# Synthesis of the first Pentacarbonyltungsten(0) Complexes with *P*-Pentamethylcyclopentadienyl-substituted 1*H*-Phosphirene Ligands: Crystal Structure of $[\{(Me_5C_5\overline{PC(H)=C}Ph\}W(CO)_5]$

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*Dedicated to Professor Reinhard Schmutzler on the Occasion of his 70th Birthday*

**Abstract.** The tungsten(0) complex $[\{Me_5C_5\overline{PC(Ph)=N}\}W(CO)_5]$ (**1**) reacts upon heating with alkyne derivatives **3a−e** in toluene to form benzonitrile and the complexes $[\{Me_5C_5\overline{PC(R^1)=C}(R^2)\}$-W(CO)5] (**4a−e**) (**4a**: $R^1$ = OEt, $R^2$ = H; **4b**: $R^1$ = OEt, $R^2$ = $SiMe_3$; **4c**: $R^1$ = Ph, $R^2$ = H; **4d** : $R^1$ = Ph, $R^2$ = Ph; **4e**: $R^1$, $R^2$ = Et), which were purified by column chromatography (except **4d**). In reaction of **1** with **3d** the tungsten(0) complex **5**, having a 2,3-dihydro-1,2,3-azadiphosphete ligand, is formed in a competing reaction. Spectroscopic and mass spectrometric data of complexes **4a−c, 4e** and **5** are discussed. The structures of complexes **4c** and **5** were determined by single-crystal X-ray diffraction In **4c** the three-membered ring has a C=C bond length of 1.312(3) Å and a C−P−C angle of 43.02(9)°. In **5** the P−P bond length is 2.2866(7) Å; the four-membered ring is slightly folded (fold angle 15° about P1−C6).

**Keywords:** Phosphorus heterocycles; 1*H*-Phosphirene complexes; Phosphinidene complexes; Tungsten

# Synthese der ersten Pentacarbonylwolfram(0)-Komplexe mit *P*-Pentamethylcyclopenta-dienyl-substituierten 1*H*-Phosphiren-Liganden: Kristallstruktur von $[\{(Me_5C_5\overline{PC(H)=C}Ph\}W(CO)_5]$

**Inhaltsübersicht.** Der Wolfram(0)-Komplex $[\{Me_5C_5\overline{PC(Ph)=N}\}$-$W(CO)_5]$ (**1**) reagiert beim Erwärmen mit den Alkinderivaten **3a−e** in Toluol zu Benzonitril und den Komplexen $[\{Me_5C_5\overline{PC(R^1)=C}(R^2)\}$-W(CO)5] (**4a−e**) (**4a**: $R^1$ = OEt, $R^2$ = H; **4b**: $R^1$ = OEt, $R^2$ = $SiMe_3$; **4c**: $R^1$ = Ph, $R^2$ = H; **4d** : $R^1$ = Ph, $R^2$ = Ph; **4e**: $R^1$, $R^2$ = Et), die bis auf **4d** säulenchromatographisch gereinigt und isoliert wurden. Im Fall der Reaktion von **1** mit **3d** entsteht in einer Konkurrenzreaktion der Wolfram(0)-Komplex **5**, der einen 2,3-Dihydro-1,2,3-azadiphosphet-Liganden aufweist. Spektroskopische und massenspektrometrische Daten der Komplexe **4a−c, 4e** und **5** werden diskutiert. Die Strukturen der Komplexe **4c** und **5** konnten durch Einkristall-Röntgendiffraktometrie aufgeklärt werden. In **4c** hat der Dreiring eine C=C-Bindungslänge von 1.312(3) Å und einen C−P−C-Winkel von 43.02(9)°. In **5** weist die P−P-Bindung eine Länge von 2.2866(7) Å auf; der Vierring ist leicht gefaltet (Faltwinkel um P1−C6: 15°).

## 1 Introduction

The chemistry of 1*H*-phosphirene complexes [1, 2] dates back to 1982, when the first synthesis was described by *Marinetti* and *Mathey* [3]. Since then numerous derivatives have been described including those with *P*- [4] and *C*-bonded [5] functional groups. Surprisingly, no stable derivative having a pentamethylcyclopentadienyl group (hereafter denoted as Cp*) bonded to phosphorus has been described, although such complexes could have interesting coordination properties. In 1999, we obtained a polycyclic phosphirane complex and proposed a *P*-Cp*-substituted 1*H*-phosphirene complex as highly reactive intermediate [6]. We decided to return to this problem and to investigate thermal reactions of the tungsten(0) complex $[\{Me_5C_5\overline{PC(Ph)=N}\}$-$W(CO)_5]$ (**1**) with alkyne derivatives; the results will be reported hereafter. Furthermore, we report the first structure of a *P*-Cp*-substituted 1*H*-phosphirene complex and of a 2,3-dihydro-1,2,3-azadiphosphete complex.

