DOI: 10.1002/zaac.200900063

Facile Synthesis of Pentacarbonyltungsten(0) Complexes with Oxaphosphirane Ligands

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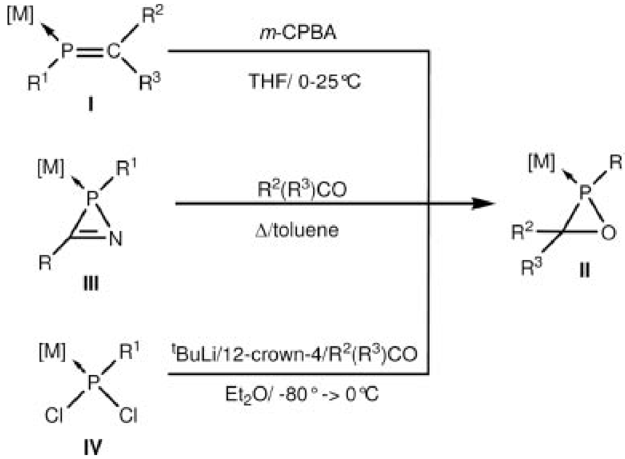
Dedicated to Professor Edgar Niecke on the Occasion of His 70th Birthday

Keywords: Phosphorus heterocycles; Phosphanylidenoid complexes; Oxaphosphirane complexes; Tungsten

Abstract. Facile synthesis of tungsten(0) complexes of the type $[\{(R^1\overline{PCH(R^2)-O})\}W(CO)_5]$ **7a–g** ($R^1 = C_5Me_5$) and **8a–g** ($R^1 = CH(SiMe_3)_2$) using transient Li/Cl phosphanylidenoid tungsten(0) complexes **4**, **5** and carbonyl derivatives **6a–g** is reported; furthermore, for all complexes NMR, IR spectroscopic, mass spectrometric investigations and, in addition, single-crystal X-ray structures of complexes **7b**,**d–g** and **8b**,**d** are presented.

Introduction

The chemistry of oxaphosphiranes involving phosphorus with high coordination number dates back to 1978, when the first synthesis of a $\sigma^4\lambda^5$-oxaphosphirane derivative was described by *Röschenthaler* and *Schmutzler* using *Niecke*'s iminophosphane and hexafluoroacetone [1]. In 1982, the intermediacy of $\sigma^4\lambda^5$-oxaphosphirane *P*-oxide derivatives in ring expansion reactions was claimed by *Bartlett* [2]. In 1988, some NMR evidence was provided by *Boisdan* and *Barrans*, who investigated a monomer-dimer equilibrium of a $\sigma^5\lambda^5$-oxaphosphirane [3]. Although recent theoretical investigations [4] predict easy decomposition into phosphane and carbonyl derivatives, further evidence for the existence of $\sigma^5\lambda^5$-oxaphosphiranes was gained by *Butenschön* [5]. In 1990, *Mathey*'s discovery that $\sigma^3\lambda^3$-oxaphosphirane complexes (**II**) can be obtained through epoxidation of phosphaalkene complexes (**I**) with *m*-CPBA was a further breakthrough (Scheme 1) [6]. Although non-ligated $\sigma^3\lambda^3$-oxaphosphirane derivatives are still unknown, theoretical investigations [7] predict their existence, although some rearrangements might occur [7, 8]. In 1994, we described a new route to oxaphosphirane complexes (**II**) using thermally induced ring cleavage of a 2*H*-azaphosphirene complex (**III**) in the presence of an aldehyde [9] or a ketone [10] derivative. In the latter case a side reaction to a benzo[c]-1,2-oxaphospholane complex occurred. A new facile protocol for the synthesis of complexes **II** was reported recently that utilized the reaction of easily available complexes **IV**, *tert*-butyllithium and aldehydes [11].



Scheme 1. Synthetic routes to oxaphosphirane complexes **II** (R denotes ubiquitous organic substituents. [M] denotes a $W(CO)_5$ group).

It should be pointed out that oxaphosphirane chemistry is still largely undeveloped, which might be attributed to the restricted accessibility. The first example of a C,O bond cleavage reaction was reported very recently, showing that $[\{Me_5C_5\overline{PCH(Ph)-O}\}W(CO)_5]$ react thermally with alde-

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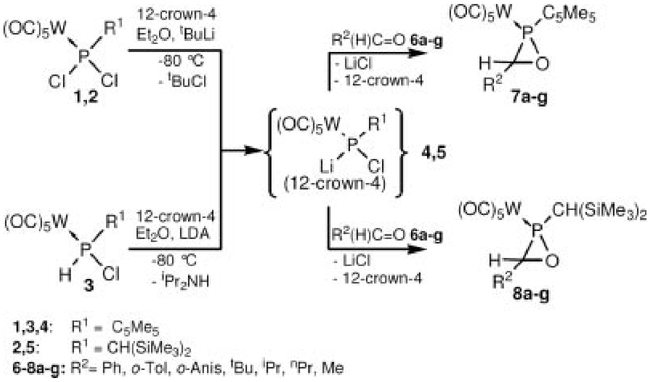
hydes to furnish new O,P,C-cage ligands [12]. Furthermore, we developed a protocol for the selective P,O bond ring expansion of $[\{(Me_3Si)_2HC\overline{PCH(Ph)-O}\}W(CO)_5]$ using trifluoromethane sulfonic acid, carbonitriles and triethylamine as base [13]. Here, we report on the synthesis of tungsten(0) complexes of the type $[\{(R^1\overline{PCH(R^2)-O})\}W(CO)_5]$ **7a**−**g** and **8a**−**g** using transient Li/Cl phosphanylidenoid tungsten(0) complexes and aldehydes **6a**−**g**; furthermore, single-crystal X-ray structures of complexes **7b**,**d**−**g** and **8b**,**d** are presented.

Results and Discussion

Synthesis

Reaction of dichloro(organo)phosphane complexes **1** ($R^1 = C_5Me_5$) [14] and **2** [$R^2 = CH(SiMe_3)_2$] [15] with *tert*-butyllithium or of monochloro(organo)phosphane **3** [$R = C_5Me_5$ (=Cp*)] [16] with LDA at low temperature in the presence of 12-crown-4 and aldehydes **6a**−**g** yielded selectively oxaphosphirane complexes **7a** [12], **7b**−**g** and **8a** [9], **8b**−**e** and **8g** [11] (Scheme 2). As our investigations showed [17], Li/Cl phosphanylidenoid tungsten(0) complexes **4** and **5** are transiently formed by chloro-lithium exchange in complexes **1** and **2** or deprotonation/lithiation of **3**.



Scheme 2. Synthesis of oxaphosphirane complexes **7**, **8a**−**g** through reaction of transiently formed Li/Cl phosphanylidenoid complexes **4**,**5**.

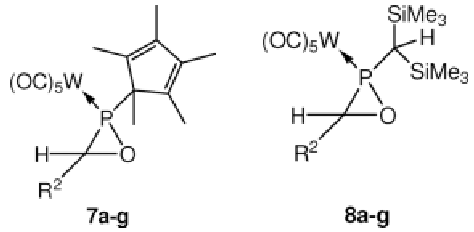
Complexes **7a**−**g** and **8a**−**f** were isolated using column chromatography at low temperature and neutral aluminum oxide as solid phases or − if **3** was used as phosphanylidenoid precursor − by extraction and washing the residue with *n*-pentane at low temperature. All complexes were fully characterized by NMR and IR spectroscopy and mass spectrometry.

Unfortunately, complex **8g** was only identified by ^{31}P NMR spectroscopy because decomposition occurred during column chromatography.

Discussion of NMR Spectroscopic and Mass Spectrometric Results

Complexes **7a**−**g** and **8a**−**g** display ^{31}P NMR spectroscopic data typical for this class of compounds (Table 1). Nevertheless, some trends are becoming apparent and thus can be described for the first time: complexes with oxaphosphirane ligands that possess a *P*−Cp* substituent always show resonances that reveal slightly more shielded phosphorus nuclei than those with a *P*−$CH(SiMe_3)_2$ substituent, and thus a $\Delta\delta$ of approx. 4−11 results. The tungsten−phosphorus coupling constant magnitude lies within the range 303 ± 6 Hz and is virtually identical for corresponding derivatives.

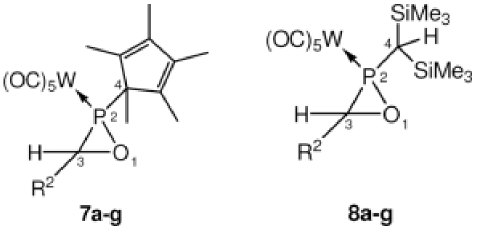
Table 1. $^{31}P\{^1H\}$ NMR spectroscopic data[a)] of *P*−C_5Me_5- and *P*−$CH(SiMe_3)_2$-substituted oxaphosphirane tungsten(0) complexes **7a**−**g**[b)] and **8a**−**g**[c)].



7/8	R^2	δ ($^{31}P\{^1H\}$) ($\lvert ^1J_{W,P}\rvert$)	δ ($^{31}P\{^1H\}$) ($\lvert ^1J_{W,P}\rvert$)
a	Ph	31.6 (309.0)	38.2 (307.7)
b	*o*-Tol	32.1 (307.7)	41.0 (306.6)
c	*o*-Anis	30.9 (306.4)	39.2 (305.5)
d	*t*Bu	11.0 (298.8)	22.5 (298.8)
e	*i*Pr	24.7 (298.8)	31.9 (298.8)
f	*n*Pr	22.8 (298.8)	27.7 (302.6)
g	Me	23.0 (297.5)	29.0 (299.8)[d)]

a) *J* values are given in Hz; b) in C_6D_6; c) in $CDCl_3$; d) only observed in reaction solution (Et_2O).

