solvents in vacuo at 20 °C. The remaining oil was distilled to give 12.0 g (56%) of **1b** as a yellow oil (b.p. ca. 100 °C at 1.5×10^{-4} bar). ^{1}H NMR (C_6D_6): δ = 1.9 (m, 11 H, C_6H_{11}), 2.56 (s, 12 H, NMe_2) ppm. ^{31}P{^{1}H} NMR (C_6D_6): δ = 57.5 (s) ppm. Because of the sensitivity of the phosphaalkene no reliable elemental analyses were obtained.

[Cp(CO)$_2$Mo{η^3-*t*BuPPC(SiMe$_3$)$_2$}] (3a): A solution of **1a** (0.24 g, 1.28 mmol) in toluene (10 mL) was added dropwise to a well-stirred, chilled solution (–30 °C) of **2** (0.52, 1.29 mmol) in toluene (15 mL). It was slowly warmed to ambient temperature and stirring was continued for 72 h. The reaction mixture was freed from solvent and volatile compounds. The black residue was transferred onto a column (d = 1.5 cm, l = 6 cm) charged with silica. A yellow phase was eluted with 40 mL of a diethyl ether/pentane mixture (1:9). Removal of solvents in vacuo afforded 0.20 g (31%) of orange crystalline **3a**. IR (KBr): $\tilde{\nu}$ = 1943 vs (CO), 1877 vs (CO), 1247 m [$\delta(SiMe_3)$], 847 m [$\rho(SiMe_3)$] cm^{-1}. ^{1}H NMR (C_6D_6): δ = 0.17 (d, $^4J_{PH}$ = 1.3 Hz, $SiMe_3$), 0.47 (d, $^4J_{PH}$ = 1.3 Hz, $SiMe_3$), 1.04 (dd, $^3J_{PH}$ = 10.8, $^4J_{PH}$ = 1.9 Hz, 9 H, *t*Bu), 4.85 (s, 5 H, Cp) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ = 4.5 (d, $^3J_{PH}$ = 9.8 Hz, $SiCH_3$), 8.8 (d, $^3J_{CP}$ = 11.3 Hz, $SiCH_3$), 32.0 [dd, J_{PC} = 14.4; 8.6 Hz, C(CH_3)$_3$],

32.6 [d, $^2J_{PC}$ = 47.1 Hz, $C(CH_3)_3$], 90.7 (s, C_5H_5), 234.3 (s, CO), 235.2 (s, CO) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ = 18.1 (d, $^1J_{PP}$ = 407 Hz, P-terminal), –6.8 (d, $^1J_{PP}$ = 407 Hz, P-central) ppm. $C_{18}H_{32}MoO_2P_2Si_2$ (494.50): calcd. C 43.72, H 6.52; found C 43.61, H 6.52.

[Cp(CO)$_2$Mo{η³-CyPPC(SiMe$_3$)$_2$}] (3b) and [{Cp(CO)$_2$Mo}$_2$-η²,η²-{P$_2$(PCy)$_3$}] (4): A solution of CyP=C(NMe$_2$)$_2$ (**1b**) (0.27 g, 1.32 mmol) in toluene (15 mL) was added dropwise at room temp. to a vigorously stirred solution of **2** (0.52 g, 1.32 mmol) in toluene (15 mL). Stirring was continued for 72 h. Solvent and volatile components were removed in vacuo to give a dark-brown solid residue. The latter was chromatographed on a column (l = 6.5 cm, d = 20 cm) filled with silica. An orange-yellow zone was eluted with *n*-pentane to afford 0.30 g (44%) of orange crystalline **3b** after recrystallization. A few orange crystals of compound **4** were isolated from the mother liquor. IR (KBr): $\tilde{\nu}$ = 1930 vs (CO), 1859 vs (CO), 1246 m [δ(SiMe$_3$)], 844 m [ρ(SiMe$_3$)] cm^{-1}. ^{1}H NMR (C_6D_6): δ = 0.18 (s, 9 H, SiMe$_3$), 0.45 (s, 9 H, SiMe$_3$), 0.88–1.90 (m, 11 H, C_6H_{11}), 4.79 (s, 5 H, C_5H_5) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 3.90 (d, $^3J_{PC}$ = 9.2 Hz, SiMe$_3$), 8.1 (d, $^3J_{PC}$ = 10.3 Hz, $SiCH_3$), 26.0 (s, C–Cy), 27.1(d, $^1J_{PC}$ = 8.1 Hz, PCH), 32.9 (dd, J_{PC} = 14.4, 5.2 Hz, C–Cy), 37.3 (dd, J_{PC} = 15.5, 2.9 Hz, C–Cy), 42.7 (d, J_{PC} = 13.8 Hz, C–Cy), 43.0 (d, J_{PC} = 13.8 Hz, C–Cy), 43.8 (dd, $^1J_{PC}$ = 95.4, $^2J_{PC}$ = 6.9 Hz, PP*C*), 91.4 (s, C_5H_5), 234.1 (d, $^2J_{PC}$ = 47.1 Hz, CO), 235.6 (s, CO) ppm. $^{31}P\{^1H\}$NMR (C_6D_6): δ = –32.9 (d, $^1J_{PP}$ = 382.2 Hz, P-central), 2.4 (d, $^1J_{PP}$ = 383.2 Hz, P-terminal). $C_{20}H_{34}MoO_2P_2Si_2$ (520.54): calcd. C 46.15, H 6.58; found C 46.13, H 6.53.

