

# Synthesis and reactions of cycloheptadienyl and cyclooctadienyl tungsten complexes: X-ray crystal structure of $[\text{W}(\text{CO})_2(\text{PPh}_3)_2(\eta^5\text{-C}_7\text{H}_9)][\text{BF}_4]$

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Received 26 September 2003; accepted 1 December 2003

## Abstract

Protonation of the cycloheptatriene complex  $[\text{W}(\text{CO})_3(\eta^6\text{-C}_7\text{H}_8)]$  with  $\text{H}[\text{BF}_4] \cdot \text{Et}_2\text{O}$  in  $\text{CH}_2\text{Cl}_2$  affords the cycloheptadienyl system  $[\text{W}(\text{CO})_3(\eta^5\text{-C}_7\text{H}_9)][\text{BF}_4]$  (**1**). Complex **1** reacts with  $\text{NaI}$  to yield  $[\text{WI}(\text{CO})_3(\eta^5\text{-C}_7\text{H}_9)]$ , which is a precursor to  $[\text{W}(\text{CO})_2(\text{NCMe})_3(\eta^3\text{-C}_7\text{H}_9)][\text{BF}_4]$ , albeit in very low yield. The dicarbonyl derivatives  $[\text{W}(\text{CO})_2\text{L}_2(\eta^5\text{-C}_7\text{H}_9)]^+$  ( $\text{L}_2 = 2\text{PPh}_3$ , **4**, or  $\text{dppm}$ , **5**) were obtained, respectively, by  $\text{H}[\text{BF}_4] \cdot \text{Et}_2\text{O}$  protonation of  $[\text{W}(\text{CO})_2(\text{PPh}_3)_2(\eta^6\text{-C}_7\text{H}_8)]$  in the presence of  $\text{PPh}_3$  and reaction of **1** with  $\text{dppm}$ . The X-ray crystal structure of **4** (as a  $1/2 \text{CH}_2\text{Cl}_2$  solvate) reveals that the two  $\text{PPh}_3$  ligands are mutually *trans* and are located beneath the central dienyl carbon and the centre of the edge bridge. The first examples of cyclooctadienyl tungsten complexes  $[\text{WBr}(\text{CO})_2(\text{NCMe})_2(1\text{-}3\text{-}\eta^5\text{-}5,6\text{-C}_8\text{H}_{11})]$  (**6**) and  $[\text{WBr}(\text{CO})_2(\text{NCMe})_2(1\text{-}3\text{-}\eta^4\text{-}4,5\text{-C}_8\text{H}_{11})]$  (**7**) were synthesised by reaction of  $[\text{W}(\text{CO})_3(\text{NCR})_3]$  ( $\text{R} = \text{Me}$  or  $\text{Pr}^n$ ) with 3-Br-1,5-cod/6-Br-1,4-cod or 5-Br-1,3-cod/3-Br-1,4-cod (cod = cyclooctadiene), respectively. Complexes **6** and **7** are precursors to the pentahapto-bonded cyclooctadienyl tungsten species  $[\text{W}(\text{CO})_2(\text{dppm})(1\text{-}3\text{-}5,6\text{-}\eta\text{-C}_8\text{H}_{11})][\text{BF}_4]$  and  $[\text{W}(\text{CO})_2(\text{dppe})(1\text{-}5\text{-}\eta\text{-C}_8\text{H}_{11})][\text{BF}_4] \cdot \text{CH}_2\text{Cl}_2$ . © 2004 Elsevier B.V. All rights reserved.

**Keywords:** Dienyl; Tungsten; Cycloheptadienyl; Cyclooctadienyl; Edge bridge

## 1. Introduction

The cyclohexadienyl ( $\text{C}_6\text{H}_7$ ), cycloheptadienyl ( $\text{C}_7\text{H}_9$ ) and cyclooctadienyl ( $\text{C}_8\text{H}_{11}$ ) ligands constitute a subclass of dienyl ligands in which the terminal dienyl carbons are linked by an edge bridge consisting of one, two or three methylene groups, respectively. Edge-bridged dienyl ligands are of interest because of the structural effects of the edge bridge and their ability to coordinate to a metal centre both as  $\eta^5$  and  $\eta^3$  ligands with inter-conversion between the two hapticity types in selected examples [1,2]. The focus of our work in this area to date has been with cycloheptadienyl [3,4] and cyclooctadienyl [5,6] complexes of molybdenum but in the current paper

we extend our investigations to the chemistry of the analogous tungsten systems. It is not our intention to provide a comprehensive and exhaustive account of cycloheptadienyl and cyclooctadienyl tungsten chemistry but rather our objectives are (i) to describe synthetic routes to the tungsten complexes and (ii) to highlight differences in reactivity resulting from exchange of molybdenum for tungsten especially with respect to  $\eta^5 \rightarrow \eta^3$  hapticity conversion processes. In addition to our preliminary account of this work [7], some aspects of cycloheptadienyl tungsten chemistry have been developed previously. These comprise the synthesis of the monosubstituted, pentahapto-cycloheptadienyl complexes (i)  $[\text{W}(\text{CO})_3\text{L}(\eta^5\text{-C}_7\text{H}_9)]^+$  ( $\text{L} = \text{P}$ -,  $\text{As}$ - or  $\text{Sb}$ -donor ligand) via reaction of  $\text{L}$  with  $[\text{W}(\text{CO})_3(\eta^5\text{-C}_7\text{H}_9)]^+$  [8] and (ii)  $[\text{WX}(\text{CO})_3(\eta^5\text{-C}_7\text{H}_9)]$  ( $\text{X} = \text{Me}$  [9] or  $\text{SnPh}_3$  [10]) derived from the anion  $[\text{W}(\text{CO})_3(\eta^5\text{-C}_7\text{H}_9)]^-$ . One case of the  $\text{C}_7\text{H}_9$  ligand-bonded trihapto to tungsten,

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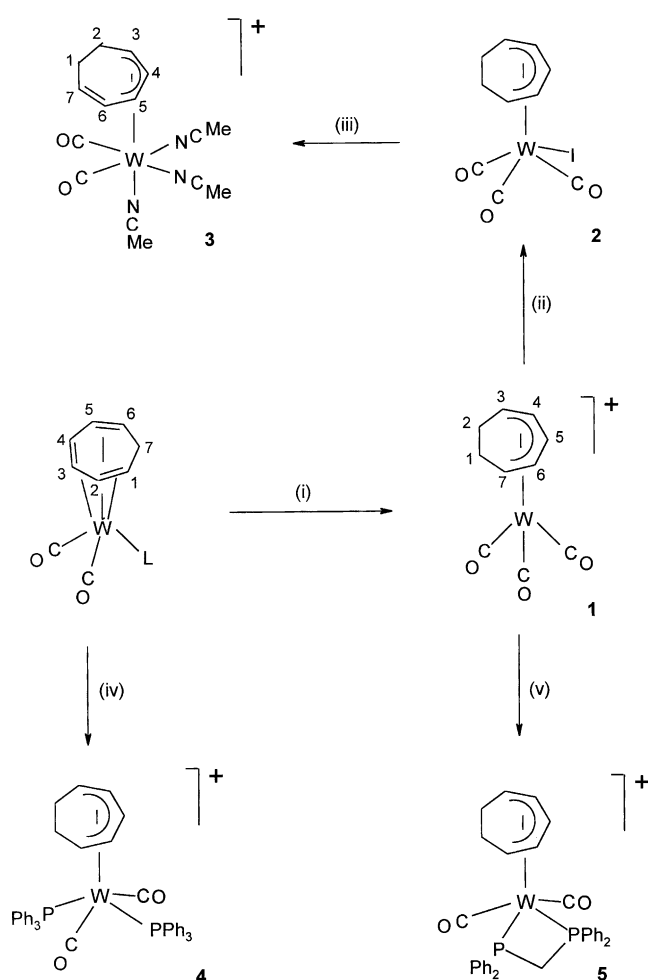
$[\text{W}(\text{CO})_2(\eta^3\text{-C}_7\text{H}_9)(\eta\text{-C}_5\text{H}_4\text{Me})]$ , has also been reported [11]. The cyclooctadienyl tungsten complexes described here represent the first examples of this system.

## 2. Results and discussion

### 2.1. Cycloheptadienyl complexes

Our investigations on the chemistry of the cycloheptadienyl tungsten system are summarised in Scheme 1. Microanalytical, infrared and mass spectroscopic data for each of the complexes are presented in Table 1 and  $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR data are given in Table 2. A full account of the spectroscopic data for analogous molybdenum complexes has been presented previously [3,4] and therefore discussion here is restricted to specific, salient points.

Progress in the development of cycloheptadienyl molybdenum chemistry has been facilitated by the



Scheme 1. Reagents and conditions: (i)  $\text{L} = \text{CO}$ ;  $\text{H}[\text{BF}_4] \cdot \text{Et}_2\text{O}$  in  $\text{CH}_2\text{Cl}_2$ , 30 min. (ii)  $\text{NaI}$  in acetone,  $-78^\circ\text{C}$ , 1 h. (iii)  $\text{Ag}[\text{BF}_4]$  in  $\text{NCMe}$ , 30 min. (iv)  $\text{L} = \text{PPh}_3$ ;  $\text{H}[\text{BF}_4] \cdot \text{Et}_2\text{O}/\text{PPh}_3$  in  $\text{THF}$ , 1 h. (v) (a)  $\text{dppm}$  in  $\text{CH}_2\text{Cl}_2$ , 1 h. (b) Reflux in 2-butanone, 30 min.

availability of  $[\text{Mo}(\text{CO})_2(\text{NCMe})_3(\eta^3\text{-C}_7\text{H}_9)]^+$  which is a versatile precursor to a wide range of derivatives  $[\text{Mo}(\text{CO})_2\text{L}_2(\eta^5\text{-C}_7\text{H}_9)]^+$  ( $\text{L}_2 = 2 \text{ PR}_3$ ,  $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$  ( $n = 1$ ,  $\text{dppm}$ ,  $n = 2$ ,  $\text{dppe}$ ), 2,2'-bipyridine, diene, etc.) [3]. The synthesis of  $[\text{Mo}(\text{CO})_2(\text{NCMe})_3(\eta^3\text{-C}_7\text{H}_9)]^+$  was effected in a two-step process involving protonation of  $[\text{Mo}(\text{CO})_3(\eta^6\text{-C}_7\text{H}_8)]$  with  $\text{H}[\text{BF}_4] \cdot \text{Et}_2\text{O}$  in  $\text{CO}$  saturated  $\text{CH}_2\text{Cl}_2$  to give  $[\text{Mo}(\text{CO})_4(\eta^5\text{-C}_7\text{H}_9)]^+$  followed by reaction with  $\text{NCMe}$  to yield  $[\text{Mo}(\text{CO})_2(\text{NCMe})_3(\eta^3\text{-C}_7\text{H}_9)]^+$ . The initial strategy in the current investigation was therefore to synthesise  $[\text{W}(\text{CO})_2(\text{NCMe})_3(\eta^3\text{-C}_7\text{H}_9)]^+$  starting from  $[\text{W}(\text{CO})_3(\eta^6\text{-C}_7\text{H}_8)]$  and to apply this as a precursor to a range of novel dicarbonyl cycloheptadienyl tungsten complexes of the type  $[\text{W}(\text{CO})_2\text{L}_2(\eta^5\text{-C}_7\text{H}_9)]^+$ . As discussed in Section 1, previously reported examples of cycloheptadienyl tungsten complexes are limited to tricarbonyl derivatives of the type  $[\text{W}(\text{CO})_3\text{L}(\eta^5\text{-C}_7\text{H}_9)]^+$  and  $[\text{WX}(\text{CO})_3(\eta^5\text{-C}_7\text{H}_9)]$  [8–10].

