



The preparation, crystal structure and some reaction chemistry of Bromo(η^5 -penta-phenylcyclopentadienyl)dicarbonylosmium(II), $[\text{Os}(\eta^5\text{-C}_5\text{Ph}_5)(\text{CO})_2\text{Br}]$

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Abstract—The preparation and characterisation of $[\text{Os}(\eta^5\text{-C}_5\text{Ph}_5)(\text{CO})_2\text{Br}]$ (**1**) are described; this complex is the first reported C_5Ph_5^- derivative of osmium. A single crystal X-ray diffraction study of (**1**) (refined to $R = 0.040$, $R_w = 0.043$) is also reported. The related complexes, $[\text{Os}\{\eta^5\text{-C}_5\text{Ph}_4(p\text{-}^t\text{BuC}_6\text{H}_4)\}(\text{CO})_2\text{Br}]$ (**2**) and $[\text{Os}\{\eta^5\text{-C}_5(p\text{-MeC}_6\text{H}_4)_5\}(\text{CO})_2\text{Br}]$ (**3**), have also been prepared. Carbonyl substitution of (**1**) in tetrahydrofuran following treatment with Me_3NO afforded $[\text{Os}(\eta^5\text{-C}_5\text{Ph}_5)(\text{CO})(\text{L})\text{Br}]$ ($\text{L} = \text{PMe}_2\text{Ph}$ (**4**), $\text{P}(\text{OEt})_3$ (**5**), $\text{P}(\text{OCH}_2)_3\text{CCH}_3$ (**6**) and $^t\text{BuNC}$ (**7**)). A single crystal X-ray diffraction study of (**6**) (refined to $R = 0.066$, $R_w = 0.073$) is described. © 1998 Elsevier Science Ltd. All rights reserved

Keywords: osmium; cyclopentadienyl; pentaphenylcyclopentadienyl; crystal structure.

Relatively few cyclopentadienyl or substituted cyclopentadienyl complexes of osmium have been described and the number of structurally characterised derivatives is correspondingly small [1–22]. Previously, the half-sandwich compounds $[\text{Os}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Br}]$ and $[\text{Os}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{H}]$ have been prepared from the reactions of $\text{Os}(\text{CO})_4\text{Br}_2$ with $(\text{C}_5\text{H}_6)_2$ in decane and $\text{Ti}(\text{C}_5\text{H}_5)$ in heptane, respectively [23]. In addition, $[\text{Os}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_2\text{Br}]$ has been synthesised by reacting $\text{Os}(\text{CO})_4\text{Br}_2$ with $\text{C}_5\text{Me}_5\text{H}$ in decane [23]; $[\text{Os}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_2\text{I}]$ from a one-pot reaction of $\text{Os}_3(\text{CO})_{12}$, I_2 and $\text{C}_5\text{Me}_5\text{H}$ in benzene [6], and $[\text{Os}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_2\text{H}]$ from $\text{Os}_3(\text{CO})_{12}$ and $\text{C}_5\text{Me}_5\text{H}$ in heptane [23]. More recently, $[\text{Os}(\eta^5\text{-C}_5\text{Me}_5)\text{Br}(\mu\text{-Br})]_2$ has been synthesised in good yield from H_2OsBr_6 and $\text{C}_5\text{Me}_5\text{H}$ [20]. This dimer proved to be a convenient intermediate in the synthesis of a wide variety of $[\text{Os}(\text{C}_5\text{Me}_5)\text{L}_n]$ complexes.

The formal oxidative addition of $\text{C}_5\text{R}_{5-n}\text{H}_n\text{X}$ ($n = 0\text{--}5$) to a transition metal precursor is an alternative synthetic route to cyclopentadienyl and substituted cyclopentadienyl complexes. This route has not been widely exploited because of the lack of ready

availability of most of the necessary $\text{C}_5\text{R}_{5-n}\text{H}_n\text{X}$ precursors. However, 1-bromo-1,2,3,4,5-penta-aryl-cyclopentadienyl species are readily prepared in high yield and their reactions with organometallic precursors provide convenient routes to pentaaryl-cyclopentadienyl complexes [24–26]. A potentially wide range of ligands with varying electronic and steric properties is accessible in this way.

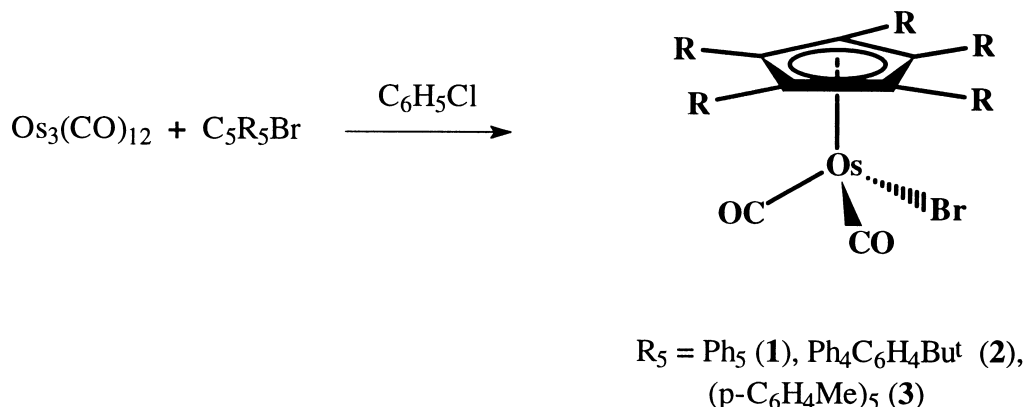
Although pentaphenylcyclopentadienyl complexes of many metals are known and several of these have been structurally characterised [27–56], no pentaphenylcyclopentadienyl complex of osmium has been reported.

Herein we describe the preparation of $[\text{Os}(\eta^5\text{-C}_5\text{Ph}_5)(\text{CO})_2\text{Br}]$ by the formal oxidative addition of $\text{C}_5\text{Ph}_5\text{Br}$ to $\text{Os}_3(\text{CO})_{12}$. The similar complexes $[\text{Os}\{\eta^5\text{-C}_5\text{Ph}_4(p\text{-}^t\text{BuC}_6\text{H}_4)\}(\text{CO})_2\text{Br}]$ and $[\text{Os}\{\eta^5\text{-C}_5(p\text{-MeC}_6\text{H}_4)_5\}(\text{CO})_2\text{Br}]$ have also been prepared. The crystal structure of $[\text{Os}(\eta^5\text{-C}_5\text{Ph}_5)(\text{CO})_2\text{Br}]$ and the preparation of several derivatives of the mono (pentaphenylcyclopentadienyl)osmium moiety are also reported.

RESULTS AND DISCUSSION

$[\text{Os}(\eta^5\text{-C}_5\text{Ph}_5)(\text{CO})_2\text{Br}]$ (**1**) was prepared by refluxing a mixture of $\text{Os}_3(\text{CO})_{12}$ and $\text{C}_5\text{Ph}_5\text{Br}$ in chloro-

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Scheme 1.

benzene. The complex was isolated as an air-stable pale yellow solid after purification on a silica gel column and crystallisation from dichloromethane/*n*-hexane, and was characterised by elemental analysis, and mass, infrared and ^1H and ^{13}C NMR spectra. Small amounts of the new complex $[\text{Os}(\eta^5\text{-C}_5\text{Ph}_5)(\text{CO})_2\text{H}]$ (similarly characterised), and of $\text{C}_5\text{Ph}_5\text{H}$ and $\text{Os}_3(\text{CO})_{10}\text{Br}_2$ were also obtained in variable amounts and were isolated after column chromatography of the reaction mixture. The analogous osmium compounds, $[\text{Os}\{\eta^5\text{-C}_5\text{Ph}_4(p\text{-BuC}_6\text{H}_4)\}(\text{CO})_2\text{Br}]$ (**2**) and $[\text{Os}\{\eta^5\text{-C}_5(p\text{-MeC}_6\text{H}_4)_5\}(\text{CO})_2\text{Br}]$ (**3**) have also been prepared by reacting the corresponding perarylcyclopentadienyl bromide with $\text{Os}_3(\text{CO})_{12}$ in chlorobenzene (Scheme 1). Although the yields of (**2**) and (**3**) were considerably lower than that of (**1**), they have not been optimised. The analytical and spectroscopic data of (**1**)–(**3**) were consistent with the formulation of the products as $[\text{Os}(\eta^5\text{-ligand})(\text{CO})_2\text{Br}]$. The mass spectra of (**1**)–(**3**) show that the main fragmentation pathway is via the loss of the two carbonyl ligands although all exhibit an (often intense) ion assigned to $[\text{Os}(\text{ligand})_2\text{-H}]^+$.

