Mononuclear η^6-p-Cymeneosmium(II) Complexes and their Reactions with Al_2Me_6 and other Methylating Reagents

Javier A. Cabeza and Peter M. Maitlis *
Department of Chemistry, University of Sheffield, Sheffield S3 7HF

An improved-yield synthesis of the η^6-p-cymeneosmium(II) chloride complex $[(p\text{-}MeC_6H_4CHMe_2)_2Os_2Cl_4]$ (**1**) has allowed the development of the chemistry of the mononuclear complexes, $[(p\text{-}MeC_6H_4CHMe_2)OsLCl_2]$ (**2**) [L = CO, $CNCMe_3$, Me_2SO, PMe_3, PPh_3, or $P(OPh)_3$]. These gave $[(p\text{-}MeC_6H_4CHMe_2)OsL(Me)Cl]$ (**3**) (L = CO, $CNCMe_3$, Me_2SO, or PMe_3) with Al_2Me_6. Reaction of $[(p\text{-}MeC_6H_4CHMe_2)Os(Me_2SO)(Me)Cl]$ with L′ [PPh_3 or $P(OPh)_3$] gave the complex $[(p\text{-}MeC_6H_4CHMe_2)OsL'(Me)Cl]$. Al_2Me_6 reacted with $[(p\text{-}MeC_6H_4CHMe_2)OsL'Cl_2]$ to give chiefly the *ortho*-metallated complexes $[(p\text{-}MeC_6H_4CHMe_2)Os\{PPh_2(o\text{-}C_6H_4)\}X]$ (**5**) (X = Cl), (**6**) (X = Me), and $[(p\text{-}MeC_6H_4CHMe_2)Os\{P(OPh)(OC_6H_4\text{-}o)_2\}]$ (**8**); however, the triphenylphosphine complex also gave the mono- and the di-methyl complexes $[(p\text{-}MeC_6H_4CHMe_2)Os(PPh_3)(Me)X]$ (X = Cl or Me). The complexes have been characterised by their i.r., ^1H, ^{13}C, and ^{31}P n.m.r. spectra and their e.i. mass spectra. The p-cymene ring remains η^6-bonded throughout these reactions and appears quite difficult to displace.

The chemistry of mononuclear η^6-arene–ruthenium(II) complexes has been widely studied in the last few years, but much less is known about their osmium analogues.[1–3] This is partly because until recently only the benzene- and p-cymene-osmium(II) complexes were accessible.[4,5] These arenes are most labile in their ruthenium complexes,[6] where they are readily displaced from the complexes by nucleophiles that attack at the metal[6–9] or are themselves attacked by nucleophilic reagents that attack at carbon.[9–11] The previously reported yields of $[(p\text{-}MeC_6H_4CHMe_2)_2Os_2Cl_4]$ (**1**) and $[(C_6H_6)_2Os_2Cl_4]$ are also rather low.[4,5]

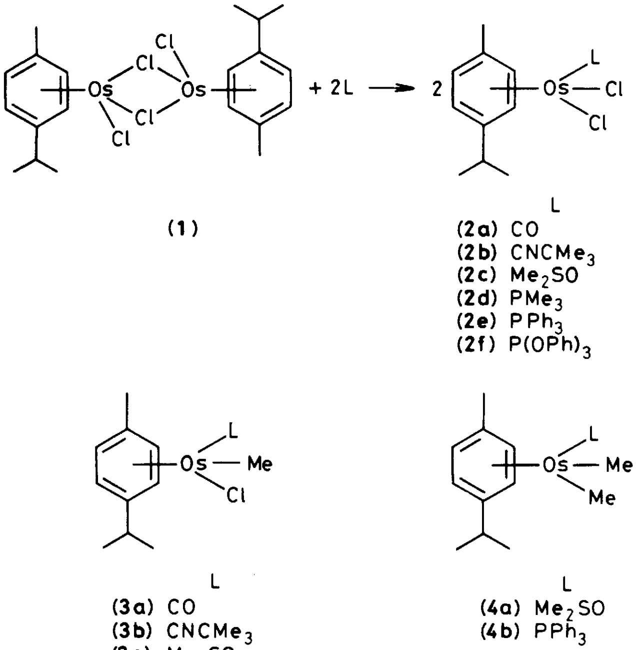
The only η^6-arene–osmium–methyl complex reported up to now is $[(C_6H_6)Os(PMe_3)_2Me]I$, prepared by oxidative addition of methyl iodide to the osmium(0) complex $[(C_6H_6)Os(PMe_3)_2]$.[12] All the other methylosmium complexes are carbonyl derivatives.[13]

In pursuance of our work on methyl derivatives of the platinum group metals,[14] we here report the syntheses and properties of some mononuclear osmium(II) complexes with p-cymene as η^6-arene ligand and their reactivity towards methylating reagents. We also describe a small modification of the published[5] synthesis of (**1**) which gives consistently high yields. Most of the new complexes are air stable and the p-cymene to osmium bond is reasonably inert. We have not observed either displacement of p-cymene or nucleophilic attack on the arene ring.

Results and Discussion

Reaction of the isoelectronic and isostructural complexes $[(C_5Me_5)_2M_2Cl_4]$ (M = Rh or Ir) with Al_2Me_6 gave a remarkable series of stable methyl, μ-methylene, and μ-methyne complexes in which the metals are often in higher formal oxidation states than the starting materials.[14] However, although reaction of the dimeric p-cymeneosmium chloride complex (**1**) occurred readily with Al_2Me_6 in toluene at −78 °C (as shown by the change in the colour of the solution from yellow to red and brown), no complexes could be isolated.

