Alkyl Compounds of Ruthenium-(III) and -(V) and Osmium(III). *X*-Ray Crystal Structures of Hexakis(trimethylsilylmethyl)- and Hexakis(neopentyl)-diruthenium(III), Dioxohexakis(trimethylsilylmethyl)diruthenium(V), and Bis-(η^3-allyl)tetrakis(neopentyl)diosmium(III)†

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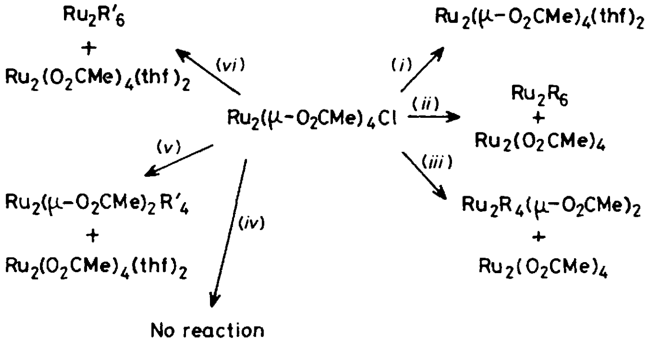
The interaction of MgRCl or MgR_2, R = CH_2SiMe_3 or CH_2CMe_3, with $Ru_2(\mu\text{-}O_2CMe)_4Cl$ or $Os_2(\mu\text{-}O_2CMe)_4Cl_2$ leads to the compounds M_2R_6 and $M_2R_4(\mu\text{-}O_2CMe)_2$; diruthenium(II) tetra-acetate, $Ru_2(\mu\text{-}O_2CMe)_4$, is formed in some of these alkylations. Interaction of $Ru_2R_4(\mu\text{-}O_2CMe)_2$ with $MgMe_2$ or $MgEt_2$ gives the corresponding mixed hexa-alkyls. Interaction of Ru_2R_6 with oxygen gives the unique ruthenium(V) oxoalkyls $R_3Ru(O)Ru(O)R_3$, while interaction of $Os_2(\mu\text{-}O_2CMe)_2(CH_2CMe_3)_4$ with allylmagnesium halide gives $Os(\eta^3\text{-}C_3H_5)_2(CH_2CMe_3)_4$. *X*-Ray crystal structures of the two diruthenium hexa-alkyls, the ruthenium oxoalkyl, and the diosmium tetra-alkylbis(allyl) have been determined. The ruthenium(V) oxo trimethylsilylmethyl has been shown to react stoicheiometrically with propene to give the epoxide. It also reacts with PhNCO and $Me_3SiN{=}PMe_3$ to give the respective ruthenium(V) imido complexes, $Ru_2(NR)_2(CH_2SiMe_3)_6$.

At the meeting of the Chemical Society in London on 21st March, 1907 at which the discovery of the first stable transition metal alkyl compound, $PtMe_3I$, was announced by Pope and Peachy[1] of the Municipal School of Technology in Manchester, the Chairman, Sir Henry Roscoe, complimented the authors in opening up an entirely new branch of investigation 'which might indeed be said to be a wonderful find.' It was to be another 40 years before the structure of $(PtMe_3Cl)_4$ was determined by Rundle and Sturdivant,[2] while the first platinum group metal with only hydrocarbon ligands, $Ru(\eta^5\text{-}C_5H_5)_2$,[3] was not synthesised until 12th February, 1952.

Until the present study[4] no neutral homoleptic alkyls or aryls of the platinum group metals were known. Unstable alkylate anions of palladium and platinum such as $[PtMe_6]^{2-}$ exist,[5] while much more stable perchlorinated aryl anions of Pt^{II} and Pt^{III}, $[Pt(C_6Cl_5)_4]^{1-,2-}$, have been characterised and shown by *X*-ray study to have square geometries.[6] More recently, the tetrahedral complexes $Os(cyclo\text{-}C_6H_{11})_4$, $Os(C_6H_4Me\text{-}o)_4$,[7] and $Ru(C_6H_4Me\text{-}o)_4$ have been structurally characterised.[8]

We now give details of work on the diruthenium(III) and diosmium(III) alkyls. Table 1 lists new compounds and analytical data.



Scheme 1. Interaction of $Ru_2(O_2CMe)_4Cl$ with Grignard or dialkylmagnesium reagents, R = CH_2SiMe_3, R′ = CH_2CMe_3, at −80°C with subsequent warming to room temperature before work up. (*i*) 4 or 6 equivalents MgRX in thf; (*ii*) as in (*i*) but in Et_2O; (*iii*) 4 equivalents MgRX in Et_2O; (*iv*) 4 or 6 equivalents MgR′X in Et_2O; (*v*) 4 equivalents MgR′X in thf; (*vi*) 6 equivalents MgR′X in thf

$$2Ru_2^{5+} \longrightarrow Ru_2^{6+} + Ru_2^{4+} \qquad (1)$$

Results and Discussion

Ruthenium Compounds.—The two alkyls Ru_2R_6, R = CH_2SiMe_3 and CH_2CMe_3, are obtained as air sensitive light petroleum soluble crystals by interaction of $Ru_2(\mu\text{-}O_2CMe)_4Cl$[9] with Grignard reagents or dialkylmagnesium. The reaction is quite complicated and the nature of the products depends upon the reaction conditions as shown in Scheme 1. Since $Ru_2^{III,III}$ species result from the $Ru_2^{II,III}$ starting material it appears that a disproportionation reaction (1) is involved. From the reaction of $Ru_2(\mu\text{-}O_2CMe)_4Cl$ with $Mg(CH_2SiMe_3)_2$ in tetrahydrofuran (thf) the reduced diruthenium(II) acetate, $Ru_2(\mu\text{-}O_2CMe)_4(thf)_2$, has been isolated[10] (this dimer is now best obtained from the blue reduced solutions of ruthenium chloride[11]). The alkylating agent could be acting here as a one-electron reducing agent, but a disproportionation seems more likely. Since the yield of $Ru_2(\mu\text{-}O_2CMe)_4(thf)_2$ is no more than 50% it must be assumed that any alkylated product formed simultaneously in a disproportionation is unstable. We have in fact shown that in tetrahydrofuran at 25 °C $Ru_2(CH_2SiMe_3)_6$ decomposes quite rapidly.

