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Synthesis of the η²-1-Phosphaallene Complexes [(η⁵-C_5H_5)(CO)(NO)W{η²-R^1P=C=C(R^2)H}] (R^1 = *t*Bu, Cy; R^2 = Ph, H) from [(η⁵-C_5H_5)(CO)(NO)-W=C=C(R^2)H] (R^2 = Ph, H) and Inversely Polarized Phosphaalkenes R^1P=C(NMe_2)$_2$ (R^1 = *t*Bu, Cy), and Their Structure

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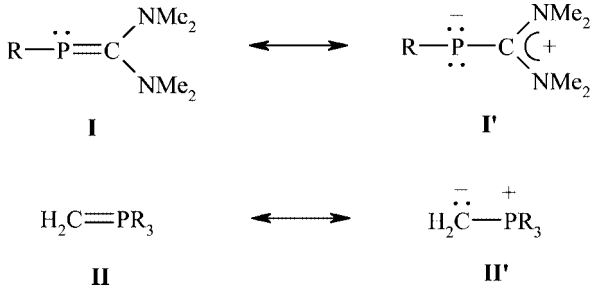
The reaction of the vinylidene complex [(η⁵-C_5H_5)(CO)(NO)-W=C=C(H)Ph] (**9**) with the phosphaalkenes RP=C(NMe_2)$_2$ (**1a**: R = *t*Bu; **1c**: R = *c*-C_6H_{11}) affords the novel η²-1-phosphaallene complexes [η²-{RP=C=C(H)Ph}W(CO)(NO)(η⁵-C_5H_5)] (**14**: R = *t*Bu; **15**: R = *c*-C_6H_{11}) in addition to the carbene complex [(η⁵-C_5H_5)(CO)(NO)W=C(NMe_2)C(Ph)=C(H)-NMe_2] (**16**). Similarly, treatment of [(η⁵-C_5H_5)(CO)(NO)-W=C=CH_2] (**12**) with the phosphaalkenes gives rise to the formation of [η²-{RP=C=CH_2}W(CO)(NO)(η⁵-C_5H_5)] (**17**: R = *t*Bu; **18**: R = *c*-C_6H_{11}). The novel compounds **14**, **15**, **17**, and **18** were characterized by elemental analysis and by spectroscopy (IR, ^{1}H, ^{13}C NMR, MS). Moreover, the molecular structures of **14** and **16** were determined by X-ray diffraction analyses.

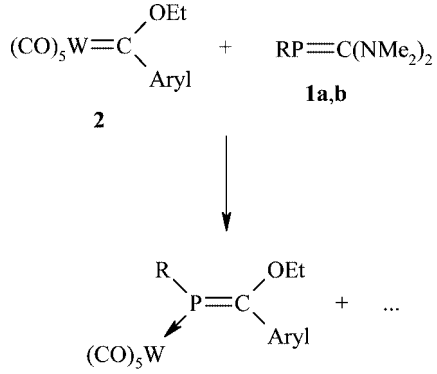
Introduction

Inversely polarized phosphaalkenes (**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 mirrors the bonding in phosphorus ylides **II** (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 be rationalized by considering the zwitterionic structures **I′** and **II′**. Phosphorus ylides are nucleophilic transfer reagents of alkylidene groups to electrophilic functionalities (e.g. Wittig reaction). The combination of phosphorus ylides and aryl(alkoxy)carbene complexes affords enol ethers.[3] Recently, we discovered that the inversely polarized phosphaalkenes RP=C(NMe_2)$_2$ [R = *t*Bu (**1a**), Me_3Si (**1b**)] react with aryl(alkoxy)carbene complexes to yield novel phosphaalkene complexes by a formal transfer of the phosphinidene unit to the carbene ligand (Scheme 2).[4]



3 (R = *t*Bu; Aryl = 2-$MeOC_6H_4$)
4 (Me_3Si; 2-$MeOC_6H_4$)
5 (Me_3Si; 2-MeC_6H_4)

Scheme 2. Reaction of Fischer carbene complexes with inversely polarized phosphaalkenes.

We have since described the smooth transfer of phosphinidine units from phosphaalkenes **1a** (R = *t*Bu) and **1c** (R = Cy) to the electrophilic ligand in the phosphavinylidene complexes **6** and **7** to produce the first η³-1,2-diphosphaallyl complexes (Scheme 3).[5] Similar transformations have been effected with inversely polarized arsaalkenes.[6]