We therefore prepared the yellow or orange-yellow crystalline mononuclear complexes (**2a**)—(**2f**) (Scheme and Table 1) by reacting (**1**) with an excess of the appropriate ligand in dichloromethane. The i.r. spectra show two strong bands in the region 270—310 cm^{-1}, assigned to ν(Os–Cl) (Table 1); those of complexes (**2a**) and (**2b**) also show the expected bands due to ν(CO) and ν(NC) respectively. The ^1H n.m.r. spectra (Table 2) of all the complexes (**2a**)—(**2f**), as expected, showed a double doublet for the aromatic protons of the p-cymene ligand; no coupling to phosphorus could be detected in (**2d**)—(**2f**). The ^{13}C n.m.r. spectra (Table 3) were also in agreement with the structures; complexes (**2d**)—(**2f**) showed small couplings of the p-cymene ring carbons to phosphorus (J 1—6 Hz).



Scheme.

The complexes (**2a**)—(**2f**) behaved well in the mass spectrometer and good electron impact (e.i.) spectra were obtained.

Table 1. Yields, analytical, i.r., and mass spectroscopic data

			Microanalysis[a] (%)				
	Compound	Yield (%)	C	H	Other	I.r.[b] (v/cm^{-1})	Mass spectrum[c] (m/z)
(2a)	$[(p\text{-MeC}_6\text{H}_4\text{CHMe}_2)\text{Os(CO)Cl}_2]$	95	31.2 (31.2)	3.3 (3.4)		1 989s, 1 953m[d] 318s, 273s[e]	424
(2b)	$[(p\text{-MeC}_6\text{H}_4\text{CHMe}_2)\text{Os(CNCMe}_3)\text{Cl}_2]$	83	37.7 (37.7)	4.9 (4.9)	N, 3.1 (3.0)	2 184s[f] 303s, 277s[e]	479
(2c)	$[(p\text{-MeC}_6\text{H}_4\text{CHMe}_2)\text{Os(Me}_2\text{SO)Cl}_2]$	89	30.7 (30.5)	4.2 (4.3)	S, 7.1 (6.8)	1 120s[g] 307s, 283s[e]	396[h]
(2d)	$[(p\text{-MeC}_6\text{H}_4\text{CHMe}_2)\text{Os(PMe}_3)\text{Cl}_2]$	73	33.0 (33.1)	4.4 (4.9)		294s, 275s[e]	472
(2e)	$[(p\text{-MeC}_6\text{H}_4\text{CHMe}_2)\text{Os(PPh}_3)\text{Cl}_2]$	92	51.3 (51.2)	4.7 (4.5)		307s, 267s[e]	658
(2f)	$[(p\text{-MeC}_6\text{H}_4\text{CHMe}_2)\text{Os}\{\text{P(OPh)}_3\}\text{Cl}_2]$	98	47.5 (47.7)	4.3 (4.2)		310s, 285s[e]	706
(3a)	$[(p\text{-MeC}_6\text{H}_4\text{CHMe}_2)\text{Os(CO)(Me)Cl}]$	53	35.5 (35.8)	4.0 (4.3)		2 820[i] 1 940s, 1 896m[d] 300s[e]	404
(3b)	$[(p\text{-MeC}_6\text{H}_4\text{CHMe}_2)\text{Os(CNCMe}_3)\text{(Me)Cl}]$	43	42.1 (42.0)	5.9 (5.7)	N, 3.4 (3.1)	2 810m[i] 2 120s, 2 070(sh)[f] 284s[e]	459
(3c)	$[(p\text{-MeC}_6\text{H}_4\text{CHMe}_2)\text{Os(Me}_2\text{SO)(Me)Cl}]$	91	35.0 (34.5)	5.3 (5.1)	S, 7.1 (7.1)	2 810m[i] 1 088s[g] 286s[e]	376[h]
(3d)	$[(p\text{-MeC}_6\text{H}_4\text{CHMe}_2)\text{Os(PMe}_3)\text{(Me)Cl}]$	72	37.1 (37.3)	5.8 (5.8)		2 805m[i] 277s[e]	452
(3e)	$[(p\text{-MeC}_6\text{H}_4\text{CHMe}_2)\text{Os(PPh}_3)\text{(Me)Cl}]$	78	54.6 (54.7)	5.1 (5.1)		2 800m[i] 290s[e]	622[j]
(3f)	$[(p\text{-MeC}_6\text{H}_4\text{CHMe}_2)\text{Os}\{\text{P(OPh)}_3\}\text{(Me)Cl}]$	94	50.7 (50.9)	4.7 (4.7)		2 814m[i] 294s[e]	671[k]
(4b)	$[(p\text{-MeC}_6\text{H}_4\text{CHMe}_2)\text{Os(PPh}_3)\text{Me}_2]$	57	58.5 (58.4)	5.9 (5.7)		2 804m[i]	618
(5)	$[(p\text{-MeC}_6\text{H}_4\text{CHMe}_2)\text{Os}\{\text{PPh}_2(o\text{-C}_6\text{H}_4)\}\text{Cl}]$	37	54.6 (54.2)	4.7 (4.6)		286s[e]	622
(6)	$[(p\text{-MeC}_6\text{H}_4\text{CHMe}_2)\text{Os}\{\text{PPh}_2(o\text{-C}_6\text{H}_4)\}\text{Me}]$	41	57.9 (58.0)	5.5 (5.2)		2 882m[i]	601
(7)	$[(p\text{-MeC}_6\text{H}_4\text{CHMe}_2)\text{Os(PPh}_3)\text{(H)Cl}]$	72	54.2 (54.0)	5.3 (4.9)		2 045br[l] 295s[e]	624
(8)	$[(p\text{-MeC}_6\text{H}_4\text{CHMe}_2)\text{Os}\{\text{P(OPh)(OC}_6\text{H}_4\text{-}o)_2\}]$	19	52.4 (53.2)	4.1 (4.3)			634
(9)	$[(p\text{-MeC}_6\text{H}_4\text{CHMe}_2)\text{Os(PMe}_3)\text{I}_2]$	36	24.2 (23.9)	3.3 (3.6)			

[a] Calculated values in parentheses. [b] Nujol mulls. [c] Strongest peak in the molecular ion group. [d] v(CO). [e] v(OsCl). [f] v(CN). [g] v(SO). [h] Observed *m/z* $(M - \text{Me}_2\text{SO})$. [i] v(CH). [j] Observed *m/z* $(M - \text{CH}_4)$. [k] Observed *m/z* $(M - \text{CH}_3)$. [l] v(OsH).

