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Phosphaalkenes $R^1C(O)–P=C(NMe_2)_2$ (R^1=Ph, 4-EtC_6H_4): Versatile Reagents for 1,3-Dipolar Cycloadditions to Phosphenium Complexes $[Cp(CO)_2M = PPh_2]$ (M = Mo, W)

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Reaction of $[Cp(CO)_2M = PPh_2]$ [where M = Mo (**2a**), W (**2b**)] with an excess of the phosphaalkenes aryl$C(O)P=C(NMe_2)_2$ [where aryl = Ph (**3**), 4-EtC_6H_4 (**5**)] afforded the metallophosphaalkenes $[Cp(CO)_2M^a–P=C(aryl)–O–P^bPh_2(M^a–P^b)]$ [where M = Mo, aryl = Ph (**4a**); M = W, aryl = Ph (**4b**); M = Mo, aryl = 4-EtC_6H_4 (**6a**); M = W, aryl = 4-EtC_6H_4 (**6b**)] as orange crystals. Compounds **4a**,**b** and **6a**,**b** were characterized by means of spectroscopy (IR, ^1H, ^{13}C and ^{31}P NMR spectroscopy and MS). Moreover, the molecular structures of **3**, **4a**, and **6b** were determined by X-ray diffraction analysis.

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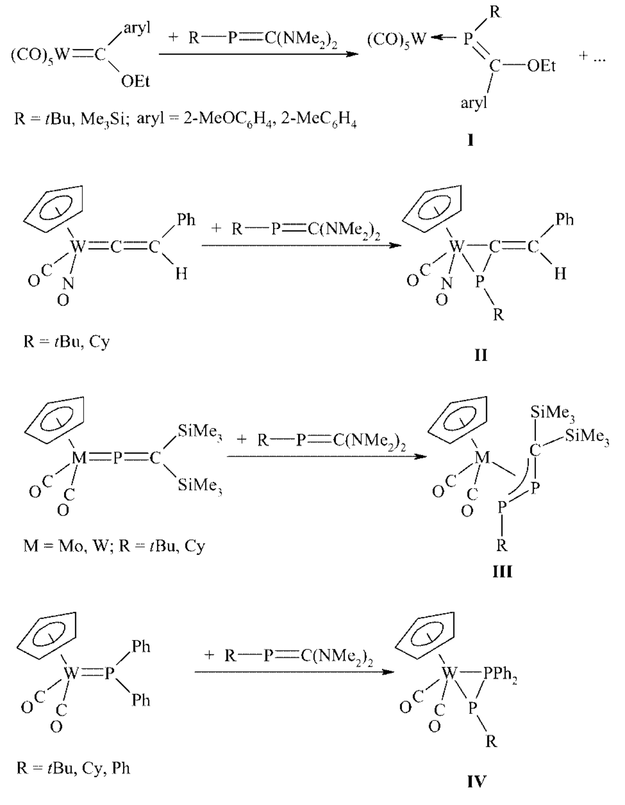
Introduction

During the course of our studies on phosphaalkenes $R–P=C(NMe_2)_2$ (R = *t*Bu, Cy, Ph), we observed a facile metal-assisted cleavage of the PC multiple bond and the formal transfer of phosphanediyls (RP) on suitable complexes with electrophilic ligands.[1] Thus, reaction with selected Fischer carbene complexes gave rise to the formation of coordination compounds **I** with novel η^1-phosphaalkene ligands,[2] whereas treatment with vinylidene complexes resulted in the formation of η^2(P,C)-phosphaallene complexes **II**.[3] η^3-1,2-Diphosphaallyl complexes **III** were obtained from the combination of phosphaalkenes and phosphavinylidene complexes.[4] Only recently we disclosed the generation of η^2-diphosphanyl complexes **IV** by reacting phosphaalkenes and phosphenium complexes[5] (Scheme 1).



Scheme 1. Phosphanediyl-transfer from phosphaalkenes onto selected organometallic electrophiles.

Results and Discussion

The purpose of this work was to study the reactivity of the *P*-benzoylphosphaalkenes $PhC(O)P=C(NMe_2)_2$ (**3**)[6] and 4-$EtC_6H_4C(O)P=C(NMe_2)_2$ (**5**) with the phosphenium complexes $[Cp(CO)_2M = PPh_2]$ (**2a**: M = Mo; **2b**: W). The latter were generated in situ by the dehydrochlorination of the functionalized phosphane complexes $[Cp(CO)_2ClMP(H)Ph_2]$[7] (**1a**: M = Mo; **1b**: W) with diazabicycloundecene (DBU). Phosphaalkene **5** was synthesized as a yellow powder in 81% yield from 4-ethylbenzoylchloride and $Me_3SiP=C(NMe_2)_2$[8] (Scheme 2).

Treatment of freshly prepared complexes **2a**,**b** with an excess of the phosphaalkenes in toluene solution over a temperature range of –30 to 20 °C afforded orange crystalline metallophosphaalkenes **4a**,**b** and **6a**,**b** in modest yields (Scheme 3).