A single crystal X-ray diffraction study of (**1**) was undertaken for comparison with those of the iron [30] and ruthenium [46] analogues. $[\text{Os}(\eta^5\text{-C}_5\text{Ph}_5)(\text{CO})_2\text{Br}]$ crystallises in the orthorhombic space group *PBCA* and is isostructural with $[\text{Fe}(\eta^5\text{-C}_5\text{Ph}_5)(\text{CO})_2\text{Br}]$ [30] and $[\text{Ru}(\eta^5\text{-C}_5\text{Ph}_5)(\text{CO})_2\text{Br}]$ [46]. The crystal structure of $[\text{Os}(\eta^5\text{-C}_5\text{Ph}_5)(\text{CO})_2\text{Br}]$ consists of discrete molecules in the solid state and no intermolecular contacts of significance were observed in the solid. The closest intermolecular contact is 3.44 Å between O(1) on molecule (*x*, *y*, *z*) and C(22) on

molecule ($1/2-x$, $1/2+y$, $+z$). The closest intermolecular non-bonding approaches to osmium are greater than 4 Å. Final atomic positional coordinates, with estimated standard deviations, bond lengths and angles and anisotropic thermal parameters are deposited.* Selected interatomic bond distances and angles, with standard deviations derived from the refinement, are given in Tables 1 and 2. The atomic nomenclature is defined in Fig. 1. Figures 1 and 2 illustrate the molecular geometry viewed along, and perpendicular to, the normal to the C_5 plane of the C_5Ph_5 ligand, respectively.

The $[\text{Os}(\eta^5\text{-C}_5\text{Ph}_5)(\text{CO})_2\text{Br}]$ molecule

Coordination by the η^5 pentaphenylcyclopentadienyl group, the bromine atom and the two carbonyl groups creates a “piano stool” environment about the osmium atom. The Os–(ring centroid) distance is 1.90 Å and the average Os–C distance of 2.27 Å may be compared with 2.214 Å for $[\text{Os}(\eta^5\text{-C}_5\text{Ph}_5)(\text{CO})_2\text{Br}]$.

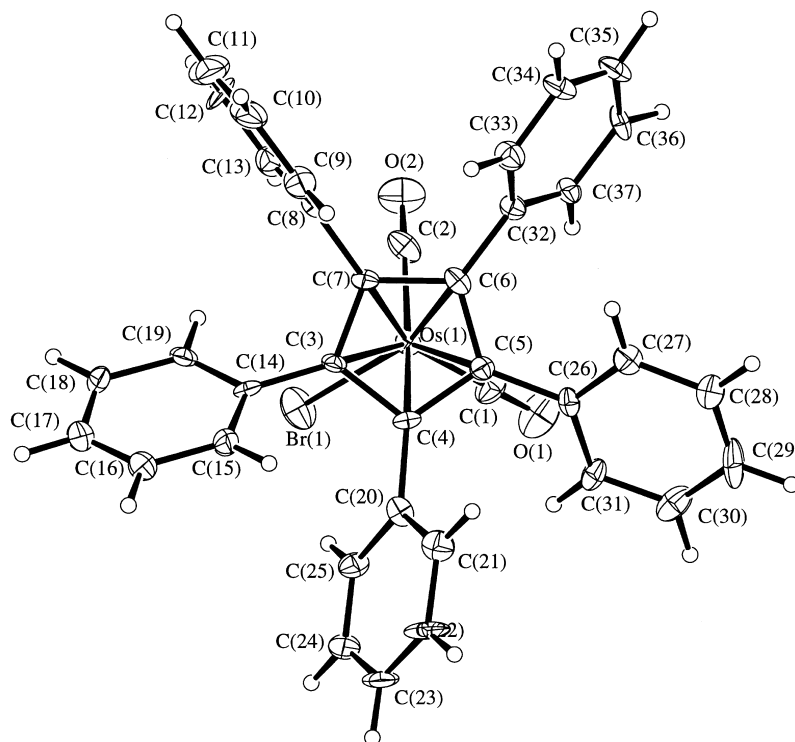
Table 1. Selected bond lengths (Å) for $[\text{Os}(\eta^5\text{-C}_5\text{Ph}_5)(\text{CO})_2\text{Br}]$ (**1**)

Atoms	<i>d</i>	Atoms	<i>d</i>
Os(1)—Br(1)	2.531(2)	Os(1)—C(1)	1.87(2)
Os(1)—C(2)	1.93(2)	Os(1)—C(3)	2.31(1)
Os(1)—C(4)	2.26(1)	Os(1)—C(5)	2.25(1)
Os(1)—C(6)	2.24(1)	Os(1)—C(7)	2.28(1)
O(1)—C(1)	1.09(2)	O(2)—C(2)	1.00(2)
C(3)—C(4)	1.48(2)	C(3)—C(7)	1.42(2)
C(4)—C(5)	1.45(2)	C(5)—C(6)	1.45(2)
C(6)—C(7)	1.47(2)	C(7)—C(8)	1.47(2)
C(3)—C(14)	1.45(2)	C(4)—C(20)	1.48(2)
C(5)—C(26)	1.48(2)	C(6)—C(32)	1.47(2)

* The atomic coordinates and thermal parameters have been submitted as supplementary material for deposition at the Cambridge Crystallographic Data Centre (see Deposition of crystallographic data).

Table 2. Selected bond angles ($^\circ$) for $[\text{Os}(\eta^5\text{-C}_5\text{Ph}_5)(\text{CO})_2\text{Br}]$ (**1**)

Atoms	Angle	Atoms	Angle
C(1)—Os(1)—Br(1)	88.1(5)	C(2)—Os(1)—Br(1)	87.4(5)
C(1)—Os(1)—C(2)	88.6(7)	C(3)—Os(1)—Br(1)	95.1(3)
C(4)—Os(1)—Br(1)	105.1(3)	C(5)—Os(1)—Br(1)	141.0(3)
C(6)—Os(1)—Br(1)	156.1(3)	C(7)—Os(1)—Br(1)	118.4(3)
O(1)—C(1)—Os(1)	178(1)	O(2)—C(2)—Os(1)	177(1)
C(4)—C(3)—C(7)	107(1)	C(4)—C(5)—C(6)	109(1)
C(3)—C(4)—C(5)	107(1)	C(5)—C(6)—C(7)	106(1)
C(3)—C(7)—C(6)	109(1)	C(4)—C(3)—C(14)	124(1)
C(5)—C(6)—C(32)	127(1)	C(7)—C(3)—C(14)	127(1)
C(7)—C(6)—C(32)	125(1)	C(3)—C(4)—C(20)	122(1)
C(3)—C(7)—C(8)	122(1)	C(5)—C(4)—C(20)	128(1)
C(6)—C(7)—C(8)	126(1)	C(4)—C(5)—C(26)	123(1)
C(6)—C(5)—C(26)	126(1)	C(6)—C(32)—C(33)	118(1)
C(7)—C(8)—C(9)	118(1)	C(6)—C(32)—C(37)	121(1)
C(7)—C(8)—C(13)	124(1)	C(5)—C(26)—C(27)	117(1)
C(4)—C(20)—C(21)	119(1)	C(5)—C(26)—C(31)	123(1)
C(4)—C(20)—C(25)	123(1)	C(3)—C(14)—C(15)	120(1)
C(3)—C(14)—C(19)	120(1)		

Fig. 1. ORTEP [69] (25% probability) illustration of the molecular structure of $[\text{Os}(\eta^5\text{-C}_5\text{Ph}_5)(\text{CO})_2\text{Br}]$ (**1**) showing the atom numbering. Viewed along the normal to the C_5Ph_5 plane.