Treatment of a  $\text{CO}$  saturated,  $\text{CH}_2\text{Cl}_2$  solution of  $[\text{W}(\text{CO})_3(\eta^6\text{-C}_7\text{H}_8)]$  with  $\text{H}[\text{BF}_4] \cdot \text{Et}_2\text{O}$  at  $0^\circ\text{C}$  followed by slow warming to ambient temperature afforded an orange-yellow solution. In contrast to the molybdenum system, no precipitate formed directly from the reaction mixture but subsequent work up led to isolation of the product as an orange oil or, on occasions, as an orange solid. Infrared spectroscopic data indicated that the isolated material was not  $[\text{W}(\text{CO})_4(\eta^5\text{-C}_7\text{H}_9)]^+[\text{BF}_4]^-$  but the formally 16-electron, tricarbonyl species  $[\text{W}(\text{CO})_3(\eta^5\text{-C}_7\text{H}_9)]^+[\text{BF}_4]^-$  (**1**). Thus, the  $\text{CH}_2\text{Cl}_2$  solution infrared spectrum of **1** has two strong bands ( $\nu(\text{CO})$  ( $\text{cm}^{-1}$ ) 2058, 1980), in contrast to the three band spectrum of  $[\text{Mo}(\text{CO})_4(\eta\text{-C}_7\text{H}_9)]^+[\text{BF}_4]^-$  ( $\nu(\text{CO})$ ,  $\text{CH}_2\text{Cl}_2$  ( $\text{cm}^{-1}$ ), 2112, 2065, 2008), but comparable with related cyclopentadienyl complexes  $[\text{M}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)]^+[\text{BF}_4]^-$  ( $\nu(\text{CO})$ ,  $\text{CH}_2\text{Cl}_2$  ( $\text{cm}^{-1}$ ),  $\text{M} = \text{Mo}$ , 2071, 1988;  $\text{M} = \text{W}$ , 2067, 1975) [12], which also possess formal 16-electron configurations although it has been suggested that these latter complexes incorporate an  $F$ -coordinated  $\text{BF}_4$  ligand. In fact the tricarbonyl cycloheptadienyl complexes  $[\text{M}(\text{CO})_3(\eta^5\text{-C}_7\text{H}_9)]^+[\text{BF}_4]^-$  ( $\text{M} = \text{Mo}$  [13] or  $\text{W}$  [8]) have been prepared previously by protonation of  $[\text{M}(\text{CO})_3(\eta^6\text{-C}_7\text{H}_8)]$  in propionic anhydride but the tungsten derivative could not be isolated free from solvent residues. The modified synthesis described here led to isolation of solvent free  $[\text{W}(\text{CO})_3(\eta^5\text{-C}_7\text{H}_9)]^+[\text{BF}_4]^-$  and this allowed us to confirm its identity by microanalysis and  $^1\text{H}$  NMR spectroscopy. It is probable that in our previous work, the tetracarbonyl  $[\text{Mo}(\text{CO})_4(\eta^5\text{-C}_7\text{H}_9)]^+[\text{BF}_4]^-$  was generated by in situ carbonylation of  $[\text{Mo}(\text{CO})_3(\eta^5\text{-C}_7\text{H}_9)]^+[\text{BF}_4]^-$  so paralleling the reactions of the cyclopentadienyl complexes  $[\text{M}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)]^+[\text{BF}_4]^-$  ( $\text{M} = \text{Mo}$  or  $\text{W}$ ) with carbon monoxide to yield  $[\text{M}(\text{CO})_4(\eta\text{-C}_5\text{H}_5)]^+[\text{BF}_4]^-$  [12]. However,  $[\text{W}(\text{CO})_3(\eta^5\text{-C}_7\text{H}_9)]^+[\text{BF}_4]^-$  appears to be unreactive towards addition of  $\text{CO}$  and complex **1** was isolated independent of whether

Table 1  
Microanalytical, infrared and mass spectroscopic data

Complex	Analysis (%) <sup>a</sup>			Infrared <sup>b</sup> $\nu(\text{CO})$ (cm <sup>-1</sup> )	Mass spectral data <sup>c</sup>
	C	H	N		
<b>1</b> [W(CO) <sub>3</sub> ( $\eta^5$ -C <sub>7</sub> H <sub>9</sub> )] [BF <sub>4</sub> ]	27.1 (26.8)	2.3 (2.0)		2058, 1980	
<b>2</b> [W(CO) <sub>3</sub> ( $\eta^5$ -C <sub>7</sub> H <sub>9</sub> )]	24.7 (24.6)	2.0 <sup>d</sup> (1.8)		2035, 1959	488 (M <sup>+</sup> ), 460 ([M – CO] <sup>+</sup> ), 432 ([M – 2CO] <sup>+</sup> ), 404 ([M – 3CO] <sup>+</sup> ), 363 ([M – I] <sup>+</sup> )
<b>3</b> [W(CO) <sub>2</sub> (NCMe) <sub>3</sub> ( $\eta^3$ -C <sub>7</sub> H <sub>9</sub> )] [BF <sub>4</sub> ]	32.9 (33.2)	3.3 (3.3)	7.8 (7.7)	1952, 1869 <sup>e</sup>	415 ([M – NCMe] <sup>+</sup> ), 374 ([M – 2NCMe] <sup>+</sup> ), 318 ([M – 2NCMe – 2CO] <sup>+</sup> )
<b>4</b> [W(CO) <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub> ( $\eta^5$ -C <sub>7</sub> H <sub>9</sub> )] [BF <sub>4</sub> ]	57.3 (57.2)	4.3 (4.1)		1974, 1898	857 (M <sup>+</sup> ), 595 ([M – PPh <sub>3</sub> ] <sup>+</sup> ) <sup>f</sup>
<b>5</b> [W(CO) <sub>2</sub> (dppm)( $\eta^5$ -C <sub>7</sub> H <sub>9</sub> )] [BF <sub>4</sub> ]	50.5 (50.8)	4.1 (3.9)		2013, 1919	717 (M <sup>+</sup> ), 687 ([M – CO – 2H] <sup>+</sup> ), 659 ([M – 2CO – 2H] <sup>+</sup> )
<b>6</b> [WBr(CO) <sub>2</sub> (NCMe) <sub>2</sub> (1-3- $\eta$ :5,6-C <sub>8</sub> H <sub>11</sub> )]	33.4 (33.0)	3.5 (3.4)	5.7 (5.5)	1936, 1847 <sup>e</sup>	469 ([M – NCMe] <sup>+</sup> ), 428 ([M – 2NCMe] <sup>+</sup> or [M – Br] <sup>+</sup> ), 400 ([M – 2NCMe – CO] <sup>+</sup> ), 388 ([M – NCMe – Br] <sup>+</sup> )
<b>7</b> [WBr(CO) <sub>2</sub> (NCMe) <sub>2</sub> (1-3- $\eta$ :4,5-C <sub>8</sub> H <sub>11</sub> )]	33.3 (33.0)	3.6 (3.4)	5.7 (5.5)	1937, 1848 <sup>e</sup>	469 ([M – NCMe] <sup>+</sup> ), 428 ([M – 2NCMe] <sup>+</sup> or [M – Br] <sup>+</sup> ), 400 ([M – 2NCMe – CO] <sup>+</sup> ), 388 ([M – NCMe – Br] <sup>+</sup> )
<b>8</b> [WBr(CO) <sub>2</sub> (dppm)(1-3- $\eta$ :5,6-C <sub>8</sub> H <sub>11</sub> )]	51.5 (51.8)	4.1 (4.1)		1932, 1843	812 (M <sup>+</sup> ), 784 ([M – CO] <sup>+</sup> ), 754 ([M – 2CO – 2H] <sup>+</sup> ), 731 ([M – Br] <sup>+</sup> ), 703 ([M – Br – CO] <sup>+</sup> ), 676 ([M – Br – 2CO] <sup>+</sup> ), 647 ([M – 2CO – C <sub>8</sub> H <sub>11</sub> ] <sup>+</sup> )
<b>9</b> [W(CO) <sub>2</sub> (dppm)(1-3:5,6- $\eta$ -C <sub>8</sub> H <sub>11</sub> )] [BF <sub>4</sub> ]	51.7 (51.4)	4.2 (4.1)		1995, 1891	731 (M <sup>+</sup> ), 701 ([M – CO – 2H] <sup>+</sup> ), 673 ([M – 2CO – 2H] <sup>+</sup> )
<b>10</b> [W(CO) <sub>2</sub> (NCMe)(dppm)(1-3- $\eta$ :5,6-C <sub>8</sub> H <sub>11</sub> )] [BF <sub>4</sub> ]	51.8 (51.7)	4.3 (4.2)	1.6 (1.6)	1951, 1862 <sup>e</sup>	772 (M <sup>+</sup> ), 731 ([M – NCMe] <sup>+</sup> ) 701 ([M – NCMe – CO – 2H] <sup>+</sup> ), 673 ([M – NCMe – 2CO – 2H] <sup>+</sup> )
<b>11</b> [WBr(CO) <sub>2</sub> (dppe)(1-3- $\eta$ :4,5-C <sub>8</sub> H <sub>11</sub> )]	51.9 (52.4)	4.3 (4.2)		1926, 1833	824 (M <sup>+</sup> ), 768 ([M – 2CO] <sup>+</sup> ), 745 ([M – Br] <sup>+</sup> ), 716 ([M – Br – CO] <sup>+</sup> ), 660 ([M – 2CO – C <sub>8</sub> H <sub>11</sub> ] <sup>+</sup> )
<b>12</b> [W(CO) <sub>2</sub> (dppe)(1-5- $\eta$ -C <sub>8</sub> H <sub>11</sub> )] [BF <sub>4</sub> ] · CH <sub>2</sub> Cl <sub>2</sub>	48.5 (48.4)	3.9 <sup>g</sup> (4.0)		1991, 1916	745 (M <sup>+</sup> ), 715 ([M – CO – 2H] <sup>+</sup> ), 685 ([M – 2CO – 4H] <sup>+</sup> )

<sup>a</sup> Calculated values in parentheses.