## 2 Preparative and Spectroscopic Results

### 2.1 Synthesis

Thermal reaction of $[\{Me_5C_5\overline{PC(Ph)=N}\}W(CO)_5]$ (**1**) [7] in toluene at 65 °C in the presence of alkynes **3a−e** yielded benzonitrile and the 1*H*-phosphirene tungsten complexes

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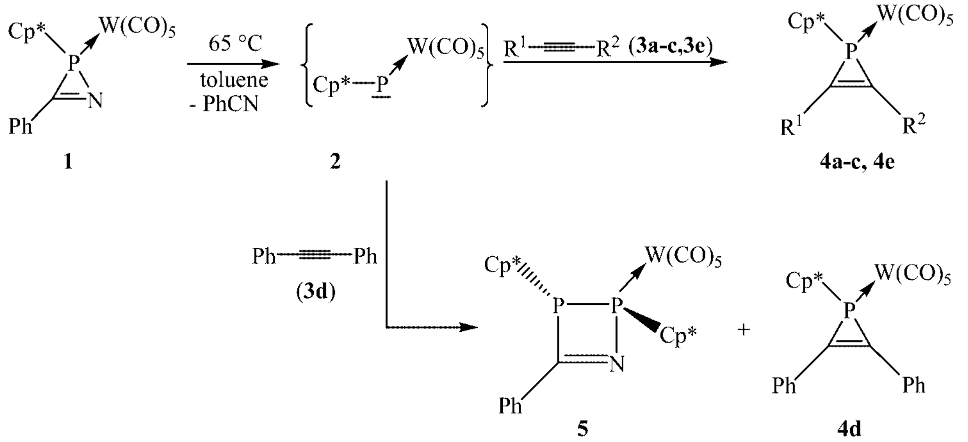


**Scheme 1** Synthesis of tungsten complexes **4a-e** and **5**.

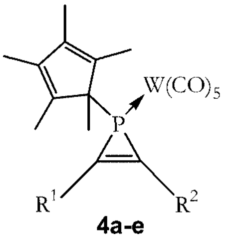
**4a−e** via [2+1]-cycloaddition of the transiently formed terminal phosphinidene complex **2** with **3a−e** [*cf.* 6, 8] (Scheme 1); complexes **4a−c** and **4e** were isolated using column chromatography at low temperature (Table 1). Unfortunately, complex **4d** was only identified by $^{31}$P NMR spectroscopy because considerable amounts of complex **5** were formed in this case, thus leading to separation problems. Although the competing reaction that leads to complex **5** could be largely suppressed by enhancing the **1**:**3d** ratio from 1:1 to 1:5 − thus decreasing the content of **5** from 55 to 25 % −, we were not able to isolate **4d**. It is noteworthy that if the [2+1]-cycloaddition reaction of the transiently formed terminal phosphinidene complex **2** is sterically hindered, as in the case of **3d**, then the formation of the tungsten complex **5** can be favored.

In contrast to complexes **4a,b** and **4d,e,** which remained stable under the reaction conditions, complex **4c** underwent further reactions upon prolonged heating, thus yielding two new products at $\delta$ ($^{31}$P) = −111.9 ($|^1J(W,P)|$ = 222.7 Hz) and −140.3 ($|^1J(W,P)|$ = 266.4 Hz), which were not separable. The former might be assigned to a complex with a polycyclic phosphorus ligand (*cf.* [6]), whereas the latter is attributable to a 1*H*-phosphirene complex with a transformed *P*-substituent.

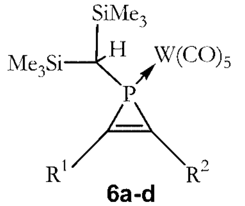
### *2.2 NMR spectroscopic and mass spectrometric results*

The 1*H*-phosphirene complexes show the expected $^{31}$P and $^{13}$C NMR parameter of the nuclei of the three-membered ring, which are displayed in Table 1 and 2 together with those of the closely related complexes **6a** [5a], **6b** [5b] and **6c** [9] and **6d** [9]. It is remarkable that, in comparison to **6**, all complexes **4** show more deshielded $^{31}$P nuclei and slightly decreased $|^1J(^{183}W,^{31}P)|$ values. Within each series, steric and electronic effects on the resonances are in accordance with trends of previously reported derivatives [1, 2, 5, 9].