[Cp(CO)$_2$W{η³-*t*BuPPC(SiMe$_3$)$_2$}] (6): A solution of **1a** (0.224 g, 1.3 mmol) in toluene (25 mL) was added dropwise at room temp. to a well-stirred solution of **5** (0.65 g, 1.3 mmol) in toluene (25 mL). After stirring for 48 h, solvent and volatile compounds were removed in vacuo. The dark-brown solid residue was chromatographed on silica with pentane, as described before. A yellow zone was eluted with pentane (230 mL). From this elute, compound **6** was isolated as a yellow solid (0.14 g, 18% yield). IR (KBr): $\tilde{\nu}$ = 1938 vs (CO), 1851 vs (CO), 1246 m [δ(SiMe$_3$)], 847 m [ρ(SiMe$_3$)] cm^{-1}. ^{1}H NMR (C_6D_6): δ = 0.16 (d, $^4J_{PH}$ = 1.3 Hz, 9 H, SiMe$_3$), 0.54 (s, 9 H, SiMe$_3$), 1.04 (dd, $^3J_{PH}$ = 10.7, $^4J_{PH}$ = 1.3 Hz, 9 H, *t*Bu), 4.89 (s, 5 H, C_5H_5) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 4.2 (d, $^3J_{PC}$ = 9.2 Hz, SiMe$_3$), 9.0 (d, $^3J_{PC}$ = 11.5 Hz, SiMe$_3$), 32.1 (dd, J_{PC} = 14.4, 8.6 Hz, $C(CH_3)_3$), 32.3 (dd, J_{PC} = 49.6, 2.5 Hz, *C*-$(CH_3)_3$), 89.1 (s, C_5H_5), 224.4 (s, CO), 222.7 (m, CO) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ = –10.7 (d, $^1J_{PP}$ = 378.8 Hz, P-terminal), –61.6 (d, $^1J_{PP}$ = 378.8 Hz, P-central) ppm. MS (ESI): m/z = 583 [M + H$^+$], 555 [M – CO + H$^+$], 527 [M – 220 + H$^+$]. $C_{18}H_{32}O_2P_2Si_2W$ (582.41): calcd. C 37.12, H 5.54; found C 37.31, H 5.67.

[Cp(CO)$_2$Mo{η²-(Me$_3$Si)$_2$CH–P=PC(NMe$_2$)$_2$}] (9): A solution of **1c** (0.17 g, 1.31 mmol) in diethyl ether (10 mL) was added dropwise with vigorous stirring to a chilled solution (–30 °C) of **2** (0.53 g, 1.31 mmol) in diethyl ether (15 mL). The brown reaction mixture was warmed to ambient temp. and stirred for 24 h. Solvent and volatile components were removed in vacuo. The black, oily residue was transferred to a column (d = 1.5 cm, l = 6 cm) filled with silica. A yellow phase, eluted with 40 mL of a diethyl ether/*n*-pentane mixture (1:9) was discarded. Subsequently, a burgundy-red phase was eluted with 40 mL of diethyl ether. Removal of solvent led to the isolation of the orange solid **9**. IR (KBr): $\tilde{\nu}$ = 1889 (s, CO), 1803 s (CO), 1260 m [δ(SiMe$_3$)], 840 s [ρ(SiMe$_3$)] cm^{-1}. ^{1}H NMR (C_6D_6): δ = 0.29 (s, ^{1}H, $CHSi_2$), 0.51 (s, 18 H, SiMe$_3$), 2.49 (s, 12 H, NMe$_2$), 5.06 (s, 5 H, C_5H_5) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 2.3 (d, $^2J_{CP}$ = 7 Hz, $SiCH_3$), 3.7 (d, $^2J_{CP}$ = 7 Hz, $SiCH_3$), 16.9 (d, $^1J_{CP}$ = 79.3 Hz, $CHSi_2$), 42.5 (br. s, NCH_3), 44.2 (br. s, NCH_3), 91.3 (s, C_5H_5), 203.7 (s, CO) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ = –70.0, –75.0 [AB-spin system, $^1J_{PP}$ = 421 Hz, (Me$_2$N)C*P* and *P*CH(SiMe$_3$)$_2$] ppm. MS (ESI): m/z = 541 [M + H$^+$]. $C_{19}H_{36}MoN_2O_2P_2Si_2$ (538.56): calcd. C 42.37 H 6.74 N 5.06, found C 41.88 H 6.64 N 5.20).