$\text{C}_5\text{H}_5)(\text{PPh}_3)_2\text{Cl}]$ [3], 2.177 Å for $[\text{Os}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2\text{Br}]$ [22], 2.25 Å for $[\text{Os}(\eta^5\text{-C}_5\text{H}_5)(\text{PMe}_3)_2(\text{NO})]^+$ [1], 2.247 Å for $[\text{Os}_2(\eta^5\text{-C}_5\text{Me}_5)_2(\text{CO})_2(\mu\text{-H})_2]$ [2] and 2.223 and 2.261 Å for the two isomeric forms of $[\text{Os}(\eta^5\text{-C}_5\text{H}_5)(\eta^2\text{-CH}_2=\text{CH}-$

$\text{C}_6\text{H}_4\text{PPh}_2)\text{Br}]$ [4]. The Os—CO distances (1.87(2) and 1.93(2) Å) are indistinguishable and may be compared, for example, with a bond length of 1.833(9) Å in $[\text{Os}_2(\eta^5\text{C}_5\text{Me}_5)_2(\text{CO})_2(\mu\text{-H})_2]$ [2], 1.879(5) Å in $[\text{Os}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})(\text{PPh}_3)(=\text{C}(\text{tBu})\text{H})][\text{BF}_4]$ [6]

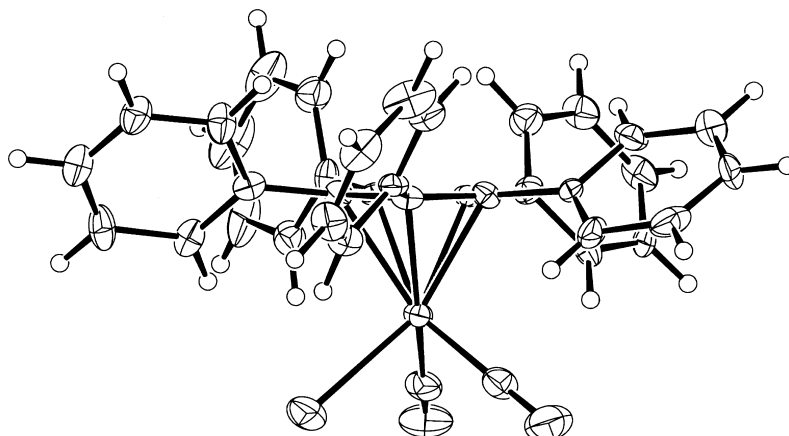


Fig. 2. ORTEP [69] (25% probability) illustration of the molecular structure of $[\text{Os}(\eta^5\text{-C}_5\text{Ph}_5)(\text{CO})_2\text{Br}]$ (**1**) viewed perpendicular to the normal to the C_5Ph_5 plane.

and 1.919(14), 1.961(15) and 1.929(15) Å in $[\text{Os}(\eta^4\text{-C}_4\text{Ph}_4\text{CO})(\text{CO})_3]$ [57]. The C=O bond lengths in (**1**) are equivalent. The Os—Br distance is 2.530(2) Å and may be compared with values of 2.5438(9) Å for $[\text{Os}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2\text{Br}]$ [22], 2.545(2) and 2.510(2) Å in two molecules of $[\text{Os}(\eta^5\text{-C}_5\text{H}_5)(\eta^2\text{-CH}_2=\text{CH-C}_6\text{H}_4\text{PPh}_2)\text{Br}]$ [4] and 2.559(1) Å for $[\text{Os}(\eta^5\text{-C}_5\text{Me}_5)\text{Br}(\mu\text{-Br})_2]$ [20].

The C_5 nucleus of the pentaphenylcyclopentadienyl ligand is planar to within 0.02 Å. The C—C bond lengths of the C_5 ring range from 1.42(2)–1.48(2) Å, the average C—C bond length being 1.45 Å, which is consistent with C_5Ph_5 rings in other metal complexes. The *ipso*-carbon atoms of each of the phenyl rings are displaced slightly from the C_5 plane by between 0.07 and 0.25 Å, with the average distance being 0.16 Å. The *ipso*-carbon atoms of all phenyl rings are on the opposite side of the C_5 plane to the osmium atom. The phenyl rings are all also planar to within 0.02 Å and are canted at between 39.5 and 88.0° to the C_5 ring in a paddle wheel arrangement. The phenyl ring defined by C(8) is almost perpendicular to the C_5 ring.

Table 3 compares some bond length data deter-

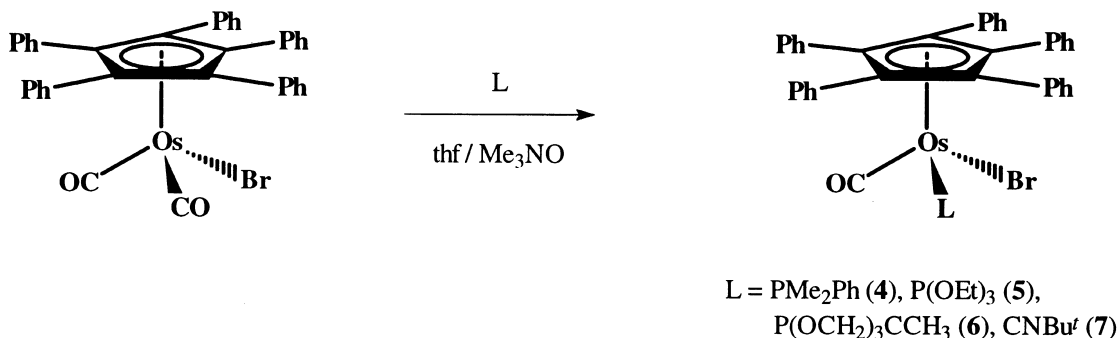
mined for $[\text{Os}(\eta^5\text{-C}_5\text{Ph}_5)(\text{CO})_2\text{Br}]$ and its iron (**8**) and ruthenium (**9**) analogues. As expected, it is evident that differences between the compounds of the three metals are generally small. For all three compounds the view of the coordination sphere of the metal as a distorted octahedron is supported by the angles subtended at the metal atom by the bromine atom and the two carbonyl carbon atoms ($\text{C}(1)\text{—M}(1)\text{—Br}(1) = 86.6(1)^\circ$, $86.8(2)^\circ$ and $88.1(5)^\circ$; $\text{C}(1)\text{—M}(1)\text{—C}(2) = 89.8(2)^\circ$, $87.9(3)^\circ$ and $88.6(7)^\circ$; $\text{C}(2)\text{—M}(1)\text{—Br}(1) = 86.6(1)^\circ$, $85.5(3)^\circ$ and $87.4(5)^\circ$ for M = Fe (**8**), Ru (**9**) and Os (**1**), respectively). The average deviation of the phenyl rings from coplanarity with the C_5 ring is 59.9° in (**1**), which is similar to that of (**8**) (58.7°) [30] and (**9**) (62.0°) [46], while both (**8**) (87.4°) and (**9**) (87.4°) also contain a phenyl ring almost perpendicular to the C_5 ring.

Mono-carbonyl substitution of (**1**) in tetrahydrofuran using Me_3NO and appropriate ligands, L, afforded $[\text{Os}(\eta^5\text{-C}_5\text{Ph}_5)(\text{CO})(\text{L})\text{Br}]$ (L = PMe_2Ph (**4**), $\text{P}(\text{OEt})_3$ (**5**), $\text{P}(\text{OCH}_2)_3\text{CCH}_3$ (**6**) and tBuNC (**7**)) (Scheme 2), which have been characterised by elemental analysis, and mass, infrared and ^1H and ^{31}P NMR

Table 3. Comparisons of selected metrical data between $[\text{M}(\eta^5\text{-C}_5\text{Ph}_5)(\text{CO})_2\text{Br}]$ (M = Fe (**8**), Ru (**9**), Os (**1**))

Bond	Fe ³⁰	Distance (Å)	
		Ru ⁴⁶	Os ^a
M—CO	1.786(5), 1.812(5)	1.902(9), 1.930(9)	1.87(2), 1.93(2)
M—Br	2.424(1)	2.537(1)	2.530(2)
M—C(C_5 ring)	2.090(3)–2.165(4)	2.215(6)–2.304(6)	2.24(1)–2.31(1)
	2.125 av.	2.258 av.	2.27 av.
M—(C_5 ring plane)	1.738(5)	not given	1.90
C—C(C_5Ph_5)	1.420(5)–1.451(5)	1.411(8)–1.462(9)	1.42(2)–1.48(2)
	1.435 av.	1.441 av.	1.45 av.
C—O	1.052(6), 1.097(6)	1.024(8), 1.102(8)	0.99(2), 1.10(2)

^aThis work



Scheme 2.

spectra. The mass spectra of compounds (4)–(7) all exhibit a molecular ion, although the dominant ion is $[M\text{-CO-L}]^+$. A single CO stretching vibration is observed in the IR spectrum in CH_2Cl_2 solution. As observed in the solid state IR spectrum of $[\text{Fe}(\eta^5\text{-C}_5\text{Ph}_5)(\text{CO})(\text{PMe}_3)\text{Br}]$ [58], the spectra of (4)–(6) in KBr show a splitting of the CO stretching absorptions observed in solution. This is thought to be due to the presence of two diastereoisomers derived from the opposite canting modes of the five phenyl groups around the C_5 rings [58]. The observation of one set of NMR signals in CD_2Cl_2 suggest, however, that in solution the five phenyl groups around the ring rotate rapidly on the NMR time scale. In none of these reactions, even when an excess of ligand and Me_3NO were used, did we observe the loss of two carbonyl ligands.