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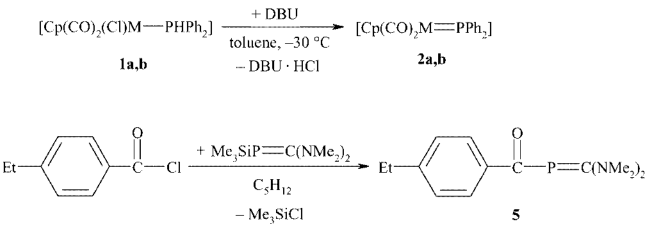
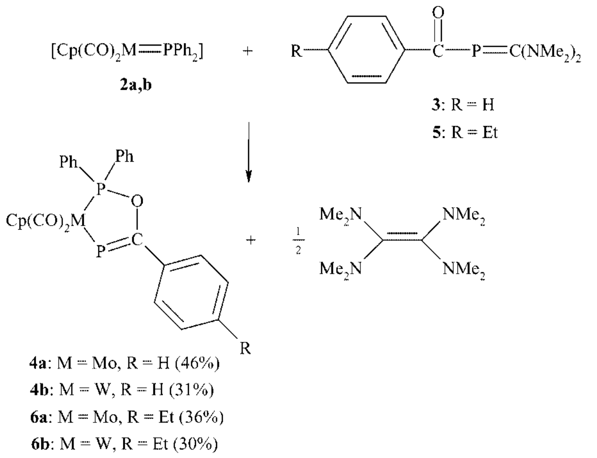


Scheme 2. Preparation of **2a**,**b** and **5**.



Scheme 3. Synthesis of metallophosphaalkenes **4a**,**b** and **6a**,**b**.

Isolation of the products was effected by column chromatography on Florisil with mixtures of pentane/diethylether as the eluents. Subsequent crystallization furnished analytically pure compounds.

The $^{31}P\{^1H\}$ NMR spectra of **4a** and **6a** show two doublets. The tetracoordinate P atoms give rise to signals at δ = 199.9 and 198.7 ppm, whereas the dicoordinate P atoms are observed at markedly lower field [**4a**: 235.5 (d); **6a**: 225.9 (d)] with PP coupling constants of 21.8 and 20.7 Hz, respectively. As expected, the corresponding doublets in tungsten complex **4b** and **6b** are more shielded and appear at δ = 170.7 (d, PPh_2) and 170.1 (d, PPh_2) ppm and δ = 209.4 (d, P=C) and 199.9 (d, P=C) with PP coupling constants of 21.8 and 22.5 Hz. Only tetracoordinate P atoms of **4b** and **6b** exhibit ^{183}W satellites with $^1J_{WP}$ = 329.3 and 330.4 Hz.

In the $^{13}C\{^1H\}$ NMR spectra of the products, the carbon atoms of the P=C bonds give rise to doublets of doublets in the typical low field region [**4a**: δ = 193.6 ppm ($^1J_{PC}$ = 85.6 Hz, $^2J_{PC}$ = 17.8 Hz); **4b**: δ = 192.9 ppm ($^1J_{PC}$ = 82.9 Hz, $^2J_{PC}$ = 18.2 Hz); **6a**: δ = 194.1 ppm ($^1J_{PC}$ = 86.2 Hz, $^2J_{PC}$ = 17.5 Hz); **6b**: δ = 193.4 ppm ($^1J_{PC}$ = 82.8 Hz, $^2J_{PC}$ = 18.4 Hz)]. The $^{13}C\{^1H\}$ NMR spectra of **4a**,**b** and **6a**,**b** show in the region of the carbonyl carbon atoms two markedly separated resonances at δ = 223.9 (s; **4b**, **6b**) and δ = 231.5 (d, $^2J_{PC}$ = 17.5 Hz; **4b**), 231.8 (d, $^2J_{PC}$ = 18.4 Hz; **6b**) and in the molybdenum compounds at δ = 234.3 (d, $^2J_{PC}$ = 12.7 Hz), 241.3 (d, $^2J_{PC}$ = 26.4 Hz) and at 234.3 (d, $^2J_{PC}$ = 12.1 Hz), 241.5 (d, $^2J_{PC}$ = 25.6 Hz) for **4a** and **6a**, respectively. We assign the resonances at higher field to the carbonyl group in the *trans* disposition of the PPh_2 unit. In keeping with the increased donor capability of the phosphaalkenyl group, the resonance of the carbonyl ligand in its *trans* disposition is attributed to the more deshielded signal. The $[M(CO)_2]$ group gives rise to two intense bands in the IR spectra at $\tilde{\nu}$ = 1935–1943 and 1864–1881 cm^{-1}, which are due to the symmetric and asymmetric CO stretching vibrations. Interestingly, the novel bidentate chelating ligand exhibits a decreased donor capacity relative to the η^2-diphosphanido ligand in complexes of the type $[Cp(CO)_2MPR^1–PR^2R^3]$, **IV** ($\tilde{\nu}$ = 1918–1933; 1837–1849 cm^{-1}).[5] The carbonyl vibration of the aryl group in precursor **4** was observed at $\tilde{\nu}$ = 1535 cm^{-1}, and does not show up in the products any longer, which means that it was involved in a cycloaddition process.

X-ray Structural Investigations

Single crystals of phosphaalkene **2** suitable for X-ray diffraction studies were grown from *n*-pentane at –30 °C. The analysis (Figure 1, Table 1) shows a benzoyl-stabilized carbenium phosphanide, in which the planar carbenium center C(8) (sum of angles is 359.6°) displays multiple bonding to planarly configured nitrogen atoms [N(1)–C(8) = 1.344(2) Å, N(2)–C(8) = 1.356(2) Å].