Table 2. Selected $^{13}C\{^1H\}$ NMR spectroscopic data[a)] of *P*−C_5Me_5- and *P*−$CH(SiMe_3)_2$-substituted oxaphosphirane tungsten(0) complexes **7a**−**g**[b)] and **8a**−**g**[c)].



7/8	R^2	δ ($^{13}C\{^1H\}$) ($\lvert J(P,C)\rvert$) C^3	C^4	δ ($^{13}C\{^1H\}$) ($\lvert J_{P,C}\rvert$) C^3	C^4
a	Ph	55.5 (17.5)	63.0 (10.0)	57.9 (27.5)	30.5 (18.8)
b	*o*-Tol	54.9 (15.5)	63.1 (10.1)	57.9 (24.5)	32.7 (20.3)
c	*o*-Anis	54.7 (20.2)	64.3 (10.0)	54.7 (28.2)	30.4 (20.2)
d	*t*Bu	63.0 (19.1)	62.6 (7.4)	67.1 (28.5)	33.6 (15.4)
e	*i*Pr	60.7 (20.0)	61.9 (8.1)	62.9 (28.7)	28.7 (17.1)
f	*n*Pr	55.2 (20.7)	61.8 (7.8)	57.4 (30.7)	28.5 (16.4)
g	Me	51.2 (22.0)	61.8 (7.8)	−[d)]	−[d)]

a) *J* values are given in Hz; b) in C_6D_6; c) in $CDCl_3$; d) not measured.

The $^{13}C\{^1H\}$ NMR spectroscopic data of complexes **7a**−**g** and **8a**−**f** reveal a similar trend for the chemical shifts of the C^3-carbon atoms (Table 2). Interestingly, here the phosphorus−carbon coupling constant magnitudes differ significantly and those of the *P*−$CH(SiMe_3)_2$ derivatives are always larger, which is also the case for the couplings with the external C^4-carbon atom. The phosphorus−carbon couplings are significantly larger than those of other three-membered, saturated phosphorus heterocyclic ligands such as phosphiranes [18] and azaphosphiridines bound to pentacarbonyl-tungsten(0) [19]; the latter is currently under investigation by us [20]. One more aspect deserves comment: there is a clear trend in the aliphatic series showing that the C^3 atom becomes more deshielded (**g** > **f** > **e** > **d**). One might be tempted to interpret this in terms of an increase in steric demand of the alkyl substituent (*t*Bu > *i*Pr > *n*Pr > Me) but as the solid-state structures reveal (see next chapter and Table 3 and Table 4) there is no trend in the structural data that parallels (and thus could support) the assumption of an increasing van-der-Waals repulsion in this series − and thus (pure) electronic effects are operative.

The mass spectrometric experiments (EI) revealed the molecular ion peak of all complexes **7a−g** and **8a−f** with relative intensities of ca. 5−20 %. For complexes **7a−g** two fragmentation pathways were observed, starting always with oxaphosphirane ring fragmentation and formation of the neutral aldehydes and $[\{(OC)_5WPC_5Me_5\}^{\cdot +}]$ (*m*/*z* 490) in the first step. Then either carbonyltungsten radical-cations of various compositions (with regard to the coordination number of CO) are formed, which still have the Cp* substituent or do not have a Cp* substituent but instead a larger number of carbon monoxide ligands. In all spectra the base peak is given by *m*/*z* 406 assigned to $[\{(OC)_2WPC_5Me_5\}^{\cdot +}]$, which then yields the fragment *m*/*z* 271 assigned to $[\{(OC)_2WP\}^{\cdot +}]$. In the case of complexes **8a−f** the oxaphosphirane ring fragmentation dominated, thus forming *m*/*z* 514, assigned to $[(CO)_5WPCH(SiMe_3)_2{}^{\cdot +}]$. Here, the base peak (*m*/*z* 486) was assigned to $[(OC)_4WPCH(SiMe_3)_2{}^{\cdot +}]$, apparently formed through loss of CO from the precursor.

Crystal Structures of Complexes 7b,d−g and 8b,d

The molecular structures of complexes **7b**,**d−g** and **8b**,**d** were unambiguously established by X-ray diffraction studies. Whereas most of the complexes crystallize triclinic (**7b**,**e−g**, **8b**) **7d** and **8d** crystallize monoclinic. In the cases of complexes **7f**,**g** and **8b** (in which 2 independent molecules are present in the unit cell), the data for only one are presented here as the other is not significantly different (**7g** and **8b**) or is disordered (**7f**). The molecular structures are displayed in Figures 1−7, crystallographic data are given in Table 3 and selected bond lengths and angles are summarized in Table 4. Characteristic structural features of the three-membered ring of the oxaphosphirane complexes are the acute endocyclic angle at phosphorus of about 52°, which, together with three significantly different endocyclic bonds (C−O ca. 1.47, P−O ca. 1.67 and P−C ca. 1.79 Å), creates a peculiar three-membered ring arrangement. The P−W distance is notably short (ca. 2.47 Å) and is unaffected by the substitution pattern of the ligand; the former clearly indicates the influence of oxygen bound to phosphorus, as it is also evidenced in many acyclic phosphite-type complexes. The only bond that seems to be affected by

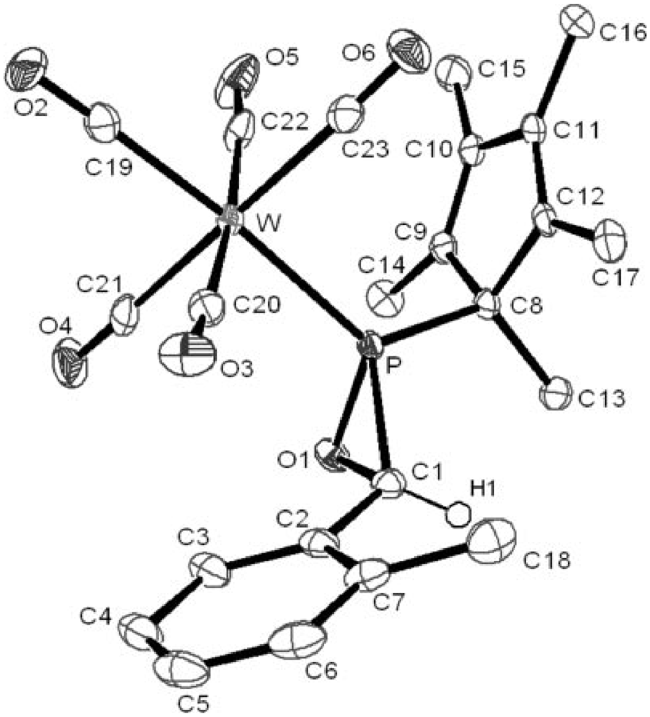


Figure 1. Molecular structure of complex **7b** in the crystal (50 % probability level; hydrogen atoms except H1 are omitted for clarity).

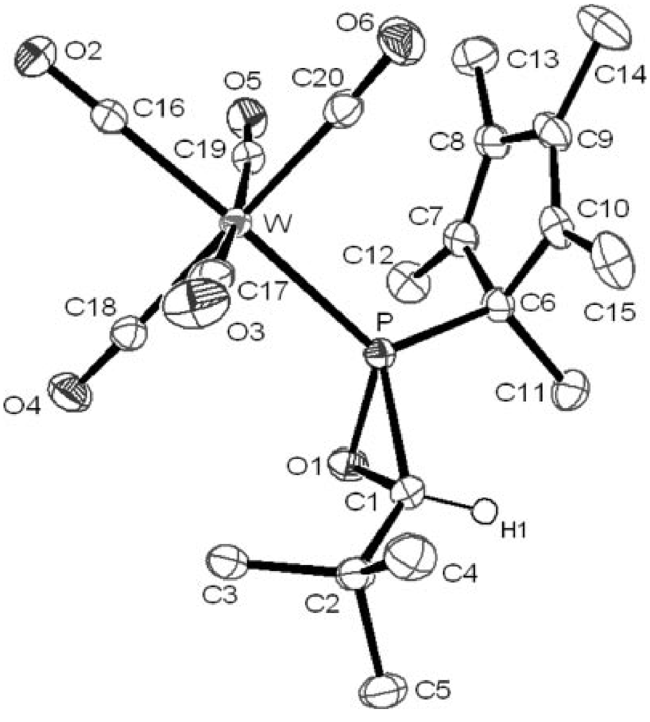


Figure 2. Molecular structure of complex **7d** in the crystal (50 % probability level; hydrogen atoms except H1 are omitted for clarity).

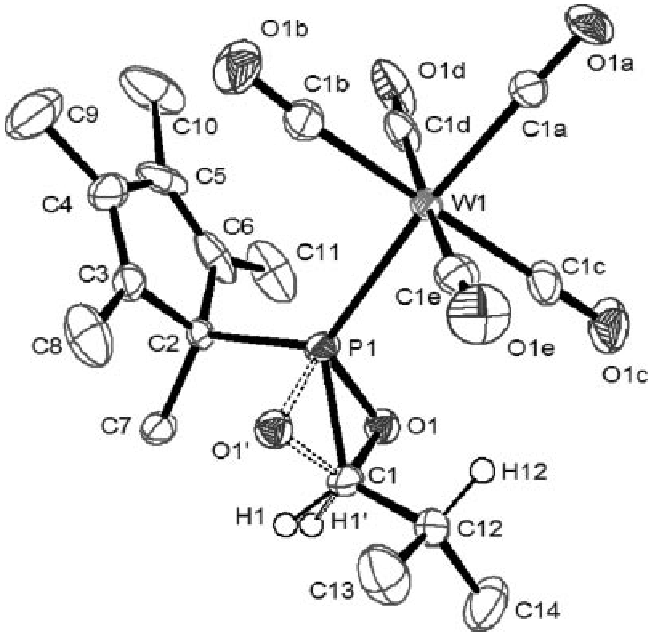


Figure 3. Molecular structure of complex **7e** in the crystal (50 % probability level; main orientation 70 %; hydrogen atoms except H1, H1′ and H12 are omitted for clarity).