Alkylation in diethyl ether by $Mg(CH_2SiMe_3)_2$ or by $Mg(CH_2SiMe_3)Cl$ gives highly coloured solutions and when the solvent is removed and the residue extracted with light petroleum, Ru_2R_6 is obtained, while the brown residue on

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

Table 1. Properties and analytical data for ruthenium and osmium compounds

			Analysis[a]/%			
Compound	Colour	M.p./°C	C	H	O	Si
$Ru_2(CH_2CMe_3)_6$	Purple	137 (decomp.)	57.5	10.5		
			(57.3)	(10.5)		
$Ru_2(CH_2SiMe_3)_6$	Blue-green	124 (decomp.)	40.0	9.1		23.0
			(39.7)	(9.1)		(22.7)
$Ru_2(\mu\text{-}O_2CMe)_2(CH_2CMe_3)_4$	Red	143 (decomp.)	47.7	8.4	10.6	
			(47.7)	(8.3)	(9.4)	
$Ru_2(\mu\text{-}O_2CMe)_2(CH_2SiMe_3)_4$	Red	112	36.0	7.5	10.0	17.1
			(35.9)	(7.5)	(9.6)	(16.8)
$Ru_2Me_2(CH_2CMe_3)_4$	Purple	178 (decomp.)	51.4	9.4		
			(51.2)	(9.7)		
$Ru_2Et_2(CH_2CMe_3)_4$	Pink	103 (decomp.)	53.4	10.0		
			(52.9)	(9.9)		
$Ru_2O_2(CH_2SiMe_3)_6$	Deep red	112 (decomp.)	37.8	8.7	4.5	22.0
			(38.0)	(8.7)	(4.3)	(22.2)
$Ru_2O_2(CH_2CMe_3)_6$	Red	136 (decomp.)	55.0	9.8	5.3	
			(54.6)	(10.0)	(4.9)	
$Ru_2(NSiMe_3)_2(CH_2SiMe_3)_6$	Orange	185—188	48.0	8.3	3.0 (N)	
			(47.7)	(8.4)	(3.1)	
$Ru_2(NPh)_2(CH_2SiMe_3)_6$	Brown	198 (decomp.)	43.0	9.4	3.4 (N)	
			(40.1)	(9.4)	(3.1)	
$Os_2(\mu\text{-}O_2CMe)_2(CH_2CMe_3)_4$	Olive green	184	34.9	*b*	8.2	
			(34.8)		(8.4)	
$Os_2(\mu\text{-}O_2CMe)_2(CH_2SiMe_3)_4$	Red	132	28.0	*b*	7.8	13.1
			(28.3)		(7.6)	(13.2)
$Os_2(\eta^3\text{-}C_3H_5)_2(CH_2CMe_3)_4$	Orange	113 (decomp.)	41.7	*b*		
			(41.8)			

[a] Required values in parentheses. [b] Hydrogen analysis not feasible.

further extraction with tetrahydrofuran or acetonitrile (solv) yields the solvates, $Ru_2(\mu\text{-}O_2CMe)_4(solv)_2$, in approximately the same yield as Ru_2R_6 [equation (2)].

$$2Ru_2{}^{II,III}(\mu\text{-}O_2CMe)_4Cl \xrightarrow{MgR_2} Ru_2{}^{II}(\mu\text{-}O_2CMe)_4 + Ru_2{}^{III}R_6 \quad (2)$$

The reaction of $Ru_2(\mu\text{-}O_2CMe)_4$ with alkylating agents leads to decomposition.

The alkylation of $Ru_2(\mu\text{-}O_2CMe)_4Cl$ can be controlled to give the partially alkylated products $Ru_2R_4(\mu\text{-}O_2CMe)_2$. Thus interaction of 4 equivalents of MgRCl, R = CH_2SiMe_3 or CH_2CMe_3, with $Ru_2(O_2CMe)_4Cl$ in diethyl ether with shortened reaction times gives red crystalline, air sensitive products after removal of ether and extraction with hexane. The yields are only *ca.* 25% and crystals suitable for *X*-ray study could not be obtained; the similar osmium compounds also failed to give *X*-ray quality crystals. The compounds have been characterised by analysis and spectroscopy. Thus the neopentyl has bridged carboxylate i.r. stretches at 1 480 and 1 563 cm^{-1}, while the ^1H n.m.r. spectrum shows three sharp singlets at δ 2.69, 1.71, and 1.28 p.p.m., relative intensity 8:6:36, corresponding to Me_3CH_2, the acetate CH_3, and CMe_3 protons, respectively. The $^{13}C\text{-}\{^1H\}$ spectrum has five sharp singlets similar to those found for comparable rhenium bridged carboxylato alkyls,[12] the low field resonance at δ 185.7 p.p.m. being characteristic for the carboxylate carbon.

The tetra-alkyldiacetates can be readily alkylated not only with the same alkyl, CH_2SiMe_3 or CH_2CMe_3, which give the hexa-alkyls, but also with dimethylmagnesium, which, in the case of the neopentyl, leads to purple $Ru_2Me_2(CH_2CMe_3)_4$ in >80% yield. There are no acetate bands in the i.r. spectrum, and although the ^1H n.m.r. spectrum still has three sharp singlets with 8:6:36 ratio the chemical shifts are different and the $^{13}C\text{-}\{^1H\}$ spectrum does not have the characteristic carboxylate carbon peak but a new singlet at δ 18.6 p.p.m. for terminal methyl (in analogous compounds with bridging methyl groups the methyl resonances occur at much higher field, *ca.* δ −5.65 p.p.m.[13]).

Interaction of the acetato alkyl with an excess of methyllithium in diethyl ether–hexane at −80 °C initially gave a bright yellow solution, possibly containing a lithium alkylate anion, but this turns purple above *ca.* −50 °C to give the same purple solution and product as above.

Alkylation by $MgEt_2$ leads to a similar pinkish purple compound, $Ru_2Et_2(CH_2CMe_3)_4$, whose ^1H n.m.r. spectrum shows a triplet, δ 1.68 p.p.m. [J(H–H) = 4 Hz], and a quartet at δ 0.51 p.p.m. with a similar J value for the C_2H_5 group.

The Structure of Ru_2R_6.—The structures of both diruthenium hexa-alkyls, Ru_2R_6 (R = CH_2CMe_3 and CH_2SiMe_3), have been determined by single crystal *X*-ray methods. Diagrams of the molecules are given in Figures 1 and 2, selected bond lengths and angles in Tables 2 and 3. Not unexpectedly, the structures of the two molecules are analogous, with a nearly staggered ethane-like arrangement of the two RuR_3 fragments (the ranges of C–Ru–Ru–C torsion angles are 52.5—65.0 and 55.5—63.4° for R = CH_2CMe_3 and CH_2SiMe_3 respectively). Whereas the neopentyl has no rigorous crystallographic but approximate $\bar{1}$ symmetry, the trimethylsilylmethyl derivative lies on a crystallographic centre of symmetry. Whilst the Ru–C distances in the two molecules are very similar, the Ru–Ru formal triple bond in the trimethylsilylmethyl is significantly shorter than that in the neopentyl, but still not as short as might be expected when compared with the values obtained for $Ru_2{}^{5+}$ systems where the bond order is formally 2.5.[14] We now consider that these data imply a lengthening of the Ru≡Ru bond due to steric compression between the two bulky RuR_3 groups which is maximised in the case of the sterically most demanding neopentyl. Further analysis of this point is underway using the methods of molecular mechanics.[15]

Finally, it may be noted that the Ru_2R_6 species are similar to, but not isostructural with, $M_2(CH_2SiMe_3)_6$, M = Mo or W,[16] and the corresponding $M_2(NR_2)_6$[17] and $M_2(OR)_6$[18] species.

The Ru_2R_6 compounds are the only examples so far of species with unsupported $Ru{\equiv}Ru$ triple bonds containing the Ru_2^{6+} core. The only other compound $[Ru_2L_2]^{2+}$, L = a dibenzotetra-aza[14]annulene dianion ($C_{22}H_{22}N_4^{2-}$), has not been fully characterised,[19] although a bridged ruthenium(III) species with a Ru–Ru bond, $Ru_2Ph_2(PhCONH)_2[NC(Ph)OPPh_2]_2$, has been reported.[20]

Reactions of Diruthenium Hexa-alkyls.—Detailed study of the chemistry of these alkyls has been hindered by the overall limited yields from ruthenium trichloride starting material. The CH_2SiMe_3 compound is generally more reactive than the neopentyl.

