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Synthesis of the sterically crowded cycloheptatrienyl complexes $[M(CO)(PPh_3)_2(\eta\text{-}C_7H_7)]^+$ (M = Mo or W): X-ray crystal structures of $[W(CO)(PPh_3)_2(\eta\text{-}C_7H_7)][BF_4]$ and $[W(CO)_2(PPh_3)(\eta\text{-}C_7H_7)][BF_4] \cdot CH_2Cl_2$

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Abstract

The first examples of complexes of the sterically crowded, bis(triphenylphosphine) auxiliary $M(PPh_3)_2(\eta\text{-}C_7H_7)$ (M = Mo or W) have been synthesised. $[Mo(CO)(PPh_3)_2(\eta\text{-}C_7H_7)][PF_6]$ (**1**) was obtained by low-temperature reaction of $[MoMe(CO)(PPh_3)(\eta\text{-}C_7H_7)]$ with $[Ph_3C][PF_6]$ in the presence of PPh_3. The tungsten analogue $[W(CO)(PPh_3)_2(\eta\text{-}C_7H_7)][BF_4]$ (**3**) was formed by reaction of $[WI(CO)(PPh_3)(\eta\text{-}C_7H_7)]$ with $Ag[BF_4]$ in acetone followed by addition of PPh_3. An X-ray crystallographic structural comparison of complex **3** with its mono-phosphine counterpart, $[W(CO)_2(PPh_3)(\eta\text{-}C_7H_7)][BF_4] \cdot CH_2Cl_2$ (**4**) reveals that the principal structural differences between **3** and **4** resulting from replacement of a carbonyl ligand by PPh_3 are: (i) an increase in the sum of the angles between the tripodal ligands and (ii) an elongation of the W–PPh_3 bond length (from 2.4950(12) Å in **4** to 2.5360(6) and 2.5496(6) Å in the bis(phosphine) complex **3**).

Keywords: Molybdenum; Tungsten; Cycloheptatrienyl; Steric crowding

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1. Introduction

Steric crowding in 18-electron organometallic complexes is an effective strategy to facilitate ligand dissociation and the formation of unsaturated 16-electron systems which can exhibit catalytic properties or new patterns of reactivity [1]. In half-sandwich systems, a key consideration is the interplay of ring size and ring substituents with the steric demands of other ligands in the complex. For example, in the complexes $[RuCl(PPh_3)_2(\eta\text{-}C_5R_5)]$ [R = H (Cp) or Me (Cp*)], the enhanced reactivity of the Cp* complex to dissociation of PPh_3 has been exploited in the synthesis of the novel neutral vinylidenes [2] $[RuCl({=}C{=}CHR')(PPh_3)Cp^*]$, a process not mirrored by the corresponding Cp system. Although ring substituents may be critical in the design of sterically crowded, half-sandwich systems, the effect of increasing ring size is also an important factor [3]. In the complexes $[ML_3(\eta^n\text{-}C_nH_n)]^{z+}$ ($n = 4$–7) an increase in n results in a corresponding decrease in the sum of the angles ($\Sigma\varphi$) between the tripodal ligands L (see Fig. 1) effectively restricting the space available to the ligands L. In fact the magnitude of this pyramidalisation effect is not strongly dependent upon the identity of ring-substituents, but rather it is controlled by changes in donor/acceptor properties of the cyclopolyene with increase in n.

The isoelectronic character of the 13-electron fragments $Ru(\eta\text{-}C_5R_5)$ and $Mo(\eta\text{-}C_7H_7)$ (C_7H_7 = cycloheptatrienyl) has been well documented by ourselves [4] and others [5] and similarities in complex type and reactivity noted.

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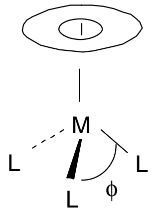


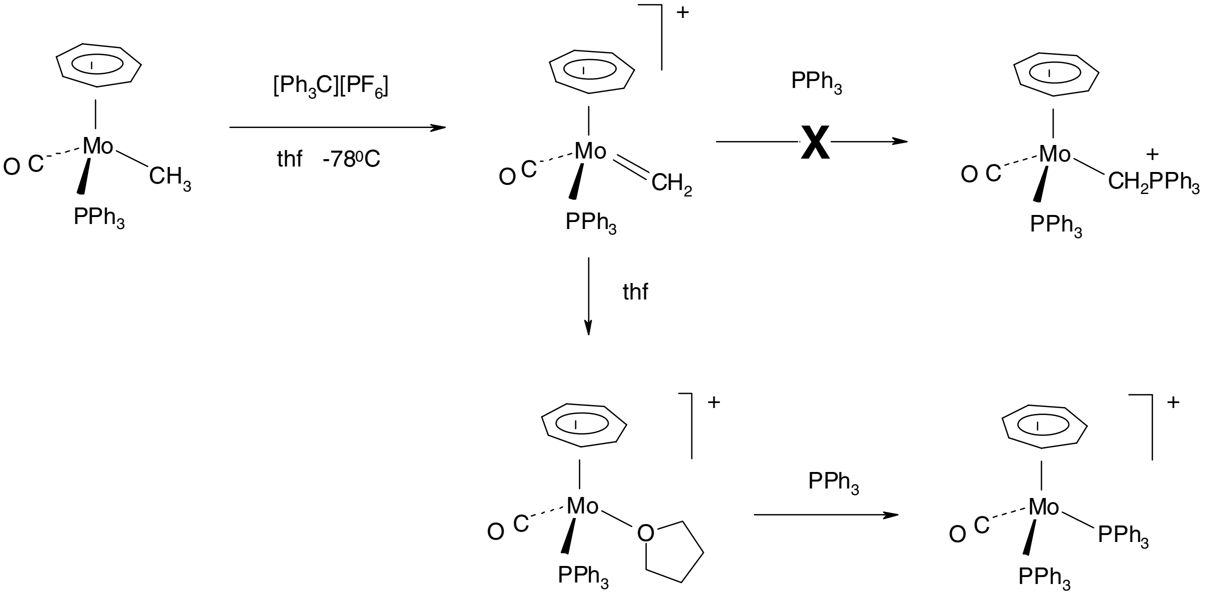
Fig. 1. Illustration of the parameter φ for $[ML_3(\eta^n\text{-}C_nH_n)]^{z+}$.