**Table 1** $^{31}$P NMR data[a)] of *P*-Cp*- und *P*-CH(SiMe$_3$)$_2$-substituted 1*H*-phosphirene tungsten complexes **4a-e** and **6a** [5a]**, 6b** [5b] and **6c** [9] and **6d** [9].[b)]



**4a-e**



**6a-d**

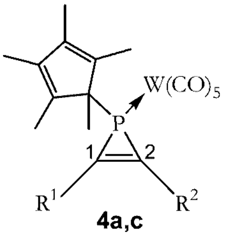
| **4/6** | R$^1$ | R$^2$ | $\delta$ $^{31}$P | $|^1J(^{183}W,^{31}P)|$ | $\delta$ $^{31}$P | $|^1J(^{183}W, ^{31}P)|$ |
|---|---|---|---|---|---|---|
| **a** | OEt | H | −82,8 | 262,7 | −90,8 | 268,0 |
| **b** | OEt | SiMe$_3$ | −100,6 | 264,8 | −110,5 | 273,5 |
| **c** | Ph | H | −129,7 | 266,0 | −136,8 | 272,1 |
| **d** | Ph | Ph | −129,8* | 264,5*) | −134,6 | 268,6 |
| **e** | Et | Et | −134,7 | 259,7 | − | − |

[a)] CDCl$_3$, *) toluene with a D$_6$-benzene capillary tube; $\delta$ in ppm; J in Hz; [b)] **6e** is unknown.

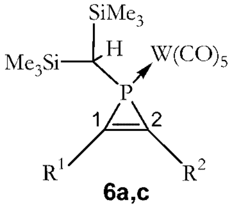
Complexes **4** and **6** show characteristically small phosphorus-carbon coupling constant magnitudes − as one might expect in such cases because only sums of the two scalar couplings $^1J(P,C)$ and $^2J(P,C)$, most probably having opposite signs [10], were determined. The $^{13}$C resonances of complexes **4a** and **6a** clearly indicate a π-donating electron interaction of the ethoxy-oxygen atom lone pair with the double bond π-system, e.g., thus leading to strongly shielded C$^2$ nuclei. This is further supported by a comparison of the $^1$H resonances of **4a** and **4c** $\delta$ ($^1$H) = 6,4, $|J(^{31}P, ^1H)|$ = 17,2 Hz (**4a**) and $\delta$ ($^1$H) = 8,5, $|J(^{31}P, ^1H)|$ = 20,9 Hz (**4c**).

Mass spectrometric investigations (EI) of complexes **4a−c** showed that ring cleavage of the three-membered ring does not occur upon ionization. There are two major fragmentation pathways of the radical cations: 1) extrusion of one (and subsequently more) CO units and 2) the cleavage of the exocyclic P−C bond, leading to the Cp* radical cat-

**Table 2** Comparison of selected $^{13}$C NMR data [a)] of the nuclei of the three-membered ring of 1*H*-phosphirene complexes **4a,c** with those of complexes **6a** [5a] and **6c** [9].



**4a,c**



**6a,c**

| **4/6** | R$^1$ | R$^2$ | $\delta^{13}C^1$ ($\lvert J(P,C^1)\rvert$) | $\delta^{13}C^2$ ($\lvert J(P,C^2)\rvert$) | $\delta^{13}C^1$ ($\lvert J(P,C^1)\rvert$) | $\delta^{13}C^2$ ($\lvert J(P,C^2)\rvert$) |
|---|---|---|---|---|---|---|
| **a** | OEt | H | 156,6 (5,0) | 84,3 *) | 158,8 (2,0) | 88,1 (4,9) |
| **c** | Ph | H | 141,6 (19,7) | 120,0 (13,0) | 145,8 (17,9) | 124,7 (6,5) |

[a)] CDCl$_3$; δ in ppm; J in Hz; *) multiplet, J was not determined

ion and its fragments. In the case of complex **5** two fragmentation pathways of the radical cation are especially interesting: the cleavage of the P−Cp* bond and/or the P−W bond (a) yielding m/z 300, which is tentatively assigned to the ion $[(Cp^*\overline{PPhC{=}NP})^+]$, and the cleavage of the four-membered ring (b) to give m/z 197, which is attributed to $[(Cp^*P_2)^+]$. All assignments are based on the comparison of simulated and measured isotope patterns and masses.

## 3 Crystal Structures of Complexes 4c and 5

The molecular structures of complexes **4c** and **5** were unambiguously established by X-ray diffraction studies. For selected bond lengths and angles see Figures 1 and 2. Characteristic structural features of the three-membered ring of the 1*H*-phosphirene complex **4c** are the very acute endocyclic angle at phosphorus of 43,02(9)° and the two endocyclic P−C bonds (P−C6 1,793(2) and P−C7 1,786(2) Å), which are close in length to the corresponding bonds of **6c** (P−C6 1,799(5) Å and P−C7 1,775(5) Å) [5a]. The C6−C7 distance of complex **4c** (1,312(3) Å) is in the range of values of "standard" $C_{sp2}-C_{sp2}$ bonds, e.g., in acyclic derivatives (1,322 Å) and cyclopropenes (1,294 Å) [11]) and virtually identical with the value of the corresponding bond of **6b** (1,311(7) Å) [5b]).

