The Synthesis and *X*-Ray Crystal Structures of Homoleptic Tetrahedral Aryls of Osmium(IV) and of Cyclohexyls of Ruthenium(IV), Osmium(IV), and Chromium(IV)†

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The interaction of *o*-tolylmagnesium bromide or $AlPh_3(OEt_2)$ with osmium tetraoxide leads to the isolation of the homoleptic, tetrahedral osmium(IV) compounds OsR_4 (R = C_6H_4Me-*o* or C_6H_5). Thermally stable $M(C_6H_{11})_4$ compounds (M = Ru, Os, or Cr; C_6H_{11} = cyclohexyl) are obtained by the interaction of the Grignard reagent with $Ru_2(O_2CMe)_4Cl$, $Os_2(O_2CMe)_4Cl_2$, and $CrCl_3(thf)_3$ (thf = tetrahydrofuran) respectively. The structures of all five compounds have been determined by *X*-ray crystallography.

Although the interest in preparing neutral, homoleptic tetra-alkyls for the platinum metals dates back to the first claims[1] of '$PtMe_4$', now known to be $[PtMe_3(OH)]_4$, such compounds have never previously been made. For the early transition metals, Ti, Zr, Hf, V, Cr,[2] for Mo,[3] W[4] and also for Mn,[5,6] Fe[6] and Co[6,7] alkyls and/or aryls have been isolated and several have been crystallographically characterized: $M(CH_2Ph)_4$ (M = Ti,[8] Zr,[9] or Hf[8]), $V(C_6H_2Me_3\text{-}2,4,6)_4$,[10] $Cr(CH_2CMe_2Ph)_4$,[11] and $Cr(CPh{=}CMe_2)_4$.[12]

The synthetic routes used for Ru and Os differ from those employed in the preparation of other tetra-alkyls which have relied almost exclusively on alkylation of metal halides or alkoxides. They include interaction of Grignard reagents or aluminium alkyls/aryls with OsO_4 and of Grignards with $Os_2(O_2CMe)_4Cl_2$ or $Ru_2(O_2CMe)_4Cl$.

Alkylation of OsO_4 has been used to synthesize $OsO(CH_2SiMe_3)_4$[13] and $OsO_2(C_6H_2Me_3\text{-}2,4,6)_2$[14] and indirectly in the preparation of nitrido-osmium alkyls[15] while the acetato-bridged osmium and ruthenium dimers have been previously converted to the binuclear Ru^{III} homoleptic alkyls Ru_2R_6 (R = CH_2CMe_3 or CH_2SiMe_3) or to the partially alkylated species $M_2(\mu\text{-}O_2CMe)_2R_4$ (M = Ru or Os, R = CH_2CMe_3 or CH_2SiMe_3).[16] New compounds and analyses are given in Table 1.

A preliminary account has been published.[17]

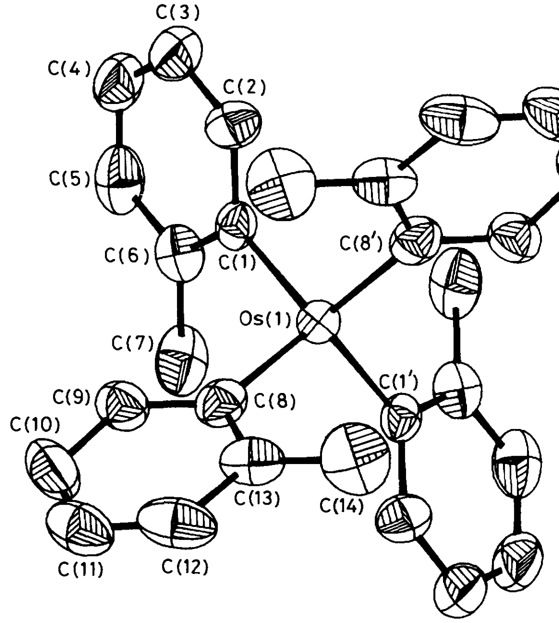

Figure 1. Molecular structure of $Os(C_6H_4Me\text{-}o)_4$

Results and Discussion

1. *Synthesis and Crystal Structure of* $Os(C_6H_4Me\text{-}o)_4$.—The interaction of osmium tetraoxide with seven equivalents of *o*-tolylmagnesium bromide in tetrahydrofuran (thf) yields a red-purple solution from which dark red-purple polyhedra of the diamagnetic compound $Os(C_6H_4Me\text{-}o)_4$ can be obtained in high yield after extraction into light petroleum and subsequent crystallization.