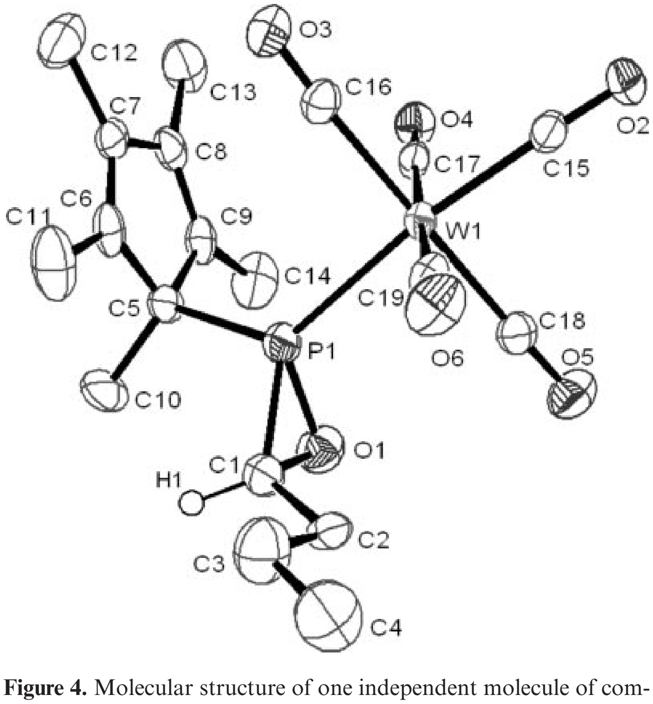


Figure 4. Molecular structure of one independent molecule of complex **7f** in the crystal (50 % probability level; hydrogen atoms except H1 are omitted for clarity).

the substitution pattern is the C−O bond, which varies from 1.473(3) Å (**7b**,**d**) to 1.522(5) Å (**7f**); the C−O bond in **7e** is even longer [1.557(6) Å] but this (most probably) is an artifact of disorder.

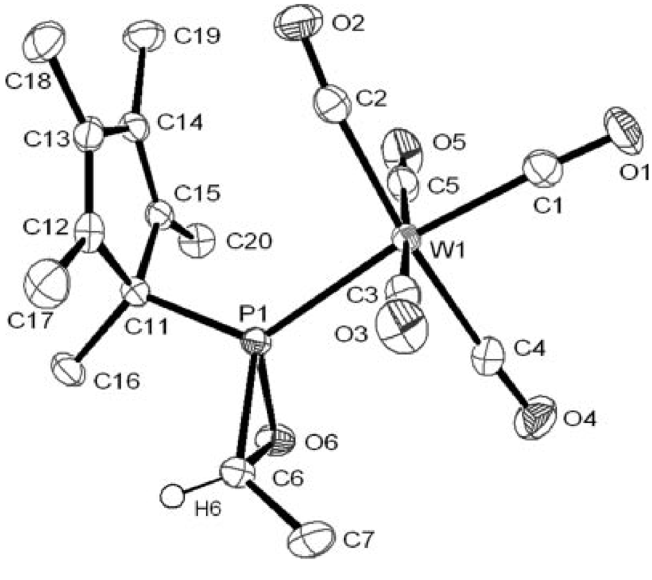


Figure 5. Molecular structure of one independent molecule of complex **7g** in the crystal (50 % probability level; hydrogen atoms except H6 are omitted for clarity).

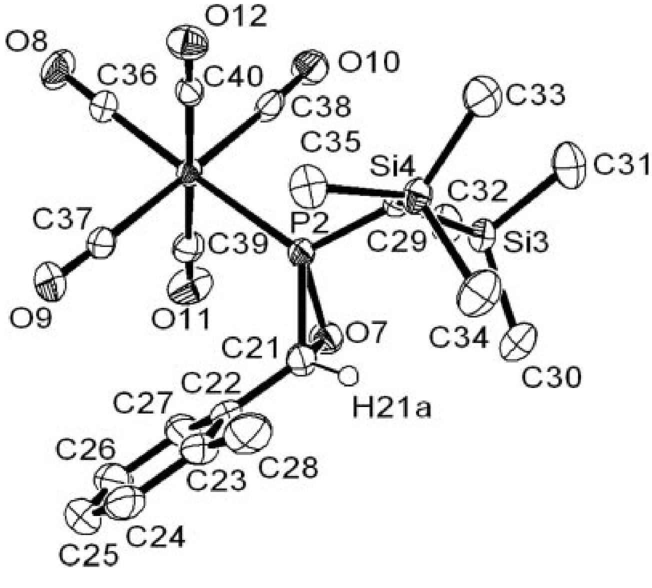


Figure 6. Molecular structure of one independent molecule of complex **8b** in the crystal (50 % probability level; hydrogen atoms except H21a are omitted for clarity).

Experimental Section

All operations were performed under deoxygenated and dry argon, using standard Schlenk techniques with conventional glassware. Solvents were distilled from sodium wire. NMR spectroscopic data were recorded with a Bruker Avance 300 spectrometer (^{13}C: 75.5 MHz; ^{31}P: 121.5 MHz) at 30 °C (**7a**,**b**,**d**−**g** and **8a**−**g**) or a Bruker DPX 500 spectrometer (^{13}C: 125.8 MHz; ^{31}P: 202.4 MHz) at 25 °C (**7c**) using C_6D_6 (**7a**−**g**) or $CDCl_3$ (**8a**−**g**) as solvent and internal standard; shifts are given relative to tetramethylsilane (^{1}H, ^{13}C) and 85 % H_3PO_4 (^{31}P). Mass spectra were recorded with a Kratos MS 50 spectrometer (EI, 70 eV). Elemental analyses were performed using an Elementa (Vario EL) analytical gaschromato-

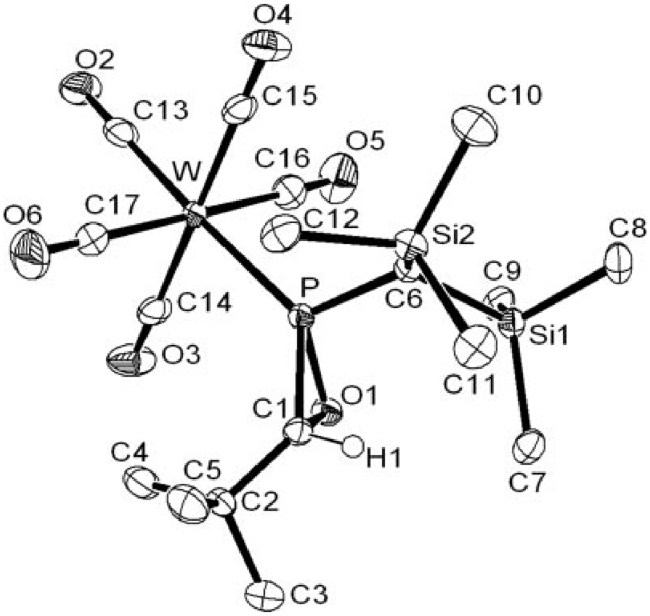


Figure 7. Molecular structure of complex **8d** in the crystal (50 % probability level; hydrogen atoms except H1 are omitted for clarity).

graph. Infrared spectra were collected with a FT-IR Nicolet 380. Melting points were obtained with a Büchi 535 capillary apparatus.

X-ray crystallographic analysis of 7b,d–g and 8b,d: Data were collected with a Nonius-KappaCCD diffractometer at 123 K using Mo-K_α radiation (λ = 0.71073 Å) (**7b**,**d–f** and **8b**,**d**) or a Bruker SMART diffractometer at 133 K (**7g**). The structures were refined by full-matrix least-squares on F^2 (SHELXL-97 [21]). All non-hydrogen atoms were refined anisotropically. The hydrogen atoms, if not found in difference density map (**7b**), were included in calculated positions using a riding model. 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-711298 (**7b**), CCDC-711299 (**7d**), CCDC-711300 (**7e**), CCDC-711301 (**7f**), CCDC-711302 (**7g**), CCDC-711303 (**8b**) and CCDC-711304 (**8d**). 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].

General Procedure for the Preparation of Complexes $[\{Me_5C_5\overline{PCH(R^2)-O}\}W(CO)_5]$ *(7a–g)*

Protocol A (7a,e,g): To a solution of $[(Me_5C_5PCl_2)W(CO)_5]$ (**1**) (230 mg, 0.41 mmol) dissolved in diethyl ether (5 mL), 12-crown-4 (74 µL, 0.46 mmol) and afterwards benzaldehyde (**a**) (46 µL, 0.46 mmol), isobutyraldehyde (**e**) (42 µL, 0.46 mmol) or acetaldehyde (**g**) (0.03 mL, 0.5 mmol) were added. The solution was cooled to −80 °C and a solution of *tert*-butyllithium in *n*-pentane (0.3 mL, 0.46 mmol, 1.5 M) diluted with diethyl ether (5 mL) (−80 °C) was added dropwise. The solutions were then stirred for 90 min while gently warming to −20 °C. Afterwards, the solvents were removed in vacuo (ca. 0.01 bar) and the residue was extracted with *n*-pentane (20 mL). The product was purified by column chromatography and the dry crude product was washed with *n*-pentane at −70 °C.

Protocol B (7a–d,f,g): To a solution of lithium diisopropylamide (LDA, freshly prepared from n-butyllithium and diisopropylamine, 1.2 equivalents) in diethyl ether cooled to −80 °C, a solution of

Table 3. Crystallographic data of oxaphosphirane tungsten(0) complexes **7b**,**d–g** and **8b**,**d**.

