

# Reactions of (THF)W(CO)<sub>5</sub> with some diphosphenes carrying bulky aryl and phenoxy groups

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## Abstract

The reaction of (THF)W(CO)<sub>5</sub> (THF = tetrahydrofuran) with asymmetrical diphosphenes carrying bulky aryl and phenoxy groups gave end-on-type complexes on either phosphorus atom. One of the complexes was analyzed by X-ray crystallography indicating that the major complex suffers less from the steric bulk.

**Keywords:** Carbonyl; Chromium; Molybdenum; Phosphorus; Tungsten; X-ray diffraction

## 1. Introduction

Physicochemical properties of low coordinated phosphorus compounds such as diphosphenes are of current interest. We have previously reported the preparation, characterization, and crystal structure of 1,2-bis(2,4,6-tri-tert-butylphenyl)diphosphene (**1**) utilizing the 2,4,6-tri-tert-butylphenyl group (abbreviated to Ar) as a sterically protecting group [1,2]. Moreover, we and others have also described some diphosphenes with the >N–P=P– skeleton [3–5], as well as diphosphene **2** containing the –O–P=P– skeleton [6]. We reported some results on the reaction of several kinds of phenoxy-diphosphenes with sulfur, dichlorocarbene and selenium, and now we report the results on the reaction of such diphosphenes having the –O–P=P– skeleton with (THF)W(CO)<sub>5</sub> (THF = tetrahydrofuran) to give complexes of end-on type coordination.

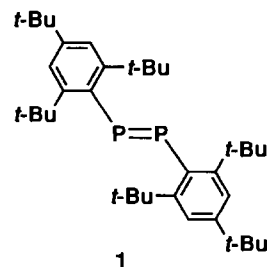
## 2. Results and discussion

### 2.1. Preparation of diphosphenes carrying bulky phenoxy and the Ar groups

Some stable diphosphenes carrying bulky phenoxy and the Ar groups were prepared as previously reported [6] as follows. Sterically hindered phenyl phospho-

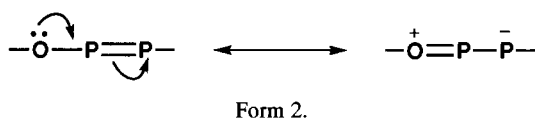
rodichloridites **3a–3c** were prepared from the corresponding phenols **4a–4c**. Reaction of **3a–3c** with lithium 2,4,6-tri-tert-butylphenylphosphide [7], followed by the dehydrochlorination reaction with 1,8-diazabicyclo-[5.4.0]undec-7-ene (DBU) gave the corresponding asymmetrical diphosphenes **2a–2c** (Scheme 1). Diphosphenes **2a–2c** were stable towards air and moisture during the silica-gel column-chromatography procedure.

The <sup>31</sup>P NMR spectra of the diphosphenes **2a–2c** showed an AB pattern, unequivocally characteristic of asymmetrical diphosphenes. The signals due to the P<sup>A</sup> of the diphosphenes **2a–2c** appear at slightly higher field ( $\delta_p = 409–411$  ppm) compared with those for **1** ( $\delta_p = 490$  ppm), where P<sup>A</sup> denotes the Ar-substituted phosphorus atom and P<sup>B</sup> denotes the other phosphorus atom except for the symmetrical **1**. The phenoxy-group-substituted phosphorus atoms (P<sup>B</sup>) of **2a–2c** resonate at significantly low field ( $\delta_p = 533–535$  ppm) compared with the P<sup>A</sup> for **2a–2c** or P<sup>A</sup> for **1**. These



Form 1.

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facts can be interpreted by considering resonance structures of the  $-O-P=P-$   $\pi$  system involving the  $P=P$  double bond perturbed by the lone-pair electrons of the oxygen atom [3,4,6].

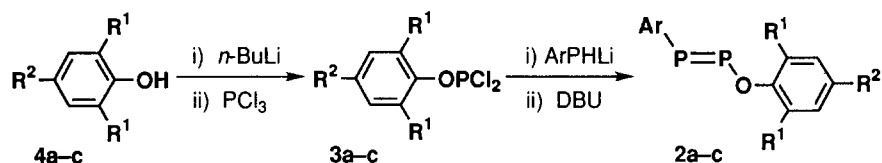
## 2.2. Reaction of the diphosphenes **2a–2c** with $(THF)W(CO)_5$