The compound has remarkable thermal stability and chemical inertness. It does not react with small molecules (O_2, CO, or NO at 25 °C) and can be refluxed in glacial acetic acid for 2 d without decomposition. The i.r. and ^1H and ^{13}C n.m.r. spectra show bands only for the C_6H_4Me-*o* group.

A diagram of the molecular structure is shown in Figure 1; selected bond lengths and angles are given in Table 2. The molecule is sited on a crystallographic two-fold axis, but its effective symmetry is very close to $\bar{4}$. The closeness of the structure to this symmetry can be seen in two aspects of the geometry: the angle between the two C–Os–C planes, which intersect on the two-fold axis, 89.4(8)° (ideal 90°), and the orientations of the two independent phenyl rings relative to the two-fold axis direction which are equal at 43.6(8)°. The 'tetrahedral' geometry for the OsC_4 unit is somewhat flattened and this may be ascribed to the steric repulsions between the three methyl groups and the methylated ring carbons on the phenyl rings across the two-fold axes, *i.e.* C(7)···C(6') 3.45(2) and C(14)···C(13') 3.47(3) Å. The methyl carbons are also in close contact with the metal atom [C(7, 14)···Os 3.35(1), 3.36(1) Å], but since the hydrogen atoms seem to be disordered (see Experimental section); there are no indications of any Os···H bonding interactions.

To our knowledge the *o*-tolyl ligand appears not to have been previously used for the preparation of homoleptic tetra-aryls; however there are well characterized tetramesityls of Ti,[18] V,[19] Cr,[20] and Mo.[3] These are more stable and chemically inert than analogous phenyl compounds which decompose *via* reductive elimination[21] and *ortho*-hydrogen abstraction decomposition pathways[22] (however, see below).‡

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

‡ *Note added in proof.* We have now synthesised and determined the crystal structures of $Re(C_6H_4Me\text{-}o)_4$ and $Ru(C_6H_4Me\text{-}o)_4$ also.

Table 1. Physical properties and analytical data for tetrahedral compounds

Compound	Colour	M.p. (°C)	Analysis (%)[a] C	Analysis (%)[a] H
$Os(C_6H_4Me\text{-}o)_4$	Red-purple	174—177	60.4 (60.6)	5.2 (5.1)
$Os(C_6H_5)_4$	Red-purple	*ca.* 200 (decomp.)[b]	58.0 (57.8)	4.2 (4.0)
$Ru(C_6H_{11})_4$	Red-orange	*ca.* 150 (decomp.)[b]	66.6 (66.5)	10.3 (10.2)
$Os(C_6H_{11})_4$	Dark red	143—145	55.3 (55.1)	8.6 (8.5)
$Cr(C_6H_{11})_4$	Dark red	*ca.* 200 (decomp.)[b]	74.2 (74.9)	11.3 (11.5)

[a] Found (required). [b] Decomposition without melting.

Table 2. Selected bond distances (Å) and angles (°) for $Os(C_6H_4Me\text{-}o)_4$ and $Os(C_6H_5)_4$

$Os(C_6H_4Me\text{-}o)_4$		$Os(C_6H_5)_4$	
Os–C(11)	2.016(9)	Os–C(1)	1.994(12)
Os–C(21)	1.977(11)		
C(1)–Os–C(1′)	114.1(3)	C(1)–Os–C(1′)	110.4(4)
C(8)–Os–C(8′)	117.1(3)	C(1)–Os–C(1″)	107.6(4)
C(1)–Os–C(8)	106.9(3)		