<sup>b</sup> Solution spectra in CH<sub>2</sub>Cl<sub>2</sub> unless stated otherwise.

<sup>c</sup> FAB mass spectra unless stated otherwise,  $m/z$  values based on <sup>184</sup>W.

<sup>d</sup> I, 26.9 (26.0).

<sup>e</sup> In CH<sub>3</sub>CN.

<sup>f</sup> Electrospray mass spectrum in NCMe.

<sup>g</sup> Cl 6.8 (7.7).

Table 2  
 $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR data<sup>a,b</sup>

	$^1\text{H}$ NMR			$^{13}\text{C}\{^1\text{H}\}$ NMR			
	H <sub>dienyl</sub>	H <sub>methylene</sub>	L	CO	C <sub>dienyl</sub>	C <sub>methylene</sub>	L
1 <sup>c</sup>	6.40, 1H, m, H <sup>5</sup> ; 6.02, 2H, m, H <sup>4,6</sup> ; 5.58, 2H, d, H <sup>3,7</sup> $J(\text{H}^{3/7}-\text{H}^{4/6})$ 8	2.50, 4H, br, H <sup>1,2</sup>					
2 <sup>de</sup>	5.78, 1H, br, H <sup>5</sup> ; 5.31, 2H, m, H <sup>4,6</sup> ; 4.88, 2H, d, H <sup>3,7</sup> $J(\text{H}^{3/7}-\text{H}^{4/6})$ 9	2.62, 4H, br, H <sup>1,2</sup>		215.5, 202.9	101.1, 91.7, 88.5	33.5	
3 <sup>ef</sup>	6.21, 1H, dd, H <sup>6</sup> , $J(\text{H}^5-\text{H}^6)$ 7, $J(\text{H}^6-\text{H}^7)$ 11; 5.26, 1H, m, H <sup>7</sup> , 4.69, 1H, m, 4.66, 1H, m, H <sup>3</sup> and H <sup>5</sup> ; 3.61, 1H, at, H <sup>4</sup> , $J(\text{H}^4-\text{H}^{3/5})$ 8	2.65, 1H, m, H <sup>2</sup> ; 2.11, 2H, m, H <sup>1</sup> and H <sup>2</sup> ; 1.40, 1H, m, H <sup>1</sup>		214.6, 213.0	131.3, 128.2, C <sup>6,7</sup> ; 70.6, 69.4, 68.4, C <sup>3,4,5</sup>	30.0, 27.8	
4	5.34, 3H, m, H <sup>4,5,6</sup> ; 4.62, 2H, br, H <sup>3,7</sup>	1.90, 2H, m, 1.17, 2H, m, H <sup>1,2</sup>	7.54, 7.48, 30H, m, Ph (PPh <sub>3</sub> )	220.9, t, $J(\text{P}-\text{C})$ 19	102.6, 101.0, 91.5	34.2	133.7, 132.1, 129.4 (PPh <sub>3</sub> )
5 <sup>e</sup>	6.15, 1H, 5.35, 1H, 5.23, 1H, 5.12 1H, 4.58, 1H, 4.33, 1H, 4.17, 1H, H <sup>3-7</sup> and dppm CH <sub>2</sub>	2.45, 1H, m, 2.33, 1H, m, 2.12, 1H, m, 2.08, 1H, m, H <sup>1,2</sup>	7.86–7.06, 6.62, 20H, m, Ph(dppm)				
6 <sup>f</sup>	5.86, 1H, m, H <sup>5</sup> ; 5.51, 1H, m, H <sup>6</sup> , 4.24, 1H, m, 4.05, 1H, m, H <sup>1</sup> and H <sup>3</sup> ; 3.22, 1H, at, H <sup>2</sup> , $J(\text{H}^2-\text{H}^{1/3})$ 8	2.50, 1H, m, H <sup>4</sup> ; 2.39–2.03, 4H, m, H <sup>4,7,8</sup> ; 1.76, 1H, m, H <sup>8</sup>		218.4, 218.2	130.7, 130.4, C <sup>5,6</sup> ; 65.4, 65.1, 64.3 C <sup>1,2,3</sup>	33.6, 32.4, C <sup>4,7,8</sup>	
7 <sup>f</sup>	6.28, 1H, dd, H <sup>4</sup> , $J(\text{H}^4-\text{H}^5)$ 10; 5.22, 1H, m, H <sup>5</sup> , 4.31, 1H, br, 3.69, 1H, m, H <sup>1</sup> and H <sup>3</sup> ; 3.56, 1H, at, H <sup>2</sup> , $J(\text{H}^2-\text{H}^{1/3})$ 7	2.97, 1H, m, 1H, H <sup>6</sup> ; 2.10, 2H, m, H <sup>6,8</sup> ; 1.65, 1H, m, 1.28, 1H, m, H <sup>7</sup> ; 0.90, 1H, m, H <sup>8</sup>		Not observed	136.5, 126.2, C <sup>5,6</sup> ; 66.2, 59.9, 59.5, C <sup>1,2,3</sup>	33.2, 31.5, 25.4, C <sup>6,7,8</sup>	
8	5.83, 1H, m, H <sup>5</sup> ; 5.49, 1H, m, H <sup>6</sup> , 4.82, 1H, br, 4.67, 1H, br, H <sup>1</sup> and H <sup>3</sup> ; 3.29, 1H, m, H <sup>2</sup>	2.59, 1H, m, H <sup>4</sup> ; 2.51, 2H, m, H <sup>4</sup> and H <sup>8</sup> ; 2.27, 2H, m, H <sup>7</sup> ; 2.10, 1H, m, H <sup>8</sup>	7.58–7.29, 20H, m, Ph; 4.87, 1H, m, 4.51, 1H, m, CH <sub>2</sub> (dppm)	219.1, m; 218.4, m	74.7, C <sup>2h</sup>	33.5, 31.6	133.7–128.9, Ph; 37.2, t, $J(\text{C}-\text{P})$ 24, CH <sub>2</sub> (dppm)
9 <sup>i</sup>	5.26, 1H, at, H <sup>2</sup> , $J(\text{H}^2-\text{H}^{1/3})$ 8; 5.13, 1H, m, H <sup>1</sup> ; 4.82, 1H, m, H <sup>6</sup> ; 4.69, 1H, m, H <sup>3</sup> , 2.98, 1H, m, H <sup>5</sup>	3.76, 1H, m, H <sup>4</sup> ; 2.68, 3H, m, H <sup>7</sup> , H <sup>8</sup> ; 2.38, 1H, m, H <sup>4</sup> ; 2.27, 1H, m, H <sup>8</sup>	7.76–7.24, 20H, m, Ph; 5.64, 1H, m; 4.53, 1H, m, CH <sub>2</sub> (dppm)	219.7, dd, $J(\text{C}-\text{P})$ 22, 5; 209.4, dd, $J(\text{C}-\text{P})$ 10, 3	111.4, C <sup>6</sup> ; 104.9, C <sup>2</sup> ; 71.4, C <sup>1</sup> ; 63.9, C <sup>3</sup> ; 57.2, C <sup>5</sup>	32.8, C <sup>7</sup> ; 29.4, C <sup>8</sup> ; 21.8, C <sup>4</sup>	134.3–129.2, Ph; 43.9, t, $J(\text{P}-\text{C})$ 29, CH <sub>2</sub> (dppm)

Table 2 (continued)

	<sup>1</sup> H NMR			<sup>13</sup> C{ <sup>1</sup> H} NMR			
	H <sub>diaryl</sub>	H <sub>methylene</sub>	L	CO	C <sub>diaryl</sub>	C <sub>methylene</sub>	L
<b>10</b> <sup>f,g,j</sup>	5.82, 1H, br, H <sup>5</sup> ; 5.55, 1H, m, H <sup>6</sup> , 4.95, 1H, br, 4.57, 1H, br, H <sup>1</sup> and H <sup>3</sup> ; 4.19, 1H, br, H <sup>2</sup>	2.68–2.15, 6H, br, H <sup>4</sup> , H <sup>7</sup> , H <sup>8</sup>	7.94–7.51, 20H, m, Ph; 5.09, m, 1H, 4.76, 1H, m, CH <sub>2</sub> (dppm)	216.9, m; 211.9, m	84.2, 82.7, 67.8 82.5 <sup>a</sup> , 79.8 <sup>a</sup> , 68.8 <sup>a1</sup>	32.4, 30.8, 29.6	132.5–125.5, Ph; 37.0, t, J(C–P) 26, CH <sub>2</sub> (dppm)
<b>11</b>	6.25, 1H, dd, H <sup>4</sup> , J(H <sup>4</sup> –H <sup>5</sup> ) 11; 5.24, 1H, m, H <sup>5</sup> , 4.90, 1H, br, H <sup>3</sup> ; 4.18, 1H, br, H <sup>1</sup> ; 3.50, 1H, at, H <sup>2</sup> , J(H <sup>2</sup> –H <sup>1/3</sup> ) 8	2.79, 1H, m, 2.03, 1H, m, H <sup>6</sup> ; 2.25, m, 1H, H <sup>8</sup> ; 1.54, 1H, H <sup>7</sup> , 1.23, 2H, m, H <sup>7</sup> , H <sup>8</sup>	7.72–7.44, 20H, m, Ph; 3.07, m, 2H, CH <sub>2</sub> , 2.41, m, 2H, CH <sub>2</sub> (dppe)	218.1, at, J(C–P) 11 215.1 at, J(C–P) 7	76.4, 66.3, 64.6, C <sup>1</sup> , C <sup>2</sup> , C <sup>3k</sup>	31.3, 29.4, 24.5	134.4–126.4, Ph, 26.7, m, CH <sub>2</sub> (dppe)
<b>12</b> <sup>e</sup>	5.44, 1H, m, H <sup>3</sup> ; 5.35, 1H, br, 4.43, 1H, br, 4.33, 1H, br, 3.73, 1H, br, H <sup>1,2,4,5</sup>	2.57, 1H, m, 2.29, 1H, br, 1.60, 2H, br, H <sup>6</sup> , H <sup>8</sup> ; 1.18, 1H, br, 0.38, 1H, m, H <sup>7</sup>	7.62–7.04, Ph; 2.96, 1H, m, 2.63, 3H, m, CH <sub>2</sub> (dppe)	220.4, 210.6	106.8, C <sup>3</sup> ; 88.5, br, 86.3, br, 84.5, br, 59.2, br, C <sup>1,2,4,5</sup>	27.9, br, 25.5, br, C <sup>6,8</sup> ; 18.8, C <sup>7</sup>	133.0–129.6, Ph; 29.5, m, CH <sub>2</sub> (dppe)

d, doublet; t, triplet; at, apparent triplet; m, multiplet; br, broad; chemical shifts downfield from SiMe<sub>4</sub>, coupling constants in hertz; in CD<sub>2</sub>Cl<sub>2</sub> solution unless stated otherwise, numbering as in Schemes 1 and 2. All spectra recorded at room temperature unless stated otherwise.