However, the chemistry of the cycloheptatrienyl molybdenum system is clearly distinct from that of the Ru(η-C_5R_5) system and this can, in part, be attributed to differences in steric parameters. The large ring cycloheptatrienyl ligand presents considerable steric demand at a metal centre with an estimated cone angle (154°) [6], larger than that of both the Cp (110°) and Cp* (142°) ligands. The experimental consequences of the effect of increasing ring size on the accommodation of sterically demanding tripodal ligands are nicely illustrated by a comparison of the known auxiliaries Ru(PR'_3)$_2$(η-C_5R_5) and Mo(PR'_3)$_2$(η-C_7H_7). Accordingly, whilst the bis(triphenylphosphine) auxiliary Ru(PPh_3)$_2$(η-C_5R_5) is one of the cornerstones of the organometallic chemistry of ruthenium [7], the chemistry of bis(phosphine) cycloheptatrienyl systems Mo(PR'_3)$_2$-(η-C_7H_7) is dominated by complexes of the chelate phosphine $Ph_2PCH_2CH_2PPh_2$ (dppe) [4,8,9] or small cone angle P-donor ligands such as P(OMe)$_3$ [10]. This paper reports the syntheses of the sterically crowded complexes [M(CO)-(PPh_3)$_2$(η-C_7H_7)]$^+$ (M = Mo or W), the first examples of derivatives of the bis(triphenylphosphine) auxiliary M(PPh_3)$_2$(η-C_7H_7), and explores the structural modifications required to accommodate the combination of sterically demanding ring and phosphine ligands in a half-sandwich complex.

2. Results and discussion

2.1. Synthetic studies

The isolation of complexes derived from the Mo(PPh_3)$_2$(η-C_7H_7) auxiliary has long been a goal of our investigations into the chemistry of the cycloheptatrienyl molybdenum system. However, following a number of unsuccessful synthetic attempts using several different strategies, it began to appear that such complexes were not accessible – an observation which might easily be rationalised by steric limitations. It was therefore with some surprise that we identified [Mo(CO)(PPh_3)$_2$(η-C_7H_7)][PF_6] (**1**) as the product of an attempt to generate and stabilise the carbene complex [Mo(=CH_2)(CO)(PPh_3)(η-C_7H_7)]$^+$ from the low temperature reaction of [Mo(CH_3)(CO)-(PPh_3)(η-C_7H_7)] with [Ph_3C][PF_6] [11]. The synthetic strategy for formation of the desired carbene complex [Mo(=CH_2)(CO)(PPh_3)(η-C_7H_7)]$^+$ and subsequent stabilisation as a phosphonium salt is summarised in Scheme 1. Following addition of PPh_3, the reaction mixture was warmed to room temperature and the product isolated as a green-brown solid by recrystallisation first from thf-diethyl ether, then CH_2Cl_2-diethyl ether. Characterisation by infrared and FAB mass spectroscopy and by ^{1}H and ^{13}C NMR spectroscopy (Table 1) revealed that the isolated product was in fact the bis(triphenylphosphine) complex [Mo(CO)(PPh_3)$_2$(η-C_7H_7)][PF_6] (**1**). Data which



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Scheme 1.