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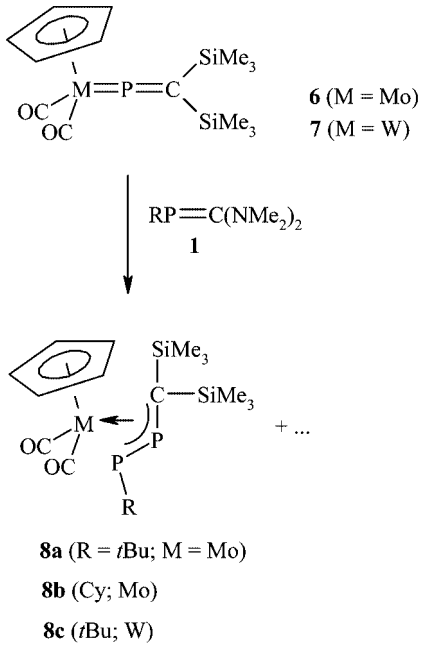
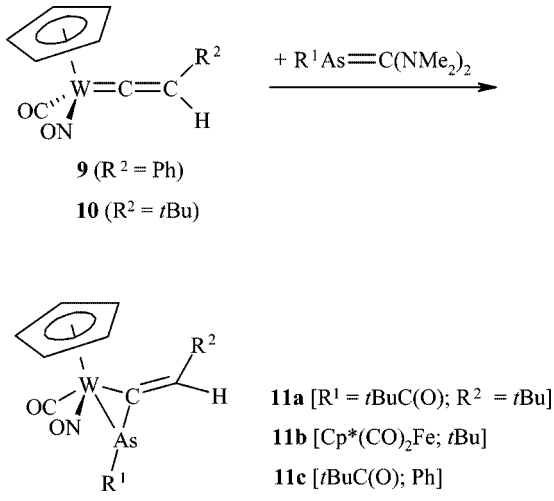


Scheme 3. Formation of 1,2-diphosphaallyl complexes **8a**–**c**.

The obvious next step was to extend our studies on the nucleophilic transfer of phosphinidenes from inversely polarized phosphaalkenes to the electrophilic ligand of vinylidene complexes. This extension seemed particularly promising in light of the previous synthesis of η^2-1-arsaallene complexes **11a**–**c** from vinylidene complexes **9** and **10** and arsaalkenes (Scheme 4).[7]

Moreover, Ipaktschi et al. have succeeded in the transformation of vinylidene complex **12** into η^2-allene complexes **13a**–**c** by treating them with diazomethane and ethyl diazoacetate (Scheme 5).[8] In this contribution we present our results on the smooth phosphinidene transfer from phosphaalkenes **1a** and **1c** to the vinylidene ligands of complexes **9** and **12**.

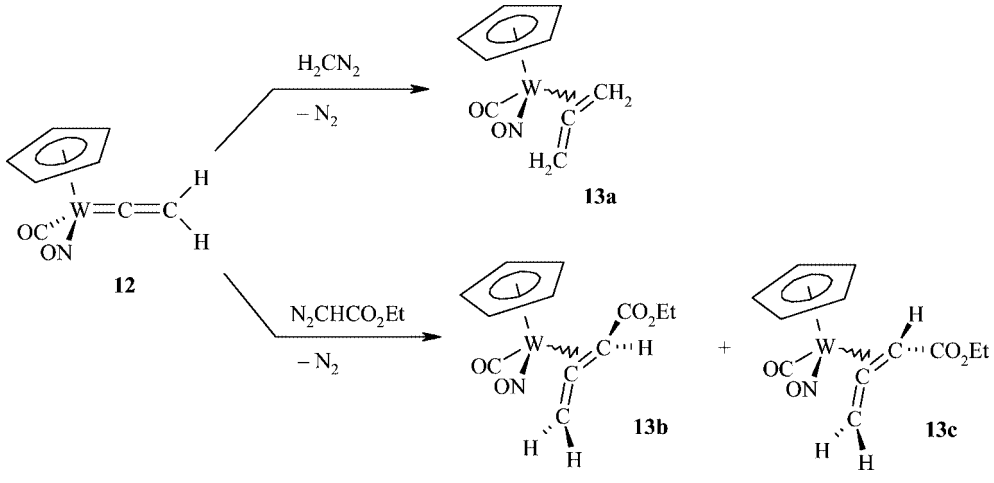


Scheme 4. Synthesis of η^2-1-arsaallene complexes **11a**–**c**.

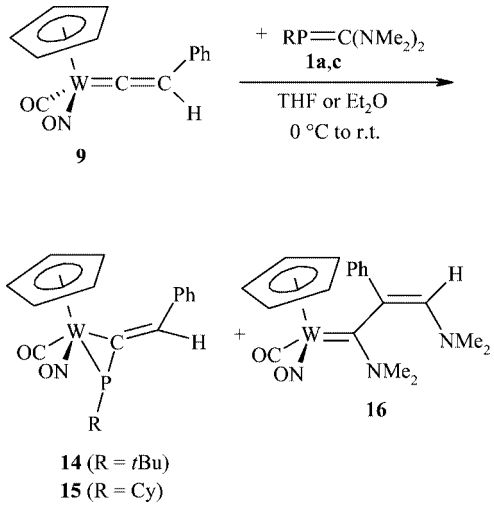
Results and Discussion

Treatment of [Cp(CO)(NO)W=C=C(H)Ph] (**9**)[9] with half a molar equivalent of phosphaalkenes $RP=C(NMe_2)_2$ (**1a**: R = *t*Bu;[4a] **1c**: R = Cy[5]) in tetrahydrofuran (**1a**) or diethyl ether (**1c**) in the range 0 to 20 °C afforded the crystalline η^2-1-phosphaallene complexes **14** (20% yield) and **15** (19% yield), respectively. Purification of the products was effected by column chromatography on Florisil with hexane as an eluent (Scheme 6).