These showed a group of molecular ion peaks with intensities in agreement with those calculated for the presence of seven different osmium and two different chlorine isotopes. The complexes had a common cracking pattern involving loss of L and of one or both chlorines; this observation underlines the considerable stability and inertness of these osmium complexes.

The i.r. spectrum of the dimethyl sulphoxide complex **(2c)** shows a strong band at 1 120 cm^{-1} which we assign to v(SO). According to the customary assignment (bands below 1 100 cm^{-1} indicate binding through sulphur while bands above 1 100 cm^{-1} are taken to indicate binding through oxygen[15]), this complex should have the dimethyl sulphoxide bonded through oxygen to the osmium(II). However, preliminary results from a single-crystal *X*-ray determination[16] show very clearly that the dimethyl sulphoxide is not bonded through the oxygen but through the sulphur [Os–S 2.31(1), Os–O 3.23(1) Å], as would have been anticipated. The methyl complex **(3c)** showed v(SO) at 1 088 cm^{-1}, quite consistent with sulphur-bonded Me_2SO. Clearly the position of the i.r. band is influenced by factors other than the precise mode of liganding of the dimethyl sulphoxide.

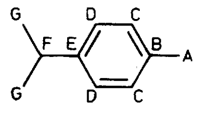
When the complexes **(2a)**—**(2f)** were reacted with Al_2Me_6 the type of product obtained depended very much on the ligand L attached to the osmium. The carbonyl, isonitrile, and trimethylphosphine complexes **(2a)**, **(2b)**, and **(2d)** gave only the monomethyl-monochloro derivatives **(3a)**, **(3b)**, and **(3d)**, even with a large excess of Al_2Me_6.

Since dimethyl sulphoxide is a labile ligand, reactions of **(2c)** with Al_2Me_6 led to decomposition unless a small additional amount of dimethyl sulphoxide was added to the solvent. In that case, reaction using a stoicheiometric amount of Al_2Me_6 gave the monomethyl complex **(3c)** as a yellow air-stable solid. When an excess of Al_2Me_6 was used the dimethyl complex **(4a)** (11%) could also be detected by ^{1}H and ^{13}C n.m.r. spectroscopy (and by mass spectrometry) in the product.

The dimethyl sulphoxide in **(3c)** is easily displaced and on treatment with triphenylphosphine, the chloro(methyl)triphenylphosphine complex **(3e)** was obtained in reasonable yield. The triphenyl phosphite complex **(3f)** was prepared similarly. Neither **(3e)** nor **(3f)** could conveniently be made by direct reaction of Al_2Me_6 with either **(2e)** or **(2f)**.

In the compounds **(3a)**—**(3f)** the Os bears four different groups and is therefore a chiral centre. This is immediately evident from the n.m.r. spectra of the co-ordinated *p*-cymene which now show doubling of both the aromatic H and C resonances and also of the isopropyl methyls. The appearance of these diastereotopic nuclei is a useful indicator of stereochemistry at the osmium.

Table 2. ^1H N.m.r. spectra[a] (δ/p.p.m.)