	7b	**7d**	**7e**$^{a)}$	**7f**$^{b)}$	**7g**$^{c)}$	**8b**$^{d)}$	**8d**
R^1	C_5Me_5	C_5Me_5	C_5Me_5	C_5Me_5	C_5Me_5	$CH(SiMe_3)_2$	$CH(SiMe_3)_2$
R^2	*o*-Tol	*t*Bu	*i*Pr	*n*Pr	Me	*o*-Tol	*t*Bu
Formula	$C_{23}H_{23}O_6PW$	$C_{20}H_{25}O_6PW$	$C_{19}H_{23}O_6PW$	$C_{19}H_{23}O_6PW$	$C_{17}H_{19}O_6PW$	$C_{20}H_{27}O_6PSi_2W$	$C_{17}H_{29}O_6PSi_2W$
Molecular weight /g·mol^{-1}	610.07	576.22	562.20	562.20	534.14	634.04	600.39
Crystal size/mm	0.28 × 0.26 × 0.07	1.00 × 0.40 × 0.20	0.40 × 0.30 × 0.20	0.60 × 0.30 × 0.2	0.20 × 0.12 × 0.08	0.32 × 0.20 × 0.16	0.36 × 0.32 × 0.20
Crystal system, space group	triclinic, $P\bar{1}$	monoclinic, $C2/c$	triclinic, $P\bar{1}$	triclinic, $P\bar{1}$	triclinic, $P\bar{1}$	triclinic, $P\bar{1}$	monoclinic $P2_1/n$
a /Å	10.1759(3)	28.6042(10)	8.6583(2)	10.7186(3)	9.3055(14)	10.7196(4)	9.5099(3)
b /Å	10.5149(4)	11.3211(4)	10.4122(2)	12.7122(3)	13.627(2)	15.8421(7)	18.8095(6)
c /Å	13.0168(5)	15.3514(5)	11.9464(3)	16.9111(5)	15.434(2)	16.9897(7)	13.6649(5)
α /°	112.382(2)	90	94.080(1)	90.1314(16)	87.147(5)	70.7067(18)	90
β /°	101.178(2)	116.9660(13)	95.639(1)	106.0680(15)	86.427(5)	80.751(2)	91.237(2)
γ /°	105.456(2)	90	90.291(1)	102.4240(14)	89.101(5)	78.910(2)	90
V /Å^3	1171.14(7)	4430.8(3)	1068.98(4)	2157.68(10)	1950.7(5)	2657.58(19)	2443.76(13)
Z	2	8	2	4	4	4	4
$2\theta_{max}$ /°	55	70	55	58	61	56	56
Collected (indpt) reflections	20461 (5251)	22464 (9384)	10643 (4788)	29512 (11156)	45983 (11802)	30787 (12469)	18592 (5796)
R_{int}	0.0504	0.0583	0.0388	0.0524	0.0342	0.0599	0.0518
μ /mm^{-1}	5.035	5.317	5.508	5.457	6.031	4.529	4.917
Refined parameters	372	262	247	520	471	602	253
R_1 (for $I > 2\sigma(I)$)	0.0228	0.0281	0.0288	0.0336	0.0230	0.0387	0.0287
wR_2 (for all data)	0.0520	0.0653	0.0693	0.0821	0.0522	0.0833	0.0556
max./min. residual electron density / e·Å^{-3}	1.233/ −1.824	1.740/ −2.385	2.379/ −1.898	3.220/ −1.674	1.109/ −1.155	1.400/ −1.692	0.984/ −1.770

a) Disordered structure, main orientation 70 %; b) two independent molecules, structure of a second disordered molecule: main orientation: 56 %; c) two independent molecules; d) two independent molecules, one molcule of *n*-pentane in the unit cell.

Table 4. Selected structural data of oxaphosphirane tungsten(0) complexes **7b**,**d**−**g** and **8b**,**d**.

	7b	**7d**	**7e**$^{a)}$	**7f**$^{b)}$	**7g**$^{c)}$	**8b**$^{d)}$	**8d**
R^1	C$_5$Me$_5$	C$_5$Me$_5$	C$_5$Me$_5$	C$_5$Me$_5$	C$_5$Me$_5$	CH(SiMe$_3$)$_2$	CH(SiMe$_3$)$_2$
R^2	*o*-Tol	*t*Bu	*i*Pr	*n*Pr	Me	*o*-Tol	*t*Bu
Bond lengths /Å							
W−P	2.465(6)	2.488(5)	2.463(1)	2.486(1)	2.469(1)	2.459(2)	2.480(8)
P−O	1.672(2)	1.672(2)	1.714(4)	1.682(3)	1.666(2)	1.667(4)	1.668(2)
P−C(ring)	1.799(3)	1.787(2)	1.847(4)	1.793(4)	1.786(3)	1.805(5)	1.784(3)
C(ring)−O(ring)	1.473(3)	1.473(3)	1.557(6)	1.522(5)	1.490(3)	1482(6)	1.487(4)
C(ring)−C(R^2)	1.488(4)	1.526(3)	1.492(6)	1.504(5)	1.498(4)	1.815(5)	1.811(3)
Bond angles /°							
C(ring)−P−O	50.1(1)	50.3(1)	52.6(2)	51.8(2)	51.0(1)	50.5(2)	50.88(1)
P−C(ring)−O	60.4(1)	60.8(1)	60.9(2)	60.3(1)	60.3(1)	59.9(2)	60.6(2)
C(ring)−O−P	69.5(1)	69.0(1)	66.5(2)	67.9(1)	68.7(1)	69.6(3)	68.7 (2)

a) Disordered structure, main orientation 70 %; b) two independent molecules, structure of a second disordered molecule: main orientation: 56 %; c) two independent molecules; d) two independent molecules, one molcule of *n*-pentane in the unit cell.

[{Me$_5$C$_5$P(H)Cl}W(CO)$_5$] (**3**), 1 equivalent of 12-crown-4 and 1 equivalent of the appropriate aldehyde in diethyl ether was slowly added (volumes and quantities see Table 5). The solution was stirred for 2 h while gently warming to −20 °C. Afterwards, the solvents were removed in vacuo (ca. 0.01 bar) and the residue was extracted with *n*-pentane (15−40 mL). The raw product was washed carefully with *n*-pentane at −70 °C.

Table 5. Reaction conditions for the synthesis of **7a**−**g**.

7	R	LDA	**3**: *m* /mg	12-c-4	**6**a−g	Et$_2$O /mL
		n / mmol	(*n* /mmol)	*V* /µL	*V* /µL	V^{LDA}/V^{R}
a	Ph	0.5	221 (0.42)	68	43	5/5
b	*o*-Tol	1.0	442 (0.84)	136	98	10/10
c	*o*-Anis	1.0	442 (0.84)	136	115$^{a)}$	10/10
d	*t*Bu	1.0	442 (0.84)	136	190	10/10
f	*n*Pr	0.5	221 (0.42)	68	38	5/5
g	Me	0.6	246 (0.47)	76	30	2/2

a) **5c**: *m* /mg.

[{Me$_5$C$_5\overline{\text{PCH(Ph)−O}}$}W(CO)$_5$] (7a) [12]: Yield: 54 mg (22 %) (A) or 182 mg (73 %) (B); m.p. 103 °C (decomp.); C$_{22}$H$_{21}$O$_6$PW (596.21 g·mol^{-1}): calc: C 44.32, H 3.55 %; exp: C 44.39, H 3.69 %; Selected NMR spectroscopic data: **^{1}H NMR**: δ = 0.83 (d, $^3J_{P,H}$ = 11.3 Hz, 3 H, Cp*-C^1-CH$_3$), 1.65 (m$_c$, 6 H, Cp*-CH$_3$), 1.68 (s, 3 H, Cp*-CH$_3$), 1.93 (s, 3 H, Cp*-CH$_3$), 4.23 (s, 1 H, POC-H), 7.05−7.37 (m, 5 H, Ph); **^{13}C{^{1}H} NMR**: δ = 9.5 (d, $J_{P,C}$ = 3.2 Hz, Cp*-CH$_3$), 10.1 (d, $J_{P,C}$ = 2.3 Hz, Cp*-CH$_3$), 10.2 (d, $J_{P,C}$ = 1.3 Hz, Cp*-CH$_3$), 10.6 (d, $J_{P,C}$ = 1.6 Hz, Cp*-CH$_3$), 12.0 (d, $J_{P,C}$ = 4.8 Hz, Cp*-C^1-CH$_3$), 55.5 (d, $J_{P,C}$ = 17.5 Hz, P-CH(Ph)), 63.0 (d, $^1J_{P,C}$ = 10.0 Hz, Cp*-C^1), 125.0 (d, $J_{P,C}$ = 2.9 Hz, Ph), 127.2 (d, $J_{P,C}$ = 2.3 Hz, Ph), 127.5 (d, $J_{P,C}$ = 2.3 Hz, Ph), 131.6 (d, $J_{P,C}$ = 7.4 Hz, Cp*), 134.0 (s, Ph), 136.8 (d, $J_{P,C}$ = 1.6 Hz, Cp*), 140.7 (d, $J_{P,C}$ = 6.1 Hz, Cp*), 143.0 (d, $J_{P,C}$ = 7.8 Hz, Cp*), 194.8 (d, $^2J_{P,C}$ = 8.4, $^1J_{W,C}$ = 125.2 Hz, *cis*-CO), 197.3 (d, $^2J_{P,C}$ = 37.5 Hz, *trans*-CO); **^{31}P{^{1}H} NMR**: δ = 31.6 (s$_{Sat}$, $^1J_{W,P}$ = 309.0 Hz). **MS**: *m*/*z* (%) = 596 (17) [M$^{\cdot+}$], 490 (57) [{(OC)$_5$WPCp*}$^{\cdot+}$], 456 (26) [(M-5CO)$^{\cdot+}$], 406 (100) [{(OC)$_2$WPCp*}$^{\cdot+}$], 378 (22) [{(OC)WPCp*}$^{\cdot+}$], 327 (13) [{(OC)$_4$WP}$^{\cdot+}$], 299 (14) [{(OC)$_3$WP}$^{\cdot+}$], 271 (5) [{(OC)$_2$WP}$^{\cdot+}$], 135 (22) [(Cp*)$^{\cdot+}$], 119 (18) [(Cp*-Me-H)$^{\cdot+}$], 105 (9) [(Cp*-2Me)$^{\cdot+}$], 91 (5) [(Cp*-2Me-CH$_2$)$^{\cdot+}$]. **IR** (KBr; ṽ(CO)): ṽ = 1937 (m), 1992 (s), 2074 (s) cm^{-1}; X-ray crystallographic analysis: structure has been deposited at the Cambridge Crystallographic Data Centre under the number CCDC-647516.