Red, crystalline carbene complex **16** was formed as a by-product in these reactions. During this process it appears that the nucleophilic carbene $C(NMe_2)_2$ is released and attacks a second equivalent of **9**. In keeping with this, if the precursors are employed in a 1:1 molar ratio half of the phosphaalkene remains unaffected. Carbene complex **16** can be eluted from the column with diethyl ether. However, only impure samples were obtained by this method. In a more efficient protocol, the phosphaallene complex **15** was extracted from the solid, red reaction residue with a diethyl ether/pentane mixture and the remaining orange residue

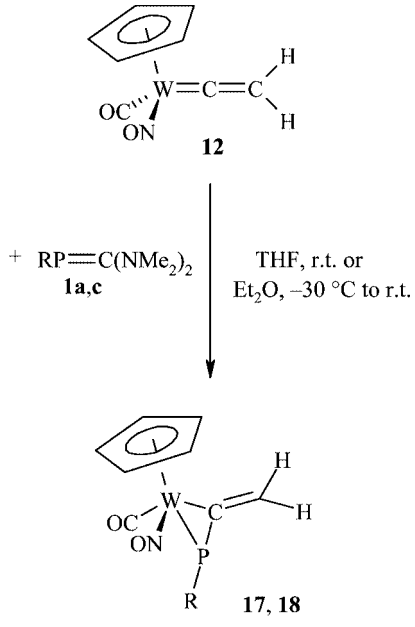


Scheme 5. Synthesis of η^2-allene complexes **13a**–**c** from **12** and diazoalkanes.



Scheme 6. Formation of the 1-phosphaallene complexes **14** and **15** and carbene complex **16**.

was dissolved in a dichloromethane/pentane mixture (3:1). Storage of the filtered solution at 4 °C afforded red crystalline **16**. The air- and moisture-sensitive complexes **14** and **15** are well soluble in saturated hydrocarbon, ethereal, and aromatic solvents. Complex **16** has been generated previously by the treatment of **9** with $[Cp^*(CO)_2FeAs{=}C(NMe_2)_2]$ in 69% yield,[7] and characterized by means of spectroscopy and elemental analyses. Similarly, yellow crystalline **17** resulted from the reaction of phosphaalkene **1a** and vinylidene complex **12**[10] in a molar ratio of 1:2 in thf at 20 °C (Scheme 7). The synthesis of **18** from **12** and **1c** was accomplished in diethyl ether at –30 °C.



Scheme 7. Preparation of the 1-phosphaallene complexes **17** and **18**.

Doublets at δ = 8.66 ($^3J_{P,H}$ = 8.2 Hz) and 8.77 ppm ($^3J_{P,H}$ = 8.8 Hz) in the ^{1}H NMR spectra of **14** and **15**, respectively, can be assigned to the proton of the exocyclic methylene group. In precursor **9** this proton gives rise to singlets at significantly higher field (δ = 6.54 and 6.59 ppm; ratio 4:5).[9] In the unsupported phosphaallene Mes*P=C=C(Ph)H a doublet at δ = 6.67 ($^3J_{P,H}$ = 27 Hz) accounts for this proton.[11] The singlets at δ = 5.81 and 5.84 ppm (ratio 5:4) for the C_5H_5 protons in **9** are markedly deshielded [δ = 4.76 (**14**), 4.79 ppm (**15**)], which is taken as an indication of the improved donor character of the η^2-phosphaallene over the vinylidene ligand in **9**. The resonances at δ = 344.64, 209.2 (210.6), and 130.95 (131.3) ppm in the $^{13}C\{^1H\}$ NMR spectrum of **9** are assigned to C_α, the carbonyl ligands, and C_β in the two isomers, respectively. The C_α atom in the η^2-phosphaallene complexes **14** and **15** is strongly shielded [**14**: δ = 166.5 ppm (d, $^1J_{P,C}$ = 97.7 Hz); **15**: δ = 167.6 ppm (d, $^1J_{P,C}$ = 94.9 Hz)], whereas the C_β atom is slightly deshielded in **14** [δ = 142.2 ppm (d, $^2J_{P,C}$ = 6.9 Hz)] and **15** [δ = 142.2 ppm (d, $^2J_{P,C}$ = 7.4 Hz)]. The C_α and C_β resonances in free phosphaallene Mes*P=C=C(Ph)H are observed as doublets at δ = 239.3 (d, $^1J_{P,C}$ = 25 Hz) and δ = 112.9 (d, $^2J_{P,C}$ = 10 Hz) ppm.[11] The carbonyl ligands in complexes **14** and **15** give rise to doublets at δ = 218.7 ($^2J_{P,C}$ = 16.1 Hz) and 218.8 ppm ($^2J_{P,C}$ = 17.3 Hz). The shift to high field of about 8 ppm in comparison to **9** [δ(CO) = 209.2 (210.6) ppm] is easily explained by the more pronounced donor capacity of the organophosphorus ligand. Pronounced bathochromic shifts of the CO and NO stretching frequencies of **14** and **15** relative to those of **9** additionally support the NMR findings. In the $^{31}P\{^1H\}$ NMR spectra of **14** and **15** singlet resonances appear at δ = –130.0 and –158.0 ppm, in the characteristic region for three-membered, phosphorus-containing rings.[12] A similar situation is encountered for the phosphaalkene complexes **17** and **18**. In the ^{31}P NMR spectra the phosphorus atoms of the three-membered rings give rise to singlets at δ = –124.0 and –153.6 ppm, respectively. Two doublets at δ = 6.48 ($^3J_{P,H}$ = 19.5 Hz) and 7.18 ppm ($^3J_{P,H}$ = 6.9 Hz) in the ^{1}H NMR spectrum of **17** and at δ = 6.46 ($^3J_{P,H}$ = 20.7 Hz) and 7.41 ppm ($^3J_{P,H}$ = 6.9 Hz) account for the magnetically different protons of the terminal methylene unit of **18**. Singlets in the ^{13}C NMR spectrum of the complexes at δ = 126.0 and 125.9 ppm account for the ^{13}C nuclei of these groups. The carbon atom C_α is observed as a doublet at δ = 169.3 ($^1J_{P,C}$ = 94.8 Hz) in **17** and at δ = 172.5 ppm ($^1J_{P,C}$ = 93.6 Hz) in **18**.