		p-Cymene				
Compound	Solvent	A	C + D	F	G	Others
(2a)	$CDCl_3$	2.43s	6.09d (6.0), 5.87d (6.0)	2.91sp (7.3)	1.32d (7.3)	
(2b)	$CDCl_3$	2.36s	5.76d (6.0), 5.55d (6.0)	2.82sp (6.7)	1.31d (6.7)	1.56s ($CNCMe_3$)
(2c)	$CDCl_3$	2.37s	5.98d (6.0), 5.81d (6.0)	3.00sp (7.1)	1.32d (7.1)	3.25s (Me_2SO)
(2d)	$CDCl_3$	2.20s	5.60s	2.78sp (6.7)	1.23d (6.7)	1.63d [10.9] (PMe_3)
(2e)	$CDCl_3$	2.00s	5.50d (6.0), 5.25d (6.0)	2.73sp (6.8)	1.15d (6.8)	7.82m, 7.46m (PPh_3)
(2f)	$CDCl_3$	1.89s	5.60d (6.0), 5.20d (6.0)	2.70sp (7.3)	1.21d (7.3)	7.31m [$P(OPh)_3$]
(3a)	C_6D_6[b]	1.74s	4.98d (5.4), 4.87d (5.4), 4.73d (5.4), 4.47d (5.4)	2.14sp (7.3)	0.89d (7.3), 0.87d (7.3)	1.56s (Os–Me)
(3b)	C_6D_6[b]	1.96s	4.98d (5.1), 4.83d (5.1), 4.79d (5.3), 4.61d (5.3)	2.37sp (7.3)	1.04d (7.3), 1.03d (7.3)	1.10s ($CNMe_3$) 1.59s (Os–Me)
(3c)	C_6D_6[b]	1.88s	5.08d (5.4), 4.90d (5.8), 4.85d (5.8), 4.67d (5.4)	2.64sp (7.3)	1.07d (7.3), 1.03d (7.3)	3.03s, 2.58s (Me_2SO) 1.43s (Os–Me)
(3d)	$CDCl_3$[b]	2.07s	5.20d (5.0), 5.11d (5.8), 4.86d (5.8), 4.57d (5.0)	2.47sp (7.3)	1.26d (7.3), 1.19d (7.3)	1.47d [10.8] (PMe_3) 0.95d [9.8] (Os–Me)
(3e)	CD_2Cl_2[b]	1.96s	5.12d (5.4), 4.78d (5.4), 4.71d (5.4), 4.60d (5.4)	2.67sp (7.3)	1.27d (7.3), 1.19d (7.3)	7.58m, 7.38m (PPh_3) 1.10d [9.8] (Os–Me)
(3f)	CD_2Cl_2[b]	1.77s	5.18d (5.7), 4.97d (5.7), 4.81d (5.7), 4.68d (5.7)	2.24sp (7.3)	1.07d (7.3), 1.03d (7.3)	7.24m [$P(OPh)_3$] 1.26d [7.8] (Os–Me)
(4a)	C_6D_6[b]	1.83s	4.81d (6.0), 4.44d (6.0)	2.67sp (7.3)	1.11d (7.3)	2.60s (Me_2SO) 0.61s (Os–Me_2)
(4b)	$(CD_3)_2CO$[b]–$CDCl_3$ (1:1)	1.80s	4.62d (5.4), 4.47d (5.4)	2.37sp (6.8)	1.13d (6.8)	7.32s (PPh_3) 0.29d [7.8] (Os–Me_2)
(5)	$(CD_3)_2CO$	1.92s	6.82d (5.8), 5.78d (6.3), 4.98d (5.8), 4.59d (6.3)	2.27sp (7.3)	1.13d (7.3), 0.97d (7.3)	7.93m, 7.63m, 7.41m, 7.25m, 7.00m [PPh_2(*o*-C_6H_4)]
(6)	$(CD_3)_2CO$[b]	1.97s	5.11d (5.8), 5.06d (5.5), 4.80d (5.8), 4.72d (5.5)	2.10sp (7.5)	1.03d (7.5), 0.94d (7.5)	7.71m, 7.32m, 7.05t [7.3], 6.83m [PPh_2(*o*-C_6H_4)] 0.91d [8.8] (Os–Me)
(7)	$(CD_3)_2CO$	2.13s	5.65d (5.8), 5.11d (5.2), 4.78d (5.8), 4.20d (5.2)	2.14sp (7.2)	1.19d (7.2), 1.13d (7.2)	7.68m, 7.38m (PPh_3) −8.42d [43.4] (Os–H)
(8)	$(CD_3)_2CO$	1.92s	5.50s	2.09sp (7.0)	0.80d (7.0)	7.47m, 7.34m, 6.71m, 6.50m [P(OPh)(*o*-$C_6H_4O)_2$]
(9)	$CDCl_3$	2.39s	5.54s	3.08sp (7.8)	1.26d (7.8)	1.89d [10.3] (PMe_3)

[a] Coupling (Hz) to H in parentheses, coupling (Hz) to P in square brackets; sp = septet. Unless otherwise stated $SiMe_4$ as internal reference. [b] Solvent peak as internal reference: $CDCl_3$, 7.27; C_6D_6, 7.17; CD_2Cl_2, 5.35; $(CD_3)_2CO$, 2.04 p.p.m.

The triphenylphosphine complex (**2e**) reacted with Al_2Me_6 to give a mixture of compounds. Longer reaction times gave a mixture of the dimethyl complex (**4b**) and the orthometallated complexes (**5**) and (**6**) (typically 1:3:3). However, when the reaction was quenched after 10 min (see Experimental section), compound (**3e**) was detected among the others and isolated. It therefore appears that (**3e**) is formed first in the reaction and that it then reacts with Al_2Me_6 to give at least (**4b**) and (**5**). Complex (**6**) must arise directly from (**3e**) or (**4b**) since (**5**) does not react with Al_2Me_6. The various complexes were separated chromatographically and characterised by their n.m.r. spectra. The ^{31}P n.m.r. spectra showed that only one type of phosphorus

Table 3. $^{13}C-\{^1H\}$ and $^{31}P-\{^1H\}$ n.m.r. spectra (δ/p.p.m.)