Table 1
Microanalytical, infrared, mass spectroscopic and NMR data

Complex	Analysis (%)[a]		Infrared, ν(CO) (cm^{-1})[b]	Mass spectral data[c]	^1H NMR data[d]		^{13}C NMR data[e]		
	C	H			PPh_3	C_7H_7	CO	PPh_3	C_7H_7
$[Mo(CO)(PPh_3)_2(\eta\text{-}C_7H_7)][PF_6] \cdot CH_2Cl_2$[f] (**1**)	55.5 (55.7)	4.0 (4.0)	1942	741 M^+ 479 $[M^+ - PPh_3]$ 451 $[M^+ - PPh_3 - CO]$	7.40, m; 7.35, m; 7.14, m	5.02, t, J(P–H) 2.2	230.6, t, J(P–C) 19.5	133.8–128.7	94.3
$[W(NCMe)(CO)(PPh_3)(\eta\text{-}C_7H_7)][BF_4]$ (**2**)	48.3 (48.5)	3.5 (3.6)	1931	606 M^+ 565 $[M^+ - NCMe]$ 537 $[M^+ - NCMe - CO]$	7.47, m; 7.29, m (1.99, d, J(P–H) 2.0, NCMe)	5.27, d, J(P–H) 2.0	230.1, d, J(P–C) 13.9	133.7–128.0 (3.2, NC*Me*)	89.8
$[W(CO)(PPh_3)_2(\eta\text{-}C_7H_7)][BF_4]$[g] (**3**)	57.7 (57.8)	4.1 (4.1)	1920	827 M^+ 565 $[M^+ - PPh_3]$ 536 $[M^+ - PPh_3 - CO]$	7.43, m; 7.32, m; 7.13, m	5.02, t, J(P–H) 2.4	224.6	135.2–128.9	90.7
$[W(CO)_2(PPh_3)(\eta\text{-}C_7H_7)][BF_4]$[g] (**4**)			2016, 1967	593 M^+ 565 $[M^+ - CO]$[h]	7.56, m; 7.35, m	5.64, d, J(P–H) 1.8	206.4, d, J(P–C) 13.4	135.0–131.1	95.4

[a] Calculated values in parentheses; **2**, $N = 1.9$ (2.0).
[b] Solution spectra in CH_2Cl_2.
[c] By FAB mass spectroscopy unless stated otherwise.
[d] 400 MHz spectra in $CDCl_3$ unless stated otherwise.
[e] 100 MHz spectra in $CDCl_3$ unless stated otherwise.
[f] 300 MHz ^1H/75 MHz ^{13}C NMR spectra.
[g] NMR spectra in CD_2Cl_2.
[h] MALDI spectrum.

specifically indicate the presence of two equivalent triphenylphosphine ligands are the triplet signal [J(P–H) = 2.2 Hz] for the C_7H_7 ligand in the ^{1}H NMR and the triplet resonance [J(P–C) = 19.5 Hz] for the carbonyl carbon in the ^{13}C NMR spectrum. The FAB and electrospray (MeOH) mass spectra show the molecular ion with the principal fragmentation arising from loss of PPh_3; the lability of the PPh_3 ligand is also demonstrated by the electrospray mass spectrum recorded in acetonitrile for which the strongest peak corresponds to the molecular ion of $[Mo(CO)(NCMe)(PPh_3)(\eta\text{-}C_7H_7)]^+$. Microanalytical data for complex **1** are for the CH_2Cl_2 solvate; the presence of CH_2Cl_2 was evident in the ^{1}H NMR spectrum of the complex and was also observed in samples of the tungsten analogue of **1** (see later) if recrystallised from CH_2Cl_2-diethylether.

The formation of complex **1** from $[Mo(CH_3)(CO)(PPh_3)(\eta\text{-}C_7H_7)]$ can be rationalised as shown in Scheme 1. The initially formed carbene ligand is displaced and the coordination site occupied by the solvent (thf) which is subsequently displaced by PPh_3; alternatively the carbene may be replaced directly by PPh_3. Inspection of the literature reveals that a similar mechanism is proposed for the reaction of $[Fe(Me)(CO)(PMe_3)(\eta\text{-}C_5Me_5)]$ with $[Ph_3C][PF_6]$ in thf [12]. In this case the solvated intermediate $[Fe(thf)(CO)(PMe_3)(\eta\text{-}C_5Me_5)]^+$ is isolable but can undergo a subsequent photochemically-induced substitution of thf by PMe_3 to yield $[Fe(CO)(PMe_3)_2(\eta\text{-}C_5Me_5)]^+$. To exploit this principle further, the synthesis and reactions of solvato complexes of the type $[M(solvent)(CO)(PPh_3)(\eta\text{-}C_7H_7)]^+$ (M = Mo or W) were explored.

Complexes of the type $[M(solvent)(CO)(PPh_3)(\eta\text{-}C_7H_7)]^+$, have been reported previously (M = Mo, solvent = NCMe), obtained by reaction of $[MoI(CO)(PPh_3)(\eta\text{-}C_7H_7)]$ with $Ag[BF_4]$ in acetonitrile [13]. In the current investigation, the tungsten derivative $[W(NCMe)(CO)(PPh_3)(\eta\text{-}C_7H_7)][BF_4]$ (**2**) was prepared for the first time by reaction of $[WI(CO)(PPh_3)(\eta\text{-}C_7H_7)]$ with $Ag[BF_4]$ in acetonitrile and characterised as detailed in Table 1. Although these complexes establish the formation of solvato systems, the NCMe ligand proved to be hard to displace. Both complexes $[M(NCMe)(CO)(PPh_3)(\eta\text{-}C_7H_7)]^+$ (M = Mo or W) reacted with strongly nucleophilic phosphines such as PMe_3 in CH_2Cl_2 at room temperature to give $[M(CO)(PPh_3)(PMe_3)(\eta\text{-}C_7H_7)]^+$ (M = Mo, W) although the outcome of the reaction was complicated by competing partial displacement of PPh_3. By contrast no reaction occurred between $[M(NCMe)(CO)(PPh_3)(\eta\text{-}C_7H_7)]^+$ and PPh_3 in CH_2Cl_2 at ambient temperature or under reflux. Therefore, in an attempt to further a rational synthesis of $[M(CO)(PPh_3)_2(\eta\text{-}C_7H_7)]^+$ (M = Mo or W), the intermediacy of complexes $[M(solvent)(CO)(PPh_3)(\eta\text{-}C_7H_7)]^+$ with more weakly coordinated, oxygen-donor solvents was investigated.