X-ray Structural Investigations

Single crystals of **14** suitable for X-ray diffraction analysis were grown from hexane at 4 °C. The analysis (Figure 1) shows a molecule with a distorted piano-stool geometry [P(1)–W(1)–C(1) 72.3(1)°, C(1)–W(1)–N(1) 91.3(2)°, N(1)–W(1)–C(2) 91.8(1)°], with nearly linear carbonyl and nitrosyl ligands [W(1)–C(1)–O(1) 178.8(4)°, W(1)–N(1)–O(2) 174.4(3)].

The most interesting part of the molecule is the 1-phosphaallene ligand, which is unsymmetrically linked to the metal atom in an η^2-fashion by the W(1)–P(1) [2.568(1) Å] and W(1)–C(2) [2.175(4) Å] bonds. The latter bond is

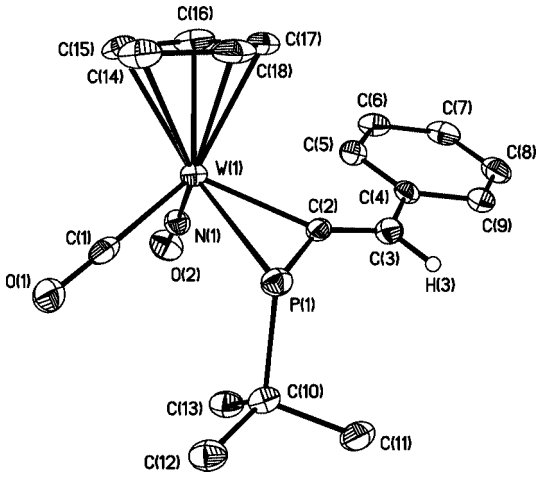
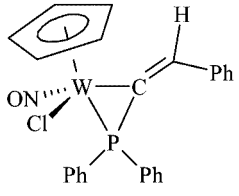


Figure 1. Molecular structure of **14** in the crystal. Selected bond lengths [Å] and angles [°]: W(1)–C(1) 2.007(4), W(1)–N(1) 1.801(3), W(1)–C(2) 2.175(4), W(1)–P(1) 2.568(1), W(1)–C(14–18) 2.335(4) – 2.382(4), P(1)–C(2) 1.742(4), P(1)–C(10) 1.904(4), C(2)–C(3) 1.353(6), C(3)–C(4) 1.468(5); W(1)–C(1)–O(1) 178.8(4), W(1)–N(1)–O(2) 174.4(3), W(1)–C(2)–P(1) 81.1(2), W(1)–C(2)–C(3) 142.2(3), C(2)–W(1)–P(1) 42.1(1), C(2)–W(1)–N(1) 91.8(1), N(1)–W(1)–C(1) 91.3(2), C(1)–W(1)–P(1) 72.3(1), W(1)–P(1)–C(10) 115.1(1), W(1)–P(1)–C(2) 56.8(1), P(1)–C(2)–C(3) 136.7(3), C(10)–P(1)–C(2) 105.3(2).