The parameters of the $[(Me_5C_5P)W(CO)_5]$ moiety, such as the angle W−P−C8 (124,38(0)°, the P−C8 distance (1,884(2) Å) and the W−P distance (2,5137(5) Å), are close to the values of $[\{Me_5C_5PC(Ph){=}N\}W(CO)_5]$ (**1**) (127,01(8)°), 1,852(5) and 2,4720(12) Å) [7]), but the values of **1** point to a different bonding situation**;** the ground state of **1** may be best represented by two structures: 1) a side-on nitrile complex to phosphorus of the phosphinidene complex moiety and 2) a covalent three-membered ring system.

The centred structural feature of complex **5** is the four-membered ring of the 2,3-dihydro-1,2,3-azadiphosphete ligand (Figure 2), which is slightly folded (mean deviation 0.07 Å; fold angle about P1···C6 15 %, distance of P1 from the plane N−C6−P2 0.41 Å).

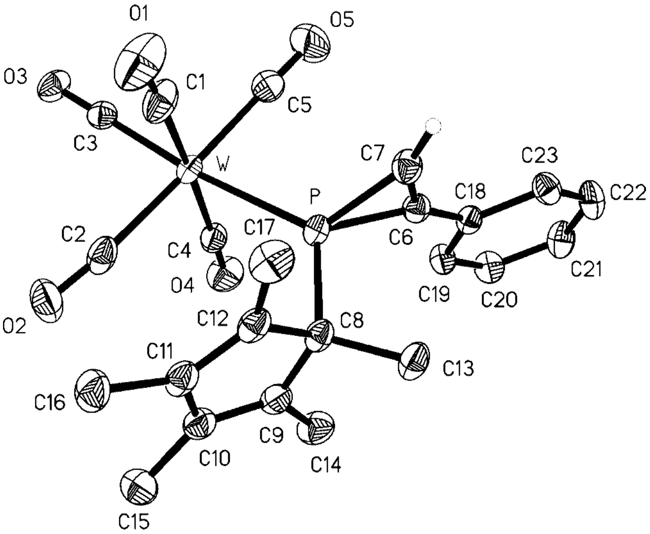


**Figure 1** Molecular structure of complex **4c** in the crystal (ellipsoids represent 50 % probability, hydrogen atoms (except at C7) are omitted for clarity). Selected bond lengths [Å] and angles [°]:

W-P 2,5137(5), P-C7 1,786(2), P-C6 1,793(2), P-C8 1,884(2), C6-C7 1,312(3), C6-C18 1,462(3); C6-P-C7 43,02(9), C6-C7-P 68,75(13), C7-C6-P 68,23(13), C6-P-C8 110,14(9), C7-P-C8 108,81(10).

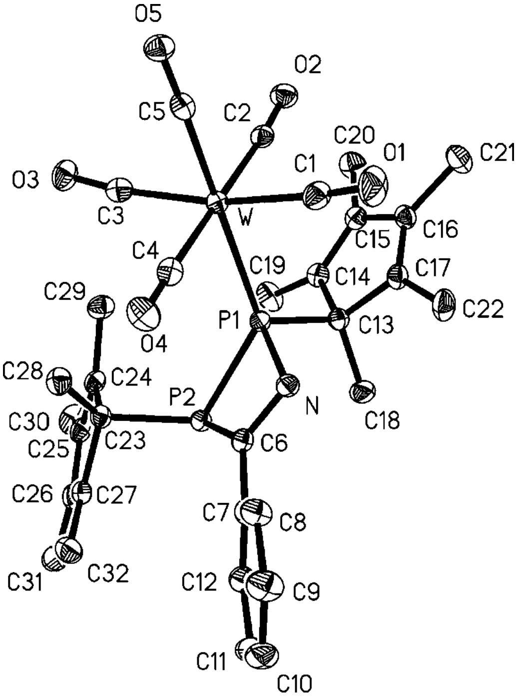


**Figure 2** Molecular structure of complex **5** in the crystal (ellipsoids represent 50 % probability, hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]:

W-P1 2,5481(5), P1-P2 2,2866(7), P2-C6 1,862(2), P1-N 1,7534(17), C6-N 1,307(3); N-P1-P2 78,36(6), C6-P2-P1 69,61(6), N-C6-P2 108,11(14), C6-N-P1 101,92(14).

The P1−P2 bond (2,2866(7) Å) is only slightly widened in comparison to complex **7** (**7**: 2,258(8) Å [12]), but represents a significantly lengthened P−P single bond (standard value 2,21 Å [11]). The dihedral angle between the four- and the six-membered rings is 33°.

Currently, studies on the coordination chemistry of *P*-Cp*-substituted 1*H*-phosphirene complexes are underway.