The compound $Ru_2(CH_2SiMe_3)_6$ does not react with dimethylamine, and addition to a hexane solution of methanol, ethanol, or propanol causes rapid decomposition; no evidence for alkoxides, $Ru_2(OR')_6$, was obtained. Interaction with phenol gives a deep red solution and after removal of solvent and excess of phenol an air sensitive brown powder which we have been unable to purify. There is no reaction with ethylene even at *ca.* 100 °C under pressure or under irradiation, nor with CH_2N_2. Hydrogen at 1 atm (101 325 Pa) rapidly causes hydrogenolysis giving alkane and metallic ruthenium. Carbon monoxide reacts rapidly with both the trimethylsilylmethyl and neopentyl and there are clearly several intermediate species but no pure products have as yet been isolated. The alkyls also react with Bu^tNC, Ph_2C_2, and NO but again pure products have not

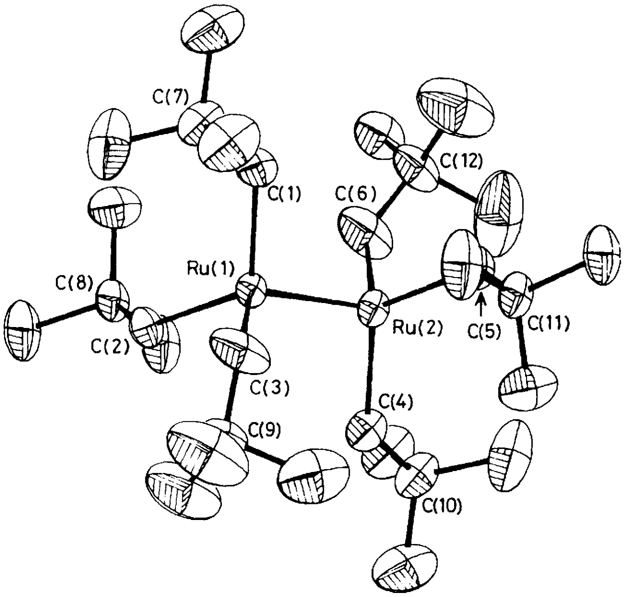


Figure 1. The molecular structure of hexakis(neopentyl)diruthenium(III)

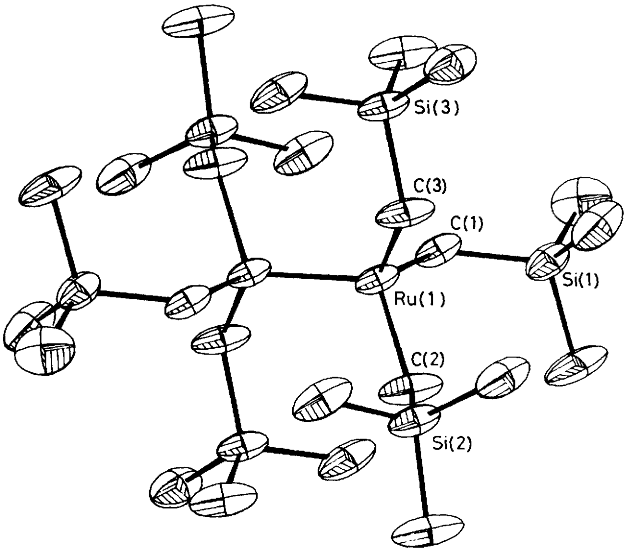


Figure 2. The molecular structure of hexakis(trimethylsilylmethyl)diruthenium(III)

Table 2. Bond lengths (Å) and angles (°) for $Ru_2(CH_2CMe_3)_6$

Ru(2)–Ru(1)	2.311(3)	C(1)–Ru(1)	2.033(7)	C(15)–C(7)	1.547(11)	C(16)–C(8)	1.526(11)
C(2)–Ru(1)	2.033(8)	C(3)–Ru(1)	2.943(8)	C(17)–C(8)	1.518(10)	C(18)–C(8)	1.531(11)
C(4)–Ru(2)	2.031(8)	C(5)–Ru(2)	2.021(8)	C(19)–C(9)	1.411(11)	C(20)–C(9)	1.427(11)
C(6)–Ru(2)	2.052(8)			C(21)–C(9)	1.569(16)	C(22)–C(10)	1.533(12)
				C(23)–C(10)	1.517(10)	C(24)–C(10)	1.520(11)
C(7)–C(1)	1.523(11)	C(8)–C(2)	1.538(9)	C(25)–C(11)	1.529(11)	C(26)–C(11)	1.520(11)
C(9)–C(3)	1.478(9)	C(10)–C(4)	1.524(10)	C(27)–C(11)	1.525(11)	C(28)–C(12)	1.399(12)
C(11)–C(5)	1.541(9)	C(12)–C(6)	1.443(10)	C(29)–C(12)	1.576(14)	C(30)–C(12)	1.517(10)
C(13)–C(7)	1.530(11)	C(14)–C(7)	1.515(13)				
C(1)–Ru(1)–Ru(2)	101.8(3)	C(2)–Ru(1)–Ru(2)	114.4(3)	C(17)–C(8)–C(16)	109.7(7)	C(18)–C(8)–C(2)	110.0(6)
C(2)–Ru(1)–C(1)	115.4(3)	C(3)–Ru(1)–Ru(2)	117.5(4)	C(18)–C(8)–C(16)	107.0(6)	C(18)–C(8)–C(3)	110.7(6)
C(3)–Ru(1)–C(1)	106.5(4)	C(3)–Ru(1)–C(2)	101.6(4)	C(19)–C(9)–C(3)	120.1(7)	C(20)–C(9)–C(3)	115.6(7)
				C(20)–C(9)–C(19)	116.5(8)	C(21)–C(9)–C(3)	103.3(8)
C(4)–Ru(2)–Ru(1)	101.3(3)	C(5)–Ru(2)–Ru(1)	115.1(3)	C(21)–C(9)–C(19)	103.2(8)	C(21)–C(9)–C(20)	91.1(9)
C(5)–Ru(2)–C(4)	117.8(3)	C(6)–Ru(2)–Ru(1)	106.4(4)	C(22)–C(10)–C(4)	110.6(6)	C(23)–C(10)–C(4)	111.4(6)
C(6)–Ru(2)–C(4)	113.2(4)	C(6)–Ru(2)–C(5)	102.8(4)	C(23)–C(10)–C(22)	109.0(7)	C(24)–C(10)–C(4)	108.3(7)
				C(24)–C(10)–C(22)	108.5(7)	C(24)–C(10)–C(23)	109.0(6)
C(7)–C(1)–Ru(1)	125.3(5)	C(8)–C(2)–Ru(1)	129.5(5)	C(25)–C(11)–C(5)	107.7(7)	C(26)–C(11)–C(5)	111.8(6)
C(9)–C(3)–Ru(1)	133.4(5)	C(10)–C(4)–Ru(2)	126.6(5)	C(26)–C(11)–C(25)	107.5(7)	C(27)–C(11)–C(5)	110.5(6)
C(11)–C(5)–Ru(2)	128.6(5)	C(12)–C(6)–Ru(2)	135.6(5)	C(27)–C(11)–C(25)	107.7(7)	C(27)–C(11)–C(26)	111.4(7)
C(13)–C(7)–C(1)	110.8(7)	C(14)–C(7)–C(1)	112.4(4)	C(28)–C(12)–C(6)	122.6(8)	C(29)–C(12)–C(6)	104.0(8)
C(14)–C(7)–C(13)	110.0(8)	C(15)–C(7)–C(1)	107.5(7)	C(29)–C(12)–C(28)	95.9(9)	C(30)–C(12)–C(6)	111.9(7)
C(15)–C(7)–C(13)	107.2(7)	C(15)–C(7)–C(14)	108.9(7)	C(30)–C(12)–C(28)	114.1(7)	C(30)–C(12)–C(29)	104.4(7)
C(16)–C(8)–C(2)	107.1(6)	C(17)–C(8)–C(2)	112.2(6)				