A single crystal X-ray diffraction study was undertaken on $[\text{Os}(\eta^5\text{-C}_5\text{Ph}_5)(\text{CO})\{\text{P(OCH}_2)_3\text{CCH}_3\}\text{Br}]$. The compound crystallises in the monoclinic space group $P2_1/n$ (#14). The pentaphenylcyclopentadienyl ligand is once again coordinated in the η^5 mode with coordination completed by the $\text{P(OCH}_2)_3\text{CCH}_3$ ligand, one carbonyl ligand and the bromide ligand, the latter two of which are disordered between two sites. Final atomic positional coordinates, with estimated standard deviations, bond lengths and angles and anisotropic thermal parameters are deposited.* Selected interatomic bond distances and angles, with standard deviations from the refinement are given in Tables 4 and 5. The atomic nomenclature is defined in Fig. 3, which illustrates the molecular geometry viewed perpendicular to the normal to the C_5 plane of the C_5Ph_5^- ligand.

Again no intermolecular contacts of significance were observed in the solid. The closest intermolecular contact is 3.13 Å between O(1a) on molecule (x, y, z) and C(29) on molecule ($-1/2-x, y-1/2, 1/2-z$). The closest intermolecular non-bonding approaches to osmium are greater than 4 Å.

The $[\text{Os}(\eta^5\text{-C}_5\text{Ph}_5)(\text{CO})\{\text{P(OCH}_2)_3\text{CCH}_3\}\text{Br}]$ molecule

The Os–(ring centroid) distance is 1.92 Å and the average Os–C distance is 2.28 Å. Disorder in the carbonyl and bromine ligands precludes any comment on the Os–CO bond distances and the C–O distances. The Os–Br distances appear to be shorter than that of (1).

The C_5 nucleus of the pentaphenylcyclopentadienyl ligand is planar to within 0.02 Å. The C–C bond lengths of the C_5 ring range from 1.43(1)–1.46(1) Å, the average being 1.45 Å. The *ipso*-carbon atom of each of the phenyl rings is displaced from the C_5 plane by between 0.11–0.35 Å, with the average being 0.18 Å. Again the *ipso* carbons of all phenyl rings are on the opposite side of the C_5 plane to the osmium atom. The phenyl rings are all planar to within 0.03 Å with normal dimensions and are canted at between 44.6 and 56.3° to the C_5 ring in the usual paddlewheel arrangement, with an average deviation from coplanarity of 52.6°.

EXPERIMENTAL

All manipulations were performed at atmospheric pressure under an atmosphere of dinitrogen by using conventional Schlenk techniques. Chlorobenzene (Merck) was dried, distilled and stored over calcium hydride. Tetrahydrofuran (thf) (Merck) was pre-dried over sodium wire and distilled from sodium benzophenone ketyl. *n*-Hexane (BDH) was distilled from sodium wire. Dichloromethane (Ajax) was distilled from calcium hydride. $\text{C}_5\text{Ph}_5\text{Br}$, [59] $\text{C}_5\text{Ph}_4(p\text{-}^t\text{Bu-C}_6\text{H}_4)\text{Br}$ [59] and $\text{C}_5(p\text{-MeC}_6\text{H}_4)_3\text{Br}$ [25] were prepared as described previously. $\text{Os}_3(\text{CO})_{12}$ (Aldrich), P(OEt)_3 (Merck), PMe_2Ph (Fluka) and $^t\text{BuNC}$ (Aldrich) were used as received. Trimethylamine *N*-oxide dihydrate (Aldrich) was dehydrated by sublimation prior to use. Flash silica (240–400 mesh) was obtained

Table 4. Selected bond lengths (Å) for $[\text{Os}(\eta^5\text{-C}_5\text{Ph}_5)(\text{CO})\{\text{P}(\text{OCH}_2)_3\text{CCH}_3\}\text{Br}]$ (**6**)

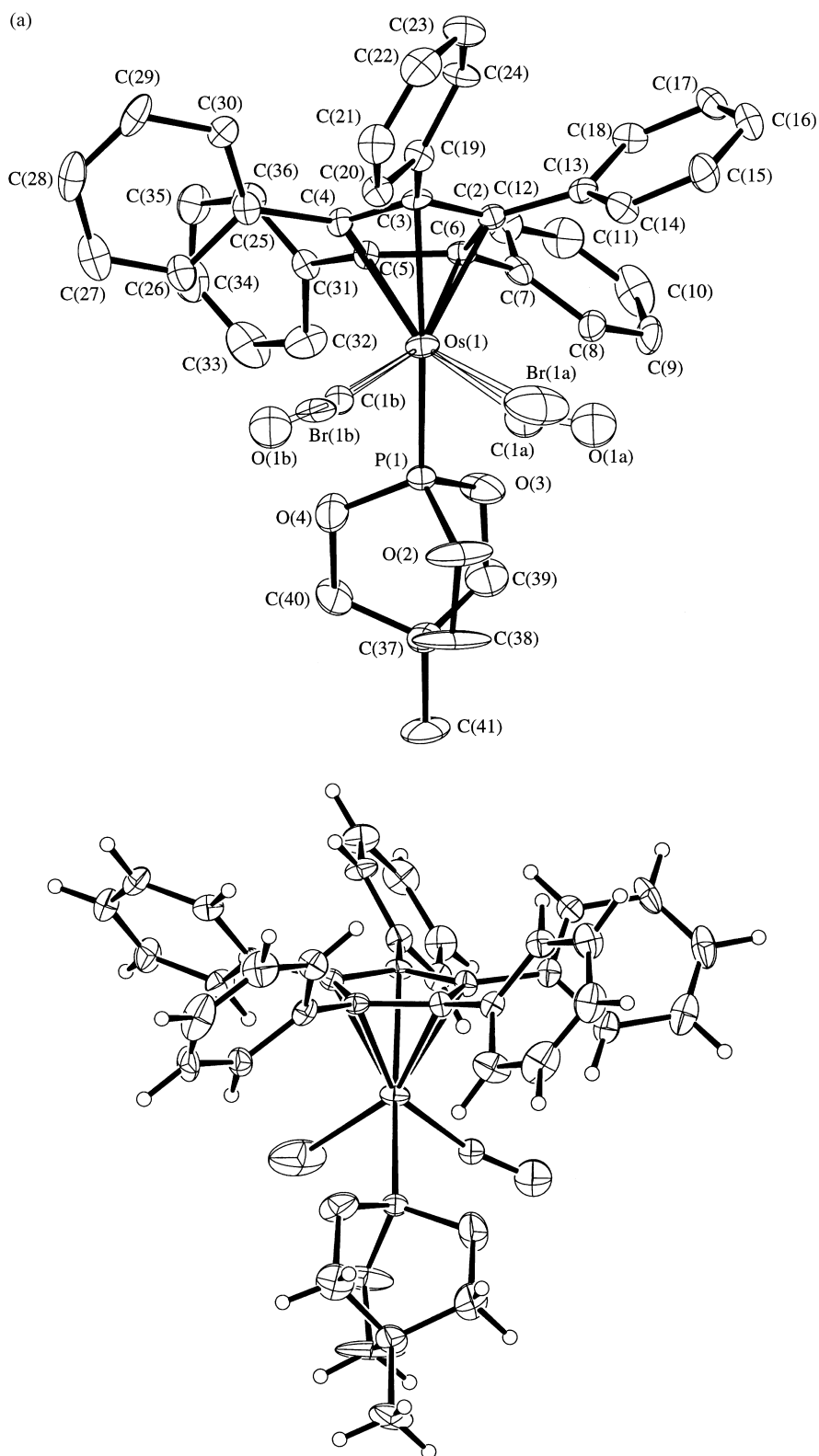
Atoms	<i>d</i>	Atoms	<i>d</i>
Os(1)—Br(1a)	2.422(5)	Os(1)—Br(1b)	2.504(2)
Os(1)—P(1)	2.239(3)	Os(1)—C(1a)	2.1292(5)
Os(1)—C(2)	2.27(1)	Os(1)—C(1b)	2.1213(5)
Os(1)—C(4)	2.28(1)	Os(1)—C(3)	2.28(1)
Os(1)—C(6)	2.255(9)	Os(1)—C(5)	2.288(9)
O(1a)—C(1a)	1.2496(1)	O(1b)—C(1b)	1.23
C(3)—C(4)	1.44(1)	C(2)—C(6)	1.43(1)
C(4)—C(5)	1.45(1)	C(5)—C(6)	1.45(1)
C(2)—C(3)	1.46(1)	C(2)—C(13)	1.47(1)
C(3)—C(19)	1.47(1)	C(4)—C(25)	1.49(1)
C(5)—C(31)	1.49(1)	C(6)—C(7)	1.46(1)
P(1)—O(2)	1.58(1)	P(1)—O(3)	1.588(9)
P(1)—O(4)	1.56(10)	O(4)—C(40)	1.44(2)
O(2)—C(38)	1.45(2)	O(3)—C(39)	1.48(2)
C(40)—C(37)	1.51(2)	C(38)—C(37)	1.44(2)
C(39)—C(37)	1.52(2)	C(37)—C(41)	1.55(2)