The reaction of **2a–2c** with a large excess amount of  $(THF)W(CO)_5$  at room temperature in THF for 3 days led to the formation of the end-on complexes **5a–5c** and **6a–6c** (Scheme 2), when the starting diphosphenes **2a–2c** were completely consumed. During the reaction of **2** with  $(THF)W(CO)_5$ , two sets of AB-pattern signals appeared in an almost equal amount. Either peak  $\delta_{P^B}$  in a lower field for **5** or  $\delta_{P^A}$  in a higher field for **6** was accompanied with satellite peaks due to  $^{183}W$ , clearly indicating the position of the coordination site of the end-on-type coordination [8]. It seems likely that the  $P^A$  atom is more electron donating than  $P^B$  but that **5** is less hindered than **6**. The  $^{31}P$  NMR data for **2**, **5** and **6** are listed in Table 1 together with **1** as a reference. The two complexes **5** and **6** were isolated after silica gel column chromatography as a mixture of the major **5** and the minor **6**, but attempted further purification of the

minor complex **6** failed. The major complexes **5** were successfully obtained as crystalline materials in every case and **5b** could be analyzed by X-ray crystallography. Although some transition metal complexes of the phenoxy-substituted diphosphene with a side-on-type coordination or mixed side-on- and end-on-type coordination have been reported [9,10], the complex formation with single end-on-type coordination such as **5** or **6** has not been reported so far. Similar results were obtained for **2b** with the other Group 6 metal carbonyls such as chromium and molybdenum to give the end-on coordination complexes **7b–10b**. Table 1 also lists the  $^{31}P$  NMR data for compounds **7b–10b**.

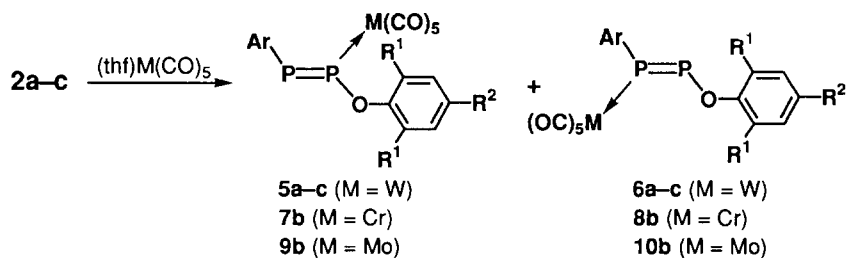
## 2.3. Structure analysis of tungsten carbonyl complex **5b**

Fig. 1 is an ORTEP drawing [11] of **5b**. Some selected bond lengths and bond angles are listed in Table 2 and Table 3 respectively. The atoms (W(1), P(1), P(2), O(1), C(1), C(16)) are coplanar within 0.012(2) Å and the atoms O(6) and C(38) are slightly off this plane by 0.339 and 0.184 Å respectively. The aromatic rings of the Ar and the bulky phenoxy groups are almost perpendicular to the diphosphene  $P=P$   $\pi$  system, making an angle of  $90.84^\circ$  and  $86.06^\circ$  respectively. The dihedral angles of  $C(16)-P(2)-P(1)-O(1)$ ,  $C(16)-P(2)-P(1)-W(1)$ ,  $P(2)-P(1)-O(1)-C(1)$  are  $179.7(3)^\circ$ ,  $1.1(3)^\circ$  and  $-2.7(6)^\circ$  respectively. The bond length  $P(1)-P(2)$  is 2.025(3) Å, which falls into the shortest lengths reported for diphosphenes so far [12]. The coordination



a:  $R^1 = R^2 = t\text{-Bu}$ ; b:  $R^1 = t\text{-Bu}$ ,  $R^2 = \text{Me}$ ; c:  $R^1 = t\text{-Bu}$ ,  $R^2 = \text{H}$ ;  
Ar = 2,4,6- $t\text{-Bu}_3\text{C}_6\text{H}_2$ ; DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene.

Scheme 1.



a:  $R^1 = R^2 = t\text{-Bu}$ ; b:  $R^1 = t\text{-Bu}$ ,  $R^2 = \text{Me}$ ; c:  $R^1 = t\text{-Bu}$ ,  $R^2 = \text{H}$ .

Scheme 2.

Table 1  
 $^{31}\text{P}$  NMR data of diphosphenes **1** and **2** and the Group 6 metal carbonyl complexes **5**–**10** (in  $\text{CDCl}_3$ )

Compound <sup>a</sup>	$\delta_{\text{P}^{\text{B}}}$ (ppm)	$^1J_{\text{P}^{\text{B}}\text{W}}$ (Hz)	$\delta_{\text{P}^{\text{A}}}$ (ppm)	$^1J_{\text{P}^{\text{A}}\text{W}}$ (Hz)	$^1J_{\text{PP}}$ (Hz)
<b>1</b>	490.0 <sup>b</sup>	—	490.0 <sup>b</sup>	—	—
<b>2a</b>	534.1	—	409.8	—	572.2
<b>2b</b>	534.4	—	409.7	—	572.3
<b>2c</b>	533.2	—	410.4	—	572.5
<b>5a</b>	444.6	289.5	343.2	—	564.3
<b>5b</b>	443.4	291.3	339.6	—	568.9
<b>5c</b>	443.2	291.6	339.9	—	569.1
<b>6a</b>	491.2	—	311.3	243.5	510.8
<b>6b</b>	491.7	—	311.8	243.6	510.6
<b>6c</b>	491.0	—	312.9	244.0	510.9
<b>7b</b>	501.1	—	378.1	—	572.9
<b>8b</b>	516.0	—	363.4	—	512.6
<b>9b</b>	484.2	—	362.9	—	565.0
<b>10b</b>	501.8	—	378.2	—	573.2