		$^{13}C-\{^1H\}$ N.m.r.[a]						
		p-Cymene						
Compound	Solvent	A	B + E	C + D	F	G	Others	$^{31}P-\{^1H\}$ N.m.r.[b]
(2a)	CD_2Cl_2	18.9s	112.5s, 109.5s	87.3s, 86.5s	32.0s	22.8s	CO[c]	
(2b)	CD_2Cl_2	18.4s	101.7s, 99.0s	79.6s, 79.2s	31.5s	22.8s	122.2s, 58.2s, 31.1s ($CNCMe_3$)	
(2c)	CD_2Cl_2	18.4s	99.7s, 93.9s	78.8s, 78.7s	30.7s	22.2s	42.3s (Me_2SO)	
(2d)	$CDCl_3$	18.1s	97.3d [1.5], 86.1d [1.5]	80.4d [4.6], 77.0d [2.3]	30.4s	22.3s	15.05d [38.0] (PMe_3)	−39.1s
(2e)	$CDCl_3$	17.8s	103.4d [4.6], 88.5d [2.0]	80.4d [2.3], 79.9d [5.3]	30.0s	22.2s	134.4d [9.2], 133.3d [52.6], 130.2d [2.3], 127.8d [9.9] (PPh_3)	−13.1s
(2f)	CD_2Cl_2	18.0s	97.9d [3.7], 97.3d [5.4]	82.5d [5.7], 81.6d [6.9]	31.1s	22.7s	152.2d [11.3], 129.9s, 125.4s, 122.0d [4.5] [$P(OPh)_3$]	57.65s
(3b)	C_6D_6	16.7s	98.5s, 96.6s	81.3s, 80.0s, 79.7s, 78.3s	30.0s	22.2s, 21.4s	136.6s, 55.3s, 30.1s ($CNCMe_3$) −21.8s (Os–Me)	
(3c)	C_6D_6	17.7s	99.9s, 92.9s	84.5s, 83.5s, 76.3s, 75.1s	30.4s	23.4s, 21.9s	49.1s, 37.6s (Me_2SO) −16.0s (Os–Me)	
(3d)	$(CD_3)_2CO$	17.8s	99.4s, 85.1s	85.4d [6.9], 80.7d [3.1], 77.7d [6.9], 73.8d [3.8]	31.1s	23.9s, 22.1s	15.6d [35.9] (PMe_3) −20.8d [13.0] (Os–Me)	−41.7s
(3e)	CD_2Cl_2	17.9s	104.0s, 93.7s	82.8d [5.0], 80.8d [4.4], 79.8d [1.8], 77.9d [3.8]	30.5s	23.8s, 22.2s	135.2d [49.6], 134.8d [9.7], 130.0d [2.0], 128.0d [9.7] (PPh_3) −17.0d [12.2] (Os–Me)	−2.13s
(3f)	C_6D_6	17.5s	102.6d [3.1], 96.8d [3.3]	88.0d [5.8], 87.8d [4.8], 79.8d [8.8], 77.6d [6.9]	30.7s	23.3s, 22.4s	152.9d [10.24], 129.5s, 124.4s, 122.2d [4.0] [$P(OPh)_3$] −23.0d [18.8] (Os–Me)	71.0s
(4a)	C_6D_6	17.3s	96.4s, 92.8s	81.9s, 77.2s	30.8s	23.4s	44.1s (Me_2SO) −19.5s ($Os–Me_2$)	
(4b)	CD_2Cl_2	17.7s	98.4d [1.3], 93.4d [1.6]	81.6d [4.8], 80.8d [2.1]	30.1s	23.4s	134.8d [27.2], 134.7d [9.7], 129.2d [2.2], 127.6d [9.4] (PPh_3) −22.99d [13.0] ($Os–Me_2$)	8.1s
(5)	$(CD_3)_2CO$	18.1	99.1s, 90.0s	80.3d [3.8], 79.7d [5.1], 79.0d [3.3], 77.5d [4.4]	31.0s	24.1s, 22.1s	152.4—120.7m [$PPh_2(o-C_6H_4)$]	−65.3s
(6)	$(CD_3)_2CO$	18.1s	98.7d [3.0], 92.8d [2.3]	79.5d [4.0], 78.6d [3.4], 78.5d [4.5], 77.0d [3.8]	32.1s	24.3s, 32.2s	148.3—122.9m [$PPh_2(o-C_6H_4)$] −19.5d [10.7] (Os–Me)	−55.8s
(7)	$(CD_3)_2CO$	18.5s	99.7d [1.5], 96.9d [1.5]	84.9d [5.3], 81.8d [1.5], 79.4d [6.9], 72.8d [1.5]	31.9s	24.6s, 23.3s	138.0d [51.9], 134.7d [9.9], 130.3d [2.3], 128.3d [9.9] (PPh_3)	7.6s
(9)	CD_2Cl_2	20.6s	102.3s, 87.8s	81.3d [3.2], 77.2d [5.0]	32.1s	22.8s	20.7d [40.6] (PMe_3)	−62.3s

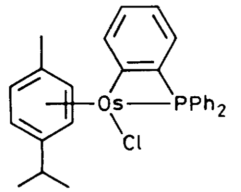
[a] Coupling (Hz) to P in square brackets; $SiMe_4$ as internal reference. See diagram in Table 2. [b] Recorded in the same solvent as the ^{13}C spectra; H_3PO_4 as external reference. [c] Carbonyl carbon not observed.

was present in each complex, and both the ^1H and the ^{13}C n.m.r. spectra showed the expected doublets at high field (low frequency) due to the Os–Me, coupled to phosphorus in complexes (**4b**) and (**6**). In compounds (**5**) and (**6**) the osmium is again a chiral centre, and the phenyl rings of the triphenylphosphine ligand are magnetically inequivalent. For this reason both the ^1H and the $^{13}C-\{^1H\}$ n.m.r. spectra of these compounds are very complicated in the phenyl region.

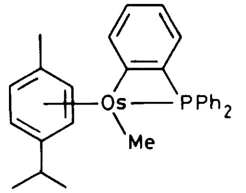
The formation of *ortho*-metallated osmium compounds with triphenylphosphine has long been known;[17] hydrogen–deuterium exchange reactions have also been reported to occur on the phosphine ligands of $[OsH(X)(CO)(PPh_3)_3]$ (X = H or Cl), but the metallated intermediates were not isolated.[18]

The *ortho*-metallated compound (**5**) was not formed on refluxing (**2e**) in ethanol containing triethylamine; this reaction gave the hydride (**7**), which was identified spectroscopically. The hydride was observed in the i.r. spectrum at 2 045 cm^{-1} and in the ^1H n.m.r. spectrum as a doublet (coupling to phosphorus) at δ −8.42 (*J* 43.4 Hz). The analogous complex $[(C_6Me_6)Ru(PPh_3)(H)Cl]$ has been prepared similarly.[19]

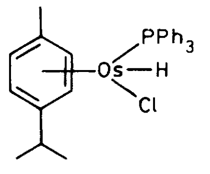
Reaction of the triphenyl phosphite complex (**2f**) with Al_2Me_6 gave a mixture of products from which the di-*ortho*-



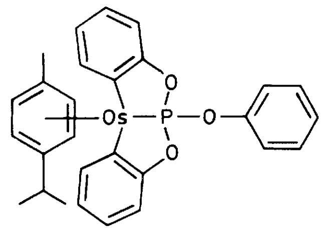
(5)



(6)



(7)



(8)

metallated complex (**8**) could be isolated by chromatography. The complex was characterised by the mass spectrum (which showed the expected molecular ion peaks) and by the ^{1}H n.m.r. spectrum; the lack of splitting of the *p*-cymene resonances showed that the osmium was not a chiral centre here, in agreement with the structure proposed. Other workers have also reported *ortho*-metallated triphenyl phosphite–osmium complexes.[20]

When a solution of the methyl–dimethyl sulphoxide complex (**3c**) was reacted with carbon monoxide [1 atm (10^5 Pa) 20 °C] in dichloromethane the carbonyl compound (**3a**) was observed in the solution by i.r. spectroscopy. However, the isolated product was always contaminated with a large amount of (**3c**), indicating that carbon monoxide and dimethyl sulphoxide were readily interchanged.