Table 3. Bond lengths (Å) and angles (°) for Ru$_2$(CH$_2$SiMe$_3$)$_6$

C(1)–Ru(1)	2.021(5)	C(2)–Ru(1)	2.036(5)
C(3)–Ru(1)	2.036(5)	Ru(1)–Ru(1a)	2.265(3)
C(1)–Si(1)	1.870(5)	C(11)–Si(1)	1.872(6)
C(12)–Si(1)	1.869(6)	C(13)–Si(1)	1.867(6)
C(2)–Si(2)	1.871(5)	C(21)–Si(2)	1.869(5)
C(22)–Si(2)	1.874(6)	C(23)–Si(2)	1.880(6)
C(3)–Si(3)	1.869(5)	C(31)–Si(3)	1.865(6)
C(32)–Si(3)	1.878(6)	C(33)–Si(3)	1.880(6)
C(2)–Ru(1)–C(1)	108.6(2)	C(3)–Ru(1)–C(1)	112.8(2)
C(3)–Ru(1)–C(2)	103.5(2)	C(1)–Ru(1)–Ru(1)	106.6(3)
C(2)–Ru(1)–Ru(1a)	112.3(2)	C(3)–Ru(1)–Ru(1)	113.1(2)
Si(1)–C(1)–Ru(1)	121.8(3)	Si(2)–C(2)–Ru(1)	124.7(3)
Si(3)–C(3)–Ru(1)	125.2(3)		
C(11)–Si(1)–C(1)	106.5(3)	C(12)–Si(1)–C(1)	110.9(3)
C(12)–Si(1)–C(11)	108.6(3)	C(13)–Si(1)–C(1)	112.2(3)
C(13)–Si(1)–C(11)	109.5(3)	C(13)–Si(1)–C(12)	109.0(3)
C(21)–Si(2)–C(2)	110.3(3)	C(22)–Si(2)–C(2)	113.9(3)
C(22)–Si(2)–C(21)	109.8(3)	C(23)–Si(2)–C(2)	107.7(3)
C(23)–Si(2)–C(21)	107.7(3)	C(23)–Si(2)–C(22)	107.2(3)
C(31)–Si(3)–C(3)	108.8(3)	C(32)–Si(3)–C(3)	112.7(3)
C(32)–Si(3)–C(31)	111.6(3)	C(33)–Si(3)–C(3)	108.4(3)
C(33)–Si(3)–C(31)	107.5(3)	C(33)–Si(3)–C(32)	107.7(3)

Key to symmetry operations relating designated atoms to reference atoms at x, y, z: (a) $-x$, $-y$, $-z$.

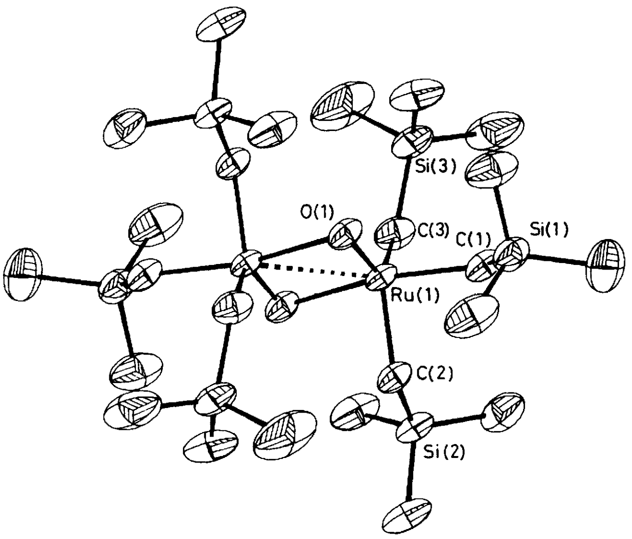


Figure 3. The molecular structure of dioxohexakis(trimethylsilylmethyl)diruthenium(v)

been isolated. Excess of trimethylphosphine in hexane at −30 °C causes metal–metal bond cleavage and gives in >60% yield (2,2-dimethyl-2-silapropane-1,3-diyl)tetrakis(trimethylphosphine)ruthenium(II), Ru(CH$_2$SiMe$_2$CH$_2$)(PMe$_3$)$_4$, identical to that previously obtained[21] by reaction of Mg(CH$_2$SiMe$_3$)$_2$ with Ru$_2$(O$_2$CMe)$_4$Cl in the presence of PMe$_3$. The mechanism of these reactions is not clear. A similar cleavage occurs with 1,2-bis(dimethylphosphino)ethane (dmpe) to give yellow needles characterised by n.m.r. as Ru(CH$_2$SiMe$_2$CH$_2$)(dmpe)$_2$: ^{31}P-{^{1}H}; two triplets δ 13.0 [J(P–P) = 14] and 21.0 p.p.m. [J(P–P) = 15 Hz]; ^{1}H, similar to that of the PMe$_3$ compound for the (CH$_2$)$_2$SiMe$_2$ moiety.

Table 4. Bond lengths (Å) and angles (°) for Ru$_2$O$_2$(CH$_2$SiMe$_3$)$_6$

O(1)–Ru(1)	1.733(6)	C(1)–Ru(1)	2.071(8)
C(2)–Ru(1)	2.031(8)	C(3)–Ru(1)	2.027(8)
Ru(1)–Ru(1a)	2.738(4)	O(1)–Ru(1a)	2.208(6)
C(1)–Si(1)	1.869(8)	C(11)–Si(1)	1.871(9)
C(12)–Si(1)	1.862(9)	C(13)–Si(1)	1.876(9)
C(2)–Si(2)	1.876(8)	C(21)–Si(2)	1.860(9)
C(22)–Si(2)	1.876(8)	C(23)–Si(2)	1.865(8)
C(3)–Si(3)	1.880(8)	C(31)–Si(3)	1.852(9)
C(32)–Si(3)	1.863(9)	C(33)–Si(3)	1.858(10)
C(1)–Ru(1)–O(1)	101.8(3)	C(2)–Ru(1)–O(1)	118.5(3)
C(2)–Ru(1)–C(1)	88.3(3)	C(3)–Ru(1)–O(1)	120.7(3)
C(3)–Ru(1)–C(1)	89.2(4)	C(3)–Ru(1)–C(2)	119.9(4)
C(1)–Ru(1)–Ru(1a)	155.5(4)	C(2)–Ru(1)–Ru(1a)	102.1(4)
C(3)–Ru(1)–Ru(1a)	104.4(4)	O(1)–Ru(1)–O(1a)	92.9(4)
C(1)–Ru(1)–O(1a)	165.2(5)	C(2)–Ru(1)–O(1a)	83.3(4)
C(3)–Ru(1)–O(1a)	84.6(4)		
Si(1)–C(1)–Ru(1)	118.5(4)	Si(3)–C(3)–Ru(1)	122.5(4)
Si(2)–C(2)–Ru(1)	118.9(4)	Ru(1)–O(1)–Ru(1a)	87.1(4)
C(11)–Si(1)–C(1)	112.6(4)	C(12)–Si(1)–C(1)	112.2(4)
C(12)–Si(1)–C(11)	107.8(5)	C(13)–Si(1)–C(1)	106.1(5)
C(13)–Si(1)–C(11)	109.5(5)	C(13)–Si(1)–C(12)	108.5(5)
C(21)–Si(2)–C(2)	112.6(4)	C(22)–Si(2)–C(2)	105.2(4)
C(22)–Si(2)–C(21)	108.9(4)	C(23)–Si(2)–C(2)	111.4(4)
C(23)–Si(2)–C(21)	109.5(5)	C(23)–Si(2)–C(22)	109.1(4)
C(31)–Si(3)–C(3)	115.0(4)	C(32)–Si(3)–C(3)	108.8(4)
C(32)–Si(3)–C(31)	107.4(5)	C(33)–Si(3)–C(3)	106.8(4)
C(33)–Si(3)–C(31)	108.1(5)	C(33)–Si(3)–C(32)	110.7(6)