## Experimental Part

All reactions and manipulations were carried out under an atmosphere of deoxygenated dry nitrogen, using standard Schlenk techniques with conventional glassware. Solvents were dried according to standard procedures. − NMR spectra were recorded on a Bruker AC-200 spectrometer (200 MHz for $^{1}H$; 50.3 MHz for $^{13}C$; 81.0 MHz for $^{31}P$) using [D]chloroform, [$D_2$]methylenedichloride and [$D_6$]benzene as solvent and internal standard; shifts are given relative to ext. tetramethylsilane ($^{1}H$, $^{13}C$) and 85 % $H_3PO_4$ ($^{31}P$); only coupling constant magnitudes are given. − Electron impact (EI) (70 eV) chemical ionization (CI) (ammonia or methane), and fast atom bombardement (FAB) (Xenon) mass spectra were recorded on a double focusing mass spectrometer Finnigan MAT-8430. − Infrared spectra were recorded on a Biorad FT-IR 165 (selected data given). Ultraviolett/vis spectra were recorded on a Hewlett Packard HP 8452. − Melting points were obtained on a Büchi 535 capillary apparatus. − Elemental analyses were performed using a Carlo Erba analytical gaschromatograph. − The *κP*-notation in the nomenclature is intended to differentiate between P- and N-coordination of the appropriate heterocycle to the metal.

### General procedure for the preparation of complexes $[\{Me_5C_5\overline{PC(R^1)=C}(R^2)\}W(CO)_5]$ (4a−e)

To a solution of 0,30 g (0.5 mmol) $[\{(Me_5C_5\overline{PC(Ph)=N}\}W(CO)_5]$ (**1**), dissolved in toluene (1.8 mL), the appropriate alkyne derivative **3a**, **3b** [15] or **3c−e** (2,5 mmol each) was added and the solution heated at 65 °C for 60−90 min ($^{31}P$ NMR control) with slow stirring. All volatile components were removed in vacuo (ca. 0.01 mbar) and the products separated by low-temperature column chromatography (neutral $Al_2O_3$, −50 °C, 15 x 2 cm, *n*-pentane/diethyl ether (1. 95:5 and 2. 90:10)). Evaporation of the first yellow fractions yielded complexes **4a, c** and **4e** as yellow solids, **4b** as yellow oil; crystallisation from *n*-pentane yielded pale-yellow crystals.

### $[\{Me_5C_5\overline{PC(OEt)=C}H\}W(CO)_5]$ (4a)

Starting material: 0,30 mL (2,5 mmol) EtOC≡CH (**3a**); Yield: 0,10 g (34 %), m.p.: 84 °C (decomp).
Elemental analysis for $C_{19}H_{21}O_6PW$ (560,18 g/mol): Calc. C 40,74; H 3,78; found: C 40,62; H 3,70 %.

**$^{1}$H-NMR**: $\delta$ = 0,89 (d, $^{3}J_{PH}$ = 13,6 Hz, 3H, Cp*(C1)-$CH_3$), 1,46 (dt, $^{3}J_{HH}$ = 7,1 Hz, $^{4}J_{PH}$ = 0,3 Hz, 3H, $OCH_2CH_3$), 1,84 (m, 12H, Cp*-$CH_3$), 4,33 (dq, $^{3}J_{HH}$ = 7,1 Hz, $^{3}J_{PH}$ = 3,0 Hz, 2H, $OCH_2CH_3$), 6,37 (d, $^{2}J_{PH}$ = 17,2 Hz, 1H, *H*-C=C). **$^{13}$C{$^{1}$H}-NMR**: $\delta$ = 10,8 (m, Cp*-$CH_3$), 11,7 (m, Cp*-$CH_3$), 14,8 (s, $OCH_2CH_3$ ), 17,2 (m, Cp*(C1)-$CH_3$), 63,6 (d, $^{1}J_{PC}$ = 38,6 Hz, Cp*-$C_{Ring}$(C1)), 71,0 (d, $^{3}J_{PC}$ = 3,4 Hz, $OCH_2CH_3$), 84,3 (m, H-*C*=C), 134,8 (s, Cp*-$C_{Ring}$), 135,3 (s, Cp*-$C_{Ring}$), 141,0 (s, Cp*-$C_{Ring}$), 141,3 (s, Cp*-$C_{Ring}$), 156,6 (d, $^{1+2}J_{PC}$ = 5,0 Hz, EtO-*C*=C), 196,0 (d, $^{2}J_{PC}$ = 8,1 Hz, *cis*-CO), 198,4 (d, $^{2}J_{PC}$ = 32,1 Hz, *trans*-CO) **$^{31}$P{$^{1}$H}-NMR**: $\delta$ = −82,8 ($s_{Sat}$, $^{1}J_{WP}$ = 262,7 Hz). **MS** (70 eV, $^{184}$W): *m*/*z* = 560 (16) [$M^+$], 504 (15) [$(M\text{-}2CO)^+$], 425 (25) [$(M\text{-}Cp^*)^+$], 419 (30) [$(M\text{-}5CO\text{-}H)^+$], 369 (62) [$(M\text{-}Cp^*\text{-}2CO)^+$], 341 (100) [$(M\text{-}Cp^*\text{-}3CO)^+$], 135 (48) [$(Cp^*)^+$], 119 (60) [$(Cp^*\text{-}Me\text{-}H)^+$], 105 (50) [$(Cp^*\text{-}2Me)^+$], 91 (42) [$(Cp^*\text{-}2Me-CH_2)^+$].