<sup>a</sup> 300 MHz <sup>1</sup>H, 75 MHz <sup>13</sup>C{<sup>1</sup>H}, 121.5 MHz <sup>31</sup>P{<sup>1</sup>H} NMR spectra unless stated otherwise.

<sup>b</sup> <sup>31</sup>P{<sup>1</sup>H} NMR data: **4**, (25 °C) 18.3; (–50 °C) 20.9, d, J(P–P) 18, J(<sup>183</sup>W–P) 169, 16.5, d, J(P–P) 18, J(<sup>183</sup>W–P) 223; **5**, (25 °C) –31.7, br; (–70 °C) AB doublet of doublets, –32.3, d, J(P–P) 63; –33.2, d, J(P–P) 63; **8**, (30 °C) –21.5, br; (–80 °C) isomer 1: –7.1, d, J(P–P) 25, J(<sup>183</sup>W–P) 189, –30.1, d, J(P–P) 25, J(<sup>183</sup>W–P) 145; isomer 2: –8.1, d, J(P–P) 23, J(<sup>183</sup>W–P) 188; –30.7, d, J(P–P) 23, J(<sup>183</sup>W–P) 146; (approximate ratio, isomer 1 to isomer 2, 2:1). **9**, –35.2, d, J(P–P) 49, J(<sup>183</sup>W–P) 201; –36.5, d, J(P–P) 49, J(<sup>183</sup>W–P) 187; **12**, (–30 °C), 43.8, d, J(P–P) 23, J(<sup>183</sup>W–P) 263; 35.2, d, J(P–P) 22, J(<sup>183</sup>W–P) 183, J(P–P) not resolved at room temperature.

<sup>c</sup> In acetone-D-6.

<sup>d</sup> In CDCl<sub>3</sub>.

<sup>e</sup> Assignments with the aid of <sup>1</sup>H–<sup>1</sup>H decoupling experiments.

<sup>f</sup> In CD<sub>3</sub>CN.

<sup>g</sup> Low temperature spectra, **5**: <sup>1</sup>H (–70 °C); **10**: <sup>13</sup>C (–30 °C); **12**: <sup>1</sup>H (–30 °C).

<sup>h</sup> C<sup>5,6</sup> obscured by dppm Ph carbons, C<sup>1,3</sup> not observed.

<sup>i</sup> 500 MHz <sup>1</sup>H, 125 MHz <sup>13</sup>C{<sup>1</sup>H} NMR spectra, assignments made with the aid of standard 2D techniques.

<sup>j</sup> Resonances for minor isomer marked with asterisk.

<sup>k</sup> C<sup>4,5</sup> obscured by dppe Ph carbons.

protonation of  $[\text{W}(\text{CO})_3(\eta^6\text{-C}_7\text{H}_8)]$  was carried out under a CO or nitrogen atmosphere.

The second step of the synthesis of  $[\text{W}(\text{CO})_2(\text{NCMe})_3(\eta^3\text{-C}_7\text{H}_9)][\text{BF}_4]$  (**3**) was attempted by dissolution of  $[\text{W}(\text{CO})_3(\eta^5\text{-C}_7\text{H}_9)][\text{BF}_4]$  in stirred NCMe. Work up of the reaction mixture gave an orange solid with infrared active carbonyl stretching frequencies ( $\nu(\text{CO})$ ,  $\text{CH}_3\text{CN}$  ( $\text{cm}^{-1}$ ) 1952, 1869) consistent with the formation of **3** (cf.  $[\text{Mo}(\text{CO})_2(\text{NCMe})_3(\eta^3\text{-C}_7\text{H}_9)][\text{BF}_4]$  ( $\nu(\text{CO})$ ,  $\text{CH}_3\text{CN}$  ( $\text{cm}^{-1}$ ) 1958, 1877) [3]. However, attempts to generate a pure form of this material were unsuccessful and ultimately complex **3** was obtained in a two step synthesis from **1**. First, reaction of  $[\text{W}(\text{CO})_3(\eta^5\text{-C}_7\text{H}_9)][\text{BF}_4]$  with excess NaI in acetone at  $-78^\circ\text{C}$  afforded  $[\text{WI}(\text{CO})_3(\eta^5\text{-C}_7\text{H}_9)]$  (**2**). Subsequent reaction of complex **2** with  $\text{Ag}[\text{BF}_4]$  in NCMe resulted in iodide abstraction and formation of low yields of an analytically pure sample of **3**. Complex **3** is a rare example of the cycloheptadienyl ligand-bonded trihapto to tungsten; its identity as an  $\eta^3\text{-C}_7\text{H}_9$  complex was established conclusively by the  $^{13}\text{C}\{^1\text{H}\}$  NMR data which reveal characteristic shifts for the olefin (C(6), C(7)) and allyl (C(3)–C(5)) carbons.

Although a synthesis of  $[\text{W}(\text{CO})_2(\text{NCMe})_3(\eta^3\text{-C}_7\text{H}_9)][\text{BF}_4]$  (**3**) was developed, the overall yield from  $[\text{W}(\text{CO})_3(\eta^6\text{-C}_7\text{H}_8)]$  was too low for **3** to be an effective precursor to further cycloheptadienyl tungsten complexes. Two alternative synthetic routes to dicarbonyl complexes  $[\text{W}(\text{CO})_2\text{L}_2(\eta^5\text{-C}_7\text{H}_9)]^+$  were therefore explored. First, the protonation of substituted cycloheptatriene complexes  $[\text{W}(\text{CO})_2\text{L}(\eta^6\text{-C}_7\text{H}_8)]$  (L = P-donor ligand) in the presence of L was investigated.  $[\text{W}(\text{CO})_2(\text{PPh}_3)(\eta^6\text{-C}_7\text{H}_8)]$  was prepared by reaction of  $[\text{W}(\text{CO})_2(\text{PPh}_3)(\eta\text{-C}_7\text{H}_7)][\text{BF}_4]$  [14,15] with  $\text{Na}[\text{BH}_4]$  in THF. Subsequent protonation with  $\text{H}[\text{BF}_4]\cdot\text{Et}_2\text{O}$  in THF in the presence of  $\text{PPh}_3$  afforded  $[\text{W}(\text{CO})_2(\text{PPh}_3)_2(\eta^5\text{-C}_7\text{H}_9)][\text{BF}_4]$  (**4**) which precipitated from the reaction mixture as a bright yellow solid. Complex **4** is the first example of the general formulation  $[\text{W}(\text{CO})_2\text{L}_2(\eta^5\text{-C}_7\text{H}_9)]^+$  and is reported not to be accessible by direct reaction of  $\text{PPh}_3$  with substitution inert  $[\text{W}(\text{CO})_3(\text{PPh}_3)(\eta^5\text{-C}_7\text{H}_9)][\text{BF}_4]$  [8].

The structure of complex **4** is of particular interest with regard to the orientation of the  $\text{W}(\text{CO})_2(\text{PPh}_3)_2$  unit with respect to the edge bridge of the dienyl ligand. In the solid state, dienyl complexes of the type  $[\text{M}(\text{L})_2(\text{PR}_3)_2(\eta^5\text{-dienyl})]^{n+}$  (dienyl = acyclic or edge-bridged ligand) exhibit two alternative arrangements of the  $\text{M}(\text{L})_2(\text{PR}_3)_2$  unit with respect to the dienyl ligand – Figs. 1(a) and (b). Structure type (a) is adopted by all complexes in which the dienyl ligand is an “open” acyclic pentadienyl ligand of the type  $\text{C}_5\text{H}_7$  (pentadienyl) or 2,4-Me<sub>2</sub>-pentadienyl. However, whilst the “open” pentadienyl system  $[\text{Re}(\text{H})_2(\text{PMe}_2\text{Ph})_2(\eta^5\text{-2,4-Me}_2\text{-pentadienyl})]$  assumes structure (a) in the solid state [16], the edge-bridged cyclohexadienyl and cyclooctadienyl ana-

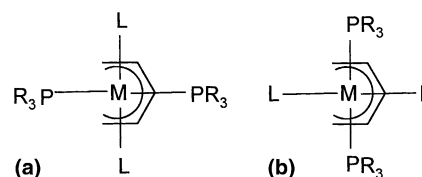


Fig. 1. (a,b) Structure types of  $[\text{M}(\text{L})_2(\text{PR}_3)_2(\eta^5\text{-dienyl})]^{n+}$  (dienyl = “open” or edge-bridged ligand).

logues  $[\text{Re}(\text{H})_2(\text{PMe}_2\text{Ph})_2(\eta^5\text{-dienyl})]$  are found to have structure (b) [17,18]. It might be speculated that the edge bridge in **4** could also promote the adoption of structure (b) – to our knowledge there are no crystallographically characterised examples of  $[\text{M}(\text{CO})_2(\text{PR}_3)_2(\eta^5\text{-dienyl})]^{n+}$  incorporating an edge-bridged dienyl ligand. Infrared data for **4** were consistent with a *trans* arrangement of the carbonyl ligands and this observation encouraged more detailed structural studies.

A spectroscopic handle on this problem is to employ variable temperature  $^{31}\text{P}\{^1\text{H}\}$  NMR methods [19]. At ambient temperature only a singlet resonance was apparent in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **4** but at  $-50^\circ\text{C}$ , a clearly resolved doublet of doublets pattern with associated  $^{183}\text{W}$  satellites was observed. The implication that structure (a), with inequivalent  $^{31}\text{P}$  environments, is adopted was confirmed by an X-ray crystallographic study. The X-ray crystal structure of  $[\text{W}(\text{CO})_2(\text{PPh}_3)_2(\eta^5\text{-C}_7\text{H}_9)][\text{BF}_4]\cdot 0.5\text{CH}_2\text{Cl}_2$ , and the crystallographic numbering scheme are presented in Fig. 2 and important bond lengths and angles are given in Table 3. It is clear that **4** adopts structure type (a) with P(1) located beneath the edge-bridge carbons C(4) and C(5) (crystallographic numbering scheme) and P(2) placed under the central dienyl carbon C(1). The structure was examined for unusual features or distortions resulting from accommodation of P(1) under the edge bridge. One response of

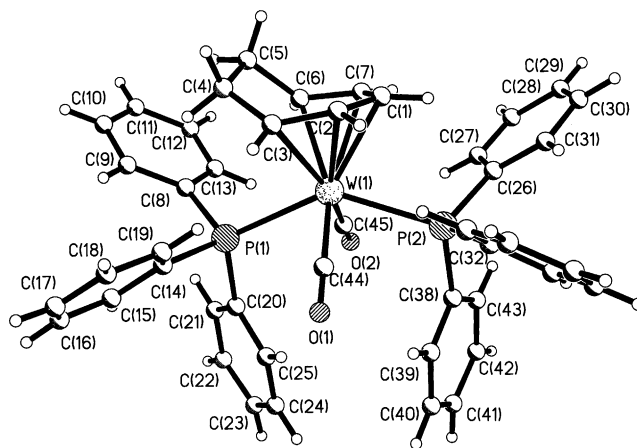


Fig. 2. Molecular structure of complex **4**;  $\text{BF}_4$  counter anion and  $\text{CH}_2\text{Cl}_2$  omitted.