<sup>a</sup>  $\text{P}^{\text{A}}$  denotes the Ar-substituted phosphorus atom and  $\text{P}^{\text{B}}$  denotes the other except for **1**.

<sup>b</sup>  $\delta_{\text{P}}$  value in  $\text{C}_6\text{D}_6$  for **1**: 492.4 [1].

length  $\text{P}(1)\text{--W}(1)$  of 2.456(2) Å is much shorter than 2.531(2) Å of  $[\text{ArP}=\text{C}=\text{CPh}_2]\text{W}(\text{CO})_5$  [13], 2.506(1) Å of  $[\text{ArP}=\text{C}=\text{C}=\text{CPh}_2]\text{W}(\text{CO})_5$  [14] and 2.522(6) and 2.517(5) Å of  $[\text{ArP}=\text{C}=\text{PAr}][\text{W}(\text{CO})_5]_2$  [15]. The two tert-butyl groups of the phenoxy moiety are disordered, and the structure with a dominant occupancy is shown in Fig. 1.

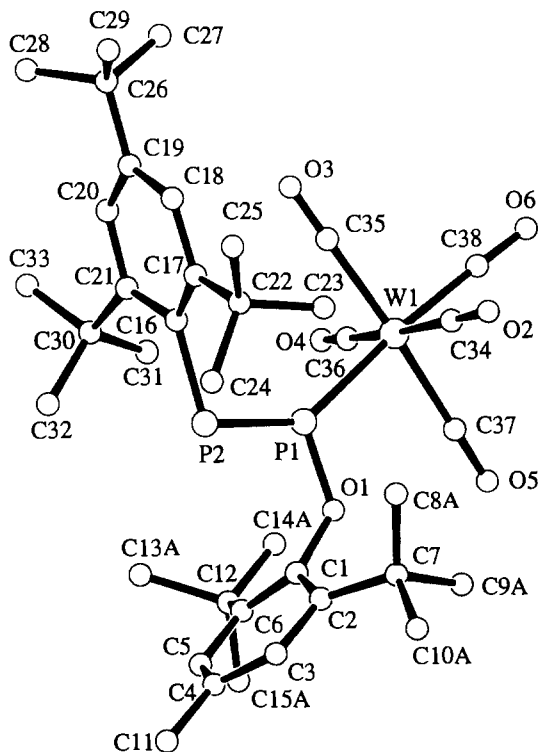


Fig. 1. Molecular structure of **5b** with atom-labeling scheme. The atoms  $\text{C}(8)\text{--C}(10)$  and  $\text{C}(13)\text{--C}(15)$  are disordered and the molecular structure with a dominant occupancy (0.76) for each is shown for clarity.

### 3. Experimental details

All experiments were carried out under an argon atmosphere with dry solvents, unless otherwise specified. All melting points were determined with a Yanagimoto MP-J3 micromelting point apparatus and were uncorrected.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were measured by either a Bruker AC-200P or AM-600 spectrometer.  $^{31}\text{P}$  NMR spectra were obtained with a Bruker AC-200P spectrometer using 85%  $\text{H}_3\text{PO}_4$  as an external standard. IR spectra were recorded on a Horiba FT-300 spectrometer. The UV–visible spectra were obtained with a Hitachi U-3210 spectrometer. X-ray reflections were recorded on a Rigaku AFC-7S four-circle diffractometer using graphite-monochromated  $\text{Mo K}\alpha$  radiation.

Table 2  
 Some selected bond distances (Å) for **5b** (numbers in parentheses are estimated standard deviations).