### $[\{Me_5C_5\overline{PC(OEt)=C}(SiMe_3)\}W(CO)_5]$ (4b)

Starting material: 0,60 g (2,5 mmol) EtOC≡C$SiMe_3$ [13] (**3b**) (50 % toluene solution); Yield: 0,09 g (28 %), yellow oil. Elemental analysis for $C_{22}H_{29}O_6PSiW$ (632.36 g/mol): Calc. C 41,79; H 4,62; found: C 41,61; H 4,50 %.

**$^{13}$C{$^{1}$H}-NMR**: $\delta$ = 1,0 (s, Si-$CH_3$), 10,4 (d, $^{3}J_{PC}$ = 2,4 Hz, Cp*(C2/5)-$CH_3$), 11,4 (d, $^{3}J_{PC}$ = 3,4 Hz, Cp*(C2/5)-$CH_3$), 11,6 (s, Cp*(C3/4)-$CH_3$), 11,8 (s, Cp*(C3/4)-$CH_3$), 15,2 (s, $OCH_2CH_3$) 17,2 (d, $J_{PC}$ = 3,3 Hz, Cp*(C1)-$CH_3$), 63,6 (d, $^{2}J_{PC}$ = 18,6 Hz, Cp*-$C_{Ring}$(C1)), 70,9 (s, $Me_3Si$-*C*=C), 135,1 (d, $J_{PC}$ = 6,0 Hz, Cp*-$C_{Ring}$), 135,6 (d, $J_{PC}$ = 2,8 Hz, Cp*-$C_{Ring}$), 140,5 (d, $J_{PC}$ = 7,0 Hz, Cp*-$C_{Ring}$), 141,0 (d, $J_{PC}$ = 6,1 Hz Cp*-$C_{Ring}$), 166,8 (d, $^{2}J_{PC}$ = 8,2 Hz, EtO-*C*=C), 196,3 (d, $^{2}J(_{PC}$ = 7,9 Hz, *cis*-CO), 198,4 (d, $^{2}J_{PC}$ = 31,9 Hz, *trans*-CO). **$^{31}$P{$^{1}$H}-NMR**: $\delta$ = −100,6 (s, $^{1}J_{WP}$ = 264,8 Hz).

### $[\{Me_5C_5\overline{PC(Ph)=C}H\}W(CO)_5]$ (4c)

Starting material: 0,30 mL (2,5 mmol) PhC≡CH (**3c**); Yield: 0,11 g (36 %), m.p.: 122 °C (decomp).
Elemental analysis for $C_{23}H_{21}O_5PW$ (592,22 g/mol): Calc. C 46,65; H 3,57; found: C 46,78; H 3,67 %.

**$^{1}$H-NMR**: $\delta$ = 0,77 (d, $^{3}J_{PH}$ = 14,3 Hz, 3H, Cp*(C1)-$CH_3$), 1,97 (m, 12H, Cp*-$CH_3$), 7,59 (m, 3 H, Ph), 7,85 (m, 2H, Ph), 8,51 (d, $^{2}J_{PH}$ = 20,9 Hz, 1 H, *H*-C=C). **$^{13}$C{$^{1}$H}-NMR**: $\delta$ = 10,7 (d, $^{3}J_{PC}$ = 3,1 Hz, Cp*(3/4)-$CH_3$), 11,4 (d, $^{3}J_{PC}$ = 3,1 Hz, Cp*(3/4)-$CH_3$), 11,7 (d, $^{2}J_{PC}$ = 4,9 Hz, Cp*(2/5)-$CH_3$), 11,8 (d, $^{2}J_{PC}$ = 5,2 Hz, Cp*(2/5)-$CH_3$), 17,9 (d, $^{3}J_{PC}$ = 3,1 Hz, Cp* (C1)-$CH_3$), 62,8 (d, $^{1}J_{PC}$ = 15,6 Hz, Cp*(C1)-$C_{Ring}$), 120,0 (d, $^{1}J_{PC}$ = 13,0 Hz, H-*C*=C), 127,6 (d, $^{2}J_{PC}$ = 7,4 Hz, *i*-Ph), 129,1 (s, *m*-Ph), 129,7 (d, $^{3}J_{PC}$ = 3,0 Hz, *o*-Ph), 131,0 (s, *p*-Ph), 135,4 (d, $^{3}J_{PC}$ = 10,0 Hz, Cp*(C3/4)-$C_{Ring}$), 135,5 (d, $^{3}J_{PC}$ = 11,4 Hz, Cp*(C3/4)-$C_{Ring}$), 141,0 (d, $^{2}J_{PC}$ = 16,5 Hz, Cp*(C2/5)-$C_{Ring}$), 141,1 (d, $^{2}J_{PC}$ = 17,3 Hz, Cp*(C2/5)-$C_{Ring}$), 141,6 (d, $^{1+2}J_{PC}$ = 19,7 Hz, Ph-*C*=C), 196,1 (d, $^{2}J_{PC}$ = 8,2 Hz, *cis*-CO), 198,1 (d, $^{2}J_{PC}$ = 32,5 Hz, *trans*-CO). **$^{31}$P{$^{1}$H}-NMR**: $\delta$ = −129,7 ($s_{Sat}$, $^{1}J_{WP}$ 266,0 Hz). **MS** (70 eV, $^{184}$W): *m*/*z* = 592 (27) [$M^+$], 564 (3) [$(M\text{-}CO)^+$], 536 (17) [$(M\text{-}2CO)^+$], 508 (13) [$(M\text{-}3CO)^+$], 480 (4) [$(M\text{-}4CO)^+$], 452 (100) [$(M\text{-}5CO)^+$], 429 (37) [$(M\text{-}Cp^*\text{-}CO)^+$], 401 (51) [$(M\text{-}Cp^*\text{-}2CO)^+$], 373 (66) [$(M\text{-}Cp^*\text{-}3CO)^+$], 317 (44) [$(M\text{-}Cp^*\text{-}5CO)^+$], 135 (27) [$(Cp^*)^+$], 119 (37) [$(Cp^*\text{-}Me\text{-}H)^+$], 105 (32) [$(Cp^*\text{-}2Me)^+$], 91 (27) [$(Cp^*\text{-}2Me-CH_2)^+$].