Table 5. Selected bond angles (°) for $[\text{Os}(\eta^5\text{-C}_5\text{Ph}_5)(\text{CO})\{\text{P}(\text{OCH}_2)_3\text{CCH}_3\}\text{Br}]$ (**6**)

Atoms	Angle	Atoms	Angle
C(1b)—Os(1)—Br(1a)	82.3(2)	P(1)—Os(1)—Br(1a)	85.3(1)
C(1a)—Os(1)—Br(1b)	88.57(7)	P(1)—Os(1)—Br(1b)	85.49(9)
P(1)—Os(1)—C(1b)	86.80(8)	P(1)—Os(1)—C(1a)	74.31(7)
C(3)—Os(1)—Br(1a)	106.2(3)	C(4)—Os(1)—Br(1a)	141.5(3)
C(5)—Os(1)—Br(1a)	155.3(3)	C(6)—Os(1)—Br(1a)	118.6(3)
C(2)—Os(1)—Br(1a)	95.9(3)	C(3)—Os(1)—Br(1b)	103.5(3)
C(4)—Os(1)—Br(1b)	93.6(3)	C(5)—Os(1)—Br(1b)	117.5(2)
C(6)—Os(1)—Br(1b)	153.9(3)	C(2)—Os(1)—Br(1b)	139.7(3)
O(1b)—C(1b)—Os(1)	157.68(1)	O(1a)—C(1a)—Os(1)	154.13(1)
C(4)—C(3)—C(2)	105.8(8)	C(4)—C(5)—C(6)	107.3(8)
C(3)—C(4)—C(5)	109.6(8)	C(5)—C(6)—C(2)	107.6(8)
C(3)—C(2)—C(6)	109.6(9)	C(4)—C(3)—C(19)	126.9(8)
C(5)—C(6)—C(7)	127.6(9)	C(5)—C(4)—C(25)	124.1(9)
C(2)—C(6)—C(7)	124.0(9)	C(3)—C(4)—C(25)	126.1(9)
C(6)—C(2)—C(13)	126.3(9)	C(6)—C(5)—C(31)	126.7(8)
C(3)—C(2)—C(13)	123.7(9)	C(4)—C(5)—C(31)	124.2(8)
C(2)—C(3)—C(19)	126.7(9)	C(6)—C(7)—C(12)	120(1)
C(2)—C(13)—C(18)	120.5(10)	C(6)—C(7)—C(8)	122(1)
C(2)—C(13)—C(14)	121.5(10)	C(5)—C(31)—C(32)	121(1)
C(4)—C(25)—C(30)	119.7(10)	C(5)—C(31)—C(36)	120(1)
C(4)—C(25)—C(26)	120(1)	C(3)—C(19)—C(24)	119(1)
C(3)—C(19)—C(20)	121(1)	P(1)—O(4)—C(40)	116.5(9)
Os(1)—P(1)—O(2)	114.7(4)	P(1)—O(2)—C(38)	113(1)
Os(1)—P(1)—O(3)	116.0(4)	P(1)—O(3)—C(39)	115.6(9)
Os(1)—P(1)—O(4)	118.0(4)	C(38)—C(37)—C(41)	111(1)
O(2)—C(38)—C(37)	113(1)	C(40)—C(37)—C(41)	110(1)
O(3)—C(39)—C(37)	109(1)	C(39)—C(37)—C(41)	110(1)
O(4)—C(40)—C(37)	110(1)		

from Merck. Elemental analyses (C, H, N, Br) were performed by the Australian Microanalytical Service. Melting points were recorded on a Reichert hot plat-

form in air and are uncorrected. Fourier transform infrared spectra were recorded on a Digilab FTS-40 spectrometer. ^1H and ^{13}C NMR spectra were recorded



on Bruker AC200F (^1H NMR 200.13 MHz, ^{13}C NMR 50.33 MHz) or Bruker AMX400 (^1H NMR 400.21 MHz) spectrometers. The spectra were referenced internally to TMS or to residual solvent resonances (CD_2Cl_2 , ^1H δ 5.30 ppm, ^{13}C δ 53.8 ppm). ^{31}P NMR spectra were recorded on a Bruker AMX400 spectrometer operating at 162.0 MHz and were referenced with respect to 85% H_3PO_4 as standard reference, with an external reference of neat trimethylphosphite (δ 140.85 ppm). Electron impact mass spectra were obtained using a Kratos MS 9 geometry mass spectrometer with a direct insertion probe, a 280°C source temperature, 70 eV ionisation voltage and 4 kV acceleration voltage.

Preparation of $[\text{Os}(\eta^5\text{-C}_5\text{Ph}_5)(\text{CO})_2\text{Br}]$ (**1**)