$\text{W}(1)\text{--P}(1)$	2.456(2)	$\text{C}(2)\text{--C}(7)$	1.57(1)
$\text{W}(1)\text{--C}(34)$	2.028(9)	$\text{C}(3)\text{--C}(4)$	1.39(1)
$\text{W}(1)\text{--C}(35)$	2.062(9)	$\text{C}(4)\text{--C}(5)$	1.38(1)
$\text{W}(1)\text{--C}(36)$	2.026(10)	$\text{C}(4)\text{--C}(11)$	1.50(1)
$\text{W}(1)\text{--C}(37)$	2.050(9)	$\text{C}(5)\text{--C}(6)$	1.40(1)
$\text{W}(1)\text{--C}(38)$	2.021(9)	$\text{C}(6)\text{--C}(12)$	1.55(1)
$\text{P}(1)\text{--P}(2)$	2.025(3)	$\text{C}(16)\text{--C}(17)$	1.423(10)
$\text{P}(1)\text{--O}(1)$	1.629(5)	$\text{C}(16)\text{--C}(21)$	1.424(9)
$\text{P}(2)\text{--C}(16)$	1.858(7)	$\text{C}(17)\text{--C}(18)$	1.399(10)
$\text{O}(1)\text{--C}(1)$	1.414(8)	$\text{C}(17)\text{--C}(22)$	1.555(10)
$\text{O}(2)\text{--C}(34)$	1.153(9)	$\text{C}(18)\text{--C}(19)$	1.373(10)
$\text{O}(3)\text{--C}(35)$	1.124(9)	$\text{C}(19)\text{--C}(20)$	1.372(10)
$\text{O}(4)\text{--C}(36)$	1.151(10)	$\text{C}(19)\text{--C}(26)$	1.535(10)
$\text{O}(5)\text{--C}(37)$	1.122(9)	$\text{C}(20)\text{--C}(21)$	1.401(10)
$\text{O}(6)\text{--C}(38)$	1.145(9)	$\text{C}(21)\text{--C}(30)$	1.56(1)
$\text{C}(1)\text{--C}(2)$	1.402(10)		
$\text{C}(1)\text{--C}(6)$	1.407(10)		
$\text{C}(2)\text{--C}(3)$	1.40(1)		

### 3.1. Synthesis of diphosphenes (2a–2c)

Diphosphenes **2** were prepared according to the method reported previously [6].

**2a**: yellow needles; melting point (m.p.), 186.5–187.5°C (hexane).  $^{31}\text{P}\{^1\text{H}\}$  NMR (81 MHz,  $\text{CDCl}_3$ ):  $\delta$  409.8 and 534.1 (AB,  $^1J_{\text{PP}} = 572.2$  Hz) ppm.

**2b**: yellow needles; m.p., 171.5–172.5°C (hexane).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  409.7, 534.4 (AB,  $^1J_{\text{PP}} = 572.3$  Hz) ppm.

**2c**: yellow needles; m.p., 167–168°C (hexane).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  410.4, 533.2 (AB,  $^1J_{\text{PP}} = 572.5$  Hz) ppm.

### 3.2. Synthesis of tungsten carbonyl complexes (5a–5c and 6a–6c)

A typical synthetic procedure is described for **5a** and **6a**. Diphosphene **2a** (210 mg, 0.37 mmol) was dissolved in THF (25 ml) and stirred at room temperature for 3 days in the presence of a large excess (about 50-fold excess) of  $(\text{THF})\text{W}(\text{CO})_5$ , prepared from photolysis of hexacarbonyltungsten in THF [16], when the starting diphosphene was almost consumed. During the reaction of **2a** with  $(\text{THF})\text{W}(\text{CO})_5$ , two sets of AB-pattern signals appeared in an almost equal intensity owing to the two complexes **5a** and **6a**. The reaction mixture was subjected to silica-gel column chromatography to give **5a** and **6a**, but the ratio of the complexes changed

to about 1:0.5, probably because of some decomposition of **6a**. The further attempted purification of **6a** has failed so far but the pure **5a** was isolated as a crystalline material with 38% yield based on the diphosphene **2a** used. Similarly, **5b** and **5c** were prepared and isolated with yields of 46 and 48% from the corresponding diphosphenes **2b** and **2c** respectively, together with the corresponding **6b** and **6c**. However, attempted purification of both **6b** or **6c** was unsuccessful.