significantly shorter than the W(1)–C distances of the [C_5H_5W] part of the molecule [2.335(4)–2.382(4) Å]. The W(1)–C(2) bond length is comparable to that in complex **19** [2.178(7) Å],[13] but much smaller than in the (η^3-2-phospha-1-arsaallyl)tungsten complex **20** [2.439(2) Å].[6]



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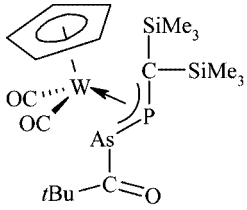
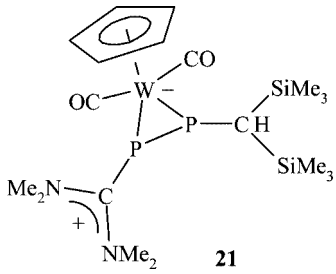


20

Thus, the situation of a π complex involving the W atom and the P=C double bond is not reflected satisfactorily by the structural data of **14**. Moreover, inspection of the W=C bond lengths in a series of carbene–tungsten complexes [1.859(4)–2.23(2) Å][14] reveals some degree of WC multiple bonding in our new complex. A similar observation was made in the molecular structure of **11b**.[7] The W(1)–P(1) separation [2.568(1) Å] markedly exceeds the WP bond length in **19** [2.434(2) Å] and may be compared with the endocyclic WP bond lengths in complexes **21** [2.5352(7) and 2.5695(7) Å][5] or **22** [2.573(4) and 2.582(4) Å].[15]

The endocyclic P(1)–C(2) bond length [1.742(4) Å] may be regarded as being a π-coordinated multiple bond. Generally, unsupported P=C bonds in acyclic phosphaalkenes range from 1.65–1.72 Å,[16] and a value of 1.63 Å has been reported for the P=C distance in the 1-phosphaallene Mes*P=C=CPh_2.[17] The carbon-carbon double bond C(2)–C(3) [1.353(6) Å] is lengthened with respect to that in Mes*P=C=CPh_2 (1.31 Å),[17] and the P(1)–C(2)–C(3) angle



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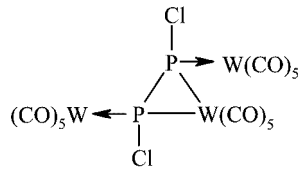

22

of 136.7(3)° is strongly compressed when compared with that in the free 1-phosphaallene (167°). Carbon atoms C(3) and C(4) are located in the plane defined by the atoms W(1), P(1), and C(2), and atom P(1) is roughly placed in a *trans* disposition to the nitrosyl ligand whereas C(2) and the carbonyl group are *trans* oriented.

Wine-red, single crystals of carbene complex **16** were grown by slow diffusion of pentane into a CH_2Cl_2 solution during a period of seven days. The analysis (Figure 2) reveals a molecule with a distorted, three-legged piano-stool geometry [N(1)–W(1)–C(6) 91.6(1)°, N(1)–W(1)–C(7) 101.1(1)°, C(6)–W(1)–C(7) 80.7(1)°] with nearly linear carbonyl and nitrosyl ligands [W(1)–C(6)–O(2) 176.5(2)°, W(1)–N(1)–O(1) 173.7(2)°]

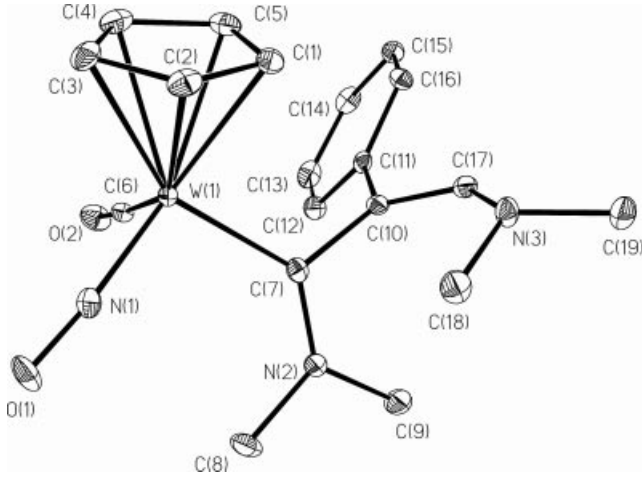

Figure 2. Molecular structure of **16** in the crystal. Selected bond lengths [Å] and angles [°]: W(1)–N(1) 1.802(2), W(1)–C(6) 1.979(2), W(1)–C(7) 2.126(2), W(1)–C(1–5) 2.373(2) – 2.407(2), N(2)–C(7) 1.339(3), N(2)–C(8) 1.478(3), N(2)–C(9) 1.481(3), C(7)–C(10) 1.516(3), C(10)–C(11) 1.491(3), C(10)–C(17) 1.369(3), N(3)–C(17) 1.383(3), N(3)–C(18) 1.437(3), N(3)–C(19) 1.467(3); N(1)–W(1)–C(6) 91.6(1), N(1)–W(1)–C(7) 101.1(1), C(6)–W(1)–C(7) 86.7(1), W(1)–C(7)–N(2) 130.4(2), W(1)–C(7)–C(10) 115.6(1), N(2)–C(7)–C(10) 114.0(2), C(7)–C(10)–C(17) 124.3(1), C(7)–C(10)–C(11) 117.8(2), C(11)–C(10)–C(17) 117.8(2), C(10)–C(17)–N(3) 132.3(2), C(17)–N(3)–C(18) 123.0(2), C(17)–N(3)–C(19) 116.5(2), C(18)–N(3)–C(19) 113.6(2).