Treatment of a green, acetone solution of $[WI(CO)(PPh_3)(\eta\text{-}C_7H_7)]$ with $Ag[BF_4]$ resulted in an immediate colour change to red then back to green. Filtration of the solution followed by addition of diethylether led to precipitation of an oily solid formulated as the solvato complex $[W(acetone)(CO)(PPh_3)(\eta\text{-}C_7H_7)][BF_4]$. The material was too unstable to characterise fully but infrared spectroscopy in CH_2Cl_2 revealed a single carbonyl band (ν(CO)(CH_2Cl_2) 1917 cm^{-1}) shifted to high wavenumber by 6 cm^{-1} from that of the starting material $[WI(CO)(PPh_3)(\eta\text{-}C_7H_7)]$. The solvato intermediate so formed, was redissolved in acetone and treated with one equivalent of PPh_3. Gentle refluxing of the reaction mixture led to the formation of the bis(triphenylphosphine) complex $[W(CO)(PPh_3)_2(\eta\text{-}C_7H_7)][BF_4]$ (**3**), which was isolated as a green-brown solid. Characterisation details for **3** including mass spectroscopic, ^{1}H and ^{13}C NMR data are presented in Table 1. The dominant fragmentation pattern in the mass spectrum is again initial loss of PPh_3 followed by loss of CO, consistent with a labile PPh_3 ligand.

Although $[W(CO)(PPh_3)_2(\eta\text{-}C_7H_7)][BF_4]$ (**3**) is the major product of the above procedure, on one occasion the formation of small quantities of the dicarbonyl complex $[W(CO)_2(PPh_3)(\eta\text{-}C_7H_7)]^+$ (**4**), [ν(CO)(CH_2Cl_2) 2016, 1967 cm^{-1}, see Table 1 for full characterisation data] was also observed. The formation of **4** as a by-product in the above reaction highlights the problems associated with an analogous synthesis of the bis(triphenylphosphine)molybdenum derivative $[Mo(CO)(PPh_3)_2(\eta\text{-}C_7H_7)][BF_4]$ (**1**). The 16-electron fragment $M(CO)(PPh_3)(\eta\text{-}C_7H_7)^+$ (M = Mo or W) is labile to ligand exchange and much more so where M = Mo than for the tungsten derivative where W–CO bonds are relatively strong. Accordingly, when an equivalent synthesis starting from $[MoBr(CO)(PPh_3)(\eta\text{-}C_7H_7)]$ and $Ag[BF_4]$ in acetone was attempted, extensive decomposition occurred and the isolated product contained significant amounts of silver–phosphine adducts $[Ag(PPh_3)_n]$, clearly identified by peaks in the mass spectrum at m/z 895, 633 with the correct isotopic pattern for Ag [14–16]. These silver–phosphine adducts were also isolated from the reaction of $[MoBr(CO)(PPh_3)(\eta\text{-}C_7H_7)]$ with $Ag[BF_4]$ in acetone in the absence of added free phosphine. It is clear therefore that a successful synthesis of **1** depends upon a low temperature route to impede ligand exchange and decomposition. For this reason the silver-free, low temperature method, starting from $[MoMe(CO)(PPh_3)(\eta\text{-}C_7H_7)]$ remains the preferred route to **1**.

2.2. Structural studies

To establish conclusively the identity of complexes **1** and **3** as bis(triphenylphosphine) systems and to investigate how the sterically demanding ligand set is accommodated at a $M(\eta\text{-}C_7H_7)$ (M = Mo or W) centre, a structural study was undertaken. Suitable crystals of the tungsten derivative **3**, were obtained by vapour diffusion of diethyl ether into an acetone solution of the complex. To provide data for a direct comparison, the structure of the dicarbonyl complex $[W(CO)_2(PPh_3)(\eta\text{-}C_7H_7)][BF_4]$ (**4**) as a CH_2Cl_2 solvate, was also determined; the crystallographic data for **3** and **4** augment a very limited series of structural determinations for the cycloheptatrienyl tungsten system [17,18]. The X-ray crystal structures of $[W(CO)(PPh_3)_2(\eta\text{-}C_7H_7)][BF_4]$ and $[W(CO)_2(PPh_3)(\eta\text{-}C_7H_7)][BF_4] \cdot CH_2Cl_2$, together with the crystallographic numbering schemes are presented in Figs. 2 and 3, respectively; important bond lengths and angles are given in Table 2. Key comparisons between the structures of **3** and **4** are presented in Table 3 together with relevant data for other complexes cited in the discussion below.