As Al_2Me_6 only gave rise to monomethyl complexes in most cases, we also reacted complexes (**2a**)—(**2f**) with methyl-lithium. Highly air-sensitive materials were obtained from most of the reactions but [(*p*-$MeC_6H_4CHMe_2$)Os(PPh_3)Me_2] (**4b**) [from reaction with (**2e**)] could be isolated and completely characterised.

The trimethylphosphine complex (**2d**) was also reacted with an excess of MgMeI, but the only isolated product from this reaction was the di iodide, [(*p*-$MeC_6H_4CHMe_2$)Os(PMe_3)I_2] (**9**).

All the methylated and the *ortho*-metallated complexes are yellow or orange-yellow and are fairly air stable as crystalline solids, but generally very air sensitive in solution.

We also note that all the methylosmium complexes prepared here show an unexpectedly low ν(CH) band in the region around 2 800 cm^{-1}. Wilkinson and co-workers[21] have found similar bands in methyl complexes of other metals and have suggested that such low-frequency C–H stretching bands may be caused by an interaction between the methyl hydrogens and the metal which, in some cases, they have confirmed by *X*-ray crystallography. However, by contrast to the complexes of Wilkinson, the osmium complexes here described are 18-electron and co-ordinatively saturated species.

Perhaps the single most novel feature of the work described here is the range of chemistry that can be accomplished at osmium using the *p*-cymene ligand as protecting group. It is not clear whether the stability of the *p*-cymene–osmium bond will be as great as, for example, the pentamethylcyclopentadienyl–rhodium or –iridium bonds but present indications are that it is surprisingly inert.

Experimental

All reactions involving methyl compounds were carried out in carefully dried Schlenk tubes under argon; manipulations were carried out using hypodermic syringes or fine cannulae through Suba-seals. Solutions of Al_2Me_6 in toluene were also made up in this way. Solvents were dried and distilled prior to use. Microanalyses (Table 1) were carried out by the University of Sheffield Microanalytical Service. I.r. spectra were recorded on a PE-157G spectrometer and far-i.r. spectra on a PE-180 instrument. Mass spectra were measured on a Kratos MS25 spectrometer; n.m.r. spectra, collected in Tables 2 and 3, on Perkin-Elmer R-12B (60 MHz, ^{1}H), R-34 (220 MHz, ^{1}H), JEOL PFT-100 (25 MHz, ^{13}C; 40.1 MHz, ^{31}P), and Bruker WP80 (20 MHz, ^{13}C; 32.4 MHz, ^{31}P) spectrometers. Since the methods used to synthesise the compounds were very similar, only typical preparations are given. The yields of isolated products are listed in Table 1. Unless otherwise stated, the reactions were carried out at room temperature.

High-yield Synthesis of [(*p*-$MeC_6H_4CHMe_2$)$_2Os_2Cl_4$] (**1**).—$Na_2[OsCl_6]$ (2 g, 4.455 mmol), α-phellandrene [2-methyl-5-(1-methylethyl)cyclohexa-1,3-diene] (10 cm^3), and absolute ethanol (20 cm^3) were refluxed under argon for 100 h. The resulting yellow-orange suspension was vacuum-concentrated to *ca.* 8 cm^3 and cooled at 0 °C overnight. The solid was filtered off, washed with cold ethanol and diethyl ether, and recrystallised from dichloromethane–hexane (after the removal of some sodium chloride) to give orange-yellow crystals (1.41 g, 80%) (Found: C, 30.3; H, 3.6. $C_{20}H_{28}Cl_4Os_2$ requires C, 30.4; H, 3.6%). ^{1}H N.m.r. ($CDCl_3$): δ 6.28 [d, *J*(H–H) 5.3, 4 H], 6.11 [d, *J*(H–H) 5.3, 4 H], 2.75 [sp, *J*(H–H) 7.6, 2 H], 2.23 (s, 6 H), 1.30 [d, *J*(H–H) 7.6 Hz, 12 H]. ^{13}C-{^{1}H} N.m.r. ($CDCl_3$): δ 92.4, 89.1, 74.0, 72.4, 31.3, 22.5, 19.4.

[(*p*-$MeC_6H_4CHMe_2$)Os(Me_2SO)Cl_2] (**2c**).—Dimethyl sulphoxide (0.5 cm^3) was added to a solution of (**1**) (175 mg, 0.222 mmol) in dichloromethane (5 cm^3). The colour changed from orange to yellow. Hexane (5 cm^3) was added and some crystals precipitated out. The suspension was vacuum-concentrated (to *ca.* 2 cm^3) and diethyl ether (5 cm^3) was added. The yellow-orange crystals were filtered off and washed with diethyl ether.

The complexes (**2b**), (**2d**), (**2f**), and (**2g**) were prepared similarly.

[(*p*-$MeC_6H_4CHMe_2$)Os(CO)Cl_2] (**2a**).—A solution of complex (**1**) (200 mg, 0.253 mmol) in dichloromethane (15 cm^3) was reacted with carbon monoxide [1 atm (10^5 Pa), 10 min]. After working up as for (**2c**) orange crystals of (**2a**) were obtained.