The third leg is a dimethylamino vinylcarbene ligand which is attached to the metal by the W(1)–C(7) double bond [2.126(2) Å]. The plane defined by the atoms C(7), C(8), C(9), C(10), and N(2) is nearly coplanar with the vector W(1)–N(1) (torsion angle 7.5°). The contact N(2)–C(7) of 1.339(3) Å represents multiple bonding. An accepted average value for a C_{sp^2}–N_{sp^2} single bond amounts to

1.41 Å.[18] Within the β-aminoalkenyl substituents the C(7)–C(17) bond [1.516(3) Å] has a bond order of unity. The C(10)–C(17) double bond of 1.369(3) Å is lengthened by conjugation with the lone pair at the slightly pyramidalized N(3) atom (sum of angles: 353.1°). As a consequence, the N(3)–C(17) distance [1.383(3) Å] is a shortened single bond. The plane defined by the atoms N(3), C(17), C(10), C(11), and C(7) is oriented nearly orthogonally to the plane of the carbene moiety.

Conclusions

The previously observed transition-metal-induced cleavage of inversely polarized phosphaalkenes to give η^3-1,2-diphosphaallyl complexes[5] has been extended to the smooth generation of η^2-1-phosphaallene complexes **14**, **15**, **17**, and **18**. This reaction underlines the ability of phosphaalkenes to act as convenient sources for phosphanediyl (phosphinidene) units under mild conditions.

Experimental Section

General: All experiments were performed under dry, oxygen-free dinitrogen using standard Schlenk techniques. Solvents were carefully dried with the appropriate drying agent and freshly distilled under N_2 before use. The following compounds were prepared according to literature procedures: [Cp(CO)(NO)W=C=C(H)Ph] (**9**),[9] [Cp(CO)(NO)W=C=CH_2] (**12**),[10] *t*BuP=C(NMe_2)$_2$ (**1a**),[4a] CyP=C(NMe_2)$_2$ (**1c**).[5] IR spectra were recorded with a Bruker FT-IR VECTOR 22 spectrometer. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded at room temperature with a Bruker AM Avance DRX 500 instrument (^{1}H: 500.13, ^{13}C: 125.75, ^{31}P: 202.46 MHz). References: $SiMe_4$ (^{1}H, ^{13}C) and 85% H_3PO_4 (^{31}P). MS: Bruker Esquire Ion Trap mass spectrometer. Florisil was purchased from Merck.

[Cp(CO)(NO)W{η^2-*t*BuP=C=CHPh}] (14): A solution of phosphaalkene **1a** (0.16 g, 0.83 mmol) in thf was added dropwise at 0 °C to a well stirred solution of complex **9** (0.61 g, 1.5 mmol) in thf (15 mL). Stirring was continued at 0 °C for 1 h. The solution was then warmed up to ambient temp. and stirred for another 2.5 h at room temp. The solvents were removed in vacuo to afford a red solid residue. The latter was suspended in hexane (150 mL) and filtered through a pad of Florisil (*l* = 1.5 cm, *d* = 2 cm). A yellow zone was eluted with hexane (4 × 30 mL). Concentration of the elute to about 15 mL and storage at 4 °C for 14 h led to the separation of product **14** as big yellow crystals. (Yield: 0.15 g, 20%). IR (KBr): $\tilde{\nu}$ = 1972 s (CO), 1630 s (NO) cm^{-1}. ^{1}H NMR (C_6D_6): δ = 1.29 (d, $^3J_{P,H}$ = 13.2 Hz, 9 H, *t*Bu), 4.76 (s, 5 H, Cp), 7.12 (t, $^3J_{H,H}$ = 7.5 Hz, 1 H, *p*-H-Ph), 7.26 (t, $^3J_{H,H}$ = 7.5 Hz, 2 H, *m*-H-Ph), 7.70 (d, $J_{H,H}$ = 6.9 Hz, 2 H, *o*-H-Ph), 8.66 [d, $^3J_{P,H}$ = 8.2 Hz, 1 H, =C(*H*)Ph] ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ = 30.4 [d, $^2J_{P,C}$ = 16.1 Hz, C(*C*H$_3$)$_3$], 35.5 [d, $^1J_{P,C}$ = 47.1 Hz, *C*(CH$_3$)$_3$], 96.7 (s, C_5H_5), 127.3 (s, Ph), 128.1 (s, Ph), 128.5 (s, Ph), 139.9 (d, ^3J = 5.7 Hz, *i*-C-Ph), 142.2 (d, $^2J_{P,C}$ = 6.9 Hz, P–C=*C*), 166.5 (d, $^2J_{P,C}$ = 97.7 Hz, P=*C*), 218.7 (d, $^2J_{P,C}$ = 16.1 Hz, CO) ppm. ^{31}P{^{1}H} NMR δ = –130.0 ppm. EI-MS: *m*/*z* 498 [M + H$^+$]. $C_{18}H_{20}NO_2PW$ (497.17): calcd. C 43.49, H 4.05, N 2.82; found C 43.51, H 4.14, N 2.86.