As in the case of rhenium,[14] the use of a di-*ortho*-substituted ligand (mesityl, R) as opposed to a mono-*ortho* one (*o*-tolyl, R′) has a significant effect on the nature of the arylation products, namely OsO_2R_2 *vs.* OsR'_4 and ReO_2R_2 *vs.* $ReOR'_4$. For rhenium, discrete tetrahedral alkyls ReR_4 were not isolated on account of the conversion to $R_4Re(\mu\text{-}N_2)ReR_4$ or $(ReR_4)_3$ under nitrogen or argon respectively.[23] Further, these Re^{IV} compounds can be obtained only from $ReCl_4(thf)_2$ or $ReCl_5$ and not from an oxochloride, *e.g.* $ReOCl_4$, and are readily oxidised to $ReOR_4$ compounds. The characteristic stability of the Re=O group towards alkylation is not encountered in osmium chemistry where even thionyl chloride can easily reduce OsO_4 to a mixture of $OsOCl_4$ and $OsCl_4$.[24] The formation of tetrahedral OsR_4 complexes is thus, not surprisingly, also consistent with a stable d^4 low-spin electronic configuration; for Os^{IV} only octahedral or distorted octahedral geometries have previously been known. It should be possible to prepare tetrahedral alkoxides, dialkylamides, and thiolates at least with bulky ligands.

2. *Synthesis and Crystal Structure of* $Os(C_6H_5)_4$.—The interaction of OsO_4 with four equivalents of $AlPh_3(OEt_2)$ in diethyl ether gives the diamagnetic compound $Os(C_6H_5)_4$ which can be crystallized from light petroleum as fine red-purple needles. The reaction is remarkably clean, showing signs of colour change above −20 °C and only slowly at *ca.* 0 °C. The i.r. and n.m.r. spectra show only phenyl absorptions.

Unstable neutral tetraphenyls are known only for Ti,[25] Zr,[26] and V,[27] and were characterized indirectly by interaction with $HgCl_2$ and formation of HgPhCl.[2] This osmium compound is the first to be stable at room temperature but it is very air sensitive and reactive towards small molecules like H_2 and CO in contrast to the inert character of $Os(C_6H_4Me\text{-}o)_4$. Slow decomposition occurs in light petroleum or toluene solutions even in the absence of light over several days, to give biphenyl and a black insoluble material.

A diagram of the structure of this molecule which has exact $\bar{4}$ symmetry is shown in Figure 2, whilst selected bond lengths and angles are given in Table 2. The OsC_4 geometry is very close to tetrahedral, with C–Os–C angles of 107.6(4) and 110.4(4)°, and the unique Os–C distance is equal to the average of the two independent Os–C distances in the *o*-tolyl complex. The bonding of the phenyl group is very symmetrical, with Os–C(1)–C(2, 6) 120.2(3) and 119.7(3)°.

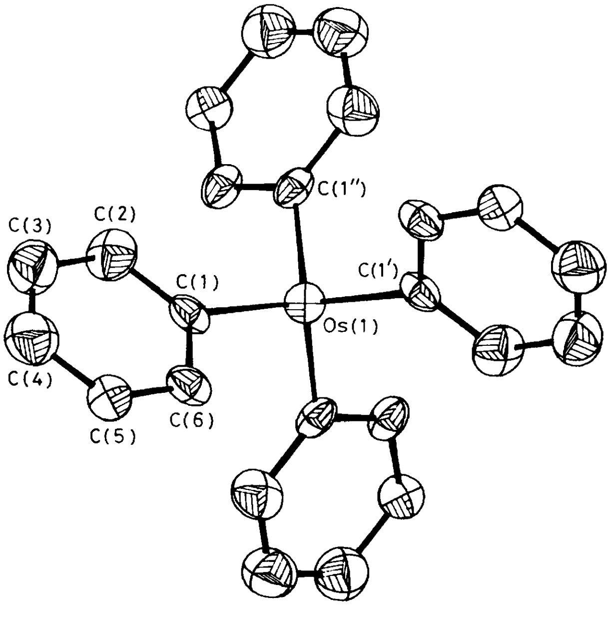

Figure 2. Molecular structure of $Os(C_6H_5)_4$

We finally note that although aluminium alkyls have found extensive use for alkylations of metal halides and in fewer cases of metal oxo species, *e.g.* synthesis using $AlMe_3$ of WMe_6 from WCl_6,[28] $ReMe_6$ from $ReOMe_4$,[29] and $Re(O)Me_2(\eta\text{-}C_5Me_5)$ from $ReO_3(\eta\text{-}C_5Me_5)$,[30] aluminium aryls have not been used.