[Cp(CO)$_2$W{η²-(Me$_3$Si)$_2$CH–P=P–C(NMe$_2$)$_2$}] (10): Analogously, equimolar amounts of **1c** (0.17 g, 1.30 mmol) and **5** (0.64 g, 1.30 mmol) were allowed to react in diethyl ether (10 mL). Analogous workup by chromatography and recrystallization from diethyl

Table 1. Crystal data and data-collection parameters.

	3a	**3b**	**4**	**10**
Empirical formula	$C_{18}H_{32}MoO_2P_2Si_2$	$C_{20}H_{34}MoO_2P_2Si_2$	$C_{32}H_{43}Mo_2O_4P_5$	$C_{19}H_{36}N_2O_2P_2Si_2W$
M_r [g mol^{-1}]	494.50	520.53	838.39	626.47
Crystal dimensions [mm]	0.30 × 0.25 × 0.10	0.16 × 0.09 × 0.04	0.15 × 0.13 × 0.04	0.24 × 0.07 × 0.03
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/n$	$P2_1/c$
a [Å]	13.7330(1)	7.8680(2)	11.6440(2)	21.437(2)
b [Å]	11.5360(1)	34.6270(5)	10.8760(2)	9.7132(8)
c [Å]	14.7690(1)	9.0300(2)	27.8690(4)	12.8112(17)
β [°]	102.1270(7)	98.5600(7)	98.9550(8)	101.664(10)
V [Å^3]	2287.55(3)	2432.77(9)	3486.31(10)	2612.5(5)
Z	4	4	4	4
$\rho_{calcd.}$ [g cm^{-3}]	1.436	1.421	1.597	1.593
μ [mm^{-1}]	0.827	0.782	0.984	4.652
F(000)	1024	1080	1704	1248
θ [°]	3.33–30.00	3.16–25.00	2.96–27.50	3.09–30.00
No. refl. collected	64677	28194	62827	58131
No. refl. unique	6649	4281	7959	7603
R (int)	0.031	0.050	0.053	0.0563
No. refl. [$I > 2\sigma(I)$]	6054	3656	6421	6213
Refined parameters	235	250	388	263
GOF	1.062	1.040	1.032	1.040
R_F [($I > 2\sigma(I)$]	0.0206	0.0248	0.0280	0.0238
wR_{F2} [$I > 2\sigma(I)$]	0.0520	0.0559	0.0637	0.0501
$\Delta\rho_{max./min.}$ [e Å^{-3}]	0.482/–0.462	0.365/–0.363	0.479/–0.384	0.932/–0.715

ether led to a few burgundy-red crystals of **10**. ^{1}H NMR (C_6D_6): δ = 0.28 (s, 1 H, $CHSi_2$), 0.51 (s, 18 H, $SiMe_3$), 2.45 (s, 12 H, NMe_2), 5.05 (s, 5 H, Cp) ppm. $^{31}P\{^1H\}$ NMR (C_6D_6): δ = –105.8 [AB spin system, $^1J_{PP}$ = 400, $^1J_{WP}$ = 46 Hz, $PCH(SiMe_3)_2$], –114.5 [AB spin system, $^1J_{PP}$ = 400 Hz, $(MeN)_2CP$] ppm.

X-ray Crystallography: Crystallographic data were collected with a Nonius Kappa CCD diffractometer with Mo-K_α radiation (graphite monochromator, λ = 0.71073 Å) at 100 K. Crystallographic programs used for the structure solution and refinement were from SHELXS-97,[19] SIR-97,[20] and SHELXL-97.[19] 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 CH_2 groups, U(H) = 1.5 U_{eq} for CH_3 groups. Crystal data of the compounds are listed in Table 1.[21]

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[21] Further details of the crystal structure investigations are available. CCDC-256916 (**3a**), -255215 (**3b**), -255216 (**4**), -255214 (**6**) and -255217 (**10**) 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., together with the names of the authors, and the journal citation.

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