Compound **16** with low purity may be extracted from the column with neat diethyl ether. The preparation of analytically pure **16** in an acceptable yield requires a slightly modified protocol. Thus, a solution of **1a** (0.33 g, 1.75 mmol) in thf (15 mL) was added dropwise to chilled solution of complex **9** (1.45 g, 3.54 mmol) in thf (15 mL). After stirring the reaction mixture for 2.5 h at room temp., solvents and other volatile components were removed in vacuo. The red solid residue was triturated with 32 mL of a diethyl ether/pentane mixture, and then the liquid phase was decanted. The solid was washed with pentane (6 × 10 mL) and dried at 10^{-6} bar. The orange solid was dissolved in a dichloromethane/pentane mixture (3:1), filtered, and the filtrate was stored at +4 °C. Carbene complex **16** separated as red crystals (0.65 g, 36% yield). The spectroscopic data were identical with a sample obtained previously by another method.

[Cp(CO)(NO)W{η^2-CyP=C=CHPh}] (15): A solution of phosphaalkene **1c** (0.24 g, 1.12 mmol) in diethyl ether (30 mL) was slowly added to a chilled solution (0 °C) of complex **9** (0.83 g, 2.03 mmol) in diethyl ether (30 mL). Stirring at 0 °C was continued for 2.5 h before the mixture was warmed to room temp. It was then evaporated to dryness and the orange-red solid residue was suspended in hexane (125 mL). It was filtered through a pad of Florisil (*l* = 1.5 cm, *d* = 2 cm). A yellow zone was eluted with hexane (4 × 30 mL). The elute was concentrated to about 15 mL and stored for 12 h at 4 °C to afford 0.20 g (19%) of orange-yellow crystalline **15**. IR (KBr): $\tilde{\nu}$ = 1990 s (CO), 1625 s (NO) cm^{-1}. ^{1}H NMR (C_6D_6): δ = 0.88–2.29 (br., 11 H, C_6H_{11}), 4.79 (s, 5 H, Cp), 7.11 (t, $^3J_{H,H}$ = 7.2 Hz, 1 H, *p*-H-Ph), 7.24 (t, $^3J_{H,H}$ = 7.5 Hz, 2 H, *m*-H-Ph), 7.71 (d, $^3J_{H,H}$ = 7.5 Hz, 2 H, *o*-H-Ph), 8.77 [d, $^3J_{P,H}$ = 8.8 Hz, =C(*H*)Ph] ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ = 96.7 (s, C_5H_5), 127.3 (s, Ph), 128.1 (s, Ph), 128.5 (s, Ph), 140.1 (d, $^3J_{P,C}$ = 6.2 Hz, *i*-C-Ph), 142.2 (d, $^3J_{P,C}$ = 7.4 Hz, P=C=*C*), 167.6 (d, $^1J_{P,C}$ = 94.9 Hz, P=C), 218.8 (d, $^2J_{P,C}$ = 17.3 Hz, CO) ppm. ^{31}P{^{1}H} NMR δ = –158.0 (s) ppm. EI-MS: *m*/*z* 524.2 [M + H$^+$], 496.2 [M – CO + H$^+$]. $C_{20}H_{22}NO_2PW$ (523.21): calcd. C 45.91, H 4.24, N 2.68; found C 46.04, H 4.27, N 2.67.

[Cp(CO)(NO)W{η^2-*t*BuP=C=CH_2}] (17): A solution of phosphaalkene **1a** (0.11 g, 0.58 mmol) in thf (5 mL) was added dropwise at ambient temp. to a solution of complex **12** (0.37 g, 1.11 mmol) in thf (10 mL). Stirring was continued for 2.5 h before the reaction mixture was evaporated to dryness. The yellow solid residue was chromatographed on a small column charged with Florisil (*l* = 4 cm, *d* = 2 cm). A yellow zone was eluted with hexane/diethyl ether (30:2). The elute was concentrated to 15 mL and stored at 4 °C for 18 h to give **17** as yellow crystals (0.14 g, 30% yield). IR (KBr): $\tilde{\nu}$ = 1979 s (CO), 1618 s (NO) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 1.11 (d, $^3J_{P,H}$ = 13.2 Hz, 9 H, *t*Bu), 5.63 (s, 5 H, Cp), 6.48 (d, $^3J_{P,H}$ = 19.5 Hz, 1 H, =CH_2), 7.18 (d, $^3J_{P,H}$ = 6.9 Hz, 1 H, =CH_2) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 30.2 [d, $^2J_{P,C}$ = 16.2 Hz, C(*C*H$_3$)$_3$], 34.4 [d, $^1J_{P,C}$ = 42.8 Hz, *C*(CH$_3$)$_3$], 96.8 (s, Cp), 126.0 (s, P=C=*C*), 169.3 (d, $^1J_{P,C}$ = 94.8 Hz, P=*C*=C), 217.3 (d, $^2J_{P,C}$ = 12.7 Hz, CO) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = –124.0 ppm. EI-MS: *m*/*z* 422.1 [M + H$^+$]. $C_{12}H_{16}NO_2PW$ (421.08): calcd. C 34.23, H 3.83, N 3.33; found C 33.51, H 3.87, N 3.30.