[{Me$_5$C$_5\overline{\text{PCH(\textit{o}-tolyl)-O}}$}W(CO)$_5$] (7b): Yield: 420 mg (73 %) (B); m.p. 108−9 °C (decomp); C$_{23}$H$_{23}$O$_6$PW (610.07 g·mol^{-1}): calc: C 45.27, H 3.80 %; exp: C 45.22, H 3.97 %. **^{1}H NMR**: δ = 0.65 (d, $J_{P,H}$ = 11.3 Hz, 3 H, Cp*-C^1-CH$_3$), 1.41−1.45 (m$_c$, 6 H, Cp*-CH$_3$), 1.52 (s, 3 H, Cp*-CH$_3$), 1.75 (s, 3 H, Cp*-CH$_3$ or Ar-CH$_3$), 1.92 (s, 3 H, Cp*-CH$_3$ or Ar-CH$_3$), 3.92 (s, 1 H, POC-H), 6.72 (d, $J_{H,H}$ = 6.99 Hz, 1 H, Ar), 6.81−6.91 (m$_c$, 2 H, Ar), 7.40 (d, $J_{H,H}$ = 6.99 Hz, 1 H, Ar); **^{13}C{^{1}H} NMR**: δ = 9.9 (d, $J_{P,C}$ = 3.0 Hz, Cp*-CH$_3$), 10.0 (d, $J_{P,C}$ = 1.8 Hz, Cp*-CH$_3$), 10.3 (d, $J_{P,C}$ = 1.2 Hz, Cp*-CH$_3$), 10.5 (d, $J_{P,C}$ = 1.8 Hz, Cp*-CH$_3$), 12.2 (d, $J_{P,C}$ = 4.8 Hz, Cp*-C^1-CH$_3$), 17.8 (s, Ar-CH$_3$), 54.9 (d, $J_{P,C}$ = 15.5 Hz, POCH), 63.1 (d, $J_{P,C}$ = 10.1 Hz, Cp*-C^1), 125.0 (d, $J_{P,C}$ = 4.8 Hz, Ar), 125.1 (d, $J_{P,C}$ = 2.4 Hz, Ar), 127.1 (d, $J_{P,C}$ = 2.4 Hz, Ar), 128.8 (d, $J_{P,C}$ = 2.4 Hz, Ar), 132.0 (d, $J_{P,C}$ = 8.3 Hz, Cp* or Ar), 132.1 (s, Cp* or Ar), 134.2 (d, $J_{P,C}$ = 1.8 Hz, Cp* or Ar), 136.5 (s, Cp* or Ar), 141.0 (d, $J_{P,C}$ = 1.2 Hz, Cp*), 142.8 (d, $J_{P,C}$ = 6.0 Hz, Cp*), 192.8 (d$_{Sat}$, $^2J_{P,C}$ = 8.3, $^1J_{W,C}$ = 125.2 Hz, *cis*-CO), 194.2 (d, $^2J_{P,C}$ = 37.6 Hz, *trans*-CO); **^{31}P{^{1}H} NMR**: δ = 32.1 (s$_{Sat}$, $^1J_{W,P}$ = 307.7 Hz). **MS**: *m*/*z* (%) = 610 (19) [M$^{\cdot+}$], 526 (13) [(M-3CO)$^{\cdot+}$], 490 (12) [{(OC)$_5$WPCp*}$^{\cdot+}$], 406 (25) [{(OC)$_2$WPCp*}$^{\cdot+}$], 299 (3) [{(OC)$_3$WP}$^{\cdot+}$], 135 (42) [(Cp*)$^{\cdot+}$], 134 (100) [(Cp*-H)$^{\cdot+}$], 119 (28) [(Cp*-Me-H)$^{\cdot+}$], 105 (7) [(Cp*-2Me)$^{\cdot+}$], 91 (3) [(Cp*-2Me-CH$_2$)$^{\cdot+}$]. **IR** (KBr; ṽ(CO)): ṽ = 1934 (s), 1990 (s), 2073 (s) cm^{-1}.

[{Me$_5$C$_5\overline{\text{PCH(\textit{o}-anisyl)-O}}$}W(CO)$_5$] (7c): Yield: 391 mg (74 %) (B); m.p. 78−80 °C (decomp); C$_{23}$H$_{23}$O$_7$PW (626.24 g·mol^{-1}): calc: C 44.11, H 3.70 %; exp: C 43.46, H 4.03 %. **^{1}H NMR** (500.1 MHz, 25 °C, C$_6$D$_6$): δ = 0.95 (d, $J_{P,H}$ = 11.3 Hz, 3 H, Cp*-C^1-CH$_3$), 1.68−1.70 (m, 6 H, Cp*-CH$_3$), 1.92 (s, 3 H, Cp*-CH$_3$), 1.98 (s, 3 H, Cp*-CH$_3$), 3.34 (s, 3 H, Ar-OCH$_3$), 4.46 (d, $J_{P,H}$ = 2.0 Hz, 3 H, POC-H), 6.46 (d, $J_{H,H}$ = 8.2 Hz, 1 H, Ar), 6.88 ("t", $J_{H,H}$ = 7.4 Hz, 1 H, Ar), 7.09 ("t", $J_{H,H}$ = 7.9 Hz, 1 H, Ar), 7.60 (d"q", $J_{H,H}$ = 7.5 Hz (d), $J_{H,H}$ = 0.7 Hz (q), 1 H, Ar); **^{13}C{^{1}H} NMR** (125.8 MHz, 25 C, C$_6$D$_6$): δ = 10.5 (d, $J_{P,C}$ = 3.0 Hz, Cp*-CH$_3$), 11.6 (d, $J_{P,C}$ = 2.0 Hz, Cp*-CH$_3$), 11.6 (s, Cp*-CH$_3$), 12.1 (s, Cp*-CH$_3$), 13.3 (d, $J_{P,C}$ = 5.0 Hz, Cp*-C^1-CH$_3$), 54.7 (d, $J_{P,C}$ = 20.2 Hz, POCH), 54.8 (s, Ar-OCH$_3$), 64.3 (d, $J_{P,C}$ = 10.0 Hz, Cp*-C^1), 110.0 (d, $J_{P,C}$ = 2.0 Hz, *m*-Ar-H), 121.0 (d, $J_{P,C}$ = 2.0 Hz, *m*-Ar-H), 124.1 (s, *i*-Ar), 127.3 (d, $J_{P,C}$ = 4.0 Hz, *o*-Ar-H), 129.5 (d, $J_{P,C}$ = 2.0 Hz, *p*-Ar-H), 133.6 (d, $J_{P,C}$ = 7.0 Hz, Cp*), 138.2 (s, Cp*), 141.9 (d, $J_{P,C}$ = 6.0 Hz, Cp*), 144.1 (d, $J_{P,C}$ = 8.0 Hz, Cp*), 157.9 (s, *o*-Ar-OCH$_3$), 194.4 (d, $J_{P,C}$ = 8.0 Hz, *cis*-CO), 195.9 (d, $J_{P,C}$ = 36.9 Hz, *trans*-CO); **^{31}P{^{1}H} NMR** (202.4 MHz, 25 °C, C$_6$D$_6$): δ = 30.9 (s$_{Sat}$, $^1J_{W,P}$ = 306.4 Hz). **MS**: *m*/*z* (%) = 626 (17) [M$^{\cdot+}$], 542 (14)

[(M-3CO)$^{\cdot+}$], 135 (100) [(Cp*)$^{\cdot+}$], 119 (32) [(Cp*-Me-H)$^{\cdot+}$], 105 (19) [(Cp*-2Me)$^{\cdot+}$], 91 (27) [(Cp*−2Me−CH$_2$)$^{\cdot+}$]. **IR** (KBr; $\tilde{\nu}$(CO)): $\tilde{\nu}$ = 1935 (m/s), 1989 (m/s), 2078 (s) cm^{-1}.