Key to symmetry operations relating designated atoms to reference atoms at x, y, z: (a) 1.0 $-x$, 1.0 $-y$, 1.0 $-z$.

The most interesting reaction of the alkyls, however, is that with oxygen which we now consider.

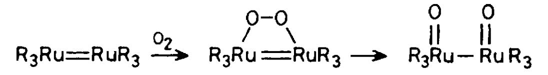
Ru$_2$(CH$_2$SiMe$_3$)$_6$ *with dioxygen*. Although the ruthenium alkyls are sensitive both to dry air and to moisture, and Ru$_2$(CH$_2$SiMe$_3$)$_6$ is pyrophoric in the solid state and decomposes very rapidly with air in solution, very careful oxygenation at −80 °C shows that the greenish solution turns red. A red crystalline compound, isolated in moderate yields, is confirmed as (RuOR$_3$)$_2$ by analysis and cryoscopic molecular weight in benzene; there is a new i.r. band at 908 cm^{-1} assignable as the Ru=O stretch. The ^{1}H n.m.r. spectrum still shows two singlets similar to those of the parent but much broadened, while the ^{13}C-{^{1}H} spectrum shows two sharp singlets shifted downfield with respect to the bands of Ru$_2$R$_6$, possibly reflecting the deshielding nature of the oxo ligands.[22]

The structure was determined by *X*-ray diffraction and a diagram of the centrosymmetric molecule is shown in Figure 3. Selected bond lengths and angles are given in Table 4. The molecule can be considered to comprise two RuO$_2$C$_3$ trigonal bipyramids in which the equator is formed from one oxo oxygen atom and two alkyl carbons (all three interbond angles are 120 ± 2°), linked *via* oxygen bridges between one axial and one equatorial site. A very similar asymmetric mode of bridging has been found in the '18-electron' osmium(v) complex, (cyclohexane-1,2-diolato)dioxo(quinuclidine)osmium,[23] in which the di-μ-oxo bridge [Os=O 1.78(1)Å, Os···O 2.22(1) Å] is between two sites on each of two OsO$_5$N octahedra.

In the present case, the ruthenium oxidation state is v and if the alkyl and oxo groups are considered to be one- and four-electron donors respectively, and the weak O···Ru link a two-electron donation, then the metal centre has formally 17 electrons. The diamagnetism of the complex results from the single Ru-Ru link in contrast to the osmium complex which dimerises only *via* oxygen bridging. The Ru–Ru bond length (2.738 Å) falls in the range typical for Ru–Ru single bonds, *e.g.* that in $Ru_4(NO)_4Cl_4(PPh_2)_4$ of 2.787 Å.[24]

The oxo compound is unusual not only in being a unique metal–metal bridged oxoruthenium(v) species (the M_2^{10+} core is not known for other platinum group metals) but in being formed by cleavage of molecular oxygen, presumably *via* an initial bridged peroxo species (Scheme 2). The compound is also formed essentially quantitatively in an instantaneous reaction of Ru_2R_6 with nitrosobenzene in toluene at −80 °C [equation (3)]. We assume that coupling of phenylnitrene to give the other product, azobenzene, is intramolecular.

$$Ru_2R_6 + 2PhNO \longrightarrow Ru_2O_2R_6 + PhN{=}NPh \qquad (3)$$



$$R_3Ru{=}RuR_3 \xrightarrow{O_2} R_3\overset{O-O}{Ru{=}Ru}R_3 \longrightarrow R_3\overset{O}{\overset{\|}{Ru}}-\overset{O}{\overset{\|}{Ru}}R_3$$

Scheme 2.

Although $Ru_2O_2(CH_2CMe_3)_6$ cannot be obtained by direct interaction of oxygen on the alkyl due to further reaction, it can be obtained in moderate yield using nitrosobenzene as dark orange-red crystals whose spectroscopic properties [ν(Ru=O) 926 cm^{-1}] are similar to those of the trimethylsilylmethyl.

It is possible to follow by n.m.r. spectroscopy the interaction of $Ru_2O_2(CH_2SiMe_3)_6$ in C_6D_6 with propene (^1H: doublet, δ 4.95; broad multiplet, δ 5.65 p.p.m.). There is no apparent reaction at +6 °C but at 10 °C in *ca.* 5 min the spectra of $Ru_2O_2R_6$, Ru_2R_6, and propene oxide (^1H: doublet, δ 1.3; multiplet, δ 3; and two symetrical multiplets, centred at δ 2.5 p.p.m.) are visible; after *ca.* 10 min decomposition occurs giving a black precipitate.

The reaction can be carried out on a larger scale when Ru_2R_6 is added to propene in hexane at −40 °C. After stirring for *ca.* 5 min at −30 °C the red solution became a dichroic reddish green; aliquots were taken during the reaction for i.r. study in solution cells. The C=C stretch of propene (1 670 cm^{-1}) disappears and is replaced by epoxide bands at 1 260 and 950 cm^{-1}. Quenching of the reaction by addition of aqueous tetrahydrofuran and fractionation of the black reaction mixture (collection of the 35—36 °C fraction) confirmed the presence of propene oxide. If the solutions containing the epoxide and alkyl are allowed to stand oxidative decomposition occurs.

The oxo alkyl reacts rapidly with excess of phenyl isocyanate[25] in hexane at −30 °C to give CO_2 and a rather low yield of the phenylimido compound $Ru_2(NPh)_2(CH_2SiMe_3)_6$. This is air sensitive, and insoluble in hexane but moderately soluble in toluene; it decomposes in acetone or thf. The i.r. spectrum has a new strong band at 1 132 cm^{-1} in the characteristic region for arylimido compounds.[26] A similar reaction with the phosphinimine, $Me_3P{=}NSiMe_3$ (phosphinimines are known to react with M=O to give M=NR[27]), in hexane over 24 h gives PMe_3O and $Ru_2(NSiMe_3)_2(CH_2SiMe_3)_6$ as air sensitive orange crystals with ν(RuN) at 1 160 cm^{-1}.