[Cp(CO)(NO)W{η^2-CyP=C=CH_2}] (18): A solution of phosphaalkene **1c** (0.22 g, 1.04 mmol) in diethyl ether (25 mL) was added dropwise to a chilled solution (–30 °C) of complex **12** (0.62 g, 1.86 mmol) in diethyl ether (30 mL). Stirring was continued at –30 °C for 1 h, and then at room temp. for another 2.5 h. The mixture was evaporated to dryness. The red solid residue was suspended in pentane (150 mL) and filtered through a pad of Florisil (*l* = 1.5 cm, *d* = 2 cm). A yellow zone was eluted with a diethyl ether/pentane mixture (1:3). The elute was concentrated to 20 mL and stored at 4 °C for 14 h, whereby product **18** separated as yellow crystals (0.10 g, 12%). IR (KBr): $\tilde{\nu}$ = 1973 s (CO), 1618 s (NO)

cm^{-1}. ^1H NMR (C_6D_6): δ = 1.10–2.29 (m, 11 H, C_6H_{11}), 4.76 (s, 5 H, Cp), 6.46 (d, $^3J_{P,H}$ = 20.7 Hz, 1 H, =CH_2), 7.41 (d, $^3J_{P,H}$ = 6.9 Hz, 1 H, =CH_2) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 26.4 (s, Cy), 27.2 (d, $J_{P,C}$ = 6.9 Hz, Cy), 27.4 (d, $J_{P,C}$ = 13.9 Hz, Cy), 32.3 (d, $J_{P,C}$ = 6.9 Hz, Cy), 33.6 (d, $J_{P,C}$ = 20.8, Cy), 40.3 (d, $J_{P,C}$ = 40.5 Hz, Cy), 95.5 (s, C_5H_5), 125.9 (s, P=C=*C*), 175.5 (d, $^1J_{P,C}$ = 93.6 Hz, P=C), 219.5 (d, $^2J_{P,C}$ = 15.0 Hz, CO) ppm. $^{31}P\{^1H\}$ NMR δ = –153.6 (s) ppm. EI-MS: *m/z* 448.1 [M^+]. $C_{14}H_{18}NO_2PW$ (447.11): calcd. C 37.61, H 4.06, N 3.13; found C 37.33, H 4.09, N 3.15.

X-ray Crystallography:[19] Crystallographic data were collected with a Nonius KappaCCD diffractometer with Mo-K_α radiation (graphite monochromator, λ = 0.71073 Å) at 100 K. The crystallographic programs used for structure solution and refinement were SHELXS-97 and SHELXL-97. The structures were solved by direct methods and refined by 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 and U(H) = 1.5 U_{eq} for CH_3 groups. The largest difference peaks for **14** are located near W(1) (0.82 and 0.89 Å). Other crystal data for both compounds are listed in Table 1.

Table 1. Crystal data and collection parameters.

	14	**16**
Empirical formula	$C_{18}H_{20}NOPW$	$C_{19}H_{23}N_3O_2W$
M_r [g mol^{-1}]	497.17	509.25
Crystal dimensions [mm]	0.30 × 0.29 × 0.26	0.18 × 0.17 × 0.10
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$
a [Å]	9.9120(3)	9.1310(4)
b [Å]	23.2500(3)	20.026(2)
c [Å]	7.6980(7)	9.9290(9)
β [°]	97.6080(11)	91.245(6)
V [Å^3]	1758.42(17)	1815.2(3)
Z	4	4
$\rho_{calcd.}$ [g m^{-3}]	1.878	1.863
μ [mm^{-1}]	6.668	6.381
F(000)	960	992
Θ [°]	3.00–25.00	2.00–30.00
Reflections collected	34975	73776
Reflections unique	3064	5277
R(int)	0.043	0.0582
Refined parameters	211	230
GOF	1.085	1.021
R_F [$I > 2\sigma(I)$]	0.0244	0.0203
wR_{F^2} [all data]	0.0664	0.0332
$\Delta\rho_{max/min}$ [e Å^{-3}]	2.476/–1.206	0.659/–0.740

CCDC-622264 (for **14**) and -622265 (for **16**) 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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