A mixture of $\text{Os}_3(\text{CO})_{12}$ (219 mg, 0.242 mmol) and $\text{C}_5\text{Ph}_5\text{Br}$ (402 mg, 0.765 mmol) in chlorobenzene (90 ml) was heated at reflux for 18 h. The solvent was removed *in vacuo*, then column chromatography was performed. Elution with *n*-hexane afforded a small amount of $\text{Os}_3(\text{CO})_{10}\text{Br}_2$. (Found: C 12.1, H < 0.1, Br 17.5. $\text{C}_{10}\text{Br}_2\text{Os}_3$ requires C 11.9, Br 15.8%). IR (cyclohexane): ν (CO) 2114 w, 2080 s, 2069 s, 2026 vs, 2012 s, 1993 w, 1989 w cm^{-1} [lit. [60]: ν (CO) 2113 w, 2080 s, 2069 s, 2026 s, 1991 sh, 1987 w cm^{-1}]. A small amount of $\text{C}_5\text{Ph}_5\text{H}$ (identified on the basis of IR (KBr) and m.p.) was similarly obtained by elution with 20% CH_2Cl_2 /80% *n*-hexane. Elution with 30% CH_2Cl_2 /70% *n*-hexane and evaporation to dryness (rotary evaporator) afforded a white solid which was crystallised from CH_2Cl_2 /*n*-hexane to give colourless crystals of $[\text{Os}(\eta^5\text{-C}_5\text{Ph}_5)(\text{CO})_2\text{H}]$ m.p. > 140°C (dec.). (Found: C 64.3, H 3.6. $\text{C}_{37}\text{H}_{26}\text{O}_2\text{Os}$ requires C 64.2, H 3.8%). ^1H NMR (CDCl_3 , 200.13 MHz): δ 7.10–7.03 (m, 25H, Ar-*H*), –13.19 (s, 1H, Os-*H*) ppm. Mass spectrum: EI (*m/e*) 694 ($[\text{M}]^+$, 100%). IR (KBr) ν_{max} 3110 vw, 3087 vw, 3061 w, 3040 vw, 3031 vw, 2077 w, 1998 vs, 1984 w, 1938 vs, 1907 w, 1734 vw, 1717 vw, 1700 vw, 1684 vw, 1653 w, 1602 w, 1577 w, 1559 w, 1540 w, 1505 w, 1457 vw, 1446 w, 1412 w, 1182 vw, 1157 vw, 1073 w, 1029 w, 922 vw, 803 w, 783 w, 758 w, 741 m, 709 (sh), 698 m, 607 w, 575 w, 562 w, 518 w, 509 w cm^{-1} . IR (CH_2Cl_2): ν (Os–H) 2087 vs, ν (CO) 2008 vs, 1945 vs, cm^{-1} . Further elution with 70% CH_2Cl_2 /30% *n*-hexane afforded a yellow solution which after evaporation and crystallisation of the solid from CH_2Cl_2 /*n*-hexane gave yellow crystals of $[\text{Os}(\eta^5\text{-C}_5\text{Ph}_5)(\text{CO})_2\text{Br}]$ (**1**) (365 mg, 65%) m.p. > 205°C (dec.). (Found: C 57.2, H 3.3, Br 10.5. $\text{C}_{37}\text{H}_{25}\text{BrO}_2\text{Os}$ requires C 57.6, H 3.3, Br 10.4%). ^1H NMR (CD_2Cl_2 , 200.13 MHz): δ 7.25–7.00 (m, 25H, Ar-*H*) ppm. ^{13}C NMR (CD_2Cl_2 , 50.33 MHz): δ 178.0 (CO), 132.9 (quaternary Ar-*C*), 129.7, 128.9, 128.3 (Ar-*CH*), 104.9 (Cp-*C*) ppm. Mass spectrum: EI (*m/e*) 1081 ($[\text{Os}(\eta^5\text{-C}_5\text{Ph}_5)_2\text{H}]^+$, 3%), 772 ($[\text{M}]^+$, 1%), 744 ($[\text{M}]^+ - \text{CO}]^+$, 1%), 716 ($[\text{M}]^+ - 2\text{CO}]^+$, 100%), 446 (HC_5Ph_5 , 12%), 445

(C_5Ph_5 , 10%). IR (KBr) ν_{max} : 3111 vw, 3090 w, 3059 w, 3046 (sh), 2028 vs, 1973 vs, 1602 w, 1579 vw, 1502 w, 1446 w, 1419 w, 1398 vw, 1379 vw, 1184 vw, 1158 vw, 1076 w, 1030 w, 1002 vw, 921 vw, 841 vw, 802 w, 782 w, 767 vw, 738 m, 707 m, 697 m, 676 vw, 593 w, 581 w, 571 w, 562 w, 544 w, 518 vw, 501 vw, 493 vw, 465 w cm^{-1} . IR (CH_2Cl_2): ν (CO) 2033 vs, 1978 vs cm^{-1} .

Preparation of $[\text{Os}\{\eta^5\text{-C}_5\text{Ph}_4(p\text{-}^t\text{BuC}_6\text{H}_4)\}(\text{CO})_2\text{Br}]$ (**2**)

A similar reaction of $\text{Os}_3(\text{CO})_{12}$ (111 mg, 0.122 mmol) and $\text{C}_5\text{Ph}_4(p\text{-}^t\text{BuC}_6\text{H}_4)\text{Br}$ (223 mg, 0.383 mmol) in chlorobenzene (50 ml) afforded after column chromatography, elution with 50% CH_2Cl_2 /50% *n*-hexane and crystallisation from CH_2Cl_2 /*n*-hexane, a pale yellow powder identified as $[\text{Os}\{\eta^5\text{-C}_5\text{Ph}_4(p\text{-}^t\text{BuC}_6\text{H}_4)\}(\text{CO})_2\text{Br}]$ (**2**) (110 mg, 36%) m.p. > 210°C (dec.). (Found: C 59.2, H 4.2, Br 9.9. $\text{C}_{41}\text{H}_{33}\text{BrO}_2\text{Os}$ requires C 59.5, H 4.0, Br 9.7%). ^1H NMR (CD_2Cl_2 , 200.13 MHz): δ 7.25–6.90 (m, 24H, Ar-*H*), 1.24 (s, 9H, ^tBu) ppm. Mass spectrum: EI (*m/e*) 1193 ($[\text{Os}(\text{C}_5\text{Ph}_4(p\text{-}^t\text{BuC}_6\text{H}_4))_2\text{H}]^+$, 37%), 772 ($[\text{M}]^+ - 2\text{CO}]^+$, 100%). IR (KBr) ν_{max} 3110 vw, 3091 vw, 3058 w, 3042 (sh), 2965 w, 2936 vw, 2905 vw, 2870 vw, 2026 vs, 1971 vs, 1684 vw, 1653 vw, 1602 vw, 1578 vw, 1559 vw, 1540 vw, 1520 vw, 1506 vw, 1502 vw, 1473 vw, 1457 vw, 1441 w, 1420 vw, 1396 vw, 1364 vw, 1269 vw, 1200 vw, 1185 vw, 1120 vw, 1108 vw, 1076 vw, 1027 vw, 1018 vw, 919 vw, 842 w, 797 vw, 756 w, 749 w, 737 w, 705 m, 699 m, 596 w, 581 w, 569 w, 558 w, 547 w, 501 vw, 493 vw, 464 w cm^{-1} . IR (CH_2Cl_2): ν (CO) 2033 vs, 1977 vs cm^{-1} .

Preparation of $[\text{Os}\{\eta^5\text{-C}_5(p\text{-MeC}_6\text{H}_4)_5\}(\text{CO})_2\text{Br}]$ (**3**)

Similarly, reaction of a mixture of $\text{Os}_3(\text{CO})_{12}$ (235 mg, 0.259 mmol) and $\text{C}_5(p\text{-MeC}_6\text{H}_4)_5\text{Br}$ (460 mg, 0.772 mmol) in chlorobenzene (60 ml) afforded after column chromatography, elution with 70% CH_2Cl_2 /30% *n*-hexane and crystallisation from CH_2Cl_2 /*n*-hexane, a pale yellow powder identified as $[\text{Os}\{\eta^5\text{-C}_5(p\text{-MeC}_6\text{H}_4)_5\}(\text{CO})_2\text{Br}]$ (**3**) (60 mg, 9%) m.p. > 210°C (dec.) (Found: C 60.1, H 4.1. $\text{C}_{42}\text{H}_{35}\text{BrO}_2\text{Os}$ requires C 59.9, H 4.2%). ^1H NMR (CD_2Cl_2 , 200.13 MHz): δ 6.90 (m, 20H, Ar-*H*), 2.27 (s, 15H, Me) ppm. Mass spectrum: EI (*m/e*) 1221 ($[\text{Os}(\text{C}_5(p\text{-MeC}_6\text{H}_4)_5)_2\text{H}]^+$, 100%), 786 ($[\text{M}]^+ - 2\text{CO}]^+$, 97%), 515 ($\text{C}_5(p\text{-MeC}_6\text{H}_4)_5$, 88%). IR (KBr) ν_{max} 3133 vw, 3089 (sh), 3057 w, 3034 w, 3023 w, 2969 (sh), 2952 (sh), 2923 w, 2864 w, 2732 vw, 2026 vs, 2022 (sh), 1973 vs, 1970 (sh), 1942 vw, 1613 vw, 1520 w, 1456 vw, 1450 vw, 1437 vw, 1406 vw, 1398 vw, 1379 vw, 1188 w, 1119 vw, 1039 vw, 1021 vw, 844 vw, 833 w, 820 w, 805 w, 749 w, 728 w, 701 w, 595 w, 578 w, 556 w, 532 w, 526 vw, 495 vw, 468 vw, 443 w cm^{-1} . IR (CH_2Cl_2): ν (CO) 2030 vs, 1974 vs cm^{-1} .