**5a**: yellow prisms; m.p., 145–146°C ( $\text{CH}_3\text{CN}$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 200 MHz):  $\delta$  1.28 (9H, s,  $p\text{-}^1\text{Bu}$ ), 1.32 (9H, s,  $p\text{-}^1\text{Bu}$ ), 1.49 (18H, s,  $o\text{-}^1\text{Bu}$ ), 1.54 (18H, s,  $o\text{-}^1\text{Bu}$ ), 7.30 (2H, s, arom.), 7.43 (2H, bs, arom.) ppm.  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta_{\text{PA}}$  343.2,  $\delta_{\text{PB}}$  444.6 (satellite,  $^1J_{\text{PW}} = 289.5$  Hz) (AB,  $^1J_{\text{PP}} = 564.3$  Hz) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 50 MHz):  $\delta$  31.06 (s,  $p\text{-CMe}_3$ ), 31.47 (s,  $p\text{-CMe}_3$ ), 33.07 (s,  $o\text{-CMe}_3$ ), 33.36 (d,  $J_{\text{PC}} = 6.47$  Hz,  $o\text{-CMe}_3$ ), 34.62 (s,  $p\text{-CMe}_3$ ), 34.90 (s,  $p\text{-CMe}_3$ ), 36.58 (s,  $o\text{-CMe}_3$ ), 38.85 (s,  $o\text{-CMe}_3$ ), 123.13 (d,  $^3J_{\text{PC}} = 2.31$  Hz,  $m\text{-arom.}$ ), 123.83 (s,  $m\text{-arom.}$ ), 124.00 (d,  $^1J_{\text{PC}} = 66.8$  Hz,  $ipso\text{-arom.}$ ), 140.12 (s, arom.), 146.48 (s, arom.), 151.16 (d,  $J_{\text{PC}} = 4.62$  Hz, arom.), 155.57 (d,  $^2J_{\text{PC}} = 12.49$  Hz,  $ipso\text{-arom.}$ ), 163.62 (s, arom.), 193.99 (d,  $^2J_{\text{PC}} = 7.86$  Hz,  $4 \times \text{CO}$ ), 198.20 (d,  $^2J_{\text{PC}} = 37.49$  Hz, CO) ppm. UV ( $\text{CH}_2\text{Cl}_2$ ):  $\Delta_{\text{max}}$  289 (log  $\epsilon = 4.18$ ), 409 (log  $\epsilon = 4.05$ ) nm. IR (KBr):  $\nu$  2077 (s), 1998, 1957 (vs)  $\text{cm}^{-1}$ . Anal. Found: C, 54.92; H, 6.60%.  $\text{C}_{41}\text{H}_{58}\text{O}_6\text{P}_2\text{W}$  calc.: C, 55.16; H, 6.55%.

**6a**:  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta_{\text{PA}}$  311.3 (satellite,

Table 3

Some selected bond angles ( $^\circ$ ) for **5b** (numbers in parentheses are estimated standard deviations)

P(1)–W(1)–C(34)	92.0(2)	C(3)–C(4)–C(11)	120.3(9)
P(1)–W(1)–C(35)	92.7(2)	C(5)–C(4)–C(11)	121.8(9)
P(1)–W(1)–C(36)	94.7(2)	C(4)–C(5)–C(6)	123.7(8)
P(1)–W(1)–C(37)	87.1(2)	C(1)–C(6)–C(5)	115.1(7)
P(1)–W(1)–C(38)	174.1(2)	C(1)–C(6)–C(12)	126.5(7)
C(34)–W(1)–C(35)	92.4(4)	C(5)–C(6)–C(12)	118.2(7)
C(34)–W(1)–C(36)	173.3(3)	P(2)–C(16)–C(17)	121.1(5)
C(34)–W(1)–C(37)	93.8(3)	P(2)–C(16)–C(21)	120.2(6)
C(34)–W(1)–C(38)	83.2(3)	C(17)–C(16)–C(21)	118.3(6)
C(35)–W(1)–C(36)	88.0(4)	C(16)–C(17)–C(18)	118.9(7)
C(35)–W(1)–C(37)	173.7(3)	C(16)–C(17)–C(22)	126.3(7)
C(35)–W(1)–C(38)	90.8(3)	C(18)–C(17)–C(22)	114.8(7)
C(36)–W(1)–C(37)	85.8(4)	C(17)–C(18)–C(19)	123.2(7)
C(36)–W(1)–C(38)	90.1(3)	C(18)–C(19)–C(20)	117.2(7)
C(37)–W(1)–C(38)	89.9(3)	C(18)–C(19)–C(26)	121.9(7)
W(1)–P(1)–P(2)	142.2(1)	C(20)–C(19)–C(26)	120.8(7)
W(1)–P(1)–O(1)	110.0(2)	C(19)–C(20)–C(21)	123.8(7)
P(2)–P(1)–O(1)	107.8(2)	C(16)–C(21)–C(20)	118.2(7)
P(1)–P(2)–C(16)	104.3(2)	C(16)–C(21)–C(30)	125.7(7)
P(1)–O(1)–C(1)	124.4(4)	C(20)–C(21)–C(30)	116.1(6)
O(1)–C(1)–C(2)	117.8(6)	W(1)–C(34)–O(2)	175.0(7)
O(1)–C(1)–C(6)	119.1(6)	W(1)–C(35)–O(3)	175.7(9)
C(2)–C(1)–C(6)	123.0(7)	W(1)–C(36)–O(4)	178.2(8)
C(1)–C(2)–C(3)	116.3(7)	W(1)–C(37)–O(5)	177.3(8)
C(1)–C(2)–C(7)	124.2(7)	W(1)–C(38)–O(6)	177.2(8)
C(3)–C(2)–C(7)	119.3(7)		
C(2)–C(3)–C(4)	122.5(8)		
C(3)–C(4)–C(5)	117.8(7)		

$^1J_{PW} = 243.5$  Hz),  $\delta_{p^A} 491.2$  (AB,  $^1J_{PP} = 510.8$  Hz) ppm.