[(*p*-$MeC_6H_4CHMe_2$)Os(CO)(Me)Cl] (**3a**).—Compound (**2a**) (126 mg, 0.298 mmol) was suspended in toluene (2 cm^3); a toluene solution of Al_2Me_6 (0.44 cm^3, 0.34 mol dm^{-3}, 0.150 mmol) was added slowly. The orange solid dissolved to give a red-orange solution. After stirring (10 min), acetone (1 cm^3) followed by water (0.05 cm^3) were added dropwise. Bubbles were released and a white solid precipitated. After stirring (20 min), diethyl ether (2 cm^3) was added and the white solid filtered off to give a brown-orange solution which was vacuum-evaporated to dryness to leave a brown oil. This was dissolved in diethyl ether–acetone (3:1, 2 cm^3) and chromatographed on a short (5 × 3 cm) column of neutral alumina (activity I) under argon. On eluting with diethyl ether a yellow band separated which yielded yellow crystals of (**3a**); the crystals were washed with light petroleum (b.p. 40—60 °C, 3 cm^3) and dried in a stream of argon.

[(*p*-$MeC_6H_4CHMe_2$)Os(Me_2SO)(Me)Cl] (**3c**).—Compound (**2c**) (168 mg, 0.335 mmol) suspended in toluene (2 cm^3) containing dimethyl sulphoxide (0.1 cm^3) was treated with a solution of Al_2Me_6 in toluene (0.55 cm^3, 0.34 mol dm^{-3}, 0.187 mmol). The solid dissolved to give a yellow solution which was worked up as for complex (**3a**) to give yellow crystals of complex (**3c**).

When a mol ratio of Al_2Me_6:**(2c)** of 1.59:1 was used in this procedure, the isolated solid contained 11% of the dimethyl complex $[(p\text{-}MeC_6H_4CHMe_2)Os(Me_2SO)Me_2]$ **(4a)** (by ^1H n.m.r.).

$[(p\text{-}MeC_6H_4CHMe_2)Os\{P(OPh)_3\}(Me)Cl]$ **(3f)**.—Triphenyl phosphite (118 mg, 0.380 mmol) was added to a solution of complex **(3c)** in toluene [prepared *in situ* as described above from **(2c)** (180 mg, 0.380 mmol) and a toluene solution of Al_2Me_6 (0.57 cm^3, 0.34 mol dm^{-3}, 0.199 mmol)]. The yellow solution was evaporated to dryness *in vacuo* to give an oily solid. Diethyl ether (2 cm^3) was added with stirring and yellow crystals of **(3f)** were obtained.

Reaction of Complex **(2e)** *with* Al_2Me_6.—A solution of Al_2Me_6 in toluene (3.5 cm^3, 0.47 mol dm^{-3}, 1.645 mmol) was slowly injected into a suspension of **(2e)** (400 mg, 0.64 mmol) in toluene (5 cm^3). After the first few drops the solid dissolved to give an orange solution which a few seconds later became yellow. After stirring (10 min[*]), acetone (2 cm^3) followed by water (0.7 cm^3) were added dropwise. A white solid formed; the resultant suspension was stirred (30 min), and the solid was filtered off. The yellow solution was evaporated to dryness to leave a yellow oil which was dissolved in diethyl ether (3 cm^3) and chromatographed on a column (30 × 3 cm) of neutral alumina (activity I). On eluting with hexane a yellow fraction was obtained which gave pale yellow crystals (160 mg) identified as a mixture of **(6)** (70%) and **(4b)** (30%). Elution with diethyl ether gave two further yellow fractions. The first one yielded orange-yellow crystals (30 mg) identified as complex **(3e)**, while the second fraction gave yellow crystals of complex **(5)** (120 mg).

$[(p\text{-}MeC_6H_4CHMe_2)Os(PPh_3)Me_2]$ **(4b)**.—A solution of LiMe in diethyl ether (10 cm^3, 0.6 mol dm^{-3}, 6 mmol) was slowly injected into a suspension of **(2e)** (230 mg, 0.35 mmol) in toluene (5 cm^3). After stirring the resultant yellow solution (30 min) acetone (3 cm^3) and water (0.7 cm^3) were added dropwise while the Schlenk tube was cooled in an ice-water bath; a white solid precipitated. This suspension was stirred for 20 min and then filtered. The yellow solution was evaporated to dryness to give a brownish yellow oil from which **(4b)** was obtained on crystallisation from light petroleum (b.p. 40—60 °C) and methanol (at −15 °C).

$[(p\text{-}MeC_6H_4CHMe_2)Os(PPh_3)(H)Cl]$ **(7)**.—Triethylamine (0.4 cm^3) was added to a suspension of **(2e)** (175 mg, 0.266 mol) in ethanol 96% (10 cm^3). After refluxing (2 h), the orange-yellow solution was concentrated, precipitating $Et_3N{\cdot}HCl$ as a white solid. Diethyl ether (2 cm^3) was added and the suspension was filtered through a column (15 × 2.5 cm) of Florisil. Elution with diethyl ether gave a yellow solution which when concentrated gave yellow crystals of the hydride **(7)**.

Reaction of Complex **(2f)** *with* Al_2Me_6.—A solution of Al_2Me_6 in toluene (0.3 cm^3, 0.47 mol dm^{-3}, 0.14 mmol) was slowly injected into a suspension of **(2f)** (190 mg, 0.27 mmol) in toluene (2 cm^3). The resultant orange solution was worked up as described for the reaction of **(2e)** with Al_2Me_6 to give an orange oil which, after purification, gave yellow crystals of complex **(8)**.

Reaction of Complex **(2d)** *with Methylmagnesium Iodide.*—Complex **(2d)** (200 mg, 0.42 mmol) was suspended in toluene (2 cm^3) and a solution of methylmagnesium iodide in diethyl ether (5 cm^3, 2.3 mol dm^{-3}, 11.5 mmol) was slowly injected. The yellow solid dissolved and an orange solid precipitated. After stirring (20 min) and a conventional work-up, only orange crystals of $[(p\text{-}MeC_6H_4CHMe_2)Os(PMe_3)I_2]$ **(9)** were obtained.