3. *Syntheses and Crystal Structures of* $M(C_6H_{11})_4$ *(M = Ru, Os, or Cr;* C_6H_{11} *= cyclohexyl)*.—The reaction of excess of cyclohexylmagnesium chloride with the dimeric acetates $Ru^{II}Ru^{III}(O_2CMe)_4Cl$ and $Os^{III}{}_2(O_2CMe)_4Cl_2$ leads to the tetrahedral alkyls $M(C_6H_{11})_4$ (M = Ru or Os). Other alkylating agents give different products[16] and the reactions are clearly complicated, probably involving disproportionation. In the present cases, no other metal compounds could be isolated.

The i.r. spectrum of $Ru(C_6H_{11})_4$ shows only cyclohexyl bands. The ^1H n.m.r. spectrum is complex, comprising two multiplets centred at δ 2.62 (probably due to the α-H) and 1.58 p.p.m.; the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum consists of four sharp

Table 3. Selected bond distances (Å) and angles (°) for $M(C_6H_{11})_4$ (M = Cr, Ru, or Os)

	Cr	Ru	Os
M–C(11)	2.009(4)	2.020(5)	2.026(8)
M–C(21)	2.010(4)	2.018(5)	2.032(8)
C(11)–M–C(11′)	114.5(2)	116.2(3)	117.1(5)
C(21)–M–C(21′)	114.5(2)	116.0(3)	117.1(5)
C(11)–M–C(21)	107.8(2)	107.1(2)	106.3(3)
C(11′)–M–C(21)	106.2(2)	105.4(2)	105.3(3)
M–C(11)–C(12)	116.0(2)	114.4(3)	114.7(5)
M–C(11)–C(16)	112.6(3)	112.4(3)	112.7(5)
M–C(21)–C(22)	116.1(3)	114.3(3)	113.9(5)
M–C(21)–C(26)	112.8(3)	113.0(3)	113.8(5)
C(12)–C(11)–C(16)	111.2(3)	111.0(4)	110.9(7)
C(22)–C(21)–C(26)	110.9(3)	110.8(4)	110.6(7)

singlets at δ 49.74, 33.50, 27.46, and 26.73 p.p.m., for the four unique carbon atoms.

The osmium compound has similar spectra. Both compounds are readily soluble in ethers, aliphatic and aromatic solvents. They are air sensitive and $Os(C_6H_{11})_4$ is remarkably thermally stable, up to 200 °C. The ruthenium compound is the only Ru^{IV} tetrahedral molecule.

The scarcity of cyclohexyls[31] has been assumed to be due to facile β-hydride transfers and the only reported homoleptic compound $Ti(C_6H_{11})_4$[32] decomposes above −30 °C. The remarkable stability of these cyclohexyls with metals of smaller radius suggested that Cr^{IV}, which is known[2] to form very stable alkyls, could give a cyclohexyl. Interaction of $CrCl_3(thf)_3$ with four equivalents of the Grignard does indeed lead to dark red polyhedra of the paramagnetic compound $Cr(C_6H_{11})_4$ (Cr^{IV}, d^2, $\mu_{eff.} = 2.77$), which decomposes only at *ca.* 200 °C. The compound does not react with CO or H_2 even under 10 atm (*ca.* 10^6 Pa) at 70 °C but will react rapidly with NO, although no well defined product could be isolated. The e.s.r spectrum (*X*-band) is virtually identical with those of other Cr^{IV} tetra-alkyls with a broad mid-field line which in frozen hexane at 77 K splits into two (g = 2.08, 1.82) while at the same time a new, weak, narrow line appears at g = 1.95. As stated before[33] this new peak cannot be assigned to any transition of the $3A_2$ ground state of the alkyl. A low-field line is also observed at g = 3.71, probably due to a forbidden transition ($\Delta m = 2$).