**5b**: yellow prisms; m.p., 201–202°C (CH<sub>3</sub>CN).  $^1H$  NMR (CDCl<sub>3</sub>, 600 MHz):  $\delta = 1.30$  (9H, s, *p*-<sup>1</sup>Bu), 1.51 (18H, s, *o*-<sup>1</sup>Bu), 1.56 (18H, s, *o*-<sup>1</sup>Bu), 2.36 (3H, s, *p*-Me), 7.12 (2H, s, arom.), 7.45 (2H, s, arom.) ppm.  $^{31}P\{^1H\}$  NMR (CDCl<sub>3</sub>):  $\delta_{p^A} 339.6$ ,  $\delta_{p^B} 443.4$  (satellite,  $^1J_{PW} = 291.3$  Hz) (AB,  $^1J_{PP} = 568.9$  Hz) ppm.  $^{13}C\{^1H\}$  NMR (CDCl<sub>3</sub>, 150 MHz):  $\delta 21.37$  (s, *p*-Me), 31.06 (s, *p*-CMe<sub>3</sub>), 33.08 (s, *o*-CMe<sub>3</sub>), 33.37 (s, *o*-CMe<sub>3</sub>), 34.90 (s, *p*-CMe<sub>3</sub>), 36.36 (s, *o*-CMe<sub>3</sub>), 38.86 (s, *o*-CMe<sub>3</sub>), 123.19 (s, *m*-arom.), 124.28 (d,  $^1J_{PC} = 66.55$  Hz, *ipso*-arom.), 127.90 (s, *m*-arom.), 133.37 (s, *p*-arom.), 140.72 (s, *o*-arom.), 151.20 (s, *p*-arom.), 151.56 (d,  $^2J_{PC} = 14.79$  Hz, *ipso*-arom.), 155.73 (d,  $J_{PC} = 9.51$  Hz, *o*-arom.), 194.02 (d,  $^2J_{PC} = 5.28$  Hz and satellite,  $^1J_{WC} = 122.08$  Hz, 4 × CO), 198.14 (d,  $^2J_{PC} = 37.58$  Hz, CO) ppm. UV (CH<sub>2</sub>Cl<sub>2</sub>):  $\Delta_{max} 289$  (log  $\epsilon = 4.20$ ), 408 (log  $\epsilon = 4.09$ ) nm. IR (KBr):  $\nu 2077$  (s), 2000, 1958 (vs), 1944 (vs) cm<sup>-1</sup>. Anal. Found: C, 53.60; H, 6.22%. C<sub>38</sub>H<sub>52</sub>O<sub>6</sub>P<sub>2</sub>W calc.: C, 53.66; H, 6.16%.

**6b**:  $^{31}P\{^1H\}$  NMR (CDCl<sub>3</sub>):  $\delta_{p^A} 311.8$  (satellite,  $^1J_{PW} = 243.6$  Hz),  $\delta_{p^B} 491.7$  (AB,  $^1J_{PP} = 510.6$  Hz) ppm.

**5c**: yellow prisms; m.p., 176–178°C (CH<sub>3</sub>CN).  $^1H$  NMR (CDCl<sub>3</sub>, 600 MHz):  $\delta 1.28$  (9H, s, *p*-<sup>1</sup>Bu), 1.49 (18H, s, *o*-<sup>1</sup>Bu), 1.56 (18H, s, *o*-<sup>1</sup>Bu), 7.14 (1H, t,  $^3J_{HH} = 7.74$  Hz, arom.), 7.34 (2H, d,  $^3J_{HH} = 7.77$  Hz, arom.), 7.44 (2H, bs, arom.) ppm.  $^{31}P\{^1H\}$  NMR (CDCl<sub>3</sub>):  $\delta_{p^A} 339.9$ ,  $\delta_{p^B} 443.2$  (satellite,  $^1J_{PW} = 291.6$  Hz) (AB,  $^1J_{PP} = 569.1$  Hz) ppm.  $^{13}C\{^1H\}$  NMR (CDCl<sub>3</sub>, 150 MHz):  $\delta 31.04$  (s, *p*-CMe<sub>3</sub>), 33.04 (s, *o*-CMe<sub>3</sub>), 33.34 (bs, *o*-CMe<sub>3</sub>), 34.89 (s, *p*-CMe<sub>3</sub>), 36.51 (s, *o*-CMe<sub>3</sub>), 38.85 (s, *o*-CMe<sub>3</sub>), 123.20 (s, arom.), 124.06 (d,  $^1J_{PC} = 66.25$  Hz, *ipso*-arom.), 124.46 (s, arom.), 127.08 (s, arom.), 141.31 (s, arom.), 151.28 (d,  $J_{PC} = 3.70$  Hz, arom.), 153.63 (dd,  $^3J_{PC} = 6.47$  Hz and  $^2J_{PC} = 16.18$  Hz, *ipso*-arom.), 155.73 (d,  $J_{PC} = 10.26$  Hz, arom.), 193.96 (d,  $^2J_{PC} = 6.49$  Hz and satellite,  $^1J_{WC} = 125.98$  Hz, 4 × CO), 198.07 (d,  $^2J_{PC} = 38.18$  Hz, CO) ppm. UV (CH<sub>2</sub>Cl<sub>2</sub>):  $\Delta_{max} 289$  (log  $\epsilon = 4.16$ ), 408 (log  $\epsilon = 4.11$ ) nm. IR (KBr):  $\nu 2079$  (s), 2000, 1965 (vs), 1936 (vs) cm<sup>-1</sup>. Anal. Found: C, 53.46; H, 6.31%. C<sub>37</sub>H<sub>50</sub>O<sub>6</sub>P<sub>2</sub>W calc.: C, 53.12; H, 6.02%.