Acknowledgements

We thank the S.E.R.C. for supporting this work, the Spanish Ministry of Education for a scholarship (to J. A. C.), Dr. B. F. Taylor for n.m.r. spectra, Mr. P. Ashton and Mr. I. Johnstone for mass spectra, and the Ethyl Corporation for a gift of trimethylaluminium.

References

1 P. M. Maitlis, *Chem. Soc. Rev.*, 1981, **10**, 1.

2 M. A. Bennett, M. I. Bruce, and T. W. Matheson, in 'Comprehensive Organometallic Chemistry,' eds. G. Wilkinson, F. G. A. Stone, and E. W. Abel, 1982, vol. 4, pp. 796—806.

3 H. Werner, *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 907.

4 G. Winkhaus, H. Singer, and M. Kricke, *Z. Naturforsch., Teil B*, 1967, **21**, 1109.

5 T. Arthur and T. A. Stephenson, *J. Organomet. Chem.*, 1981, **208**, 369.

6 M. A. Bennett and A. K. Smith, *J. Chem. Soc., Dalton Trans.*, 1974, 233.

7 R. A. Zelonka and M. C. Baird, *Can. J. Chem.*, 1972, **50**, 3063.

8 D. R. Robertson and T. A. Stephenson, *J. Organomet. Chem.*, 1976, **116**, C29; D. R. Robertson, T. A. Stephenson, and T. Arthur, *ibid.*, 1978, **162**, 121.

9 S. D. Robertson, I. W. Robertson, and T. A. Stephenson, *J. Organomet. Chem.*, 1980, **202**, 309.

10 H. Werner, R. Werner, and C. Burscha, *Chem. Ber.*, 1984, **117**, 152; H. Werner and R. Werner, *ibid.*, p. 161 and refs. therein.

11 R. J. Restivo, G. Ferguson, D. J. O'Sullivan, and F. J. Lalor, *Inorg. Chem.*, 1975, **14**, 3046; H. Werner and R. Werner, *J. Organomet. Chem.*, 1981, **210**, C11; S. L. Grundy and P. M. Maitlis, *J. Chem. Soc., Chem. Commun.*, 1982, 379; H. Werner and R. Werner, *Chem. Ber.*, 1984, **117**, 142.

12 H. Werner and R. Werner, *J. Organomet. Chem.*, 1980, **194**, C7.

13 F. L'Eplattenier and C. Pelicket, *Helv. Chim. Acta*, 1970, **53**, 1091; J. R. Norton, *Acc. Chem. Res.*, 1979, **2**, 139; K. M. Motyl, J. R. Norton, C. K. Shauer, and O. P. Anderson, *J. Am. Chem. Soc.*, 1982, **104**, 7325; W. J. Carter, J. W. Kelland, S. J. Okrasinski, K. E. Warner, and J. R. Norton, *Inorg. Chem.*, 1982, **21**, 3955; J. C. Shapley, M. E. Cree-Uchiyama, and G. M. St. George, *J. Am. Chem. Soc.*, 1983, **105**, 140.

14 K. Isobe, P. M. Bailey, and P. M. Maitlis, *J. Chem. Soc., Chem. Commun.*, 1981, 807; A. Vázquez de Miguel, K. Isobe, B. F. Taylor, A. Nutton, and P. M. Maitlis, *ibid.*, 1982, 758; K. Isobe, A. Vázquez de Miguel, P. M. Bailey, S. Okeya, and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 1983, 1441; K. Isobe and P. M. Maitlis, *J. Organomet. Chem.*, 1983, **250**, C25; A. Vázquez de Miguel, M. Gómez, K. Isobe, B. F. Taylor, B. E. Mann, and P. M. Maitlis, *Organometallics*, 1983, **2**, 1724; A. Vázquez de Miguel, K. Isobe, P. M. Bailey, N. J. Meanwell, and P. M. Maitlis, *ibid.*, 1982, **1**, 1604.

15 F. A. Cotton, R. Francis, and W. J. Horrocks, *J. Phys. Chem.*, 1960, **64**, 1534; W. L. Reinolds, *Prog. Inorg. Chem.*, 1970, **12**, 10; C. White, S. J. Thompson, and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 1977, 1654.

16 A. J. Smith and H. Adams, personal communication.

17 C. W. Bradford, R. S. Nyholm, G. J. Gainsford, J. M. Guss, P. R. Ireland, and R. Mason, *J. Chem. Soc., Chem. Commun.*, 1972, 87; G. J. Gainsford, J. M. Guss, P. R. Ireland, R. Mason, C. W. Bradford, and R. S. Nyholm, *J. Organomet. Chem.*, 1972, **40**, C70.

18 F. G. Moers and J. P. Langhout, *Recl. Trav. Chim. Pays-Bas*, 1972, **91**, 591.

19 M. A. Bennett, J. P. Ennett, and K. I. Gell, *J. Organomet. Chem.*, 1982, **233**, C17.

20 C. A. Tolman, A. D. English, S. D. Ittel, and J. P. Jesson, *Inorg. Chem.*, 1978, **17**, 2374; E. W. Ainscough, T. A. James, S. D. Robinson, and J. N. Wingfield, *J. Chem. Soc., Dalton Trans.*, 1974, 2384.

21 See, for example, C. G. Howard, G. Wilkinson, M. Thornton-Pett, and M. E. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1983, 2025.

Received 18*th June* 1984; *Paper* 4/1031

---

[*] If this solution is stirred for 30 min, a mixture of **(4b)** (16%), **(5)** (42%), and **(6)** (42%) is obtained.