Osmium Compounds.—For osmium, unlike ruthenium, the $Os_2^{III,III}$ acetate chloride, $Os_2(\mu\text{-}O_2CMe)_4Cl_2$, is known[28] but alkylation yields only the acetato bridged species $Os_2R_4(\mu\text{-}O_2CMe)_2$ even when large excesses of Grignard or MgR_2 are used; excesses lead only to more rapid reaction. This behaviour is similar to that observed in alkylation reactions of $Re_2(\mu\text{-}O_2CMe)_4Cl_2$[12] where the last two acetate bridges cannot be removed.

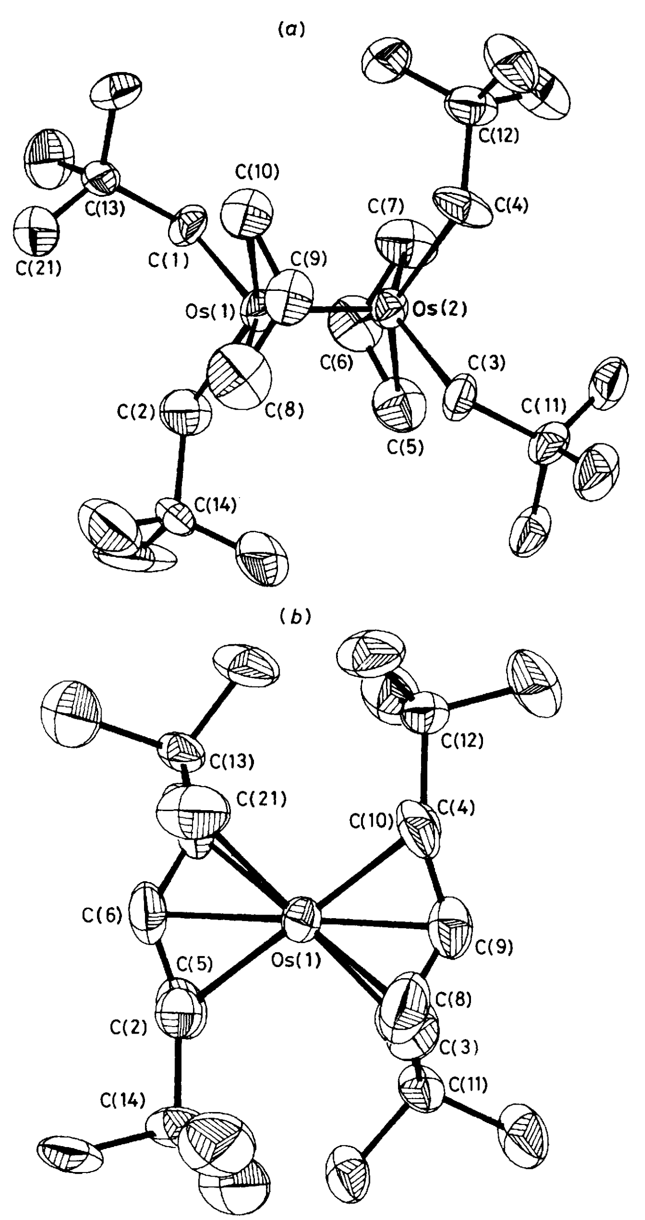


Figure 4. (*a*) The molecular structure of bis(η^3-allyl)tetrakis(neopentyl)diosmium(III). (*b*) View of the molecule along the Os–Os axis

Action of methyl, ethyl, or benzyl Grignard or alkyl-lithium reagents, on $Os_2R_4(O_2CMe)_2$ leads to decomposition in all cases where reaction occurred. The only success in removing the two bridging acetate groups was achieved by using allyl Grignard, probably since the allyl ligand can act as a three-electron η^3 ligand, like acetate; however, the use of *o*-methoxyphenyl Grignard again led to failure despite its potential for acting as a three-electron ligand.

Although we have been unable to obtain adequate crystals for structural determinations on the acetate bridged osmium species due to twinning, the spectroscopic data are adequate to characterise them.

X-Ray study of $Os_2(\eta^3\text{-}C_3H_5)_2(CH_2CMe_3)_4$ shows that the crystal structure contains two symmetry independent molecules; one is sited across a crystallographic centre of symmetry whilst the other lies in a general position. The molecular structures are very similar however and differ only in orientations of the CMe_3 groups. A diagram of the general position molecule is given in Figure 4 (*a*); selected bond lengths and angles for both are given in Table 5. The main point of interest in this structure is that whilst the Os–C(alkyl) distances are some 0.1 Å larger than the

Table 5. Bond lengths (Å) and angles (°) for $Os_2(\eta^3\text{-}C_3H_5)_2(CH_2CMe_3)_4$

Os(2)–Os(1)	2.194(3)	C(1)–Os(1)	2.145(18)	C(29)–C(12)	1.462(26)	C(21)–C(13)	1.486(24)
C(2)–Os(1)	2.145(20)	C(8)–Os(1)	2.211(19)	C(22)–C(13)	1.547(33)	C(23)–C(13)	1.493(25)
C(9)–Os(1)	2.123(18)	C(10)–Os(2)	2.223(19)	C(24)–C(14)	1.499(36)	C(25)–C(14)	1.530(29)
C(3)–Os(2)	2.195(17)	C(4)–Os(2)	2.147(21)	C(26)–C(14)	1.473(29)	C(27)–Os(3)	2.144(15)
C(5)–Os(2)	2.228(20)	C(6)–Os(2)	2.153(18)	C(28)–Os(3)	2.159(16)	C(29)–Os(3)	2.219(17)
C(7)–Os(2)	2.230(18)	C(13)–C(1)	1.545(23)	C(30)–Os(3)	2.126(14)	C(31)–Os(3)	2.230(17)
C(14)–C(2)	1.603(25)	C(11)–C(3)	1.563(23)	Os(3)–Os(3a)	2.199(3)	C(32)–C(27)	1.540(25)
C(12)–C(4)	1.591(24)	C(6)–C(5)	1.454(27)	C(33)–C(28)	1.520(24)	C(30)–C(29)	1.454(24)
C(7)–C(6)	1.437(28)	C(9)–C(8)	1.466(30)	C(31)–C(30)	1.452(23)	C(34)–C(32)	1.550(24)
C(10)–C(9)	1.486(27)	C(15)–C(11)	1.520(27)	C(35)–C(32)	1.516(24)	C(36)–C(32)	1.542(31)
C(16)–C(11)	1.551(31)	C(17)–C(11)	1.527(25)	C(37)–C(33)	1.549(25)	C(38)–C(33)	1.508(24)
C(18)–C(12)	1.460(29)	C(19)–C(12)	1.526(35)	C(39)–C(33)	1.528(29)		