Table 3  
Important bond lengths (Å) and angles (°) for complex 4

W(1)–P(1)	2.568(3)	C(44)–O(1)	1.131(13)
W(1)–P(2)	2.522(3)	C(45)–O(2)	1.135(12)
W(1)–C(1)	2.334(12)	C(1)–C(2)	1.422(17)
W(1)–C(2)	2.350(12)	C(2)–C(3)	1.358(16)
W(1)–C(3)	2.399(13)	C(3)–C(4)	1.448(17)
W(1)–C(6)	2.371(11)	C(4)–C(5)	1.542(19)
W(1)–C(7)	2.339(11)	C(5)–C(6)	1.516(17)
W(1)–C(44)	1.994(14)	C(6)–C(7)	1.387(16)
W(1)–C(45)	1.984(12)	C(7)–C(1)	1.403(17)
P(1)–W(1)–P(2)	136.46(9)	C(1)–C(2)–C(3)	128.1(13)
C(44)–W(1)–C(45)	106.4(5)	C(2)–C(3)–C(4)	128.4(13)
P(1)–W(1)–C(44)	79.0(3)	C(3)–C(4)–C(5)	115.5(11)
P(1)–W(1)–C(45)	74.8(3)	C(4)–C(5)–C(6)	111.3(11)
P(2)–W(1)–C(44)	79.8(3)	C(5)–C(6)–C(7)	122.5(12)
P(2)–W(1)–C(45)	75.4(3)	C(6)–C(7)–C(1)	121.1(11)
W(1)–C(44)–O(1)	179.3(11)	C(7)–C(1)–C(2)	123.5(12)
W(1)–C(45)–O(2)	178.5(11)		

the cycloheptadienyl ligand could be to bend the edge bridge C(4)–C(5) away from P(1) and the associated phenyl groups by increasing the fold angle  $\alpha$  between the best planes defined by [C(3)–C(4)–C(5)–C(6)] and [C(3)–C(2)–C(1)–C(7)–C(6)]. For **4**, the fold angle  $\alpha$  is estimated as 135.3° (measured on the face of the ligand remote from the metal centre). The equivalent angle in [Mo(CO)<sub>2</sub>(dppm)( $\eta^5$ -C<sub>7</sub>H<sub>9</sub>)] [BF<sub>4</sub>], in which a carbonyl ligand is located beneath the edge bridge is 133.4°, indicating no significant effect on this parameter. An alternative response could be manifest in distortion of the W(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> unit through elongation of W–P bond lengths or a decrease in the P(1)–W(1)–P(2) angle. However, yet again no unusual parameters were observed. The W–P bond lengths in **4** (W(1)–P(1) 2.568(3) Å; W(1)–P(2) 2.522(3) Å) lie within a range of W–P distances reported for [WBr<sub>2</sub>(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (2.481(9) Å; 2.486(9) Å) [20] and [NEt<sub>4</sub>][WCl<sub>2</sub>(CO)<sub>2</sub>(PPh<sub>3</sub>)( $\eta$ -C<sub>3</sub>H<sub>5</sub>)] (2.581(3) Å) [21]. Moreover, the geometry of the W(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> as defined by the angles P(1)–W–P(2) ( $\beta$  = 136.46(9)°) and C(44)–W(1)–C(45) ( $\gamma$  = 106.4(5)°) is remarkably similar to the geometry of the Nb(CO)<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub> unit in [Nb(CO)<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>( $\eta^5$ -2,4-Me<sub>2</sub>-pentadienyl)] for which the corresponding angles are:  $\beta$  = 135.5(1)°,  $\gamma$  = 107.0(2)° [19]. There is, however, some difference in the barrier to dienyl rotation for [Nb(CO)<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>( $\eta^5$ -2,4-Me<sub>2</sub>-pentadienyl)] and complex **4**. Variable temperature <sup>31</sup>P{<sup>1</sup>H} NMR studies on **4** reveal a coalescence temperature for the two phosphorus environments of 260 K leading to an estimate of  $\Delta G^\ddagger$  for dienyl rotation as 48.1 ± 1 kJ mol<sup>-1</sup>. This is higher than the value of  $\Delta G^\ddagger$  = 43.9 ± 1 kJ mol<sup>-1</sup> calculated [19] for the equivalent process in [Nb(CO)<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>( $\eta^5$ -2,4-Me<sub>2</sub>-pentadienyl)] although clearly the different identities of M(CO)<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub> units preclude a direct comparison of the effect of the dienyl ligand.

To complete our investigations on the cycloheptadienyl tungsten system, the synthesis of the chelate phosphine derivatives [W(CO)<sub>2</sub>(P-P)( $\eta^5$ -C<sub>7</sub>H<sub>9</sub>)]<sup>+</sup> (P-P = dppm or dppe) was explored. The initial synthetic approach, which attempted to employ cycloheptatriene complexes of the type [W(CO)<sub>2</sub>(P-P')( $\eta^5$ -C<sub>7</sub>H<sub>8</sub>)] (P-P' = pendant dppm or dppe) in a synthesis analogous to that of complex **4** was unproductive. The alternative, successful strategy is based on the direct reaction of [W(CO)<sub>3</sub>( $\eta^5$ -C<sub>7</sub>H<sub>9</sub>)] [BF<sub>4</sub>] with phosphines L, which is reported to give [W(CO)<sub>3</sub>L( $\eta^5$ -C<sub>7</sub>H<sub>9</sub>)] [BF<sub>4</sub>] (with the exception of the bidentate phosphine, dppe, for which a ligand-bridged product, [{W(CO)<sub>3</sub>( $\eta^5$ -C<sub>7</sub>H<sub>9</sub>)}<sub>2</sub>( $\mu$ -dppe)] [BF<sub>4</sub>]<sub>2</sub> is obtained) [8]. When a CH<sub>2</sub>Cl<sub>2</sub> solution of [W(CO)<sub>3</sub>( $\eta^5$ -C<sub>7</sub>H<sub>9</sub>)] [BF<sub>4</sub>], generated in situ from [W(CO)<sub>3</sub>( $\eta^6$ -C<sub>7</sub>H<sub>8</sub>)] and H[BF<sub>4</sub>] · Et<sub>2</sub>O, was treated with dppm, a product tentatively formulated as the pendant phosphine complex [W(CO)<sub>3</sub>(dppm-P')( $\eta^5$ -C<sub>7</sub>H<sub>9</sub>)] [BF<sub>4</sub>] was obtained ( $\nu$ (CO) CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>, 2041, 1978, 1938). Subsequent reflux of this intermediate in butanone resulted in chelation of the dppm ligand and formation of [W(CO)<sub>2</sub>(dppm)( $\eta^5$ -C<sub>7</sub>H<sub>9</sub>)] [BF<sub>4</sub>], **5**, which was isolated as an orange solid following purification by column chromatography on silica. Spectroscopic data for **5** are similar to the molybdenum analogue including the requirement to acquire NMR spectroscopic data at low temperature to obtain well resolved spectra.

Complex **5** is of particular interest for potential  $\eta^5 \rightarrow \eta^3$  hapticity conversion at the cycloheptadienyl ligand. In the case of the analogous molybdenum complexes [Mo(CO)<sub>2</sub>{Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>n</sub>PPh<sub>2</sub>}( $\eta^5$ -C<sub>7</sub>H<sub>9</sub>)]<sup>+</sup>, the dppe derivative dissolves in NCME to give an equilibrium mixture of the ring slipped, trihapto-bonded cycloheptadienyl complex [Mo(CO)<sub>2</sub>(NCMe)(dppe)( $\eta^3$ -C<sub>7</sub>H<sub>9</sub>)]<sup>+</sup> and starting material. By contrast the dppm derivative remains unchanged as [Mo(CO)<sub>2</sub>(dppm)( $\eta^5$ -C<sub>7</sub>H<sub>9</sub>)]<sup>+</sup> when dissolved in NCME [4]. It has been shown

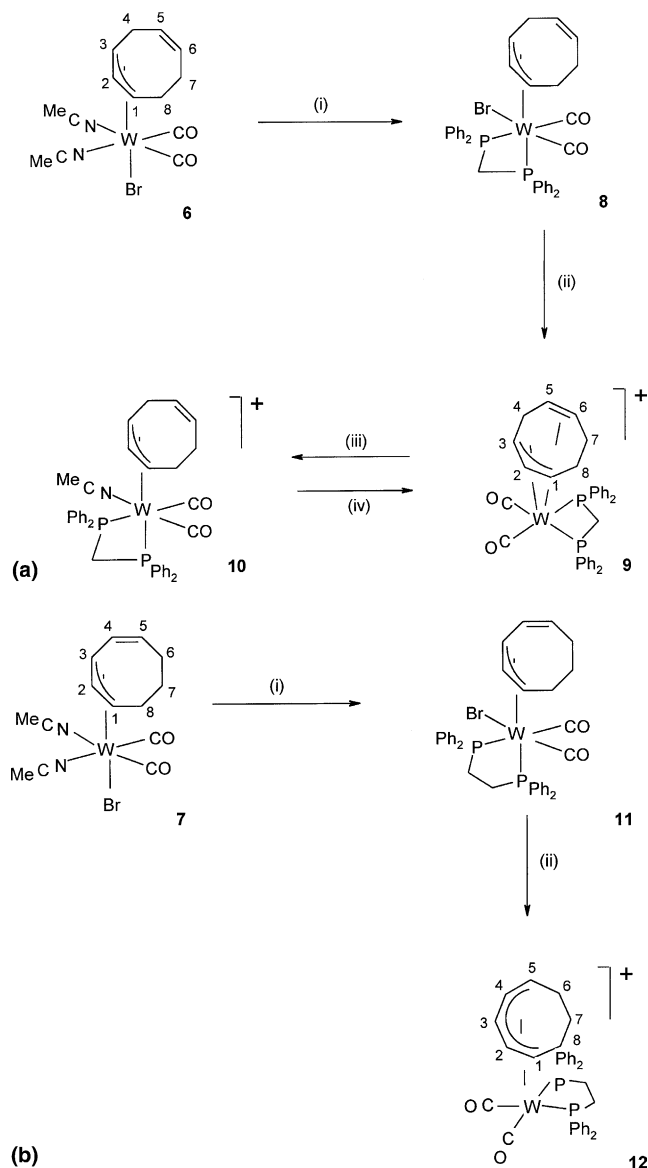
that hapticity conversions in cycloheptatrienyl complexes, driven by addition of NCMe at the metal centre, are facilitated by exchange of Mo for W [22]. However, when **5** was dissolved in NCMe, there was no spectroscopic evidence for the formation of the ring slipped acetonitrile adduct  $[\text{W}(\text{CO})_2(\text{NCMe})(\text{dppm})(\eta^3\text{-C}_7\text{H}_9)] [\text{BF}_4]$ . We conclude, therefore, that exchange of Mo for W has a relatively small effect on the preferred hapticity of the cycloheptadienyl ligand and, in this example, the  $\eta^5$  bonding mode is retained for both Mo and W.