Preparation of $[\text{Os}(\eta^5\text{-C}_5\text{Ph}_5)(\text{CO})(\text{PMe}_2\text{Ph})\text{Br}]$ (4)

A portion of Me_3NO (18 mg, 0.24 mmol) was added to a mixture of $[\text{Os}(\eta^5\text{-C}_5\text{Ph}_5)(\text{CO})_2\text{Br}]$ (141 mg, 0.183 mmol) and PMe_2Ph (0.030 ml, 0.21 mmol) in thf (25 ml) giving a colour change from yellow to orange-yellow. After stirring at room temperature for 1 h spot TLC ($\text{CH}_2\text{Cl}_2/n\text{-hexane}$ 1:1) and solution IR (CH_2Cl_2) showed that no starting material remained. The reaction mixture was evaporated *in vacuo* and then column chromatography was performed. Elution with 50% $\text{CH}_2\text{Cl}_2/50\%$ *n*-hexane afforded an orange solution which after evaporation and crystallisation of the solid from $\text{CH}_2\text{Cl}_2/n\text{-hexane}$ afforded orange crystals of $[\text{Os}(\eta^5\text{-C}_5\text{Ph}_5)(\text{CO})(\text{PMe}_2\text{Ph})\text{Br}]$ (4) (135 mg, 84%) m.p. > 250°C (dec.). (Found: C 59.7, H 4.1, Br 8.7. $\text{C}_{44}\text{H}_{36}\text{BrO}_5\text{OsP}$ requires C 59.9, H 4.1, Br 9.1%). ^1H NMR (CD_2Cl_2 , 200.13 MHz): δ 7.71–7.61, 7.31–7.26 (2 $\times$ m, 5H, P-Ar-*H*), 7.15–6.85 (m, 25H, Ar-*H*), 2.04 (d, J (PH) = 10 Hz, 3H, Me), 1.97 (d, J (PH) = 10 Hz, 3H, Me) ppm. ^{31}P $\{^1\text{H}\}$ NMR (CD_2Cl_2 , 162.0 MHz): δ 100.3 ppm. Mass spectrum: EI (m/e) 882 ($[\text{M}]^+$, 95%), 854 ($[\text{M}-\text{CO}]^+$, 62%), 716 ($[\text{M}-\text{CO}-\text{PMe}_2\text{Ph}]^+$, 100%), 138 (PMe_2Ph , 89%). IR (KBr) ν_{max} 3154 vw, 3106 vw, 3085 vw, 3058 (sh), 3053 w, 3039 vw, 3031 (sh), 3006 vw, 2988 vw, 2915 vw, 1928 s, 1919 vs, 1600 w, 1580 vw, 1502 w, 1481 vw, 1445 w, 1436 w, 1415 vw, 1378 vw, 1317 vw, 1298 vw, 1284 vw, 1265 vw, 1181 vw, 1154 vw, 1099 vw, 1076 w, 1028 w, 1004 vw, 944 w, 914 w, 842 w, 799 w, 782 w, 747 (sh), 740 m, 707 m, 701 s, 682 w, 620 vw, 598 w, 592 w, 565 w, 561 w, 550 w, 533 vw, 514 w, 493 w, 434 w cm^{-1} . IR (CH_2Cl_2): ν (CO) 1928 vs cm^{-1} .

Preparation of $[\text{Os}(\eta^5\text{-C}_5\text{Ph}_5)(\text{CO})\{\text{P}(\text{OEt})_3\}\text{Br}]$ (5)

A similar reaction and workup of $[\text{Os}(\eta^5\text{-C}_5\text{Ph}_5)(\text{CO})_2\text{Br}]$ (112 mg, 0.145 mmol), $\text{P}(\text{OEt})_3$ (0.030 ml, 0.173 mmol) and Me_3NO (15 mg, 0.20 mmol) in thf (22 ml) afforded yellow crystals of $[\text{Os}(\eta^5\text{-C}_5\text{Ph}_5)(\text{CO})\{\text{P}(\text{OEt})_3\}\text{Br}]$ (5) (97 mg, 74%) m.p. > 230°C (dec.). (Found: C 55.9, H 4.6, Br 9.2. $\text{C}_{42}\text{H}_{40}\text{BrO}_4\text{OsP}$ requires C 55.4, H 4.4, Br 8.8%). ^1H NMR (CD_2Cl_2 , 400.21 MHz): δ 7.14–7.00 (m, 25H, Ar-*H*), 4.23–3.98 (m (32 peaks), 6H, CH_2), 1.07 (t, $2J$ (HH) = 7 Hz, 9H, CH_3) ppm. ^{31}P $\{^1\text{H}\}$ NMR (CD_2Cl_2 , 162.0 MHz): δ 214.0 ppm. Mass spectrum: EI (m/e) 910 ($[\text{M}]^+$, 11%), 882 ($[\text{M}-\text{CO}]^+$, 6%), 716 ($[\text{M}-\text{CO}-\text{P}(\text{OEt})_3]^+$, 100%). IR (KBr) ν_{max} 3110 vw, 3087 vw, 3057 w, 3041 vw, 3033 vw, 2977 w, 2928 vw, 2905 vw, 2867 vw, 1947 (sh), 1936 vs, 1890 vw, 1602 w, 1503 w, 1445 w, 1392 w, 1319 vw, 1286 vw, 1183 vw, 1159 w, 1093 w, 1061 w, 1028 s, 955 m, 936 w, 849 vw, 801 w, 783 w, 765 w, 744 m, 711 m, 703 s, 678 vw, 668 vw, 622 vw, 591 w, 565 w, 559 w, 549 w, 537 w, 517 w, 482 vw cm^{-1} . IR (CH_2Cl_2): ν (CO) 1940 vs cm^{-1} .

Preparation of $[\text{Os}(\eta^5\text{-C}_5\text{Ph}_5)(\text{CO})\{\text{P}(\text{OCH}_2)_3\text{CCH}_3\}\text{Br}]$ (6)

A mixture of $[\text{Os}(\eta^5\text{-C}_5\text{Ph}_5)(\text{CO})_2\text{Br}]$ (228 mg, 0.295 mmol), $\text{P}(\text{OCH}_2)_3\text{CCH}_3$ (125 mg, 0.844 mmol) and Me_3NO (37 mg, 0.49 mmol) in thf (30 ml) was stirred at room temperature for 24 h after which time column chromatography was performed. Elution with 50% $\text{CH}_2\text{Cl}_2/50\%$ *n*-hexane, evaporation of the solvent and crystallisation of the solid from $\text{CH}_2\text{Cl}_2/n\text{-hexane}$ afforded $[\text{Os}(\eta^5\text{-C}_5\text{Ph}_5)(\text{CO})_2\text{Br}]$ (1) (80 mg, 35%). Subsequent elution with 100% CH_2Cl_2 and crystallisation of the solid from $\text{CH}_2\text{Cl}_2/n\text{-hexane}$ afforded bright yellow crystals of $[\text{Os}(\eta^5\text{-C}_5\text{Ph}_5)(\text{CO})\{\text{P}(\text{OCH}_2)_3\text{CCH}_3\}\text{Br}]$ (6) (128 mg, 49%) m.p. > 270°C. (Found: C 55.1, H 3.7, Br 9.4. $\text{C}_{41}\text{H}_{34}\text{BrO}_5\text{OsP}$ requires C 55.2, H 3.8, Br 9.0%). ^1H NMR (CD_2Cl_2 , 200.13 MHz): δ 7.19–7.03 (m, 25H, Ar-*H*), 4.23 (d, J (PH) = 5 Hz, 6H, CH_2), 0.76 (s, 3H, CH_3) ppm. ^{31}P $\{^1\text{H}\}$ NMR (CD_2Cl_2 , 162.0 MHz): δ 216.7 ppm. Mass spectrum: EI (m/e) 892 ($[\text{M}]^+$, 26%), 864 ($[\text{M}-\text{CO}]^+$, 11%), 716 ($[\text{M}-\text{CO}-\text{P}(\text{OCH}_2)_3\text{CCH}_3]^+$, 100%). IR (KBr) ν_{max} 3108 vw, 3085 vw, 3055 w, 3037 vw, 3031 (sh), 2966 vw, 2960 (sh), 2943 vw, 2884 w, 1960 vs, 1952 (sh), 1912 vw, 1601 w, 1579 vw, 1501 w, 1484 vw, 1463 w, 1445 w, 1415 vw, 1395 w, 1184 w, 1174 w, 1155 vw, 1075 w, 1030 s, 988 vw, 959 w, 928 w, 860 w, 802 w, 795 m, 788 m, 742 w, 711 w, 700 m, 658 m, 621 vw, 587 w, 561 w, 547 w, 524 w, 516 w, 498 vw, 417 w cm^{-1} . IR (CH_2Cl_2): ν (CO) 1963 vs cm^{-1} .