C(1)–Os(1)–Os(2)	97.6(5)	C(2)–Os(1)–Os(2)	102.8(5)	C(22)–C(13)–C(21)	105.5(17)	C(23)–C(13)–C(1)	111.6(16)
C(2)–Os(1)–C(1)	82.5(7)	C(8)–Os(1)–Os(2)	123.2(7)	C(23)–C(13)–C(21)	110.4(16)	C(23)–C(13)–C(22)	107.6(15)
C(8)–Os(1)–C(1)	138.8(7)	C(8)–Os(1)–C(2)	92.1(8)	C(24)–C(14)–C(2)	107.0(17)	C(25)–C(14)–C(2)	110.3(15)
C(9)–Os(1)–Os(2)	104.8(6)	C(9)–Os(1)–C(1)	131.0(7)	C(25)–C(14)–C(24)	106.2(18)	C(26)–C(14)–C(2)	112.9(16)
C(9)–Os(1)–C(2)	131.6(6)	C(10)–Os(1)–Os(2)	114.8(6)	C(26)–C(14)–C(24)	110.5(18)	C(26)–C(14)–C(25)	109.7(19)
C(10)–Os(1)–C(1)	91.2(7)	C(10)–Os(1)–C(2)	142.3(6)	C(11)–C(3)–Os(2)	120.3(11)	C(12)–C(4)–Os(2)	128.9(15)
C(3)–Os(2)–Os(1)	96.8(5)	C(4)–Os(2)–Os(1)	103.3(5)				
C(4)–Os(2)–C(3)	83.7(7)	C(5)–Os(2)–Os(1)	114.4(6)	C(27)–Os(3)–Os(3a)	97.10(6)	C(28)–Os(3)–Os(3a)	102.92(5)
C(5)–Os(2)–C(3)	92.8(7)	C(5)–Os(2)–C(4)	142.3(6)	C(29)–Os(3)–Os(3a)	122.66(7)	C(30)–Os(3)–Os(3a)	104.21(5)
C(6)–Os(2)–Os(1)	103.9(5)	C(6)–Os(2)–C(3)	131.5(6)	C(31)–Os(3)–Os(3a)	112.92(6)		
C(6)–Os(2)–C(4)	131.2(6)	C(7)–Os(2)–Os(1)	121.2(6)				
C(7)–Os(2)–C(3)	141.4(6)	C(7)–Os(2)–C(4)	93.0(8)	C(28)–Os(3)–C(27)	82.6(6)	C(29)–Os(3)–C(27)	139.5(6)
C(13)–C(1)–Os(1)	122.8(12)	C(14)–C(2)–Os(1)	129.8(14)	C(29)–Os(3)–C(28)	93.5(7)	C(30)–Os(3)–C(27)	130.8(6)
C(11)–C(3)–Os(2)	120.3(11)	C(12)–C(14)–Os(2)	128.9(14)	C(30)–Os(3)–C(28)	132.5(7)	C(31)–Os(3)–C(27)	92.0(6)
C(7)–C(6)–C(5)	116.7(17)	C(10)–C(9)–C(8)	115.9(18)	C(31)–Os(3)–C(28)	144.1(6)	C(32)–C(27)–Os(3)	121.9(11)
C(15)–C(11)–C(3)	109.0(16)	C(16)–C(11)–C(3)	106.7(14)	C(33)–C(28)–Os(3)	130.4(9)	C(31)–C(30)–C(29)	118.0(14)
C(16)–C(11)–C(15)	106.9(14)	C(17)–C(11)–C(3)	113.3(14)	C(34)–C(32)–C(27)	111.8(15)	C(35)–C(32)–C(27)	109.3(14)
C(17)–C(11)–C(15)	110.1(15)	C(17)–C(11)–C(16)	110.5(17)	C(35)–C(32)–C(34)	106.3(13)	C(36)–C(32)–C(27)	113.9(14)
C(28)–C(12)–C(4)	115.6(18)	C(19)–C(12)–C(4)	105.1(16)	C(36)–C(32)–C(34)	111.5(15)	C(36)–C(32)–C(35)	103.5(16)
C(19)–C(12)–C(18)	108.9(17)	C(20)–C(12)–C(4)	109.0(14)	C(37)–C(33)–C(28)	114.8(16)	C(38)–C(33)–C(28)	108.6(13)
C(20)–C(12)–C(18)	111.6(18)	C(20)–C(12)–C(19)	106.0(19)	C(38)–C(33)–C(37)	108.2(14)	C(39)–C(33)–C(28)	110.6(14)
C(21)–C(13)–C(1)	114.0(14)	C(22)–C(13)–C(1)	107.3(15)	C(39)–C(33)–C(37)	118.8(15)	C(39)–C(33)–C(38)	105.4(16)

Key to symmetry operations relating designated atoms to reference atoms at *x*, *y*, *x*: (a) 1.0 $-x$, 1.0 $-y$, 1.0 $-z$.

Ru–C(alkyl) distances in the structures described earlier, the Os–Os distance is some 0.2 Å shorter than the Ru–Ru distances. Again, we feel that this could be a reflection of the reduction in steric compression or substitution of two bulky CH_2CMe_3 groups by the allyl groups, although of course the electronic situation is also different since the allyl is acting as a three-electron donor. In particular, we may consider that the η^3-allyl group is occupying two co-ordination sites so that the Ru atoms are now 'equatorially' four-co-ordinate and adopting a mutually eclipsed orientation, Figure 4(*b*), so that the M–M bonding orbitals have maximised overlap.

The ^1H n.m.r. spectrum is as expected for a η^3-alkyl with three sets of signals, a multiplet centred at δ 3.99 p.p.m. due to the central proton, two doublets at δ 3.27 [*J*(H–H) = 4] and 1.50 p.p.m. [*J*(H–H) = 4 Hz] due to *exo* and *endo* protons, with the ^{13}C-{^1H} spectra having only two sharp singlets at δ 102 and 46 p.p.m.

Apart from the anion $[Os_2Cl_8]^{2-}$, which was reported[29] after our studies were complete, this compound is the only one with an Os≡Os triple bond and an Os_2^{6+} core. It may be noted that both these compounds have very short bonds, 2.197 Å in the alkyl as compared to *ca.* 2.30 Å in the carboxylates and 2.195 Å in $[Os_2Cl_8]^{2-}$. This short distance may be connected with the eclipsed geometry adopted by the ligands which is found in both compounds. Steric repulsion in triply bonded complexes normally leads to a staggered conformation as in $W_2(CH_2SiMe_3)_6$. For bond orders of 3.5 or 4, electronic factors dominate and there is a δ bonding component, which unlike σ or π orbitals does not possess cylindrical symmetry and whose strength is highly sensitive to rotation above the metal–metal bond. The eclipsed conformation in the alkyl seems to indicate that steric influences are not determining (although these probably cause the *trans* disposition of bulky neopentyl groups) and implies a greater electronic contribution in triply bonded species than has been assumed.

Experimental

Microanalyses were by Pascher, Bonn. Spectrometers employed were: i.r., Perkin-Elmer 683, Nujol mulls; n.m.r., JEOL FX90Q and Bruker WM-250, in C_6D_6 or $C_6D_5CD_3$ referenced to $SiMe_4$.

General.—Solvents were purified by standard methods and distilled under argon before use. The light petroleum had b.p. 40—60 °C. All operations were carried out under argon or in vacuum. Infrared bands are given in the text where there are special features; all of the compounds gave the usual CH_2SiMe_3 or CH_2CMe_3 peaks.

In the reactions in Scheme 1 and below, $Ru_2(O_2CMe)_4$ was obtained after removal of solvent and extraction of the alkyls with light petroleum as an insoluble residue. The tetrahydrofuran or acetonitrile adducts could be crystallised but both readily lose solvent in vacuum; good analytical data could be obtained only on the unsolvated $Ru_2(O_2CMe)_4$ (see ref. 11).

In all of the reactions either the Grignard or the dialkylmagnesium can be used.