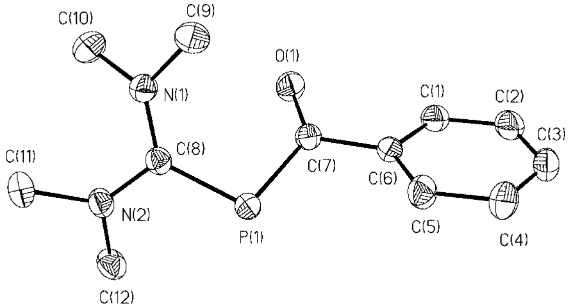


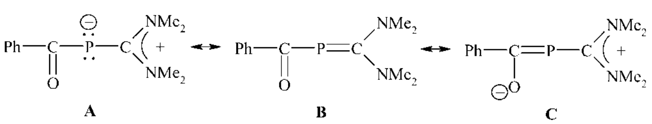
Figure 1. Molecular crystal structure of **2**. Selected bond lengths [Å] and angles [°]: P(1)–C(8) 1.800(1), P(1)–C(7) 1.806(1), O(1)–C(7) 1.240(2), N(1)–C(8) 1.344(2), N(1)–C(9) 1.462(2), N(1)–C(10) 1.468(2), N(2)–C(8) 1.356(2), N(2)–C(11) 1.461(2), N(2)–C(12) 1.457(2), C(6)–C(7) 1.511(2). C(8)–P(1)–C(7) 101.34(6), C(8)–N(1)–C(9) 123.0(1), C(8)–N(1)–C(10) 122.5(1), C(9)–N(1)–C(10) 113.4(1), C(8)–N(2)–C(11) 122.9(1), C(8)–N(2)–C(12) 123.3(1), C(11)–N(2)–C(12) 113.8(1), N(1)–C(8)–N(2) 116.8(1), N(1)–C(8)–P(1) 124.6(1), N(2)–C(8)–P(1) 118.2(1), P(1)–C(7)–O(1) 127.0(1), O(1)–C(7)–C(6) 118.0(1), C(6)–C(7)–P(1) 115.0(1).

The former P=C bond of the precursor [cf. $HP=C(NMe_2)_2$; *d*(P=C) = 1.740(1) Å] is markedly lengthened to 1.800(1) Å. A bond length of 1.806(1) Å is found between the phosphorus atom and the carbon atom of the carbonyl group in **2**, which compares well with the other PC bond of the molecule. Both bonds are best regarded as single bonds. The bonds between the phosphorus atom and the carbon atoms of both carbonyl groups in bis(pivaloyl)-phenylphosphane $[tBuC(O)]_2PPh$, however, are much longer [1.893(4) and 1.922(5) Å].[9] The CO double bond in **2** [1.240(1) Å] is slightly elongated relative to the CO bonds in $[tBuC(O)]_2PPh$ [1.201(6) and 1.217(6) Å]. The backbone of the compound defined by the atoms N(2), C(8), P(1), C(7), and C(6) deviates severely from a plane, as indicated

Table 1. Crystal data and data collection parameters.

Compound	**3**	**4a**	**6b**
Empirical formula	$C_{12}H_{17}N_2OP$	$C_{26}H_{20}MoO_3P_2$	$C_{28}H_{24}O_3P_2W$
M_r [g mol^{-1}]	236.25	538.30	654.26
Crystal dimensions [mm]	1.1 × 1.0 × 0.6	0.27 × 0.16 × 0.07	0.30 × 0.30 × 0.24
Crystal system	monoclinic	monoclinic	triclinic
Space group	$C2/c$	$P2_1/n$	$P\bar{1}$
a [Å]	18.295(7)	9.2032(7)	8.6693(10)
b [Å]	7.867(2)	16.8512(9)	11.5833(14)
c [Å]	17.562(5)	14.8462(9)	13.0253(3)
α [°]	90	90	90.573(6)
β [°]	96.62(3)	95.457(5)	103.736(5)
γ [°]	90	90	101.577(16)
V [Å^3]	2510.8(14)	2292.0(3))	1242.4(2)
Z	8	4	2
$\rho_{calcd.}$ [g cm^{-3}]	1.250	1.560	1.749
μ [mm^{-1}]	0.201	0.738	4.806
F(000)	1008	1088	640
θ [°]	2.24–30.00	3.01–27.50	3.23–30.00
refl. collected	3720	37211	45461
refl. unique	3619	5237	7238
R (int)	0.0262	0.0294	0.0553
Refined parameters	213	289	309
GOF	1.067	1.079	1.091
R_F [$I > 2\sigma(I)$]	0.0404	0.0215	0.0155
wR_{F2} [all Data]	0.1073	0.0489	0.0388
$\Delta\rho$ max/min [e Å^{-3}]	0.521/–0.350	0.406/–0.496	0.686/–0.771

by the torsion angles O(1)–C(7)–P(1)–C(8) (–16.2°) and C(6)–C(7)–P(1)–C(8) (167.3°) and an interplanar angle of 40.5° between the plane defined by the atoms N(1),N(2), C(8) and P(1), C(7), C(8). From the X-ray structural data it can be concluded that compound **2** is best described by the zwitterionic limiting formula **A** and not by **B** or **C** (Scheme 4).