The three cyclohexyls are isostructural. The molecular structure of the chromium compound is shown in Figure 3; selected bond lengths and angles for all three molecules are collected in Table 3. As with $Os(C_6H_4Me\text{-}o)_4$ the molecules are sited on a crystallographic two-fold axis, but this time the effective molecular symmetry approaches closely to $\bar{4}$. Thus the two independent M–C bonds are equal within the limits of error in all three cases, the twists of the two independent rings [*i.e.* representative torsion angles about the M–C bonds, *e.g.* C(*n*1′)–Cr–C(*n*1)–C(*n*2) (*n* = 1 or 2)], differ by only 1 or 2°, and the dihedral angles between the C(11′)–M–C(11), C(21′)–M–C(21) planes are 91.1 (Cr), 91.1 (Ru), and 90.7° (Os). As with $Os(C_6H_4Me\text{-}o)_4$ the MC_4 tetrahedra are slightly flattened in the direction of the two-fold axis with C(11,11′)–M–C(21,21′) 114.5—117.1° and C(11,11′)–M–C(21,21′) 105.3—107.8° (Table 2).

Experimental

Microanalyses were by Pascher, Bonn. Spectrometers used were as follows: i.r., Perkin-Elmer 683 (spectra in Nujol mulls or KBr discs, values in cm^{-1}); n.m.r., Bruker WM-250 and JEOL FX 90Q (data in deuteriobenzene in p.p.m. relative to $SiMe_4$); e.s.r., Varian E-12 (*X*-band). Magnetic susceptibilities were determined in the solid state at ambient temperature on an Evans balance.[34]

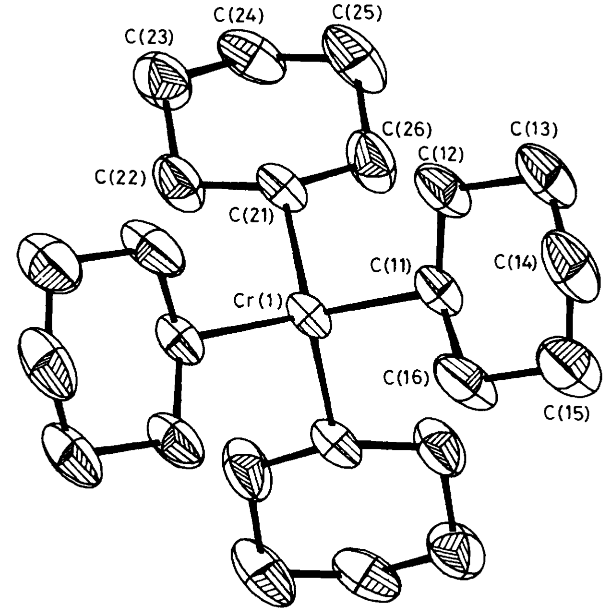

Figure 3. Molecular structure of $Cr(C_6H_{11})_4$

Osmium tetraoxide was from Johnson Matthey PLC. The compounds $Os_2(O_2CMe)_4Cl_2$,[35] $Ru_2(O_2CMe)_4Cl$,[36] $CrCl_3(thf)_3$,[37] and $AlPh_3(OEt_2)$[38] were prepared using literature methods. Solvents were refluxed over sodium or sodium–benzophenone under nitrogen and distilled before use. The light petroleum used had b.p. 40—60 °C. All operations were carried out under vacuum or purified argon.

1. *Tetrakis(o-tolyl)osmium*(IV).—To a stirred solution of OsO_4 (0.6 g, 2.36 mmol) in thf (40 cm^3) at −78 °C was added *o*-tolylmagnesium bromide (16.50 cm^3 of a 1.00 mol dm^{-3} solution in Et_2O, 16.50 mmol) under stirring. The solution was warmed slowly and held at room temperature for *ca.* 2 h. The resulting red-purple solution was evaporated and the residue extracted with light petroleum (3 × 20 cm^3). Concentration of the filtrate to *ca.* 20 cm^3 and cooling at −20 °C overnight gave red-purple polyhedra. Yield: 0.35 g, 27%. The compound is readily soluble in most common organic solvents including halogenated ones. I.r.: 3 020m, 1 560s, 1 555(sh), 1 240m, 1 180m, 1 150w, 1 050m, 1 024s, 1 020(sh), 970w, 930w, 860m, 850m, 740(sh), 730s, 700m, 650m, 495m, 435s, 400w, and 390m. N.m.r.: ^1H, 2.34 (3 H, s, *o*-Me), 7.10 (1 H, d, C_6H_4), 6.80 (1 H, m, C_6H_4), and 6.62 (2 H, m, C_6H_4); ^{13}C, 25.83 (s, *o*-Me) and 140.69, 137.89, 135.51, 128.49, 128.37, and 124.89 (s, C_6H_4).