## 2.2. Cyclooctadienyl complexes

Our investigations on the chemistry of the cyclooctadienyl tungsten system are summarised in Scheme 2(a) and (b). Microanalytical, infrared and mass spectroscopic data for each of the complexes are presented in Table 1, and  $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR data are given in Table 2. Again, a full account of the spectroscopic data for analogous molybdenum complexes has been presented previously [5,6] and, therefore, further discussion here is restricted. Both commonly observed forms of the cyclooctadienyl ligand are included in this study. In the first case (1–5- $\eta\text{-C}_8\text{H}_{11}$ ) all three methylene carbons are adjacent and these bridge the terminal dienyl carbons but in the second isomeric form (1–3:5,6- $\eta\text{-C}_8\text{H}_{11}$ ) one methylene group is located between isolated allyl and olefin components of the “dienyl” unit.

The synthetic route that we developed to cyclooctadienyl molybdenum complexes [5] is closely paralleled in the corresponding tungsten chemistry. Thus reaction of acetonitrile solutions of  $[\text{W}(\text{CO})_3(\text{NCR})_3]$  ( $\text{R} = \text{Me}$  or  $\text{Pr}^n$ ) with mixtures of either 3-Br-1,5-cod/6-Br-1,4-cod or 5-Br-1,3-cod/3-Br-1,4-cod (cod = cyclooctadiene) led, respectively, to the formation and precipitation of  $[\text{WBr}(\text{CO})_2(\text{NCMe})_2(1\text{-}3\text{-}\eta\text{:}5,6\text{-}\text{C}_8\text{H}_{11})]$  (**6**) and  $[\text{WBr}(\text{CO})_2(\text{NCMe})_2(1\text{-}3\text{-}\eta\text{:}4,5\text{-}\text{C}_8\text{H}_{11})]$  (**7**). As in the analogous chemistry of molybdenum, complexes **6** and **7** are potential precursors to an extensive chemistry of the cyclooctadienyl tungsten system. However, our studies focus on two investigations which explore possible modifications in reactivity imposed by the exchange of molybdenum for tungsten.

We have previously described the synthesis and reactivity of three pentahapto-bonded cyclooctadienyl molybdenum complexes  $[\text{Mo}(\text{CO})_2(\text{P-P})(\eta^5\text{-C}_8\text{H}_{11})]^+$  ( $\eta^5\text{-C}_8\text{H}_{11} = 1\text{-}3\text{:}5,6\text{-}\eta\text{-C}_8\text{H}_{11}$ , P-P = dppe or dppm;  $\eta^5\text{-C}_8\text{H}_{11} = 1\text{-}5\text{-}\eta\text{-C}_8\text{H}_{11}$ , P-P = dppm) [6]. The fourth combination ( $\eta^5\text{-C}_8\text{H}_{11} = 1\text{-}5\text{-}\eta\text{-C}_8\text{H}_{11}$ , P-P = dppe) was not accessible; attempts to generate this complex led instead to isolation of  $[\text{Mo}(\text{CO})_3(\text{dppe})(1\text{-}3\text{-}\eta\text{:}4,5\text{-}\text{C}_8\text{H}_{11})]^+$  probably via partial decomposition of  $[\text{Mo}(\text{CO})_2(\text{dppe})(\eta^5\text{-}1\text{-}5\text{-}\text{C}_8\text{H}_{11})]^+$  and CO exchange. We have also described the reactions of these complexes with 2-electron donor ligands  $L'$  such as NCMe or CO



Scheme 2. (a) Reagents and conditions: (i) dppe in  $\text{CH}_2\text{Cl}_2$ , 20 min; (ii)  $\text{Ag}[\text{BF}_4]$  in  $\text{CH}_2\text{Cl}_2$ ,  $1\frac{1}{2}$  h; (iii) Stir in NCMe, 2 h; (iv) Stir in  $\text{CH}_2\text{Cl}_2$ , 18 h. (b) Reagents and conditions: (i) dppe in  $\text{CH}_2\text{Cl}_2$ ,  $1\frac{1}{2}$  h; (ii)  $\text{Ag}[\text{BF}_4]$  in  $\text{CH}_2\text{Cl}_2$ , 1 h.

leading to adducts of the type  $[\text{Mo}(\text{CO})_2L'(\text{P-P})(\eta^3\text{-C}_8\text{H}_{11})]^+$  with accompanying  $\eta^5 \rightarrow \eta^3$  hapticity conversion at the cyclooctadienyl ring [6]. However, this reactivity is moderated both by the identity of the cyclooctadienyl ligand and the supporting phosphine ligand with the combination  $\eta^5\text{-C}_8\text{H}_{11} = 1\text{-}3\text{:}5,6\text{-}\eta\text{-C}_8\text{H}_{11}$ , P-P = dppm, least reactive towards addition of  $L'$ . These observations suggested two objectives for our work with the cyclooctadienyl tungsten system: (i) an investigation of the synthesis of  $[\text{W}(\text{CO})_2(\text{dppm})(1\text{-}3\text{:}5,6\text{-}\eta\text{-C}_8\text{H}_{11})]^+$  and the stability of its ligand adducts  $[\text{W}(\text{CO})_2L'(\text{dppm})(1\text{-}3\text{-}\eta\text{:}5,6\text{-}\text{C}_8\text{H}_{11})]^+$  and (ii) the synthesis of  $[\text{W}(\text{CO})_2(\text{dppe})(1\text{-}5\text{-}\eta\text{-C}_8\text{H}_{11})]^+$ , a complex which has no direct analogue in molybdenum chemistry.



Reaction of  $[\text{WBr}(\text{CO})_2(\text{NCMe})_2(1-3-\eta:5,6-\text{C}_8\text{H}_{11})]$  (**6**) with *dppm* in  $\text{CH}_2\text{Cl}_2$  affords  $[\text{WBr}(\text{CO})_2(\text{dppm})(1-3-\eta:5,6-\text{C}_8\text{H}_{11})]$  (**8**), which is a precursor to  $[\text{W}(\text{CO})_2(\text{dppm})(1-3:5,6-\eta-\text{C}_8\text{H}_{11})][\text{BF}_4]$  (**9**) by treatment with  $\text{Ag}[\text{BF}_4]$  in  $\text{CH}_2\text{Cl}_2$ . Complex **9**, which was isolated as an orange-pink solid, is a unique example of the 1-3:5,6- $\eta-\text{C}_8\text{H}_{11}$  ligand co-ordinated to tungsten. When **9** was dissolved in *NCMe*, the ligand adduct  $[\text{W}(\text{CO})_2(\text{NCMe})(\text{dppm})(1-3-\eta:5,6-\text{C}_8\text{H}_{11})][\text{BF}_4]$  (**10**) was fully formed and isolable as a stable yellow solid. The purpose of the synthesis of **10** was to establish the effect of *M* (*M* = Mo or W) on the stability of  $[\text{M}(\text{CO})_2(\text{NCMe})(\text{dppm})(1-3-\eta:5,6-\text{C}_8\text{H}_{11})][\text{BF}_4]$  with respect to dissociation of *NCMe* and accompanying  $\eta^3 \rightarrow \eta^5$  hapticity conversion of the cyclooctadienyl ligand. When  $[\text{Mo}(\text{CO})_2(\text{NCMe})(\text{dppm})(1-3-\eta:5,6-\text{C}_8\text{H}_{11})][\text{BF}_4]$  is dissolved in  $\text{CH}_2\text{Cl}_2$ , it rapidly eliminates *NCMe* with complete conversion to  $[\text{Mo}(\text{CO})_2(\text{dppm})(1-3:5,6-\eta-\text{C}_8\text{H}_{11})][\text{BF}_4]$  [**6**]. However, when **10** was dissolved in  $\text{CH}_2\text{Cl}_2$ , reversion to  $[\text{W}(\text{CO})_2(\text{dppm})(1-3:5,6-\eta-\text{C}_8\text{H}_{11})][\text{BF}_4]$  (**9**) proceeded much more slowly. Thus, for similar concentrations (ca. 0.05 g in 5  $\text{cm}^3$ ), the molybdenum derivative lost *NCMe* almost instantaneously whereas monitoring by infrared spectroscopy in  $\text{CH}_2\text{Cl}_2$  revealed that the tungsten complex **10**, required several hours to complete conversion to **9**.

The second target of this investigation was to prepare  $[\text{W}(\text{CO})_2(\text{dppe})(1-5-\eta-\text{C}_8\text{H}_{11})][\text{BF}_4]$ . The molybdenum analogue of this complex is unstable with respect to decomposition to  $[\text{Mo}(\text{CO})_3(\text{dppe})(1-3-\eta:4,5-\text{C}_8\text{H}_{11})]^+$  [**6**]; however, we anticipated that stronger W–CO bonds might render the tungsten derivative more resistant to this decomposition pathway. Reaction of  $[\text{WBr}(\text{CO})_2(\text{NCMe})_2(1-3-\eta:4,5-\text{C}_8\text{H}_{11})]$  (**7**) with *dppe* in  $\text{CH}_2\text{Cl}_2$  gave  $[\text{WBr}(\text{CO})_2(\text{dppe})(1-3-\eta:4,5-\text{C}_8\text{H}_{11})]$  (**11**) via ligand substitution. Subsequent reaction of **11** with  $\text{Ag}[\text{BF}_4]$  in  $\text{CH}_2\text{Cl}_2$  led to the successful isolation of  $[\text{W}(\text{CO})_2(\text{dppe})(1-5-\eta-\text{C}_8\text{H}_{11})][\text{BF}_4]$ .  $\text{CH}_2\text{Cl}_2$  (**12**) as an orange-pink solid. The  $\text{CH}_2\text{Cl}_2$  solvation of **12** is consistent with our observations for  $[\text{Mo}(\text{CO})_2(\text{dppe})(1-3:5,6-\eta-\text{C}_8\text{H}_{11})][\text{BF}_4]$ .  $\text{CH}_2\text{Cl}_2$  [**6**]. Complex **12** provides the first example of the 1-5- $\eta-\text{C}_8\text{H}_{11}$  coordinated to tungsten and has no direct analogue in cyclooctadienyl molybdenum chemistry. Its successful synthesis highlights a further effect of the exchange of molybdenum for tungsten.