Scheme 4. Canonical formulae for phosphaalkene **3**.

Single crystals of **4a** suitable for X-ray diffraction analysis were grown from *n*-pentane at +4 °C. The analysis (Figure 2, Table 1) displays a molecule with a distorted four-legged piano-stool geometry [C(6)–Mo(1)–C(7) 78.79(7)°, C(6)–Mo(1)–P(2) 72.86(5)°, C(7)–Mo(1)–P(1) 80.57(5)°, P(1)–Mo(1)–P(2) 70.86(1)°] with two nearly linear carbonyl ligands [Mo(1)–C(6)–O(1) 177.9(2), Mo(1)–C(7)–O(2) 177.8(2)°]. The remaining two legs are represented by a 1,4,2-diphosphaoxabuten-3-yl ligand, which is chelating the metal atom through bonds Mo(1)–P(1) [2.3754(4) Å] and Mo(1)–P(2) [2.5602(5) Å]. The latter bond length compares well to the Mo–P distance in the metallophosphaalkene [$Cp(CO)_3Mo–P=C(SiMe_3)_2$] [2.568(1) Å].[10] The bond length between the metal atom and the tetracoordinated phosphorus atom of 2.3754(4) Å is slightly longer than the Mo–P contact in [$Cp(CO)_2Mo^a–PMe_2–C^b(SiMe_3)_2(Mo^a–C^b)$] [2.348(2) Å].[11]

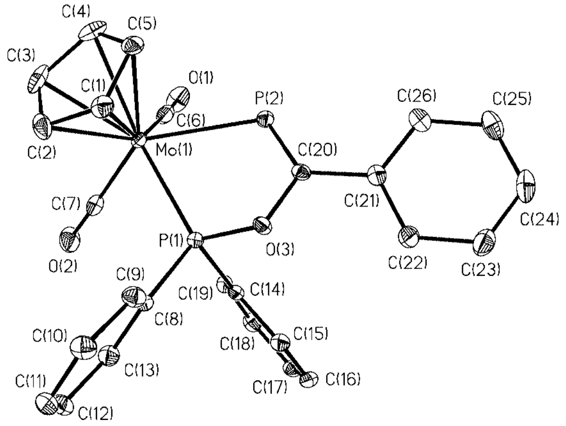


Figure 2. Molecular crystal structure of **4a**. Selected bond lengths [Å] and angles [°]: Mo(1)–C(6) 1.974(2), Mo(1)–C(7) 1.971(2), Mo(1)–P(1) 2.3754(4), Mo(1)–P(2) 2.5602(5), P(2)–C(20) 1.707(2), C(20)–O(3) 1.402(2), C(20)–C(21) 1.472(2), P(1)–O(3) 1.666(1), P(1)–C(8) 1.819(2), P(1)–C(14) 1.830(2); C(6)–Mo(1)–C(7) 78.8(1), C(6)–Mo(1)–P(2) 72.9(1), C(7)–Mo(1)–P(1) 80.6(1), P(1)–Mo(1)–P(2) 70.86(1), Mo(1)–P(1)–O(3) 112.51(4), P(1)–O(3)–C(20) 107.5(1), O(3)–C(20)–P(2) 121.7(1), Mo(1)–P(2)–C(20) 105.3(1), O(3)–C(20)–C(21) 112.7(1), P(2)–C(20)–C(21) 125.3(1), Mo(1)–C(6)–O(1) 177.9(2), Mo(1)–C(7)–O(2) 177.8(2)°.

Repulsion between the lone pair of electrons at P(2) and the electron-rich Mo atom may be responsible for the increased bond length relative to the Mo(1)–P(1) distance. This novel chelating ligand features the double bond P(2)–C(20) [1.707(2) Å], which compares well to the PC separation in the ferriophosphaalkene [$Cp(CO)_2Fe–P=C(OSiMe_3)t$Bu] [1.701(4) Å],[12] but it is markedly longer than that in the molybdophosphaalkene [$Cp(CO)_3Mo$–

$P{=}C(SiMe_3)_2$] [1.665(3) Å]. The contact P(1)–O(3) [1.666(1) Å] is shorter than the sum of the covalent radii (1.76 Å) but still reflects a bond order of unity.[13] Bond C(20)–O(3), which in precursor **2** exists as a carbonyl group with a bond length of 1.240(2) Å, is lengthened to a single bond of length 1.402(2) Å. The metalloheterocycle is slightly puckered (sum of endocyclic angles 517.9°).