**6c**:  $^{31}P\{^1H\}$  NMR (CDCl<sub>3</sub>):  $\delta_{p^A} 312.9$  (satellite,  $^1J_{PW} = 244.0$  Hz),  $\delta_{p^B} 491.0$  (AB,  $^1J_{PP} = 510.9$  Hz) ppm.

### 3.3. Synthesis of the other Group 6 metal carbonyl complexes (7b, 8b, 9b and 10b)

Similarly to the preparation of tungsten complexes, the following chromium and molybdenum complexes of diphosphene **2b** were prepared and characterized.

**7b**: yield, 53%; orange prisms; m.p., 182.5–183.5°C (CH<sub>3</sub>CN).  $^1H$  NMR (CDCl<sub>3</sub>, 200 MHz):  $\delta 1.31$  (9H, s, *p*-<sup>1</sup>Bu), 1.52 (18H, s, *o*-<sup>1</sup>Bu), 1.58 (18H, s, *o*-<sup>1</sup>Bu), 2.38

(3H, s, *p*-Me), 7.14 (2H, s, arom.), 7.46 (2H, s, arom.) ppm.  $^{31}P\{^1H\}$  NMR (CDCl<sub>3</sub>):  $\delta_{p^A} 378.1$ ,  $\delta_{p^B} 501.1$  (AB,  $^1J_{PP} = 572.9$  Hz) ppm.  $^{13}C\{^1H\}$  NMR (CDCl<sub>3</sub>, 50 MHz):  $\delta 21.37$  (s, *p*-Me), 31.06 (s, *p*-CMe<sub>3</sub>), 33.09 (s, *o*-CMe<sub>3</sub>), 33.21 (dd,  $J_{PC} = 6.95$  Hz and  $J_{PC} = 2.14$  Hz, *o*-CMe<sub>3</sub>), 34.88 (s, *p*-CMe<sub>3</sub>), 36.39 (s, *o*-CMe<sub>3</sub>), 38.76 (s, *o*-CMe<sub>3</sub>), 123.06 (d,  $J_{PC} = 3.02$  Hz, *m*-arom.), 124.95 (d,  $^1J_{PC} = 58.43$  Hz, *ipso*-arom.), 127.93 (d,  $J_{PC} = 1.66$  Hz, *m*-arom.), 133.29 (d,  $J_{PC} = 1.61$  Hz, arom.), 140.55 (s, *o*-arom.), 151.34 (d,  $J_{PC} = 4.03$  Hz, arom.), 151.80 (dd,  $^2J_{PC} = 17.69$  Hz and  $^3J_{PC} = 7.62$  Hz, *ipso*'-arom.), 155.69 (dd,  $J_{PC} = 11.25$  Hz and  $J_{PC} = 3.25$  Hz, arom.), 213.00 (dd,  $^2J_{PC} = 14.34$  Hz and  $^3J_{PC} = 2.62$  Hz, 4 × CO), 220.58 (s, CO) ppm. UV (CH<sub>2</sub>Cl<sub>2</sub>):  $\Delta_{max} 282$  (log  $\epsilon = 4.23$ ), 410 (log  $\epsilon = 3.95$ ) nm. IR (KBr):  $\nu 2071$ , 1963, 1948 cm<sup>-1</sup>.

**8b**:  $^{31}P\{^1H\}$  NMR (CDCl<sub>3</sub>):  $\delta_{p^A} 363.4$ ,  $\delta_{p^B} 516.0$  (AB,  $^1J_{PP} = 512.6$  Hz) ppm.