Focusing initially on a comparison of the cycloheptatrienyl tungsten complexes **3** and **4**, the results of replacing CO in **4** with the more sterically demanding ligand PPh_3 in **3** are examined. The principal effects of increased steric crowding at the W centre are (i) a decrease in pyramidalisation of the tripodal ligands (**4**, $\Sigma\varphi = 254^\circ$; **3**, $\Sigma\varphi = 264^\circ$) and (ii) an elongation of the average W–P bond distance by approximately 0.05 Å (from 2.495 to 2.543 Å). The increase in W–P distances contrasts with the trend in the W–CO distance which decreases from 2.004(6) Å in **4** to 1.974(2) Å in **3**, in accord with the expected behaviour of a π-acceptor ligand as electron density at the metal centre increases. The change in $\Sigma\varphi$ from 254° to 264° essentially spans the known limiting values for $[ML_3(\eta\text{-}C_7H_7)]^{z+}$ complexes (L = monodentate ligand) as exemplified by $[Mo(CO)_3(\eta\text{-}C_7H_7)][BF_4]$ (255°) [19] and the sterically crowded system $[MoI(CO)(PN^*)(\eta\text{-}C_7H_7)]$ {$PN^* = Ph_2PN(Me)CHMePh$} (263°) [20]. Clearly both structural responses (i) and (ii) afford more space to accommodate the additional PPh_3 ligand at the W centre as a P(1)–W(1)–P(2) angle of 100.5° is achieved. However, there is some evidence to suggest that the movement of the PPh_3 ligands towards the C_7H_7 ring consistent with the increase in $\Sigma\varphi$, may be close to a limiting case. The average W–ring carbon distance in **3** and **4** is almost identical (2.33 Å). However, the range of values in **3** (2.262(2)–2.364(2) Å) is much greater than observed for **4** (2.312(5)–2.346(5) Å) and closer inspection of the structure of **3** reveals that the longest W–ring carbon distances W–C(1), W–C(2), W–C(3) and W–C(7) are disposed towards the PPh_3 ligands whereas the shortest distance W–C(5) is located above the carbonyl ligand. The cycloheptatrienyl ring in **3** is therefore tilted away from the sterically crowded side of the molecule but even this does not prevent a very short intramolecular contact between H(1) and H(20) (2.22 Å); for comparison, in **4**, the closest cycloheptatrienyl ring-phosphine contact is between H(27) and H(6) (2.50 Å).

Table 2
Important bond lengths (Å) and angles (°)

Complex 3			
W(1)–P(1)	2.5360(6)	W(1)–C(4)	2.346(2)
W(1)–P(2)	2.5496(6)	W(1)–C(5)	2.262(2)
W(1)–C(8)	1.974(2)	W(1)–C(6)	2.323(2)
W(1)–C(1)	2.364(2)	W(1)–C(7)	2.319(2)
W(1)–C(2)	2.3565(19)	C(8)–O(1)	1.152(2)
W(1)–C(3)	2.352(2)		
P(1)–W(1)–P(2)	100.531(19)	Ct–W(1)–P(1)	123.5
P(1)–W(1)–C(8)	82.60(6)	Ct–W(1)–P(2)	126.8
P(2)–W(1)–C(8)	81.06(6)	Ct–W(1)–C(8)	128.6
W(1)–C(8)–O(1)	174.8(7)		
Complex 4			
W(1)–P(1)	2.4950(12)	W(1)–C(24)	2.312(5)
W(1)–C(19)	2.012(5)	W(1)–C(25)	2.323(5)
W(1)–C(20)	2.004(6)	W(1)–C(26)	2.336(5)
W(1)–C(21)	2.324(5)	W(1)–C(27)	2.344(5)
W(1)–C(22)	2.346(5)	C(19)–O(1)	1.138(7)
W(1)–C(23)	2.316(5)	C(20)–O(2)	1.145(7)
P(1)–W(1)–C(19)	83.91(15)	W(1)–C(20)–O(2)	177.4(5)
P(1)–W(1)–C(20)	87.67(16)	Ct–W(1)–P(1)	129.8
C(19)–W(1)–C(20)	82.5(2)	Ct–W(1)–C(19)	128.5
W(1)–C(19)–O(1)	178.3(5)	Ct–W(1)–C(20)	128.3

Ct = centroid of C_7H_7 ring.

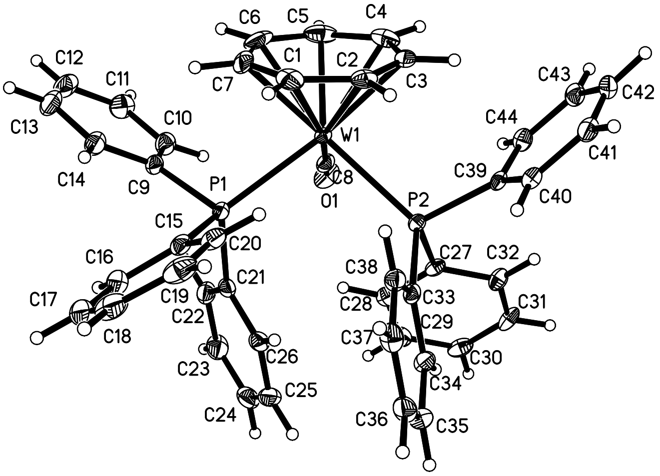

Fig. 2. Molecular structure of complex **3**; BF_4^- counter anion omitted.