Single crystals of **6b** were grown from *n*-pentane/diethyl ether at + 4 °C (Figure 3). Like **3a**, this complex has the geometry of a four-legged piano stool [C(6)–W(1)–C(7) 79.1(1), C(6)–W(1)–P(2) 72.9(1), C(7)–W(1)–C(7) 79.9(1), P(1)–W(1)–P(2) 72.77(2)°]. A 1,4,2-diphosphaoxabuten-3-yl ligand chelates the tungsten atom through bonds W(1)–P(1) [2.3632(5) Å] and W(1)–P(2) [2.5556(5) Å]. The former bond length is slightly shorter than the coordinative W–P bond in **7** [2.432(2) Å][7] or **8** [2.434(2) Å].[14]

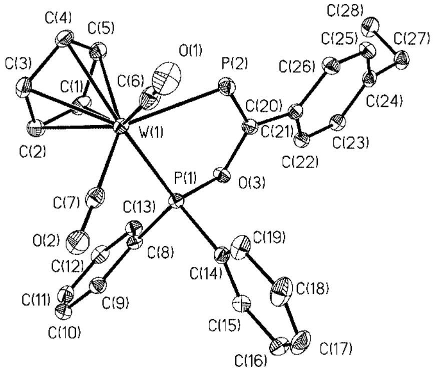
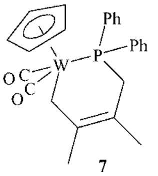


Figure 3. Molecular crystal structure of **6b**. Selected bond lengths [Å] and angles [°]: W(1)–C(6) 1.980(2), W(1)–C(7) 1.966(2), W(1)–P(1) 2.3632(5), W(1)–P(2) 2.5556(5), P(2)–C(20) 1.700(2), C(20)–O(3) 1.402(2), C(20)–C(21) 1.468(2), P(1)–C(8) 1.824(2), P(1)–C(14) 1.827(2); C(6)–W(1)–C(7) 79.1(1), C(6)–W(1)–P(2) 74.0(1), C(6)–W(1)–P(1) 116.2(1), C(7)–W(1)–P(1) 79.9(1), C(7)–W(1)–P(2) 127.1(1), P(1)–W(1)–P(2) 72.77(2), W(1)–P(1)–O(3) 113.64(4), P(1)–O(3)–C(20) 111.2(1), O(3)–C(20)–P(2) 121.7(1), W(1)–P(2)–C(20) 105.3(1), O(3)–C(20)–C(21) 112.0(1), P(2)–C(20)–C(21) 126.1(1), W(1)–C(6)–O(1) 177.4(2), W(1)–C(7)–O(2) 178.8(2).



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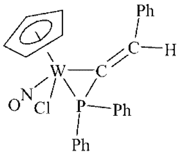

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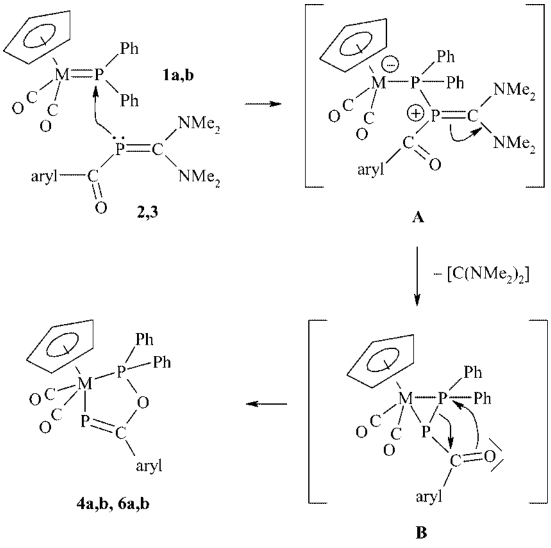
Bonding parameters within the chelating ligand of **6b** are close to those in **4a** and merit no particular discussion at this point. The five-membered metalloheterocycle of **6b** is more flattened (sum of endocyclic angles 529.6°) relative to that of **4a** (517.9°).

Mechanisms

It is conceivable that the path towards the formation of complexes **4a**, **4b**, **6a**, and **6b** begins with nucleophilic attack of phosphaalkenes **2**,**3** by its electron-abundant phosphorus atom at the phosphenium center of **1a**,**b**, which affords zwitterion **A**. Release of a carbene unit and metal–phosphorus bond formation then affords intermediate **B**. Finally, ring enlargement leads to the final products; however, intermediates **A** and **B** were not detected by ^{31}P NMR spectroscopic monitoring of the reaction (Scheme 5).



Scheme 5. Proposed mechanism for the synthesis of **4a**,**b** and **6a**,**b**.

Conclusions

Transition-metal-induced cleavage of inversely polarized phosphaalkenes with concomitant transfer of the phosphanediyl unit on carbene- or phosphenium ligands to give η^1-phosphaalkene[2] and η^2-diphosphanido complexes[5] have previously been described. Here the smooth generation of complexes **4a**,**b** and **6a** featuring the chelating 1,4,2-diphosphaoxabutene-3-yl ligand underlines the ability of phosphaalkenes to act as convenient sources for phosphanediyl units under mild conditions.

Experimental Section

General: All experiments were performed under a dry, oxygen-free nitrogen atmosphere by using standard Schlenk techniques. Solvents were carefully dried with an appropriate drying agent and freshly distilled under an atmosphere of N_2 before use. The following compounds were prepared according to literature procedures: $[Cp(CO)_2ClMo{-}PHPh_2]$ (**1a**),[7] $[Cp(CO)_2ClW{-}PHPh_2]$ (**1b**),[7] $PhC(O)P{=}C(NMe_2)_2$ (**3**),[6] and $Me_3SiP{=}C(NMe_2)_2$.[8] Diazabicycloundecene (DBU), 4-$EtC_6H_4C(O)Cl$, and Florisil (0.150–0.250 mm) were purchased commercially. IR spectra were recorded with a Bruker FTIR VECTOR 22 spectrometer. ^1H-, ^{13}C-, and ^{31}P NMR spectra were recorded at room temp. with a Bruker AM Avance DRX 500 instrument. References: $SiMe_4$ (^1H, ^{13}C) and 85% H_3PO_4 (^{31}P). MS was conducted with a Bruker Esquire Ion trap mass spectrometer autospec, sector field.