2. *Tetraphenylosmium*(IV).—To a stirred solution of OsO_4 (0.5 g, 1.97 mmol) in Et_2O (40 cm^3) at −78 °C was added a cooled (−78 °C) suspension of $AlPh_3(OEt_2)$ (2.62 g, 7.88 mmol) in Et_2O (40 cm^3); the mixture was allowed to warm slowly to room temperature and stirred for 2 h to give a red-purple solution which was evaporated. Extraction of the residue with warm light petroleum (4 × 20 cm^3) and concentration of the filtered extracts to *ca.* 30 cm^3 with cooling overnight (−20 °C) afforded dark red-purple needles. Yield: 0.24 g, 24%. The compound is soluble in common organic solvents but is very air sensitive. I.r.: 3 040m, 1 545m br, 1 280m, 1 245m, 1 165m, 1 055m, 1 020s, 980w, 875w, 850w, 730s, 725(sh), 680m, 665m, 470m, and 455w. N.m.r.: ^1H, 6.93 (m, C_6H_5); ^{13}C, 132.46, 128.24, and 126.96 (s, C_6H_5).

Table 4. Crystallographic data for $Os(C_6H_4Me\text{-}o)_4$, $Os(C_6H_5)_4$, and $M(C_6H_{11})_4$ (M = Cr, Ru, or Os)

(*a*) Crystal data					
Formula	$C_{28}H_{28}Os$	$C_{24}H_{20}Os$	$C_{24}H_{44}Cr$	$C_{24}H_{44}Ru$	$C_{24}H_{44}Os$
M	554.734	498.600	384.592	433.692	522.792
Crystal system	Orthorhombic	Tetragonal	Monoclinic	Monoclinic	Monoclinic
a/Å	16.321(3)	11.674(2)	17.540(2)	17.544(2)	17.636(4)
b/Å	8.083(2)	11.674	8.633(1)	8.586(1)	8.528(2)
c/Å	8.510(2)	6.820(1)	17.396(1)	17.394(2)	17.505(3)
α/°	90	90	90	90	90
β/°	90	90	118.30(1)	118.25(2)	118.41(2)
γ/°	90	90	90	90	90
U/Å^3	1 122.66	929.44	2 319.31	2 307.76	2 315.67
Space group	*Pba*2	$P\bar{4}2_1c$	$C2/c$	$C2/c$	$C2/c$
D_c/g cm^{-3}	1.64	1.78	1.10	1.25	1.50
Z	2	2	1	4	4
F(000)	544	480	848	928	1 056
μ(Mo-K_α)/cm^{-1}	56.4	68.65	4.84	6.70	55.14
(*b*) Data collection[a]					
Total data measured	2 183	1 025	2 370	2 357	2 365
Total data unique	1 058	485	2 045	2 033	2 037
Total data observed	855	294	1 545	1 819	1 718
Significance test	$F_o > 2\sigma(F_o)$	$F_o > 3\sigma(F_o)$	$F_o > 4\sigma(F_o)$	$F_o > 3\sigma(F_o)$	$F_o > 3\sigma(F_o)$
(*c*) Refinement					
No. of parameters	164	46	202	202	202
Absorption correction	ψ-scan/DIFABS	ψ-scan	ψ-scan	ψ-scan	ψ-scan
Weighting scheme[b] parameter *g*	0.000 08	0.0001	0.000 01	unit weight	unit weight
Final R[c]	0.0193	0.0341	0.0312	0.0229	0.0260
Final R'[d]	0.0201	0.0278	0.0304	0.0264	0.0315

[a] $\theta_{min.,max.} = 1.5, 25$ throughout. [b] $w = 1/[\sigma^2(F_o) + gF_o^2]$. [c] $R = \Sigma|\Delta F|/\Sigma|F_o|$. [d] $R' = [\Sigma w(\Delta F)^2/\Sigma w|F_o^2|]^{\frac{1}{2}}$.