### $[\{Me_5C_5\overline{PC(Ph)=C}(Ph)\}W(CO)_5]$ 4d

Starting material: 0.45 g (2,5 mmol) PhC≡CPh (**3d**): product **4d** was not isolated.

**$^{31}$P{$^{1}$H}-NMR**: $\delta$ = −129,3 ($s_{Sat}$, $^{1}J_{WP}$ = 264,5 Hz).

### $[\{Me_5C_5\overline{PC(Et)=C}(Et)\}W(CO)_5]$ (4e)

Starting material: 0.25 mL (2,5 mmol) EtC≡CEt (**3e**); Yield: 0,09 g (21 %).
Elemental analysis for $C_{21}H_{25}O_5PW$ (572,23 g/mol): Calc.: C 44,08, H 4,40, found: C 44,48, H 4,69 %.

**$^{1}$H-NMR**: $\delta$ = 0,75 (d, $^{3}J_{PH}$ = 13,6 Hz, 3H, Cp*(C1)-$CH_3$), 1,43 (t, $^{3}J_{HH}$ = 7,5 Hz, 6H, $CH_2CH_3$), 1,88 (d, $^{4}J_{PH}$ = 4,3 Hz, 6H, Cp*(C2/5)-$CH_3$), 1,96 (s, 6H, Cp*(C3/4)-$CH_3$), 2,88 (m, 4H, $CH_2CH_3$). **13C{$^{1}$H}-NMR**: $\delta$ = 10,9 (s, Cp*(C2/5)-$CH_3$), 11,7 (s, Cp*(C3/4)-$CH_3$), 12,4 (s, $CH_2CH_3$), 17,5 (s, Cp* (C1)-$CH_3$), 21,4 (d, $^{2+3}J_{PC}$ = 6.6 Hz, $CH_2CH_3$), 134,4 (d, $^{1+2}J_{PC}$ = 18.1 Hz, Et-*C*=*C*-Et), 135,6 (d, $J_{PC}$ = 4.3 Hz, Cp*-$C_{Ring}$), 140,3 (d, $J_{PC}$ = 6.4 Hz, Cp*-$C_{Ring}$), 196,5 (d, $^{2}J_{PC}$ = 8.2 Hz, *cis*-CO). <cf31>31**P{$^{1}$H}-NMR**: $\delta$ = −134,7 ($s_{Sat}$, $^{1}J_{WP}$ = 259,7 Hz).

### *Preparation of complex* $[\{Me_5C_5\overline{PC(Ph)=N}PC_5Me_5\}W(CO)_5]$ (5)

A solution of 0,95 g (1,6 mmol) $[\{(Me_5C_5PC(Ph)=N\}W(CO)_5]$ (**1**), dissolved in toluene (6,5 mL), was heated at 65 °C for 120 min with slow stirring ($^{31}P$ NMR control). All volatile components were removed in vacuo (ca. 0.01 mbar) and the product separated by low-temperature column chromatography (neutral $Al_2O_3$, −50 °C, 8 x 2 cm, *n*-pentane/diethyl ether (1. 95:5 and 2. 90:10)). Evaporation of the first yellow fractions yielded complex **5** as yellow solid; crystallisation from *n*-pentane yielded pale-yellow crystals. Yield: 0.47 g (78 %); m.p.: 132 °C (decomp.).