4-$EtC_6H_4C(O)P{=}C(NMe_2)_2$ (5): A solution of $Me_3SiP{=}C(SiMe_3)_2$ (0.25 g, 1.20 mmol) in *n*-pentane (20 mL) was added dropwise at –30 °C to the solution of 4-$EtC_6H_4C(O)Cl$ (0.20 g, 1.20 mmol) in *n*-pentane(20 mL), whereby a yellow precipitate formed. Stirring was continued at –30 °C for 1 h. The cold slurry was filtered, and the filtercake was washed with cold *n*-pentane (3 × 20 mL, –30 °C). The filtercake was dried at 10^{-3} bar to afford **5** as a bright yellow powder (yield: 0.26 g, 81%). ^{1}H NMR (500.13 MHz, C_6D_6): δ = 0.99 (t, $^{3}J_{\mathrm{HH}}$ = 7.5 Hz, 3 H, CH_2CH_3), 2.36 (q, $^{3}J_{\mathrm{HH}}$ = 7.5 Hz, 2 H, CH_2CH_3), 2.59 (s, 12 H, NCH_3), 7.05 (m, 2 H, *m*-H-Ph), 8.54 (m, 2 H, *o*-H-Ph) ppm. ^{13}C{^{1}H} NMR (125.75 MHz, C_6D_6): δ = 15.7 (s, CH_2CH_3), 29.0 (s, CH_2CH_3), 42.8 (d, $^{3}J_{\mathrm{PC}}$ = 4.6 Hz, NCH_3), 126.9 (s, Ph), 127.0 (s, Ph), 142.9 (d, $^{2}J_{\mathrm{PC}}$ = 48.3 Hz, *i*-C-Ph), 147.1 (s, *p*-C-Ph), 200.2 (d, $^{1}J_{\mathrm{PC}}$ = 78.2 Hz, P=*C*), 215.4 (d, $^{1}J_{\mathrm{PC}}$ = 78.2 Hz, PC=O) ppm. ^{31}P{^{1}H} NMR (202.46 MHz, C_6D_6): δ = 30.8 (s) ppm. IR (KBr): $\tilde{\nu}$ = 1535 [s (CO)] cm^{-1}. MS (EI): *m*/*z* = 264 [M]$^+$, 133 [4 – EtC_6H_4CO]$^+$, 131 [P=C(NMe_2)$_2$]$^+$, 105 [4 – EtC_6H_4]$^+$. $C_{14}H_{21}N_2OP$ (264.30): calcd. C 63.62, H 8.01, N 10.60; found C 63.13, H 8.15, N 10.60.

[Cp(CO)$_2$Mo^a–P=C(Ph)O–P^{b}Ph$_2$(*Mo^a–P^b*)] (4a): A solution of [Cp(CO)$_2$ClMoPHPh$_2$] (**1a**; 0.80 g, 1.82 mmol) in toluene (40 mL) was added dropwise to a chilled solution (–30 °C) of PhC(O)-P=C(NMe_2)$_2$ (**3**; 1.29 g, 5.46 mmol) and DBU (0.42 g, 2.76 mmol) in toluene (30 mL). After 2 h, the addition was complete, and stirring at –30 °C was continued for 1 h. The mixture was then warmed to room temp. and stirred overnight. Solvent and volatile components were removed in vacuo. To the residue was added Florisil (3 g) and toluene (15 mL), and the slurry was evaporated to dryness. The remaining powder was brought on a column filled with Florisil and pentane (*l* = 5 cm, *d* = 2 cm). First the column was developed with pentane/diethyl ether (30:1) to separate a yellow zone. This zone was eluted with pentane/diethyl ether (30:5, ca. 250 mL). Concentration of the elute to ca. 120 mL and storage for 12 h at –30 °C furnished product **4a** as orange crystals (yield: 0.45 g, 46%). ^{1}H NMR (500.13 MHz, C_6D_6): δ = 4.56 (s, 5 H, Cp), 6.80–7.08 (m, 9 H, Ph), 7.64 (m, 2 H, Ph), 7.81 (m, 2 H, Ph), 8.23 (m, 2 H, Ph) ppm. ^{13}C{^{1}H} NMR (125.75 MHz, C_6D_6): δ = 93.0 (s, C_5H_5), 125.4, 125.5, 127.9, 128.1, 128.3, 128.4, 128.5, 128.6, 128.7, 129.8, 129.9, 130.3, 131.7, 132.4, 132.5, 137.9 (s, Ph), 138.2 (m, Ph), 141.7, 142.1 (s, Ph), 193.6 (dd, $^{1}J_{\mathrm{PC}}$ = 85.6 Hz, $^{2}J_{\mathrm{PC}}$ = 17.8 Hz, P=C), 234.3 (d, $^{2}J_{\mathrm{PC}}$ = 12.7 Hz, CO), 241.3 (d, $^{2}J_{\mathrm{PC}}$ = 26.4 Hz, CO) ppm. ^{31}P{^{1}H} NMR (202.46 MHz, C_6D_6): δ = 199.3 (d, $^{2}J_{\mathrm{PP}}$ = 21.8 Hz, PPh$_2$), 235.5 (d, $^{2}J_{\mathrm{PP}}$ = 21.8 Hz, P=C) ppm. IR (KBr): $\tilde{\nu}$ = 1943 [s (CO)], 1874 [s (CO)] cm^{-1}. MS (EI): *m*/*z* = 540 [M]$^+$, 484 [M – 2 CO]$^+$. $C_{26}H_{20}MoO_3P_2$ (538.32): calcd. C 58.01, H 3.74; found C 57.20, H 3.42.