The NMR spectroscopic data for the  $\eta^3-\text{C}_8\text{H}_{11}$  complexes **6–8**, **10** and **11** are very similar to the Mo analogues including the observation of isomeric forms of  $[\text{WBr}(\text{CO})_2(\text{dppm})(1-3-\eta:5,6-\text{C}_8\text{H}_{11})]$  (**8**) and  $[\text{W}(\text{CO})_2(\text{NCMe})(\text{dppm})(1-3-\eta:5,6-\text{C}_8\text{H}_{11})][\text{BF}_4]$  (**10**) at low temperature. The NMR data for the  $\eta^5-\text{C}_8\text{H}_{11}$  complexes **9** and **12** are again typical of 1-3:5,6- $\eta-\text{C}_8\text{H}_{11}$  and 1-5- $\eta-\text{C}_8\text{H}_{11}$  ligands although well resolved spectra for **12** were obtained only on cooling to  $-30^\circ\text{C}$ .

### 3. Conclusions

New synthetic routes to cycloheptadienyl and cyclooctadienyl tungsten complexes have been developed. The synthetic route previously applied to a range of dicarbonyl cycloheptadienyl molybdenum complexes of the type  $[\text{Mo}(\text{CO})_2\text{L}_2(\eta^5-\text{C}_7\text{H}_9)]^+$  (based on reaction of ligands  $\text{L}_2$  with  $[\text{Mo}(\text{CO})_2(\text{NCMe})_3(\eta^3-\text{C}_7\text{H}_9)]^+$ ) was not viable in the corresponding chemistry of tungsten. However, representative examples of the hitherto unknown general formulation  $[\text{W}(\text{CO})_2\text{L}_2(\eta^5-\text{C}_7\text{H}_9)]^+$  ( $\text{L}_2 = 2 \text{PPh}_3, \text{dppm}$ ) were obtained via specific methods. The solid-state structure of  $[\text{W}(\text{CO})_2(\text{PPh}_3)_2(\eta^5-\text{C}_7\text{H}_9)][\text{BF}_4]$  shows no unusual features attributable to the edge bridge of the cycloheptadienyl ligand. The first examples of cyclooctadienyl tungsten complexes  $[\text{WBr}(\text{CO})_2(\text{NCMe})_2(1-3-\eta:5,6-\text{C}_8\text{H}_{11})]$  and  $[\text{WBr}(\text{CO})_2(\text{NCMe})_2(1-3-\eta:4,5-\text{C}_8\text{H}_{11})]$  were synthesised by reaction of  $[\text{W}(\text{CO})_3(\text{NCR})_3]$  with appropriate bromo-cyclooctadienes in a procedure directly analogous to that employed for molybdenum. These complexes served as precursors to the first examples of the pentahapto-bonded ligands 1-3:5,6- $\eta-\text{C}_8\text{H}_{11}$  and 1-5- $\eta-\text{C}_8\text{H}_{11}$  coordinated to tungsten.

Three examples of differences between the chemistry of analogous molybdenum and tungsten systems have been noted. First, the reactivity of  $[\text{M}(\text{CO})_3(\eta^5-\text{C}_7\text{H}_9)]^+$  (*M* = Mo or W) towards CO addition and formation of  $[\text{M}(\text{CO})_4(\eta^5-\text{C}_7\text{H}_9)]^+$  is *M* dependent and proceeds only for *M* = Mo. This proved to be a major limitation on the development of cycloheptadienyl tungsten chemistry because  $[\text{W}(\text{CO})_3(\eta^5-\text{C}_7\text{H}_9)]^+$  is isolable only in relatively low yield. Second, comparison of the stability of  $[\text{M}(\text{CO})_2(\text{NCMe})(\text{dppm})(1-3-\eta:5,6-\text{C}_8\text{H}_{11})][\text{BF}_4]$  (*M* = Mo or W) towards loss of *NCMe* suggests that the  $\eta^3-\text{C}_8\text{H}_{11}$  acetonitrile adduct is marginally stabilised by *M* = W. However, the effect is insufficient to promote significant differences in reactivity between  $[\text{M}(\text{CO})_2(\text{dppm})(\eta^5-\text{C}_7\text{H}_9)]^+$  (*M* = Mo or W) both of which are inert towards adduct formation with *NCMe*. Finally the contrasting stability of  $[\text{M}(\text{CO})_2(\text{dppe})(1-5-\eta-\text{C}_8\text{H}_{11})]^+$  (*M* = Mo or W) towards decomposition to  $[\text{M}(\text{CO})_3(\text{dppe})(1-3-\eta:4,5-\text{C}_8\text{H}_{11})]^+$  may be accounted for in part, by the enhanced metal carbonyl bond strength in the tungsten derivative.

### 4. Experimental

#### 4.1. General procedures

The preparation, purification and reactions of the complexes described were carried out under dry nitrogen. All solvents were dried by standard methods, distilled and deoxygenated before use. The compound  $[\text{W}(\text{CO})_3(\eta^6-\text{C}_7\text{H}_8)]$  [23] and bromocyclooctadienes

[24,25] were prepared by published procedures. Silica for column chromatography (70–230 mesh) was purchased from Lancaster Synthesis and  $\text{HBF}_4$  (as a 54 wt% solution in diethyl ether) was supplied by Aldrich. 300 MHz  $^1\text{H}$  and 75 MHz  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra were recorded on Bruker AC 300 E, Varian Associates XL 300 or Varian Unity Inova 300 spectrometers; 121.5 MHz  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra were recorded on the Varian Unity Inova 300 instrument. Infrared spectra were obtained on a Perkin–Elmer FT 1710 spectrometer and mass spectra were recorded using Kratos Concept 1S (FAB spectra) or Micromass Platform II (ES spectra) instruments. Microanalyses were by the staff of the Microanalytical Service of the Department of Chemistry, University of Manchester.

#### 4.2. Preparation of $[\text{W}(\text{CO})_3(\eta^5\text{-C}_7\text{H}_9)][\text{BF}_4]$ (1)

A purple solution of  $[\text{W}(\text{CO})_3(\eta^6\text{-C}_7\text{H}_8)]$  (0.148 g, 0.41 mmol) in  $\text{CH}_2\text{Cl}_2$  (20  $\text{cm}^3$ ) was treated with  $\text{H}[\text{BF}_4] \cdot \text{Et}_2\text{O}$  (0.330 g of a 54 wt% solution in diethyl ether) at 0 °C. The reaction mixture was allowed to warm to room temperature, stirred for 30 min, then reduced in volume to initiate precipitation of a pale orange solid which was completed by addition of 40  $\text{cm}^3$  of diethyl ether. The mother liquors were removed and the product was washed with diethyl ether and then recrystallised from  $\text{CH}_2\text{Cl}_2$ -diethyl ether; yield 0.046 g (25%).

#### 4.3. Preparation of $[\text{W}(\text{CO})_3(\eta^5\text{-C}_7\text{H}_9)]$ (2)

A purple solution of  $[\text{W}(\text{CO})_3(\eta^6\text{-C}_7\text{H}_8)]$  (0.501 g, 1.39 mmol) in diethyl ether (30  $\text{cm}^3$ ) was cooled to 0 °C, then treated with  $\text{H}[\text{BF}_4] \cdot \text{Et}_2\text{O}$  (0.260 g of a 54 wt% solution in diethyl ether). The reaction mixture was stirred for 1 h at 0 °C. Then the volume was reduced to ca. 2  $\text{cm}^3$ . The reaction mixture was redissolved in AR acetone (50  $\text{cm}^3$ ), cooled to –78 °C and NaI (0.625 g, 4.17 mmol) added. After stirring for 1 h, solvent was removed and the residue recrystallised from  $\text{CH}_2\text{Cl}_2$ -hexane then diethyl ether-hexane to give **2** as a yellow-orange solid; yield 0.262 g (39%). Complex **2** can also be purified by chromatography on a silica-*n*-hexane column from which it is eluted as a yellow band with  $\text{CH}_2\text{Cl}_2$ /*n*-hexane (1:1).

#### 4.4. Preparation of $[\text{W}(\text{CO})_2(\text{NCMe})_3(\eta^3\text{-C}_7\text{H}_9)][\text{BF}_4]$ (3)

An orange solution of  $[\text{W}(\text{CO})_3(\eta^5\text{-C}_7\text{H}_9)]$  (0.506 g, 1.04 mmol) in NCMe (40  $\text{cm}^3$ ) was treated with  $\text{Ag}[\text{BF}_4]$  (0.201 g, 1.03 mmol). The solution turned green with precipitation of AgI and after 30 min, the reaction mixture was filtered, reduced in volume and diethyl ether added to precipitate the crude product. Sub-

sequent recrystallisation from NCMe-diethyl ether followed by  $\text{CH}_2\text{Cl}_2$ -diethyl ether yielded **3** as an orange solid; yield 0.050 g (9%).

#### 4.5. Preparation of $[\text{W}(\text{CO})_2(\text{PPh}_3)(\eta^6\text{-C}_7\text{H}_8)]$

A stirred suspension of  $[\text{W}(\text{CO})_2(\text{PPh}_3)(\eta\text{-C}_7\text{H}_7)][\text{BF}_4]$  (2.704 g, 3.98 mmol) in THF (120  $\text{cm}^3$ ) was cooled to 0 °C and treated with  $\text{Na}[\text{BH}_4]$  (0.227 g, 5.96 mmol) over a period of 20 min. The reaction mixture was then allowed to warm to room temperature and stirred for 1 h to give a deep red solution which was filtered and evaporated to dryness. The residue was recrystallised from  $\text{CH}_2\text{Cl}_2$ -*n*-hexane to give  $[\text{W}(\text{CO})_2(\text{PPh}_3)(\eta^6\text{-C}_7\text{H}_8)]$  as a bright red solid; yield 1.445 g (61%).  $\text{IR}_{\nu}(\text{CO})(\text{CH}_2\text{Cl}_2)(\text{cm}^{-1})$  1903, 1817; Microanalysis: Found (Calc.) C, 54.0 (54.5); H, 3.8 (3.9);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz), numbering as in Scheme 1: 7.50, 7.40, m, 15H, Ph; 5.70, m, 2H,  $\text{H}^{3,4}$ ; 4.68, m, 2H,  $\text{H}^{2,5}$ ; 3.20, m, 2H,  $\text{H}^{1,6}$ ; 2.94, m, 2H,  $\text{H}^{7,7'}$ .

#### 4.6. Preparation of $[\text{W}(\text{CO})_2(\text{PPh}_3)_2(\eta^5\text{-C}_7\text{H}_9)][\text{BF}_4]$ (4)

A mixture of  $[\text{W}(\text{CO})_2(\text{PPh}_3)(\eta^6\text{-C}_7\text{H}_8)]$  (1.445 g, 2.43 mmol) and  $\text{PPh}_3$  (0.637 g, 2.43 mmol) in solution in THF (50  $\text{cm}^3$ ) was cooled in ice. The reaction mixture was treated with  $\text{HBF}_4 \cdot \text{Et}_2\text{O}$  (0.648 g of a 54 wt% solution in diethyl ether) resulting in a rapid colour change from red to yellow brown and after 10 min the ice bath was removed. Further stirring for 1 h resulted in precipitation of the product as a bright yellow solid which was collected by filtration and washed with THF (15  $\text{cm}^3$ ) then diethyl ether; yield 1.731 g (75%).