Table 5. Fractional atomic co-ordinates (× 10^4) for $Os(C_6H_4Me\text{-}o)_4$

Atom	*x*	*y*	*z*
Os(1)	5 000*	5 000*	0*
C(1)	4 325(5)	6 581(9)	−1 285(13)
C(2)	4 302(6)	8 238(10)	−785(11)
C(3)	3 827(6)	9 398(13)	−1 531(17)
C(4)	3 369(7)	8 920(13)	−2 822(17)
C(5)	3 381(6)	7 322(14)	−3 348(12)
C(6)	3 870(5)	6 108(9)	−2 579(10)
C(7)	3 888(8)	4 347(15)	−3 228(13)
C(8)	4 208(6)	3 650(9)	1 217(15)
C(9)	3 405(6)	3 587(9)	785(12)
C(10)	2 849(8)	2 529(14)	1 515(16)
C(11)	3 071(8)	1 559(12)	2 755(15)
C(12)	3 858(9)	1 654(11)	3 284(12)
C(13)	4 470(6)	2 679(9)	2 592(10)
C(14)	5 314(9)	2 759(17)	3 258(17)

* Invariant parameter.

Table 6. Fractional atomic co-ordinates (× 10^4) for $Os(C_6H_5)_4$

Atom	*x*	*y*	*z*
Os(1)	5 000*	5 000*	5 000*
C(2)	3 946(8)	3 593(7)	1 885(14)
C(3)	3 806(8)	2 621(7)	720(14)
C(4)	4 542(8)	1 689(7)	943(14)
C(5)	5 419(8)	1 729(7)	2 331(14)
C(6)	5 559(8)	2 701(7)	3 495(14)
C(1)	4 823(8)	3 633(7)	3 272(14)

* Invariant parameter.

3. *Tetrakis(cyclohexyl)ruthenium*(IV).—To a stirred solution of $Ru_2(O_2CMe)_4Cl$ (1.0 g, 2.11 mmol) in thf (50 cm^3) at −78 °C was added cyclohexylmagnesium bromide (16.9 cm^3 of a 1.0 mol dm^{-3} solution in Et_2O, 16.9 mmol) and the mixture warmed to 0 °C. After *ca.* 1 h volatile material was removed under reduced pressure and the residue extracted with light petroleum (2 × 30 cm^3). Concentration of the filtered extracts to *ca.* 25 cm^3 and cooling overnight (−20 °C) afforded a red-orange crystalline solid. Yield: 0.14 g, 15%. I.r.: 1 320br, 1 280s, 1 240s, 1 025(sh), 1 005m, 970s, 820m, and 790s. N.m.r.: ^{1}H, 2.62 (1 H, m, α-H) and 1.58 (10 H, m br, β-, γ-, and δ-H); ^{13}C, 49.74, 33.50, 27.46, and 26.73 (s, C_6H_{11}).

4. *Tetrakis(cyclohexyl)osmium*(IV).—To a suspension of $Os_2(O_2CMe)_4Cl_2$ (1.0 g, 1.45 mmol) in thf (40 cm^3) at −78 °C was added cyclohexylmagnesium chloride (18.4 cm^3 of a 0.63 mol dm^{-3} solution in Et_2O, 11.6 mmol) and the stirred mixture warmed slowly to 0 °C. After *ca.* 1 h the volatile materials were removed under reduced pressure, the residue extracted with light petroleum (2 × 25 cm^3), and the combined extracts filtered and reduced to *ca.* 10 cm^3. Cooling at −20 °C overnight gave dark red crystals. Yield: 0.18 g, 24%. Spectra are similar to those of $Ru(C_6H_{11})_4$.

5. *Tetrakis(cyclohexyl)chromium*(IV).—To a stirred suspension of $CrCl_3(thf)_3$ (2.5 g, 6.7 mmol) in Et_2O (40 cm^3) at −78 °C was added cyclohexylmagnesium bromide (26.7 cm^3 of a 1.0 mol dm^{-3} solution in Et_2O, 27 mmol) and the mixture warmed slowly to room temperature. The volatile materials were removed under reduced pressure and the residue was extracted with light petroleum (2 × 30 cm^3). Concentration of the filtered extracts to *ca.* 35 cm^3 and cooling overnight (−5 °C) afforded dark red crystals. Yield: 0.56 g, 22%. I.r.: 2 908s, 2 835(sh), 2 772m, 1 625br, 1 425s, 1 397s, 1 340w, 1 320w, 1 278w, 1 245(sh), 1 150s, 1 135s, 1 022m, 1 000m, 795s, and 602s.