[Cp(CO)$_2$W^a–P=C(Ph)O–P^{b}Ph$_2$(*W^a–P^b*)] (4b): A solution of [Cp(CO)$_2$ClWPHPh$_2$] (**1b**; 0.86 g, 1.63 mmol) in toluene (40 mL) was added dropwise (2 h) to a cold solution (–10 °C) of PhC(O)-P=C(NMe_2)$_2$ (**3**; 0.39 g, 1.63 mmol) and DBU (0.42 g, 2.76 mmol) in toluene (20 mL). The mixture was warmed to ambient temperature and stirred for 12 h. Volatile components were removed in vacuo, and the oily residue was combined with Florisil (2 g) and toluene and then chromatographed on Florisil as described above. A yellow zone was eluted with pentane/diethyl ether (3:2, ca. 300 mL). The elute was concentrated, and the residue was crystallized from toluene/pentane (1:1, 20 mL) at –30 °C over 24 h. The product separated as orange crystals (yield: 0.31 g, 31%). ^{1}H NMR (500.13 MHz, C_6D_6): δ = 4.55 (s, 5 H, Cp), 6.82 (m, 1 H, Ph), 6.89 (m, 2 H, Ph), 6.99–7.11 (m, 6 H, Ph), 7.64 (m, 2 H, Ph), 7.81 (m, 2, Ph), 8.24 (m, 2 H, Ph) ppm. ^{13}C{^{1}H} NMR (125.75 MHz, C_6D_6): δ = 91.6 (s, C_5H_5), 125.6, 125.8, 130.0, 130.1, 130.4, 131.8, 132.9, 133.0 (s, Ph), 192.9 (dd, $^{1}J_{\mathrm{PC}}$ = 82.9 Hz, $^{2}J_{\mathrm{PC}}$ = 18.2 Hz, P=C), 223.9 (s, CO), 231.5 (d, $^{2}J_{\mathrm{PC}}$ = 17.5 Hz, CO) ppm. ^{31}P{^{1}H} NMR (202.46 MHz, C_6D_6): δ = 170.7 (d, J_{PP} = 21.8 Hz, $^{1}J_{\mathrm{WP}}$ = 329.3 Hz, PPh$_2$), 209.4 (d, $^{2}J_{\mathrm{PP}}$ = 21.8 Hz, P=C) ppm. IR (KBr): $\tilde{\nu}$ = 1935 [s (CO)], 1864 [s (CO)] cm^{-1}. MS (EI): *m*/*z* = 626 [M]$^+$, 570 [M – CO]$^+$. $C_{26}H_{20}O_3P_2W$ (626.22): calcd. C 49.87, H 3.22; found C 48.97, H 3.10.

[Cp(CO)$_2$Mo^a–P=C(4-Et-C$_6$H$_4$)O–P^{b}Ph$_2$(*Mo^a–P^b*)] (6a): As described above, solutions of [Cp(CO)$_2$ClMoPHPh$_2$] (**1a**; 0.68 g, 1.55 mmol) in toluene (30 mL), 4-EtC_6H_4C(O)P=C(NMe_2)$_2$ (**5**; 0.41 g, 1.55 mmol), and DBU (0.36 g, 2.33 mmol) in toluene (20 mL) were combined at –30 °C. Stirring was continued for 1 h at –30 °C and 12 h at 20 °C. The solvent and the volatile components were removed in vacuo, and the residue was chromatographed on Florisil. A yellow zone was eluted with a pentane/diethyl ether (10:3, ca. 350 mL). The elute was concentrated to ca. 50 mL and stored at –30 °C for 12 h. Product **6a** separated as orange crystals (yield: 0.32 g, 36%). ^{1}H NMR (500.13 MHz, C_6D_6): δ = 0.98 (t, $^{3}J_{\mathrm{HH}}$ = 7.5 Hz, 3 H, CH_2CH_3), 2.31 (q, $^{3}J_{\mathrm{HH}}$ = 7.5 Hz, 2 H, CH_2CH_3), 4.59 (s, 5 H, Cp), 6.84 (m, 1 H, Ph), 6.89–6.91 (m, 4 H, Ph), 7.05–7.11 (m, 4 H, Ph), 7.66 (m, 2 H, Ph), 7.84 (m, 2 H, Ph), 8.19 (m, 2 H, Ph) ppm. ^{13}C{^{1}H} NMR (125.75 MHz, C_6D_6): δ = 15.6 (s, CH_2CH_3), 28.9 (s, CH_2CH_3), 93.0 (s, C_5H_5), 125.6, 125.8, 128.3, 128.4, 128.7, 128.8, 129.9, 130.1, 131.7, 132.5, 132.6 (s, Ph), 194.1 (dd, $^{1}J_{\mathrm{PC}}$ = 86.2 Hz, $^{2}J_{\mathrm{PC}}$ = 17.5 Hz, P=C), 234.3 (d, $^{2}J_{\mathrm{PC}}$ = 12.1 Hz, CO), 241.5 (d, $^{2}J_{\mathrm{PC}}$ = 25.6 Hz, CO) ppm. ^{31}P{^{1}H} NMR (202.46 MHz, C_6D_6): δ = 198.7 (d, $^{2}J_{\mathrm{PP}}$ = 20.7 Hz, PPh$_2$), 225.9 (d, $^{2}J_{\mathrm{PP}}$ = 20.7 Hz, P=C) ppm. IR (KBr): $\tilde{\nu}$ = 1942 [s (CO)], 1881 [s (CO)] cm^{-1}. MS (EI): *m*/*z* = 568 [M]$^+$, 540 [M – CO]$^+$, 512 [M – 2 CO]$^+$. $C_{28}H_{24}MoO_3P_2$ (566.38): calcd. C 59.38, H 4.27; found C 59.50, H 4.24.