$[\{Me_5C_5\overline{PCH(tBu)-O}\}W(CO)_5]$ (7d): Yield: 418 mg (86 %) (B); m.p. 104 °C; $C_{20}H_{25}O_6PW$ (576.22 g·mol^{-1}): calc: C 41.69, H 4.37 %; exp: C 41.76, H 4.39 %. **^{1}H NMR**: δ = 0.74 (d, $^3J_{P,H}$ = 10.4 Hz, 3 H, Cp*-C^1-CH$_3$), 1.08 (s, 9 H, *t*Bu-CH$_3$), 1.61−1.64 (m$_c$, 9 H, Cp*-CH$_3$), 1.88 (s, 3 H, Cp*-CH$_3$), 2.92 (s, 1 H, POC-H); **^{13}C{^{1}H} NMR**: δ = 9.3 (d, $J_{P,C}$ = 3.2 Hz, Cp*-CH$_3$), 10.0 (d, $J_{P,C}$ = 1.3 Hz, Cp*-CH$_3$), 10.5 (d, $J_{P,C}$ = 2.3 Hz, Cp*-CH$_3$), 10.7 (d, $J_{P,C}$ = 1.0 Hz, Cp*-CH$_3$), 13.1 (d, $J_{P,C}$ = 4.8 Hz, Cp*-C^1-CH$_3$), 26.6 (d, $J_{P,C}$ = 3.6 Hz, *t*Bu-CH$_3$ (3 ×)), 31.1 (s, *t*Bu), 62.6 (d, $J_{P,C}$ = 7.4 Hz, Cp*-C^1), 63.0 (d, $J_{P,C}$ = 19.1 Hz, POCH), 132.6 (d, $J_{P,C}$ = 8.1 Hz, Cp*), 138.4 (d, $J_{P,C}$ = 2.6 Hz, Cp*), 140.1 (d, $J_{P,C}$ = 6.1 Hz, Cp*), 142.5 (d, $J_{P,C}$ = 7.4 Hz, Cp*), 194.2 (d$_{Sat}$, $J_{P,C}$ = 8.1, $J_{W,C}$ = 125.8 Hz, *cis*-CO), 194.5 (d, $J_{P,C}$ = 35.9 Hz, *trans*-CO); **^{31}P{^{1}H} NMR**: δ = 11.0 (s$_{Sat}$, $^1J_{W,P}$ = 298.8 Hz). **MS**: *m*/*z* (%) = 576 (7) [M$^{\cdot+}$], 490 (42) [{(OC)$_5$WPCp*}$^{\cdot+}$], 406 (100) [{(OC)$_2$WPCp*}$^{\cdot+}$], 378 (19) [{(OC)WPCp*}$^{\cdot+}$], 327 (11) [{(OC)$_4$WP}$^{\cdot+}$], 299 (13) [{(OC)$_3$WP}$^{\cdot+}$], 271 (6) [{(OC)$_2$WP}$^{\cdot+}$], 166 (7) [(PCp*)$^{\cdot+}$], 135 (30) [(Cp*)$^{\cdot+}$], 119 (15) [(Cp*-Me-H)$^{\cdot+}$], 105 (11) [(Cp*-2Me)$^{\cdot+}$], 91 (5) [(Cp*-2Me-CH$_2$)$^{\cdot+}$]. **IR** (KBr; $\tilde{\nu}$(CO)): $\tilde{\nu}$ = 1921 (s), 1947 (s), 1991 (m), 2074 (m) cm^{-1}.

$[\{Me_5C_5\overline{PCH(iPr)-O}\}W(CO)_5]$ (7e): Yield: 102 mg (44 %) (A); m.p. 118 °C; $C_{19}H_{23}O_6PW$ (562.20 g·mol^{-1}): calc: C 40.59, H 4.12 %; exp: C 40.45, H 4.27 %. **^{1}H NMR**: δ = 0.75 (d, $^3J_{P,H}$ = 11.3 Hz, 3 H, Cp*-C^1-CH$_3$), 0.95 (d, $^3J_{H,H}$ = 6.6 Hz, 3 H, *i*Pr-CH$_3$), 1.09 (dd, $^3J_{P,H}$ = 1.2, $^3J_{H,H}$ = 6.6 Hz, 3 H, *i*Pr-CH$_3$), 1.62 (s, 3 H, Cp*-CH$_3$), 1.64 (m$_c$, 3 H, Cp*-CH$_3$), 1.66 (m$_c$, 3 H, Cp*−CH$_3$), 1.68-1.82 (m, 1 H, POC−CH), 1.88 (s, 3 H, Cp*-CH$_3$), 2.71 (d, $^3J_{PH}$ = 10.1 Hz, 1 H, POC-H); **^{13}C{^{1}H} NMR**: δ = 9.2 (d, $J_{P,C}$ = 3.2 Hz, Cp*-CH$_3$), 10.0 (d, $J_{P,C}$ = 1.3 Hz, Cp*-CH$_3$), 10.2 (d, $J_{P,C}$ = 1.9 Hz, Cp*-CH$_3$), 10.6 (d, $J_{P,C}$ = 1.6 Hz, Cp*-CH$_3$), 12.0 (d, $J_{P,C}$ = 5.2 Hz, Cp*-C^1-CH$_3$), 17.9 (s, *i*Pr-CH$_3$(1)), 18.1 (d, $J_{P,C}$ = 10.0 Hz, *i*Pr-CH$_3$(2)), 28.9 (d, $J_{P,C}$ = 3.2 Hz, POC-CH), 60.7 (d, $J_{P,C}$ = 20.0 Hz, POC-H), 61.9 (d, $J_{P,C}$ = 8.1 Hz, Cp*-C^1), 131.7 (d, $J_{P,C}$ = 7.1 Hz, Cp*), 137.3 (d, $J_{P,C}$ = 1.9 Hz, Cp*), 140.2 (d, $J_{P,C}$ = 6.1 Hz, Cp*), 142.9 (d, $J_{P,C}$ = 7.8 Hz, Cp*), 193.5 (d$_{Sat}$, $^1J_{W,C}$ = 125.4, $^2J_{P,C}$ = 8.4 Hz, *cis*-CO), 194.9 (d, $^2J_{P,C}$ = 35.6 Hz, *trans*-CO); **^{31}P{^{1}H} NMR**: δ = 24.7 (s$_{Sat}$, $^1J_{W,P}$ = 298.8 Hz). **MS**: *m*/*z* (%) = 562 (17) [M$^{\cdot+}$], 490 (34) [{(OC)$_5$WPCp*}$^{\cdot+}$], 406 (100) [{(OC)$_2$WPCp*}$^{\cdot+}$], 378 (21) [{(OC)WPCp*}$^{\cdot+}$], 327 (11) [{(OC)$_4$WP}$^{\cdot+}$], 299 (14) [{(OC)$_3$WP}$^{\cdot+}$], 271 (7) [{(OC)$_2$WP}$^{\cdot+}$], 135 (22) [(Cp*)$^{\cdot+}$], 119 (16) [(Cp*-Me-H)$^{\cdot+}$], 105 (13) [(Cp*-2Me)$^{\cdot+}$], 91 (5) [(Cp*-2Me-CH$_2$)$^{\cdot+}$]. **IR** (KBr; $\tilde{\nu}$(CO)): $\tilde{\nu}$ = 1934 (m), 2077 (s) cm^{-1}.

$[\{Me_5C_5\overline{PCH(nPr)-O}\}W(CO)_5]$ (7f): Yield: 171 mg (72 %) (B); m.p. 62 °C; $C_{19}H_{23}O_6PW$ (562.20 g·mol^{-1}): calc: C 40.59, H 4.12 %; exp: C 41.26, H 4.48 %. **^{1}H NMR**: δ = 0.75 (d, $^3J_{P,H}$ = 11.4 Hz, 3 H, Cp*-C^1-CH$_3$), 0.90 (t, $^3J_{H,H}$ = 7.3 Hz, 3 H, *n*Pr-CH$_3$), 1.36−1.48 (m, 2 H, *n*Pr-CH$_2$), 1.61−1.72 (m, 11 H, 3 × Cp*-CH$_3$ and *n*Pr-CH$_2$), 1.88 (s, 3 H, Cp*-CH$_3$), 3.00 (t, $J_{H,H}$ = 6.7 Hz, 1 H, POC-H); **^{13}C{^{1}H} NMR**: δ = 9.3 (d, $J_{P,C}$ = 3.2 Hz, Cp*-CH$_3$), 10.0 (d, $J_{P,C}$ = 1.6 Hz, Cp*-CH$_3$), 10.1 (d, $J_{P,C}$ = 2.3 Hz, Cp*-CH$_3$), 10.6 (d, $J_{P,C}$ = 1.9 Hz, Cp*-CH$_3$), 11.9 (d, $J_{P,C}$ = 5.2 Hz, Cp*-C^1-CH$_3$), 12.5 (s, POC(H)CH$_2$CH$_2$-CH$_3$), 18.9 (d, $J_{P,C}$ = 4.8 Hz, POC(H)CH$_2$-CH$_2$), 31.7 (d, $J_{P,C}$ = 2.6 Hz, POC(H)-CH$_2$), 55.2 (d, $J_{P,C}$ = 20.7 Hz, POCH), 61.8 (d, $J_{P,C}$ = 7.8 Hz, Cp*-C^1), 131.8 (d, $J_{P,C}$ = 7.1 Hz, Cp*), 137.2 (d, $J_{P,C}$ = 1.6 Hz, Cp*), 140.2 (d, $J_{P,C}$ = 6.1 Hz, Cp*), 142.7 (d, $J_{P,C}$ = 7.8 Hz, Cp*), 193.6 (d$_{Sat}$, $^1J_{W,C}$ = 125.4, $^2J_{P,C}$ = 8.4 Hz, *cis*-CO), 194.9 (d, $^2J_{P,C}$ = 35.6 Hz, *trans*-CO); **^{31}P{^{1}H} NMR**: δ = 22.8 (s$_{Sat}$, $^1J_{W,P}$ = 298.8 Hz). **MS**: *m*/*z* (%) = 562 (10) [M$^{\cdot+}$], 490 (39) [{(OC)$_5$WPCp* }$^{\cdot+}$], 406 (100) [{(OC)$_2$WPCp*}$^{\cdot+}$], 378 (20) [{(OC)WPCp*}$^{\cdot+}$], 327 (11) [{(OC)$_4$WP}$^{\cdot+}$], 299 (11) [{(OC)$_3$WP}$^{\cdot+}$], 271 (6) [{(OC)$_2$WP}$^{\cdot+}$], 135 (30) [(Cp*)$^{\cdot+}$], 119 (14) [(Cp*-Me-H)$^{\cdot+}$], 105 (10) [(Cp*-2Me)$^{\cdot+}$], 91 (4) [(Cp*-2Me-CH$_2$)$^{\cdot+}$]. **IR** (KBr; $\tilde{\nu}$(CO)): $\tilde{\nu}$ = 1923 (s), 1939 (s), 1965 (s), 1994 (m), 2075 (m) cm^{-1}.