Elemental analysis for $C_{32}H_{35}NO_5P_2W$ (759.41 g/mol): Calc.: C 50,61, H 4,65, N 1,84; found: C 50,42, H 4,73, N 1,79 %.

**$^1$H-NMR** ($CD_2Cl_2$): $\delta$ = 1,46 (t, $^{3+4}J_{PH}$ = 6,4 Hz, 6 H, Cp*(C1)-C$H_3$),1,80 (s, 12 H, Cp*-C$H_3$), 1,87 (s, 6 H, Cp*-C$H_3$), 1,96 (s, 6 H, Cp*-C$H_3$). **$^{13}$C{$^1$H}-NMR** ($CD_2Cl_2$): $\delta$ = 11,5 (m, Cp*-$C$H$_3$), 11,7 (s, Cp*-$C$H$_3$), 12,8 (m, Cp*-$C$H$_3$), 15,4 (m, Cp*-$C$H$_3$), 64,6 (s, Cp*-$C_{Ring}$), 121,1 (s, Cp*-$C_{Ring}$), 127,5 (s, Ph), 128,0 (s, Ph), 128,5 (s, Ph), 132,2 (s, Ph), 136,0 (s, Cp*-$C_{Ring}$),137,5-138.5 (m, Cp*-$C_{Ring}$), 140,9 (m, Cp*-$C_{Ring}$), 142,1 (m, Cp*-$C_{Ring}$), 197,3 (t, $J_{P,C}$ = 3.5 Hz, CO). **$^{31}$P{$^1$H}-NMR** ($CD_2Cl_2$): $\delta$ = 82.6 (br. s). **MS** (70 eV, $^{184}$W): *m*/*z* = 759 (1) [M$^+$], 624 (4) [(M-Cp*)$^+$], 521 (3) [(M-PhCN-Cp*)$^+$], 540 (1) [(M-Cp*-3CO)$^+$], 484 (1) [(M-Cp*-5CO)$^+$], 437 (5) [(M-PhCN-Cp*-3CO)$^+$], 381 (5) [(M-PhCN-Cp*-5CO)$^+$], 300 (4) [(M-Cp*-W(CO)$_5$)$^+$], 197 (14) [(Cp*P$_2$)$^+$], 135 (100) [(Cp*)$^+$], 119 (24) [(Cp*-Me-H)$^+$], 105 (16) [(Cp*-2Me)$^+$], 91 (14) [(Cp*-2Me−CH$_2$)$^+$].

## *X-ray structure analyses*

### Compound **4c**

$M_r$= 592,22, monoclinic, space group $P2_1/c$, unit cell dimensions: a = 9,9214(6), b = 17,9002(10) and c = 13,7381(8) Å, $\beta$ = 110,643(3)°, V = 2283,2(2) Å$^3$, Z = 4; $\rho_{calcd}$ = 1,723 Mg/m$^3$, Mo$K_\alpha$ radiation, $\lambda$ = 0,71073 Å, T = 133 K, yellow prism (0,20 x 0,13 x 0,13 mm). Of 37434 reflections collected to 2 $\theta_{max}$ x 56.6° on a Bruker Smart 1000 CCD, 5673 were independent ($R_{int}$ = 0,0264) and used for all calculations (program SHELXL-97). Number of parameters: 276. After absorption correction (multiple scan ), all non-hydrogen atoms were refined anisotropically using full matrix least-squares based on $F^2$ to give R1 = 0,0172, wR2 = 0,0442 (all data). Res. electr. dens: 1.8 e/ Å$^3$. Hydrogen atoms were included using a riding model or rigid methyl groups, except for H7 (at C7; refined freely).

### Compound **5**

$M_r$= 759,40, triclinic, space group $P\bar{1}$, unit cell dimensions: a = 9,3828(6), b = 11,2993(8) and c = 16,3614(12) Å; $\alpha$ = 84,593(3)°, $\beta$ = 79,344(3), $\gamma$ = 67,801(3)°, V = 1577,78(19) Å$^3$, Z = 2, $\rho_{calcd}$ = 1,598 Mg/m$^3$, Mo$K_\alpha$ radiation, $\lambda$ = 0,71073 Å, T = 133 K; yellow tablet (0,41 x 0,23 x 0,09 mm). Of 25931 reflections collected to 2$\theta_{max}$ 52.7°, 6454 were independent ($R_{int}$ = 0,0299). Number of parameter: 380. The structure was refined as above to give R1 = 0,0177, wR2 = 0,0473 (all data). Res. electr. dens. 1.3 e/ Å$^3$. Hydrogen atoms were refined using a riding model or rigid methyl groups.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-240380 and 240381. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ (Fax: (+44) 1223-336-033; E-mail: deposit@ccdc.cam.ac.uk).

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