[Cp(CO)$_2$W^a–P=C(4-Et-C$_6$H$_4$)O–P^{b}Ph$_2$(*W^a–P^b*)] (6b): As described above, a solution of [Cp(CO)$_2$ClWPHPh$_2$] (**1b**; 0.91 g, 1.73 mmol) in toluene (40 mL) was combined with a mixture of 4-EtC_6H_4C-(O)P=C(NMe_2)$_2$ (**5**; 0.47 g, 1.78 mmol) and DBU (0.36 g, 2.33 mmol) in chilled toluene (20 mL, –10 °C). After stirring at room temp. for 14 h, the mixture was evaporated to dryness, and the residue was chromatographed on Florisil. A yellow zone was eluted with pentane/diethyl ether (10:3, 250 mL; then 2:1, 200 mL). The elute was concentrated to ca. 120 mL and stored at –30 °C for 24 h, whereby product **6b** separated as yellow crystals (yield: 0.34 g, 30%). ^{1}H NMR (500.13 MHz, C_6D_6): δ = 0.98 (t, $^{3}J_{\mathrm{HH}}$ = 7.5 Hz, 3 H, CH_2CH_3), 2.31 (q, $^{3}J_{\mathrm{HH}}$ = 7.5 Hz, 2 H, CH_2CH_3), 4.58 (s, 5 H, Cp), 6.83 (m, 1 H, Ph), 6.91 (m, 4 H, Ph), 7.03–7.11 (m, 3 H, Ph), 7.68 (m, 2 H, Ph), 7.84 (m, 2 H, Ph), 8.23 (m, 2 H, Ph) ppm. ^{13}C{^{1}H} NMR (125.75 MHz, C_6D_6): δ = 15.6 (s, CH_2CH_3), 28.9 (s, CH_2CH_3), 91.6 (s, C_5H_5), 125.8, 125.9, 127.9, 128.3, 128.4, 128.6, 128.7, 130.1, 130.2, 130.4, 131.7, 132.9, 133.1, 135.7, 135.9, 136.0, 137.6, 138.0, 141.4, 141.8, 144.9, 145.0 (s, Ph), 193.4 (dd, $^{1}J_{\mathrm{PC}}$ = 82.8 Hz, $^{2}J_{\mathrm{PC}}$ = 18.4 Hz, P=C), 223.9 (br., CO), 231.8 (d, $^{2}J_{\mathrm{PC}}$ = 18.4 Hz, CO) ppm. ^{31}P{^{1}H} NMR (202.46 MHz, C_6D_6): δ = 170.1 (d, J_{PP} = 22.5 Hz, J_{PW} = 330.4 Hz, PPh$_2$), 199.9 (d, J_{PP} = 22.5 Hz, P=C) ppm. IR (KBr): $\tilde{\nu}$ = 1935 [s (CO)], 1870 [s (CO)] cm^{-1}. MS (EI): *m*/*z* = 654 [M]$^+$, 626 [M – CO]$^+$, 598 [M – 2 CO]$^+$. $C_{28}H_{24}O_3P_2W$ (654.28): calcd. C 51.40, H 3.69; found C 51.47, H 3.51.

X-ray Crystallography: Crystallographic data for **3** was collected with a Siemens P3 diffractometer with Mo-K_α at 173 K, data for **4a** and **6b** were collected with a Nonius Kappa CCD diffractometer with Mo-K_α (graphite monochromator, λ = 0.71073 Å) at 100 K. Crystallographic programs used for the structure solution and refinement were from SHELX-97.[15] The structures were solved by direct methods and 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 for **3** were refined isotropically, for **4a** and **6b** they were included at calculated positions with $U(\mathrm{H}) = 1.2\,U_{\mathrm{eq}}$ for CH_2 groups, $U(\mathrm{H}) = 1.5\,U_{\mathrm{eq}}$ for CH_3 groups. Crystal data of the compounds are listed in Table 1.[16]

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[16] CCDC-141724, -644445, and -644446 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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