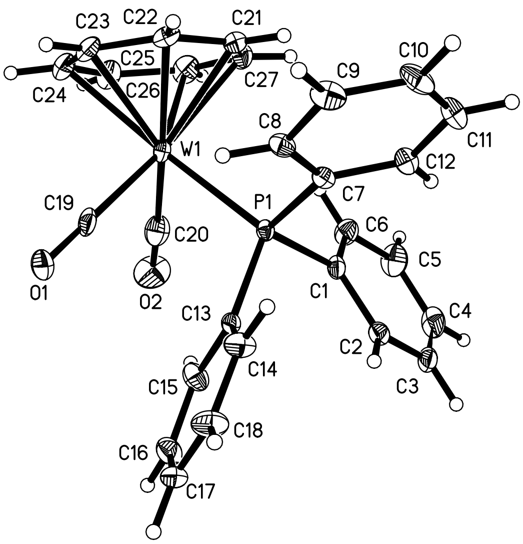

Fig. 3. Molecular structure of complex **4**; BF_4^- counter anion and solvent of crystallisation omitted.

One further mechanism by which steric crowding might be relieved in complex **3** is by reducing the effective cone

Table 3
Selected bond lengths and angles for complexes $[RuL(CO)(PPh_3)(\eta\text{-}C_5R_5)]^+$ and $[RuL(PPh_3)_2(\eta\text{-}C_5R_5)]^+$ (R = H or Me)

Complex	M–P (Å)	$\Sigma\varphi$ (°)	P–M–P (°)	Ref.
3	2.5360(6), 2.5496(6)	264	100.531 (19)	This work
4	2.4950(12)	254	n/a	This work
$[Ru(CO)(PPh_3)_2Cp]^+$	2.340(1), 2.327(1)	n/a	99.47(2)	[26]
$[Ru(CO)(PPh_3)_2Cp]^+$	2.347(13), 2.361(7)	287	97.8(4)	[27]
$[Ru(CO)_2(PPh_3)Cp^*]^+$	2.361(2)	271	n/a	[28]
$[Ru\{=C(OMe)Et\}(PPh_3)_2Cp]^+$	2.347(2), 2.349(2)	278	101.0(1)	[29]
$[Ru(=C=CMePh)(PPh_3)_2Cp]^+$	2.341(3), 2.363(3)	286	99.6(1)	[29]
$[Ru\{=C=CH(CO_2Me)\}(PPh_3)_2Cp^*]^+$	2.359(3), 2.388(3)	281	98.4(1)	[30]
$[Ru\{=CCH(Ph)CH_2CH_2O\}(CO)(PPh_3)Cp]^+$	2.335(2)	271	n/a	[31]
$[Ru(IC_6H_5Me)(CO)(PPh_3)Cp]^+$	2.324(2)	278	n/a	[32]

n/a = not applicable or data not available.

angle of the PPh_3 ligands. Although the Tolman cone angle for PPh_3 (145 ± 2°) [21] is often employed in initial considerations of sterics, this does not account for aspects of ligand conformation and meshing effects and a number of groups have studied the detailed conformation of PPh_3 ligands [22] and the application of solid cone angles [23,24]. One very useful approach is to calculate the experimental cone angle of the PPh_3 ligand from X-ray crystallographic data for the structure under consideration according to the method described by Müller and Mingos [25]. Using this procedure (r_H, the van der Waals radius for hydrogen was taken as 1.00 Å and the metal–phosphorus distance was taken as the crystallographically determined W–P distance and not 2.28 Å of the Tolman definition) the experimental cone angles for the PPh_3 ligands in complexes **3** and **4** were calculated as **3** [P(1)Ph_3: 134°; P(2)Ph_3: 135°] and **4** (137°) (atoms defining the angles were H(11), H(20), H(25), H(28), H(38) and H(43) in **3** and H(6), H(9) and H(15) in complex **4**). Experimentally determined cone angles for the PPh_3 ligand lie in the region 130–170° (with the lower limit characteristic of significant steric crowding) although values outside the range 135–160° are uncommon. There is also an approximate correlation between the M–P distance and the PPh_3 cone angle with the trend that cone angle decreases as the M–P distance increases [25]. From the cone angles computed for **3** and **4** above, it is clear that both complexes have small values for the PPh_3 cone angle consistent with steric crowding. However, the values for **3** are not at the extreme limit, nor is the decrease in cone angle between **4** and **3** particularly large especially in view of the trend for cone angle to decrease with increase in the M–P distance. We therefore conclude that although reduction of the experimental PPh_3 cone angle may be a minor response of the system to accommodation of an additional PPh_3 ligand, the increase in W–P distance remains the most significant factor.