**9b**: yield, 33%; yellow prisms; m.p., 174–175°C (CH<sub>3</sub>CN).  $^1H$  NMR (CDCl<sub>3</sub>, 200 MHz):  $\delta 1.32$  (9H, s, *p*-<sup>1</sup>Bu), 1.52 (18H, s, *o*-<sup>1</sup>Bu), 1.57 (18H, s, *o*-<sup>1</sup>Bu), 2.38 (3H, s, *p*-Me), 7.14 (2H, s, arom.), 7.49 (2H, s, arom.) ppm.  $^{31}P\{^1H\}$  NMR (CDCl<sub>3</sub>):  $\delta_{p^A} 362.9$ ,  $\delta_{p^B} 484.2$  (AB,  $^1J_{PP} = 565.0$  Hz) ppm.  $^{13}C\{^1H\}$  NMR (CDCl<sub>3</sub>, 50 MHz):  $\delta 21.38$  (s, *p*-Me), 31.09 (s, *p*-CMe<sub>3</sub>), 33.09 (s, *o*-CMe<sub>3</sub>), 33.39 (dd,  $J_{PC} = 6.89$  Hz and  $J_{PC} = 2.42$  Hz, *o*-CMe<sub>3</sub>), 34.89 (s, *p*-CMe<sub>3</sub>), 36.35 (s, *o*-CMe<sub>3</sub>), 38.83 (s, *o*-CMe<sub>3</sub>), 123.19 (d,  $J_{PC} = 2.77$  Hz, *m*-arom.), 124.14 (dd,  $^1J_{PC} = 66.33$  Hz and  $^2J_{PC} = 1.72$  Hz, *ipso*-arom.), 127.85 (d,  $J_{PC} = 1.56$  Hz, *m*-arom.), 133.27 (d,  $J_{PC} = 1.56$  Hz, arom.), 140.72 (s, arom.), 151.01 (d,  $J_{PC} = 3.87$  Hz, *o*-arom.), 151.66 (dd,  $^2J_{PC} = 16.71$  Hz and  $^3J_{PC} = 7.25$  Hz, *ipso*'-arom.), 155.66 (dd,  $J_{PC} = 11.30$  Hz and  $J_{PC} = 2.94$  Hz, arom.), 202.76 (dd,  $^2J_{PC} = 10.37$  Hz and  $^3J_{PC} = 1.14$  Hz, 4 × CO), 209.86 (dd,  $^2J_{PC} = 37.09$  Hz and  $^3J_{PC} = 0.95$  Hz, CO) ppm. UV (CH<sub>2</sub>Cl<sub>2</sub>):  $\Delta_{max} 283$  (sh, log  $\epsilon = 4.23$ ), 316 (sh, log  $\epsilon = 3.89$ ), 406 (log  $\epsilon = 4.11$ ) nm. IR (KBr):  $\nu 2079$ , 1963, 1950 cm<sup>-1</sup>. Anal. Found: C, 59.87; H, 6.64%. C<sub>38</sub>H<sub>52</sub>O<sub>6</sub>P<sub>2</sub>Mo calc.: C, 59.84; H, 6.87%.

**10b**:  $^{31}P\{^1H\}$  NMR (CDCl<sub>3</sub>):  $\delta_{p^A} 378.2$ ,  $\delta_{p^B} 501.8$  (AB,  $^1J_{PP} = 573.2$  Hz) ppm.

### 3.4. X-ray structure determination of 5b

The compound **5b** was recrystallized from acetonitrile.

Crystal data for **5b**: C<sub>38</sub>H<sub>52</sub>O<sub>6</sub>P<sub>2</sub>W;  $M_r = 850.62$ ; triclinic, space group,  $P1$ ;  $a = 11.358(3)$ ,  $b = 18.508(3)$  and  $c = 10.087(4)$  Å;  $\alpha = 97.81(3)^\circ$ ,  $\beta = 105.16(3)^\circ$  and  $\gamma = 97.81(2)^\circ$ ;  $U = 1994(1)$  Å<sup>3</sup>;  $Z = 2$ ;  $D_c = 1.416$  g cm<sup>-3</sup>;  $\mu = 30.20$  cm<sup>-1</sup>. Unique 7015 reflections with  $2\theta \leq 50.0^\circ$  were recorded and 6105 of these with  $I > 3.00\sigma(I)$  were judged as observed. The structure was solved using SHELXS86 [17]. Non-hydrogen atoms were refined anisotropically except for the disordered carbon atoms of C(8)–C(10) and C(13)–C(15). Both of the

occupancy factors for the dominant tert-butyl group were 0.76. Hydrogen atoms were included but not refined.  $R = 0.038$  and  $R_w = 0.049$ .

### 3.5. Supplementary material available

Tables of atomic coordinates, anisotropic thermal parameters, H-atom coordinates, bond distances and angles, and structure factors for **5b** (31 pages) are available on request from the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, UK.

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