Preparation of $[\text{Os}(\eta^5\text{-C}_5\text{Ph}_5)(\text{CO})(\text{CNBu}')\text{Br}]$ (7)

To a mixture of $[\text{Os}(\eta^5\text{-C}_5\text{Ph}_5)(\text{CO})_2\text{Br}]$ (128 mg, 0.166 mmol) and $^t\text{BuNC}$ (0.030 ml, 0.27 mmol) in thf (25 ml) was added Me_3NO (16 mg, 0.21 mmol), giving a colour change from pale yellow to orange-yellow. After stirring at room temperature for 1 h, the solution IR ν (CO) (CH_2Cl_2) showed that no starting material remained. The reaction mixture was evaporated to dryness (*in vacuo*) and column chromatography was performed. Elution with 70% $\text{CH}_2\text{Cl}_2/30\%$ *n*-hexane afforded a yellow-orange solution which after evaporation and crystallisation of the solid from $\text{CH}_2\text{Cl}_2/n\text{-hexane}$ gave yellow crystals of $[\text{Os}(\eta^5\text{-C}_5\text{Ph}_5)(\text{CO})(\text{CNBu}')\text{Br}]$ (7) (124 mg, 90%) m.p. > 240°C (dec.). (Found: C 59.9, H 4.1, Br 9.7, N 1.8. $\text{C}_{41}\text{H}_{34}\text{BrNOOs}$ requires C 59.6, H 4.1, Br 9.7, N 1.7%). ^1H NMR (CD_2Cl_2 , 200.13 MHz): δ 7.20–7.05 (m, 25H, Ar-*H*), 1.40 (s, 9H, ^tBu) ppm. Mass spectrum: EI (m/e) 827 ($[\text{M}]^+$, 26%), 799 ($[\text{M}-\text{CO}]^+$, 6%), 771 ($[\text{M}-\text{C}(\text{CH}_3)_2\text{CH}_2]^+$, 10%), 743 ($[\text{M}-\text{CNBu}'-\text{H}]^+$, 67%), 716 ($[\text{M}-\text{CO}-\text{CNBu}']^+$, 100%). IR (KBr) ν_{max} 3110 vw, 3087 vw, 3084 vw, 3056 w, 3037 vw, 3033 vw, 2984 w, 2937 vw, 2147 m, 2072 (sh), 2024 vw, 1954 vs, 1905 vw, 1602 w, 1504 w, 1473 w, 1457 w, 1445 w, 1419 w, 1398 w, 1370 w, 1232 w, 1206 w, 1183 w, 1074 w, 1029 w, 919

w, 802 w, 783 w, 739 m, 698 vs, 587 w, 567 s, 555 w, 541 vw, 517 vw, 464 w cm⁻¹. IR (CH₂Cl₂): ν (CN) 2156 m, ν (CO) 1960 vs cm⁻¹.

Structure determinations

(a) [Os(η^5 -C₅Ph₅)(CO)₂Br] (**1**). Primitive orthorhombic cell constants were obtained from a least-square refinement against the setting angles of 25 reflections in the range $16.18 < 2\theta < 24.08^\circ$ measured and refined on an Enraf-Nonius CAD-4 four-circle diffractometer, employing graphite monochromated Mo-K α radiation. The intensities of three representative reflections measured every hour did not change significantly during the course of the data collection. An analytical absorption correction was applied to the data and the data were also corrected for Lorentz and polarisation effects. All calculations were performed using the teXsan [61] crystallographic software package. The structure was solved in the space group PBCA (#61) by direct methods [62] and expanded using Fourier techniques [63]. Non-hydrogen atom sites were modelled anisotropically and hydrogen parameters were included in the full matrix least squares refinement with calculated positions and group temperature factors. Neutral atom scattering factors were taken from Cromer and Waber [64]. Anomalous dispersion effects were included in the structure factor calculation [65], and the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley [66]. The values for the mass attenuation coefficients are those of Creagh and Hubbel [67].

Crystal data for [Os(η^5 -C₅Ph₅)(CO)₂Br] (**1**)

C₃₇H₂₅BrO₂Os, *M* = 771.71, orthorhombic, space group, PBCA (#61), *a* = 18.028(3), *b* = 14.921(2), *c* = 21.718(3) Å, *U* = 5842(1) Å³, *D*_c(*Z* = 8) = 1.76 g cm⁻³, *F*(000) = 2992, μ (Mo-K α) = 57.67 cm⁻¹. Specimen: yellow blade, 0.525 × 0.125 × 0.012 mm. *N* = 4162, *N*_{unique} = 3976, *N*_o = 2249, range of *hkl* 0 → 15, 0 → 18, 0 → 22, *R*_{merge} = 0.166, *R* = 0.040, *R*_w = 0.043, residual extrema -1.15 and 1.01 eÅ⁻³, *T*_{min,max} = 0.27, 0.86.

(b) [Os(η^5 -C₅Ph₅)(CO){P(OCH₂)₃CCH₃}Br] (**6**). Lattice parameters at 21°C were obtained from a least squares refinement to the setting angles of 25 reflections in the range $19.77 < 2\theta < 113.36^\circ$, measured and refined on a Rigaku AFC7R diffractometer, employing graphite monochromated CuK α radiation, generated from a direct drive rotating anode. Intensity data were collected with $\omega/2\theta$ scans to a maximum 2θ value of 120.1° , with a scan width of $(1.1 + 0.35 \tan \theta)^\circ$. An empirical absorption correction based on azimuthal scans of three reflections was applied to the data. The data were corrected for Lorentz and polarisation effects and a small correction for secondary extinction applied (coefficient = 1.11

× 10⁻⁶). All calculations were performed using the teXsan structure determination software package [61]. The structure was solved by direct methods [68] and extended with Fourier maps [63]. The refinement weighting scheme was based on counting statistics. Generally the non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were included in the full matrix least squares refinement at calculated positions with group temperature factors. The carbonyl and bromide ligands were found to be site disordered. Although the carbonyl groups could be located they could not be successfully refined; possibly because of orientation disorder or a consequence of the site disorder. Neutral atom scattering factors were taken from Cromer and Waber [64]. Anomalous dispersion effects were included in the structure factor calculation [65], and the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley [66]. The values for the mass attenuation coefficients are those of Creagh and Hubbel [67].

Crystal data for [Os(η^5 -C₅Ph₅)(CO){P(OCH₂)₃CCH₃}Br] (**6**)

C₄₁H₃₄BrO₄OsP, *M* = 891.80, monoclinic, space group, P2₁/n (#14), *a* = 12.230(3), *b* = 16.135(9), *c* = 18.331(3) Å, β = 101.63(2), *U* = 3543(1) Å³, *D*_c(*Z* = 4) = 1.672 g cm⁻³, *F*(000) = 1752, μ (Cu-K α) = 88.89 cm⁻¹. Specimen: yellow prism, 0.260 × 0.250 × 0.140 mm. *N* = 5787, *N*_{unique} = 5496, *N*_o = 4242, range of *hkl* 0 → 13, 0 → 18, -20 → 20, *R*_{merge} = 0.0327, *R* = 0.066, *R*_w = 0.073, residual extrema -2.75 and 2.31 eÅ⁻³, *T*_{min,max} = 0.48, 0.98.

CONCLUSION

The preparation and crystal structure of [Os(η^5 -C₅Ph₅)(CO)₂Br], the first osmium complex of the pentaphenylcyclopentadienyl ligand, has been described. This completes the preparation and characterisation of the iron-triad [M(η^5 -C₅Ph₅)(CO)₂Br] series of this ligand. The crystal structure of the osmium complex is isostructural with those of its iron and ruthenium analogues. The osmium complex is stable in air and readily undergoes monocarbonyl substitution with a variety of ligands. The crystal structure of one such resultant complex, [Os(η^5 -C₅Ph₅)(CO){P(OCH₂)₃CCH₃}Br], is also reported.

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