Having established the structural changes in the $W(\eta\text{-}C_7H_7)$ system imposed to accommodate a second PPh_3 ligand, the remaining consideration is to examine an equivalent pair of complexes of the $Ru(\eta\text{-}C_5R_5)$ auxiliary. Two structural determinations are available for $[Ru(CO)(PPh_3)_2Cp]^+$ [26,27] and essential parameters are summarised in Table 3. Unfortunately, data for a direct comparison with $[Ru(CO)_2(PPh_3)Cp]^+$ are not available but data for the Cp* analogue have been reported [28]. Comparison of structural parameters for $[Ru(CO)_2(PPh_3)Cp^*]^+$ and $[Ru(CO)(PPh_3)_2Cp]^+$ reveal a large increase in $\Sigma\varphi$ from 271° to 287° through substitution of an additional PPh_3 ligand. However, in contrast to the pair of cycloheptatrienyltungsten complexes **3** and **4**, the change in the Ru–PPh_3 distance is much less evident (Ru–$P_{average}$: $[Ru(CO)_2(PPh_3)Cp^*]^+ = 2.36$ Å; $[Ru(CO)(PPh_3)_2Cp]^+ = 2.34$ Å). Clearly this comparison must be qualified by differences imposed by Cp vs. Cp* but the data in Table 3 [29–32] suggest that typical Ru–PPh_3 distances in cationic, mono-triphenylphosphine complexes $[RuL(CO)(PPh_3)Cp]^+$ are in the range 2.32–2.34 Å and that the effect of replacement of Cp by Cp* is to increase the Ru–PPh_3 bond length by 0.02–0.03 Å. Therefore, at least in complexes of the $Ru(PPh_3)_2Cp$ auxiliary, it is probable that accommodation of the second PPh_3 ligand results only in a relatively small lengthening and weakening of the Ru–PPh_3 bond. The contrasting behaviour of the $Ru(PPh_3)_2Cp$ and $W(PPh_3)_2(\eta\text{-}C_7H_7)$ systems in this respect may be important in rationalising the relative stability of their complexes.

3. Conclusions

The complexes $[M(CO)(PPh_3)_2(\eta\text{-}C_7H_7)]^+$ (M = Mo or W) are the first examples of derivatives of the sterically crowded bis(triphenylphosphine) auxiliary $M(PPh_3)_2(\eta\text{-}C_7H_7)$. An X-ray crystallographic structural comparison of the tungsten complex $[W(CO)(PPh_3)_2(\eta\text{-}C_7H_7)][BF_4]$ (**3**) with its mono-phosphine counterpart, $[W(CO)_2\text{-}(PPh_3)(\eta\text{-}C_7H_7)][BF_4] \cdot CH_2Cl_2$ (**4**) reveals that the additional PPh_3 ligand is accommodated in the structure by a series of modifications to the molecular geometry including an increase in the sum of the angles between the tripodal ligands, tilting of the cycloheptatrienyl ring and a small decrease in the experimental cone angle of the PPh_3ligands. However, the most significant change appears to be an elongation of the W–PPh_3 bond lengths by approximately 0.05 Å. Although the W–PPh_3 distances in complex **3** (2.5360(6) and 2.5496(6) Å) are not exceptionally long {for example: $[WBr_2(CO)_2(PPh_3)_2]$ (W–P = 2.481(9), 2.486(9) Å) [33]; $[WCl(CO)_2(PPh_3)(\eta\text{-}C_9H_7)]$ (C_9H_7 = indenyl, W–P = 2.516(1) Å) [34]; $[W(CO)_2(PPh_3)_2(\eta^5\text{-}C_7H_9)]^+$ (C_7H_9 = cycloheptadienyl, W–P = 2.568(3), 2.522(3) Å) [35]} they are towards the upper end of observed values and moreover $[W(CO)_2(PPh_3)_2(\eta^5\text{-}C_7H_9)]^+$ is also labile to PPh_3 ligand dissociation. The chemistry of the $M(PPh_3)_2(\eta\text{-}C_7H_7)$ auxiliary should therefore be dominated by PPh_3 ligand dissociation with the prospect of similar or enhanced reactivity compared to that of the $Ru(PPh_3)_2Cp^*$ system.

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 compounds $[MX(CO)(PPh_3)(\eta\text{-}C_7H_7)]$ (M = Mo, X = Br [11]; M = W, X = I [10]), $[MoMe(CO)(PPh_3)(\eta\text{-}C_7H_7)]$ [11], $[Mo(NCMe)(CO)(PPh_3)(\eta\text{-}C_7H_7)][BF_4]$ [13] and $[W(CO)_2(PPh_3)(\eta\text{-}C_7H_7)][BF_4]$ [36] were prepared by published procedures. 300 MHz ^1H and 75 MHz $^{13}C\{^1H\}$ NMR spectra were recorded on Varian Inova 300 or Varian Inova 400 spectrometers. Infrared spectra were obtained on a Perkin–Elmer FT 1710 spectrometer and mass spectra were recorded using Kratos Concept 1S (FAB spectra), Micromass Platform II (ES spectra) or Micromass/Waters Tof Spec 2E (MALDI spectra) instruments. Microanalyses were by the staff of the Microanalytical Service of the School of Chemistry, University of Manchester.

4.2. Preparation of $[Mo(CO)(PPh_3)_2(\eta\text{-}C_7H_7)][PF_6] \cdot CH_2Cl_2$ (1)

A green, stirred solution of $[Mo(CH_3)(CO)(PPh_3)(\eta\text{-}C_7H_7)]$ (0.132 g, 0.27 mmol) in thf (30 cm^3) was cooled to −78 °C, then treated with $[Ph_3C][PF_6]$ (0.110 g, 0.28 mmol) immediately followed by PPh_3 (0.079 g, 0.30 mmol). On warming slowly to room temperature the colour changed first to yellow-brown, then green brown. The reaction mixture was then reduced to dryness in vacuo and the residue recrystallised from thf-diethyl ether then CH_2Cl_2-diethyl ether to give **1** as a green brown solid. Yield: 0.13 g (50%, as CH_2Cl_2 solvate).