Table 7. Fractional atomic co-ordinates (× 10^4) for $Cr(C_6H_{11})_4$

Atom	*x*	*y*	*z*
Cr(1)	0*	603(1)	2 500*
C(11)	1 072(1)	1 861(3)	2 815(1)
C(12)	1 093(2)	2 745(3)	2 075(2)
C(13)	1 950(2)	3 592(4)	2 363(2)
C(14)	2 166(2)	4 614(4)	3 141(2)
C(15)	2 165(2)	3 730(4)	3 883(2)
C(16)	1 307(2)	2 900(4)	3 599(2)
C(21)	−243(1)	−656(3)	1 436(1)
C(22)	−1 102(2)	−1 502(4)	1 009(2)
C(23)	−1 252(2)	−2 338(4)	175(2)
C(24)	−512(2)	−3 408(3)	337(2)
C(25)	343(2)	−2 568(4)	749(2)
C(26)	493(2)	−1 736(4)	1 582(2)

* Invariant parameter.

Table 8. Fractional atomic co-ordinates (× 10^4) for $Ru(C_6H_{11})_4$

Atom	*x*	*y*	*z*
Ru(1)	0*	610(0.5)	2 500*
C(11)	1 088(2)	1 852(3)	2 825(2)
C(12)	1 079(2)	2 791(4)	2 076(2)
C(13)	1 933(2)	3 645(5)	2 353(3)
C(14)	2 166(2)	4 650(4)	3 147(3)
C(15)	2 189(2)	3 716(5)	3 895(2)
C(16)	1 333(2)	2 873(4)	3 623(2)
C(21)	−239(2)	−635(3)	1 425(2)
C(22)	−1 085(2)	−1 536(4)	1 038(2)
C(23)	−1 256(2)	−2 373(5)	192(2)
C(24)	−502(2)	−3 424(4)	337(2)
C(25)	338(3)	−2 525(5)	715(3)
C(26)	506(2)	−1 687(4)	1 556(2)

* Invariant parameter.

Table 9. Fractional atomic co-ordinates (× 10^4) for $Os(C_6H_{11})_4$

Atom	*x*	*y*	*z*
Os(1)	0*	609(1)	2 500*
C(11)	1 091(4)	1 849(8)	2 822(4)
C(12)	1 081(5)	2 803(10)	2 083(5)
C(13)	1 935(6)	3 654(11)	2 355(6)
C(14)	2 185(6)	4 664(10)	3 143(6)
C(15)	2 210(5)	3 713(11)	3 906(5)
C(16)	1 357(5)	2 866(10)	3 630(5)
C(21)	−239(4)	−635(8)	1 419(4)
C(22)	−1 085(5)	−1 561(11)	1 035(5)
C(23)	−1 257(6)	−2 392(12)	196(6)
C(24)	−510(6)	−3 419(9)	324(6)
C(25)	326(6)	−2 495(11)	683(6)
C(26)	502(5)	−1 685(11)	1 531(5)

* Invariant parameter.

X-*Ray Crystallography.*—Crystals used for the *X*-ray work were sealed under argon in thin-walled glass capillaries. All crystallographic measurements were made at 293 K using a Nonius CAD4 diffractometer and graphite-monochromated Mo-K_α radiation (λ = 0.710 69 Å), following previously detailed procedures.[39] The structures were solved *via* the heavy-atom method and refined by full-matrix least squares. For $Os(C_6M_4Me\text{-}o)_4$ and all the cyclohexyl complexes, non-hydrogen atoms were refined anisotropically and phenyl hydrogens, which were experimentally located on difference maps, isotropically. Hydrogens on the methyl of the *o*-tolyl ligand could not be located and were presumed disordered; therefore none of these was included. For $Os(C_6H_5)_4$ the refinement was rather unstable, probably due to the heavy-atom pseudosymmetry (the Os atoms define a body-centred lattice), and it was necessary to represent the phenyl groups with idealized C_6H_5 geometry (C–C = 1.395, C–H = 1.08 Å), with carbon atoms refined anisotropically and hydrogens with a common group isotropic *U* value. Details of the crystal data, data collection, and refinement are given in Table 4. Atomic co-ordinates are given in Tables 5—9. Computer programs and sources of scattering factor data are as previously indicated.[39]

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