$[\{Me_5C_5\overline{PCH(Me)-O}\}W(CO)_5]$ (7g): Yield 112 mg (51 %) (A) or 240 mg (98 %) (B); m.p. 108 °C; $C_{17}H_{19}O_6PW$ (534.14 g·mol^{-1}): calc: C 38.23 %, H 3.59 %; exp: C 38.01, H 3.66 %. **^{1}H NMR**: δ = 0.70 (d, $^3J_{P,H}$ = 11.3 Hz, 3 H, Cp*-C^1-CH$_3$), 1.28 (dd, $^3J_{P,H}$ = 14.2, $^3J_{H,H}$ = 5.9 Hz, 3 H, POC-CH$_3$), 1.55 (s, 3 H, Cp*-CH$_3$), 1.63 (m$_c$, 3 H, Cp*-CH$_3$), 1.65 (m$_c$, 3 H, Cp*-CH$_3$), 1.86 (m$_c$, 3 H, Cp*-CH$_3$), 2.94 (q, $J_{P,H}$ = 0.6, $^3J_{H,H}$ = 5.9 Hz, 1 H, POC-H); **^{13}C{^{1}H} NMR**: δ = 9.3 (d, $J_{P,C}$ = 2.9 Hz, Cp*-CH$_3$), 10.0 (d, $J_{P,C}$ = 1.6 Hz, Cp*-CH$_3$), 10.1 (d, $J_{P,C}$ = 2.3 Hz, Cp*-CH$_3$), 10.6 (d, $J_{P,C}$ = 1.6 Hz, Cp*-CH$_3$), 11.7 (d, $J_{P,C}$ = 4.8 Hz, Cp*-C^1-CH$_3$), 15.4 (d, $J_{P,C}$ = 2.9 Hz, POC-CH$_3$), 51.2 (d, $J_{P,C}$ = 22.0 Hz, POCH), 61.8 (d, $J_{P,C}$ = 7.8 Hz, Cp*-C^1), 131.9 (d, $J_{P,C}$ = 7.1 Hz, Cp*), 137.1 (d, $J_{P,C}$ = 1.9 Hz, Cp*), 140.2 (d, $J_{P,C}$ = 5.8 Hz, Cp*), 142.7 (d, $J_{P,C}$ = 7.8 Hz, Cp*), 193.5 (d$_{Sat}$, $^2J_{P,C}$ = 8.7, $^1J_{W,C}$ = 125.3 Hz, *cis*-CO), 195.0 (d, $^2J_{P,C}$ = 35.6 Hz, *trans*-CO); **^{31}P{^{1}H} NMR**: δ = 23.0 (s$_{Sat}$, $^1J_{W,P}$ = 297.5 Hz). **MS**: *m*/*z* (%) = 534 (15) [M$^{\cdot+}$], 490 (48) [{(OC)$_5$WPCp*}$^{\cdot+}$], 406 (100) [{(OC)$_2$WPCp*}$^{\cdot+}$], 378 (33) [{(OC)WPCp*}$^{\cdot+}$], 327 (18) [{(OC)$_4$WP}$^{\cdot+}$], 299 (16) [{(OC)$_3$WP}$^{\cdot+}$], 271 (9) [{(OC)$_2$WP}$^{\cdot+}$], 135 (23) [(Cp*)$^{\cdot+}$], 119 (18) [(Cp*-Me-H)$^{\cdot+}$], 105 (14) [(Cp*-2Me)$^{\cdot+}$], 91 (6) [(Cp*-2Me-CH$_2$)$^{\cdot+}$]. **IR** (KBr; $\tilde{\nu}$(CO)): $\tilde{\nu}$ = 1931 (m), 1990 (s), 2076 (s) cm^{-1}.

General Procedure for the Preparation of Complexes $[\{(Me_3Si)_2HC\overline{PCH(R^2)-O}\}W(CO)_5]$ (8a−f)

To a solution of [{(Me$_3$Si)$_2$HCPCl$_2$}W(CO)$_5$] (**2**) (200 mg, 0.31 mmol) and 12-crown-4 (0.31 mmol) in diethyl ether (10 mL), a *tert*-butyllithium solution (0.2 mL, 0.31 mmol, 1.6 M) was added dropwise at −80 °C while stirring. The mixture was stirred for five minutes at this temperature and afterwards the corresponding aldehyde (0.31 mmol) was added. The solution was stirred for additional 90 min while gently warming to 0 °C and then warmed up to ambient temperature. The solvents were then removed in vacuo (ca. 0.01 bar) and the residue was extracted with *n*-pentane (20 mL). The products were purified by column chromatography (Al$_2$O$_3$, −30 °C, petroleum ether.

$[\{(Me_3Si)_2HC\overline{PCH(Ph)-O}\}W(CO)_5]$ (8a): Yield 127.4 mg (60 %); m.p. 96 °C. $C_{19}H_{25}O_6PSi_2W$ (620.04 g·mol^{-1}): calc: C 36.78, H 4.06 %; exp: C 36.99, H 4.36 %. **^{1}H NMR**: δ = 0.30 (s, 9 H, Si(CH$_3$)$_3$), 0.39 (s, 9 H, Si(CH$_3$)$_3$), 1.28 (s, 1 H, CH(Si(CH$_3$)$_3$)$_2$), 4.40 (d, 1 H, $^2J_{P,H}$ = 1.9 Hz, PhC(H)O), 7.10 (m$_c$, 3 H, Ph), 7.36 (m$_c$, 2 H, Ph); **^{13}C{^{1}H} NMR**: δ = −0.4 (d, $^3J_{P,C}$ = 4.2 Hz, Si(CH$_3$)$_3$), 0.0 (d, $^3J_{P,C}$ = 2.2 Hz, Si(CH$_3$)$_3$), 30.5 (d, $^1J_{P,C}$ = 18.8 Hz, *C*H(Si(CH$_3$)$_3$)$_2$), 57.9 (d, $^1J_{P,C}$ = 27.5 Hz, PC(H)O), 123.5 (d, $^3J_{P,C}$ = 3.2 Hz, Ph), 126.1 (d, J = 2.9 Hz, Ph), 126.7 (d, J = 2.3 Hz, Ph), 133.3 (s, *p*-Ph), 192.7 (d, $^2J_{P,C}$ = 8.4 Hz, *cis*-CO); 194.9 (d, $^2J_{P,C}$ = 35.6 Hz, *trans*-CO); **^{31}P{^{1}H} NMR**: δ = 38.2 (s$_{sat}$, $^1J_{W,P}$ = 307.7 Hz). **MS**: *m*/*z* (%) = 620 (20) [M$^{\cdot+}$], 514 (15) [(M-Ph(H)CO)$^{\cdot+}$], 486 (15) [(M-Ph(H)CO-CO)$^{\cdot+}$], 428 (50) [(M-PhC(H)O-3CO)$^{\cdot+}$], 400 (60) [(M-Ph(H)CO-4CO)$^{\cdot+}$]; 86 (100) [CH(Si(CH$_3$)$_3$)$_2$$^{\cdot+}$]. **IR** (KBr; $\tilde{\nu}$(CO)): $\tilde{\nu}$ = 1880 (s), 1924 (m), 2077 (s), 2067(s) cm^{-1}.

$[\{(Me_3Si)_2HC\overline{PCH(o\text{-}Tol)-O}\}W(CO)_5]$ (8b): Yield 130.2 mg (60 %); m.p. 65 °C. $C_{20}H_{27}O_6PSi_2W$ (634.04 g·mol^{-1}): calc: C 37.86, H 4.29 %; exp: C 38.12, H 4.57 %. **^{1}H NMR**: δ = 0.16 (s, 9 H, $Si(CH_3)_3$), 0.22 (s, 9 H, $Si(CH_3)_3$), 1.14 (s, 1 H, $CH(Si(CH_3)_3)_2$), 2.33 (s, 3 H, *o*-CH_3), 4.26 (s, 1 H, PhC(H)O), 7.00 (m, 4 H, Ph); **^{13}C{^{1}H} NMR**: δ = 1.6 (d, $^3J_{P,C}$ = 3.14 Hz, $Si(CH_3)_3$), 1.8 (d, $^3J_{P,C}$ = 2.3 Hz, $Si(CH_3)_3$), 32.7 (d, $^1J_{P,C}$ = 20.3 Hz, *C*$H(Si(CH_3)_3)_2$), 57.9 (d, $^1J_{P,C}$ = 24.5 Hz, PC(H)O), 125.6 (d, $^3J_{P,C}$ = 2.1 Hz, Ar), 125.7 (d, $J_{P,C}$ = 4.4 Hz, Ar), 127.6 (d, $J_{P,C}$ = 2.6 Hz, Ar), 129.7 (d, $J_{P,C}$ = 2.3 Hz, Ar), 128.0 (s, Ar), 131.3 (s, Ar), 193.9 (d, $^2J_{P,C}$ = 8.4 Hz, *cis*-CO), 195.1 (d, $^2J_{P,C}$ = 34.9 Hz, *trans*-CO); **^{31}P{^{1}H} NMR**: δ = 41.0 (s_{sat}, $^1J_{W,P}$ = 306.6 Hz). **MS**: *m*/*z* (%) = 634(10) [M$^{\cdot+}$], 514 (40) [M-Ar-C(H)O$^{\cdot+}$], 486 (100) [M-Ar-C(H)O-CO$^{\cdot+}$]. **IR** (KBr; $\tilde{\nu}$(CO)): $\tilde{\nu}$ = 1923 (w), 1993 (s), 2075 (s), 2957 (s) cm^{-1}.