4.3. Preparation of $[W(NCMe)(CO)(PPh_3)(\eta\text{-}C_7H_7)][BF_4]$ (2)

Addition of $Ag[BF_4]$ (0.35 g, 1.79 mmol) to a green, stirred solution of $[WI(CO)(PPh_3)(\eta\text{-}C_7H_7)]$ (1.00 g, 1.45 mmol) in NCMe (40 cm^3) rapidly produced a precipitate of AgI. Reaction was continued for 1 h then the reaction mixture was filtered and solvent removed from the filtrate. Recrystallisation of the residue from CH_2Cl_2-diethyl ether gave complex **2** as a lime green solid. Yield: 0.85 g (85%).

4.4. Preparation of $[W(CO)(PPh_3)_2(\eta\text{-}C_7H_7)][BF_4]$ (3)

Reaction of a stirred acetone solution (30 cm^3) of $[WI(CO)(PPh_3)(\eta\text{-}C_7H_7)]$ (0.70 g, 1.01 mmol) with $Ag[BF_4]$ (0.20 g, 1.03 mmol) resulted in a colour change from green to red then back to green. After 15 min the reaction mixture was filtered and PPh_3 (0.265 g, 1.01 mmol) added. The reaction mixture was gently refluxed on a water bath for 2 h, then solvent removed in vacuo. The resulting residue was redissolved in CH_2Cl_2 and gentle refluxing continued for 30 min. The resulting green solution was filtered, reduced in volume and diethyl ether added to precipitate the crude product. Recrystallisation from CH_2Cl_2-diethyl ether gave **3** as a green-brown solid as the first precipitated fraction. Yield: 0.14 g (14%). This sample gave microanalytical data indicative of CH_2Cl_2 solvent of crystallisation (C, 54.8%, H, 3.9%, Cl, 5.60%; required for $C_{44}H_{37}OP_2\text{-}WBF_4CH_2Cl_2$: C, 54.1%, H, 3.9%, Cl, 7.1%); the microanalytical data given in Table 1 were obtained by further recrystallisation of the complex from acetone-diethyl ether.

4.5. X-ray crystal structures of $[W(CO)(PPh_3)_2(\eta\text{-}C_7H_7)][BF_4]$ (3) and $[W(CO)_2(PPh_3)(\eta\text{-}C_7H_7)][BF_4] \cdot CH_2Cl_2$ (4)

The majority of details of the structure analyses carried out on complexes **3** and **4** are given in Table 4. Data collection, cell refinement and data reduction were carried out with Bruker SMART and Bruker SAINT software;

Table 4
Crystal data and refinement parameters for $[W(CO)(PPh_3)_2(\eta\text{-}C_7H_7)][BF_4]$ (**3**) and $[W(CO)_2(PPh_3)(\eta\text{-}C_7H_7)][BF_4] \cdot CH_2Cl_2$ (**4**)

Complex	3	4
Formula	$WC_{44}H_{37}P_2OBF_4$	$WC_{27}H_{22}PO_2BF_4 \cdot CH_2Cl_2 \cdot O$
Mass	914.34	781.00
Temperature (K)	100(2)	100(2)
λ (Å)	0.71073 (Mo Kα)	0.71073 (Mo Kα)
Crystal System	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a (Å)	15.4445(19)	10.9042(7)
b (Å)	13.4246(13)	18.6959(11)
c (Å)	17.891(3)	14.3821(9)
β (°)	97.721(13)	92.6390(10)
V ($Å^3$); Z	3675.8(8); 4	2928.9(3); 4
Absorption coefficient (cm^{-1})	32.86	42.35
θ Range (°)	1.90–26.39	1.79–28.27
Limiting indices (hkl)	±19; ±16; ±22	−14/14; −23/24; −18/19
Total reflections	28,680	25,089
Independent reflections, $I > 2\sigma(I)$	7506	6930
R_1	0.0173	0.0392
wR_2	0.0417	0.1081
Completeness to theta (%)	99.6	95.3

SHELXS-97 [37] was employed for the computing of structure solution and SHELXL-97 [38] for the computing of structure refinement. In each case an absorption correction was applied with the aid of the SADABS programme [39]. Both structures were solved by direct methods with refinement by full-matrix least-squares based on F^2 and all non-hydrogen atoms were refined anisotropically; hydrogen atoms were included in calculated positions.

Single crystals of **3** were obtained as green blocks by vapour diffusion of diethyl ether into an acetone solution of the complex. A crystal of dimensions $0.25 \times 0.25 \times 0.25$ mm was selected for analysis. Single crystals of $\mathbf{4} \cdot CH_2Cl_2$ were obtained as red blocks by vapour diffusion of diethyl ether into a CH_2Cl_2 solution of the complex. A crystal of dimensions $0.20 \times 0.10 \times 0.05$ mm was selected for analysis. The asymmetric unit of complex **4** contains the W complex, a BF_4 ion, one CH_2Cl_2 molecule and one additional molecule, probably H_2O although only the O atom was detected.

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Appendix A. Supplementary data

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre. CCDC 288657 contains the supplementary crystallographic data for complex **3** and CCDC 288658 the data for complex **4**. These may be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.01.013.

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