#### 4.7. Preparation of $[\text{W}(\text{CO})_2(\text{dppm})(\eta^5\text{-C}_7\text{H}_9)][\text{BF}_4]$ (5)

A purple solution of  $[\text{W}(\text{CO})_3(\eta^6\text{-C}_7\text{H}_8)]$  (0.500 g, 1.39 mmol) in  $\text{CH}_2\text{Cl}_2$  (40  $\text{cm}^3$ ), cooled in an ice bath (0 °C), was treated with  $\text{H}[\text{BF}_4] \cdot \text{Et}_2\text{O}$  (0.40 g of a 54 wt% solution in diethyl ether). The reaction mixture was stirred for 30 min. Then, dppm (0.64 g 1.67 mmol) was added followed by warming to room temperature and stirring for 40 min. After this time the solution was reduced in volume and transferred to a silica- $\text{CH}_2\text{Cl}_2$  chromatography column. Elution with  $\text{CH}_2\text{Cl}_2$ /acetone (1:1) gave a yellow band followed by an orange band, which was collected and evaporated to dryness. The residue, tentatively formulated as  $[\text{W}(\text{CO})_3(\text{dppm-P})(\eta^5\text{-C}_7\text{H}_9)][\text{BF}_4]$ , was dissolved in 2-butanone (40  $\text{cm}^3$ ) and the solution refluxed for 30 min, then evaporated to dryness. The residue was dissolved in  $\text{CH}_2\text{Cl}_2$  and transferred to a silica- $\text{CH}_2\text{Cl}_2$  chromatography column and the product eluted as an orange-red band with  $\text{CH}_2\text{Cl}_2$ /acetone (1:1). The band was collected,

evaporated to dryness and the residue recrystallised from  $\text{CH}_2\text{Cl}_2$ -diethyl ether to give **5** as an orange-red solid; yield 0.116 g (10% based on  $[\text{W}(\text{CO})_3(\eta^6\text{-C}_7\text{H}_8)]$ ).

#### 4.8. Preparation of $[\text{WBr}(\text{CO})_2(\text{NCMe})_2(1\text{-}\eta^3\text{-}\eta^5\text{-}6\text{-C}_8\text{H}_{11})]$ (**6**)

$\text{W}(\text{CO})_6$  (4.15 g, 11.79 mmol) was refluxed in NCMe (50  $\text{cm}^3$ ) for 4 days after which time a yellow solution of  $[\text{W}(\text{CO})_3(\text{NCMe})_3]$  had formed. This was cooled to room temperature and a mixture of 3-Br-1,5-cod and 6-Br-1,4-cod (2.30 g, 12.30 mmol) added, resulting in an orange solution. The solution was stirred for 1 h and then the volume was reduced under vacuum, initiating precipitation of the product. The reaction mixture was refrigerated for 24 h. Then the mother liquors were removed giving **6** as an orange solid; yield 1.60 g (27% based on  $\text{W}(\text{CO})_6$ ).

#### 4.9. Preparation of $[\text{WBr}(\text{CO})_2(\text{NCMe})_2(1\text{-}\eta^3\text{-}\eta^4\text{-}5\text{-C}_8\text{H}_{11})]$ (**7**)

A stirred solution of  $[\text{W}(\text{CO})_3(\text{NCP}^n)_3]$  (0.919 g, 1.93 mmol) in NCMe (30  $\text{cm}^3$ ) was treated with a mixture of 5-Br-1,3-cod and 3-Br-1,4-cod (0.470 g, 2.51 mmol) resulting in an orange solution. The solution was stirred for 1 h and then the volume was reduced under vacuum, initiating precipitation of the product. The mother liquors were separated giving **7** as an orange-yellow solid; yield 0.362 g (37%).

#### 4.10. Preparation of $[\text{WBr}(\text{CO})_2(\text{dppm})(1\text{-}\eta^3\text{-}\eta^5\text{-}6\text{-C}_8\text{H}_{11})]$ (**8**)

Reaction of  $[\text{WBr}(\text{CO})_2(\text{NCMe})_2(1\text{-}\eta^3\text{-}\eta^5\text{-}6\text{-C}_8\text{H}_{11})]$  (0.992 g, 1.95 mmol) with dppm (0.748 g, 1.95 mmol) in  $\text{CH}_2\text{Cl}_2$  (40  $\text{cm}^3$ ) gave a red solution which was stirred at room temperature for 20 min. The reaction mixture was then filtered and the product precipitated as an orange solid by addition of hexane and reduction of the volume of the solution in vacuo; yield 1.42 g (90%). Orange  $[\text{WBr}(\text{CO})_2(\text{dppe})(1\text{-}\eta^3\text{-}\eta^4\text{-}5\text{-C}_8\text{H}_{11})]$  (**11**) was similarly prepared in 89% yield starting from  $[\text{WBr}(\text{CO})_2(\text{NCMe})_2(1\text{-}\eta^3\text{-}\eta^4\text{-}5\text{-C}_8\text{H}_{11})]$  (0.248 g, 0.487 mmol) and dppe (0.198 g, 0.497 mmol) stirred in  $\text{CH}_2\text{Cl}_2$  for 1 h and 30 min.

#### 4.11. Preparation of $[\text{W}(\text{CO})_2(\text{dppm})(1\text{-}\eta^3\text{-}\eta^5\text{-}6\text{-C}_8\text{H}_{11})][\text{BF}_4]$ (**9**)

A yellow-orange solution of  $[\text{WBr}(\text{CO})_2(\text{dppm})(1\text{-}\eta^3\text{-}\eta^5\text{-}6\text{-C}_8\text{H}_{11})]$  (1.00 g, 1.23 mmol) was dissolved in  $\text{CH}_2\text{Cl}_2$  (40  $\text{cm}^3$ ) and treated with  $\text{Ag}[\text{BF}_4]$  (0.30 g, 1.54 mmol). After stirring for 1 h and 30 min, the reaction mixture was filtered to give a red solution which was reduced in volume and diethyl ether added to give the

crude product as an orange solid. Subsequent recrystallisation from  $\text{CH}_2\text{Cl}_2$  afforded **9** as an orange solid; yield 0.544 g (54%). Orange-pink  $[\text{W}(\text{CO})_2(\text{dppe})(1\text{-}\eta^3\text{-}\eta^4\text{-}5\text{-C}_8\text{H}_{11})][\text{BF}_4]$  (**12**) was similarly prepared in 40% yield starting from  $[\text{WBr}(\text{CO})_2(\text{dppe})(1\text{-}\eta^3\text{-}\eta^4\text{-}5\text{-C}_8\text{H}_{11})]$  (0.186 g, 0.225 mmol) and  $\text{Ag}[\text{BF}_4]$  (0.044 g, 0.226 mmol) stirred in  $\text{CH}_2\text{Cl}_2$  for 1 h.

#### 4.12. Preparation of $[\text{W}(\text{CO})_2(\text{NCMe})(\text{dppm})(1\text{-}\eta^3\text{-}\eta^5\text{-}6\text{-C}_8\text{H}_{11})][\text{BF}_4]$ (**10**)

A solution of  $[\text{W}(\text{CO})_2(\text{dppm})(1\text{-}\eta^3\text{-}\eta^5\text{-}6\text{-C}_8\text{H}_{11})][\text{BF}_4]$  (**9**) (0.540 g, 0.66 mmol) in NCMe (30  $\text{cm}^3$ ) was stirred for 2 h, then reduced in volume and treated with diethyl ether to precipitate **10** as a bright yellow solid; yield 0.454 g (80%).

#### 4.13. X-ray crystal structure of $[\text{W}(\text{CO})_2(\text{PPh}_3)_2(\eta^5\text{-C}_7\text{H}_9)][\text{BF}_4] \cdot 0.5\text{CH}_2\text{Cl}_2$ (**4**)

The majority of details of the structure analyses carried out on **4** are given in Table 4; data were collected on a Bruker APEX diffractometer. Data collection, cell refinement and data reduction were carried out with BRUKER SMART and BRUKER SAINT software; SHELXS 97 [26] was employed for the computing structure solution and SHELXL 97 [27] for the computing structure refinement. Single crystals of **4**·0.5 $\text{CH}_2\text{Cl}_2$  were obtained as yellow needles by vapour diffusion of diethyl ether into a  $\text{CH}_2\text{Cl}_2$  solution of the complex. A crystal of dimensions 0.20 × 0.08 × 0.02 mm was selected for analysis. An absorption correction was applied with the

Table 4  
Crystal data and refinement parameters for  $[\text{W}(\text{CO})_2(\text{PPh}_3)_2(\eta^5\text{-C}_7\text{H}_9)][\text{BF}_4] \cdot 0.5\text{CH}_2\text{Cl}_2$

Formula	$\text{C}_{45}\text{H}_{39}\text{P}_2\text{O}_2\text{BF}_4 \cdot 0.5\text{CH}_2\text{Cl}_2$
Mass	986.83
Crystal system	Monoclinic
Temperature (K)	293(2)
$\lambda$ (Å)	0.71073 (Mo K $\alpha$ )
Crystal system	monoclinic
Space group	C2/c
<i>a</i> (Å)	35.267(4)
<i>b</i> (Å)	11.2128(13)
<i>c</i> (Å)	23.720(3)
$\beta$ (°)	120.395(2)
<i>V</i> (Å <sup>3</sup> ); <i>Z</i>	8090.7(17); 8
Absorption coefficient (cm <sup>-1</sup> )	30.58
$\theta$ range (°)	1.75–25.03
Limiting indices ( <i>h</i> , <i>k</i> , <i>l</i> )	±41, ±13, ±28
Total reflections	7132
Independent reflections, <i>I</i> > 2 $\sigma$ ( <i>I</i> )	5455
<i>R</i> <sub>1</sub>	0.0792
<i>wR</i> <sub>2</sub>	0.1402
Maximum and minimum difference Fourier peaks (e Å <sup>-3</sup> )	2.601/–3.457

aid of the *SADBS* programme [28]. The structure was solved by the Patterson method with refinement by full-matrix least squares based on  $F^2$ . The asymmetric unit contains the W complex, a  $\text{BF}_4$  ion and one half of a  $\text{CH}_2\text{Cl}_2$  molecule. The F atoms of the  $\text{BF}_4$  ion were disordered such that there were two sites for each F and the occupancies were constrained to sum to 1.0. All non-hydrogen atoms were refined anisotropically with the exception of F(1A); hydrogen atoms were included in calculated positions.

## 5. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 219846 for compound **4**. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) (or from the CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

## Acknowledgements

We are grateful to the EPSRC for the award of Research Studentships (to J.R.H. and D.M.S.).

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