$[\{(Me_3Si)_2HC\overline{PCH(o\text{-}Anis)-O}\}W(CO)_5]$ (8c): Yield 142.5 mg (64 %); m.p. 99 °C. $C_{20}H_{27}O_7PSi_2W$ (650.41 g·mol^{-1}): calc: C 36.93, H 4.18 %; exp: C 37.30, H 4.42 %. **^{1}H NMR**: δ = 0.22 (s, 9 H, $Si(CH_3)_3$), 0.30 (s, 9 H, $Si(CH_3)_3$), 1.16 (s, 1 H, $CH(SiCH_3)_2$), 3.79 (s, 3 H, OCH_3), 4.46 (s, 1 H, ArC(H)O), 6.79 (m, 3 H, Ar), 6.79 (m, 1 H, Ar). **^{13}C{^{1}H} NMR**: δ = −0.8 (d, $^3J_{P,C}$ = 4.2 Hz, $Si(CH_3)_3$), 0.0 (d, $^3J_{P,C}$ = 2.2 Hz, $Si(CH_3)_3$), 30.4 (d, $^1J_{P,C}$ = 20.2 Hz, *C*$H(Si(CH_3)_3)_2$), 52.6 (s, OCH_3), 54.7 (d, $^1J_{P,C}$ = 28.2 Hz, PC(H)O), 107.3 (d, $^3J_{P,C}$ = 2.2 Hz, Ar), 118.3 (d, $J_{P,C}$ = 2.4 Hz, Ar), 121.7 (s, Ar), 124.3 (d, $J_{P,C}$ = 4.4 Hz, Ar), 126.8 (d, $J_{P,C}$ = 2.6 Hz, Ar), 155.2 (d, $J_{P,C}$ = 2.6 Hz, Ar), 192.9 (d, $^2J_{P,C}$ = 8.4 Hz, *cis*-CO), 195.2 (d, $^2J_{P,C}$ = 34.7 Hz, *trans*-CO); **^{31}P{^{1}H} NMR**: δ = 39.2 (s_{sat}, $^1J_{W,P}$ = 305.5 Hz). **MS**: *m*/*z* (%) = 650 (60) [M$^{\cdot+}$], 566 (40) [M-3CO$^{\cdot+}$], 514 (15) [M-Ar-C(H)O$^{\cdot+}$], 73 (100) [$Si(CH_3)_3{}^{\cdot+}$].

$[\{(Me_3Si)_2HC\overline{P(tBu)-O}\}W(CO)_5]$ (8d): Yield 100.4 mg (50 %); m.p. 94 °C. $C_{17}H_{29}O_6PSi_2W$ (600.39 g·mol^{-1}): calc: C 34.01, H 4.87 %; exp: C 33.88, H 4.86 %. **^{1}H NMR**: δ = 0.24 (s, 9 H, $Si(CH_3)_3$), 0.31 (s, 9 H, $Si(CH_3)_3$), 1.1 (s, 9 H, $(CH_3)_3$), 1.25 (s, 1 H, C*H*$(Si(CH_3)_3)_2$), 2.7 (s, PC(H)O); **^{13}C{^{1}H} NMR**: δ = 0.7 (d, $^3J_{P,C}$ = 4.5 Hz, $Si(CH_3)_3$), 1.5 (d, $^3J_{P,C}$ = 2.3 Hz, $Si(CH_3)_3$), 24.5 (d, $^2J_{P,C}$ = 4 Hz, CH_3) 27.3 (d, $^2J_{P,C}$ = 4 Hz, $2CH_3$), 31.0 (s, $C(CH_3)_3$), 33.6 (d, $^2J_{P,C}$ = 15.4 Hz, *C*$H(Si(CH_3)_3)_2$), 67.1 (d, $^1J_{P,C}$ = 28.49 Hz, PC(H)O), 195.5 (d, $^2J_{P,C}$ = 8.4 Hz, *cis*-CO), 196.5 (d, $^2J_{P,C}$ = 33.6 Hz, *trans*-CO); **^{31}P{^{1}H} NMR**: δ = 22.5 (s_{sat}, $^1J_{W,P}$ = 298.8 Hz). **MS**: *m*/*z* (%) = 600 (13) [M$^{\cdot+}$], 557 (30) [M-CO-O$^{\cdot+}$], 527 (20) [M-CO-O$^{\cdot+}$], 514 (40) [M-*t*Bu-C(H)O$^{\cdot+}$], 486 (100) [M-*t*Bu-C(H)O-CO$^{\cdot+}$]. **IR** (KBr; $\tilde{\nu}$(CO)): $\tilde{\nu}$ = 1934 (m), 1986(s), 2076 (s) cm^{-1}.

$[\{(Me_3Si)_2HC\overline{PCH(iPr)-O}\}W(CO)_5]$ (8e): Yield 106.3 mg (53 %); m.p. 86 °C. $C_{16}H_{27}O_6PSi_2W$ (586.37 g·mol^{-1}): calc: C 32.77, H 4.64 %; exp: C 32.68, H 4.65 %. **^{1}H NMR**: δ = 0.25 (s, 9 H, $Si(CH_3)_3$), 0.30 (s, 9 H, $Si(CH_3)_3$), 1.05 (m, 1 H, C*H*$(Si(CH_3)_3)_2$), 1.17 (d, 3 H, $^2J_{H,H}$ = 6.5 Hz, CH_3), 1.21 (d, 3 H, $^2J_{H,H}$ = 6.7 Hz, CH_3), 1.60 (m, 1 H, C*H*$(CH_3)_2$), 2.75 (d, 1 H, $^2J_{P,H}$ = 9.82 Hz, PC(H)O); **^{13}C{^{1}H} NMR**: δ = −0.4 (d, $^3J_{P,C}$ = 4.5 Hz, $Si(CH_3)_3$), 0.0 (d, $^3J_{P,C}$ = 2.6 Hz, $Si(CH_3)_3$), 17.2 (s, CH(*C*$H_3)_2$), 17.4 (d, $^1J_{P,C}$ = 11.6 Hz, CH(*C*$H_3)_2$), 29.0 (d, *C*$H(CH_3)_2$, $^3J_{P,C}$ = 3.3 Hz), 28.7 (d, *C*$H(Si(CH_3)_3)_2$, $^3J_{P,C}$ = 17.1 Hz), 62.9 (d, $^1J_{P,C}$ = 28.7 Hz, PC(H)O), 193.4 (d, $^2J_{P,C}$ = 8.4 Hz, *cis*-CO), 195 (d, $^2J_{P,C}$ = 33.6 Hz, *trans*-CO); **^{31}P{^{1}H} NMR**: δ = 31.9 (s_{sat}, $^1J_{W,P}$ = 298.8). **MS**: *m*/*z* (%) = 586 (15) [M$^{\cdot+}$], 543 (30) [M-*i*Pr$^{\cdot+}$], 514 (40) [M-*i*Pr-C(H)O$^{\cdot+}$], 486 (100) [M-*i*Pr-C(H)O-CO$^{\cdot+}$]. **IR** (KBr; $\tilde{\nu}$(CO)): $\tilde{\nu}$ = 1930 (m), 1986 (s), 2067(s) cm^{-1}.

$[\{(Me_3Si)_2HC\overline{PCH(nPr)-O}\}W(CO)_5]$ (8f): Yield 110.1 mg (55 %); m.p. 68 °C; $C_{16}H_{27}O_6PSi_2W$ (586.37 g·mol^{-1}): calc: C 32.77, H 4.64 %; exp: C 32.20, H 4.56 %. **^{1}H NMR**: δ = 0.25 (s, 9 H, $Si(CH_3)_3$), 0.29 (s, 9 H, $Si(CH_3)_3$), 1.05 (t, 3 H, $^2J_{H,H}$ = 6.5, CH_3), 1.15 (s, 1 H, $CH(Si(CH_3)_3)_2$), 1.6 (m, 2 H, CH_2), 1.8 (m, 2 H, CH_2), 3.1 (t, 1 H, $^2J_{P,H}$ = 9 Hz, PC(H)O); **^{13}C{^{1}H} NMR**: δ = −0.6 (d, $^3J_{P,C}$ = 4.5 Hz, $Si(CH_3)_3$), 0.0 (d, $^3J_{P,C}$ = 2.2 Hz, $Si(CH_3)_3$), 11.9 (s, CH_2CH_3), 17.8 (d, $^2J_{P,C}$ = 6.1 Hz, CH_2), 28.5 (d, $^3J_{P,C}$ = 16.4 Hz, $CH(Si(CH_3)_3)_2$), 31.4 (d, $^3J_{P,C}$ = 30.7 Hz, CH_2), 57.4 (d, $^1J_{P,C}$ = 30.7 Hz, PC(H)O), 193.5 (d, $^2J_{P,C}$ = 8.4 Hz, *cis*-CO), 195 (d, $^2J_{P,C}$ = 33.6 Hz, *trans*-CO); **^{31}P{^{1}H} NMR**: δ = 27.7 (s_{sat}, $^1J_{W,P}$ = 302.6 Hz). **MS**: *m*/*z* (%) = 586 (20) [M$^{\cdot+}$], 543 (27) [M-*n*Pr$^{\cdot+}$], 514 (35) [M-*n*Pr-C(H)O$^{\cdot+}$], 486 (100) [M-*n*Pr-C(H)O-CO$^{\cdot+}$]; **IR** (KBr; $\tilde{\nu}$(CO)): $\tilde{\nu}$ = 1930 (m), 1986 (s), 2076 (s) cm^{-1}.

Acknowledgement

Financial support by *ThermPhos International* is gratefully acknowledged.

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Received: January 22, 2009