Table 6. Crystal data, intensity data, collection parameters, and details of refinement*

Crystal data	$Ru_2(CH_2CMe_3)_6$	$Ru_2(CH_2SiMe_3)_6$	$Ru_2O_2(CH_2SiMe_3)_6$	$Os_2(\eta^3\text{-}C_3H_5)_2(CH_2CMe_3)_4$
M	628.028	725.508	757.508	747.092
a/Å	20.013(4)	10.299(1)	11.397(5)	11.547(2)
b/Å	9.848(10)	12.152(2)	16.184(4)	19.239(3)
c/Å	9.757(4)	9.717(1)	12.156(6)	19.949(3)
α/°	117.83(5)	97.28(1)	90	90
β/°	86.89(5)	110.24(1)	115.20(3)	105.05(2)
γ/°	97.82(5)	113.67(1)	90	90
U/Å^3	1 684.66	993.817	2 028.77	4 279.703
System	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P2_1/c$
D_c/g cm^{-3}	1.24	1.21	1.24	1.74
Z	2	1	2	6
F(000)	668	382	796	2 172
μ/cm^{-1}	8.93	9.34	9.21	89.14
Data collection				
θ/° (min., max.)	1.5, 25	1.5, 25	1.5, 25	1.5, 25
T/K	270	255	r.t.	r.t.
Total data				
measured	7 577	3 652	4 069	8 471
unique	6 317	3 502	3 573	7 537
observed	4 715	2 929	2 726	3 929
Significant test	$F_o > 3\sigma(F_o)$	$F_o > 4\sigma(F_o)$	$F_o > 4\sigma(F_o)$	$F_o > 4\sigma(F_o)$
Refinement				
No. of parameters	351	199	208	482
Absorption correction	ψ-scan	ψ-scan/DIFABS	ψ-scan/DIFABS	ψ-scan/DIFABS
Weighting scheme	unit	$1/[\sigma^2(F_0) + 0.0001F_o^2]$	$1/[\sigma^2(F_0) + 0.0001F_o^2]$	$1/[\sigma^2(F_0) + 0.000\,01F_o^2]$
R =	0.0428	0.0281	0.0456	0.0448
R' =	0.0481	0.0320	0.0548	0.0398

* r.t. = Room temperature.

Table 7. Fractional co-ordinates (× 10^4) for $Ru_2(CH_2CMe_3)_6$

Atom	x	y	z
Ru(1)	1 912(0.5)	2 313(1)	2 099(1)
Ru(2)	3 049(0.5)	3 019(1)	1 905(1)
C(1)	1 845(3)	2 714(7)	4 340(6)
C(2)	1 292(3)	3 415(6)	1 484(7)
C(3)	1 537(5)	47(7)	769(8)
C(4)	3 106(3)	2 644(7)	−326(7)
C(5)	3 675(3)	2 002(6)	2 594(7)
C(6)	3 250(5)	5 312(7)	3 488(9)
C(7)	1 240(4)	2 156(7)	5 044(7)
C(8)	1 265(3)	5 159(6)	2 117(7)
C(9)	1 373(4)	−902(7)	−899(7)
C(10)	3 682(4)	3 268(7)	−1 046(7)
C(11)	3 734(3)	267(6)	1 945(7)
C(12)	3 717(4)	6 208(7)	4 765(8)
C(13)	1 212(5)	425(8)	4 533(9)
C(14)	580(4)	2 490(10)	4 647(9)
C(15)	1 340(5)	3 015(9)	6 824(8)
C(16)	604(4)	5 333(8)	1 542(9)
C(17)	1 293(4)	6 019(7)	3 874(7)
C(18)	1 837(4)	5 846(7)	1 431(8)
C(19)	1 239(7)	−184(10)	−1 796(9)
C(20)	1 021(7)	−2 408(10)	−1 337(10)
C(21)	2 043(7)	−1 600(12)	−1 606(12)
C(22)	4 361(4)	2 956(9)	−673(9)
C(23)	3 697(4)	4 995(7)	−467(8)
C(24)	3 580(5)	2 437(9)	−2 795(8)
C(25)	4 354(4)	126(8)	2 698(9)
C(26)	3 840(5)	−511(8)	204(8)
C(27)	3 120(4)	−541(8)	2 385(9)
C(28)	3 866(7)	5 697(10)	5 819(10)
C(29)	4 430(5)	6 058(11)	3 975(13)
C(30)	3 655(4)	7 924(7)	5 500(8)

Ruthenium Compounds.—(*a*) *Hexakis*(*neopentyl*)*diruthenium*(III). To a suspension of $Ru_2(O_2CMe)_4Cl$ (1 g, 2.1 mmol) in thf (50 cm^3) held at −80 °C was added neopentylmagnesium chloride (36 cm^3 of a 0.35 mol dm^{-3} solution in Et_2O). The reaction mixture was allowed to warm slowly to room temperature, becoming deep red and apparently homogeneous at about −25 °C. After stirring for 18 h the volatile materials were removed under reduced pressure, and the residue extracted with hexane (2 × 25 cm^3), giving a purple solution. The combined extracts were reduced to *ca.* 20 cm^3 whereupon cooling to −20 °C overnight yielded purple crystals. Yield: 0.32 g, 24%. N.m.r.: ^{1}H, δ 2.81 (s, 12 H, CH_2CMe_3) and 1.15 (s, 54 H, CH_2CMe_3); ^{13}C-{^{1}H}, 51.70 (s, CH_2CMe_3), 33.10 (s, CH_2CMe_3), and 31.60 p.p.m. (s, CH_2CMe_3).

(*b*) *Hexakis*(*trimethylsilylmethyl*)*diruthenium*(III). To a suspension of $Ru_2(O_2CMe)_4Cl$ (1 g, 2.1 mmol) in Et_2O (50 cm^3) held at −80 °C was added $Mg(CH_2SiMe_3)Cl$ (17.26 cm^3 of a 0.73 mol dm^{-3} solution in Et_2O). The reaction mixture was allowed to warm slowly to room temperature becoming bright blue-green at about −20 °C. After stirring at room temperature (1 h or until all the starting material disappeared) the volatiles were removed under reduced pressure, the residue extracted

Table 8. Fractional atomic co-ordinates (× 10^4) for $Ru_2(CH_2SiMe_3)_6$

Atom	*x*	*y*	*z*
Ru(1)	392(0.5)	1 048(0.5)	358(0.5)
Si(1)	1 510(1)	3 196(1)	3 703(1)
Si(2)	−1 682(1)	1 931(1)	−2 518(1)
Si(3)	4 041(1)	2 067(1)	319(1)
C(1)	1 046(4)	1 589(3)	2 650(4)
C(2)	−1 373(4)	1 441(4)	−731(4)
C(3)	2 119(4)	2 078(3)	−228(4)
C(11)	2 598(5)	3 443(4)	5 804(4)
C(12)	−337(4)	3 288(4)	3 376(5)
C(13)	2 761(5)	4 465(3)	3 122(5)
C(21)	−174(4)	3 603(3)	−2 052(5)
C(22)	−1 672(5)	884(3)	−4 102(4)
C(23)	−3 672(4)	1 853(4)	−3 275(4)
C(31)	3 749(4)	699(3)	−1 095(4)
C(32)	4 919(4)	2 041(4)	2 353(4)
C(33)	5 475(4)	3 548(3)	161(5)

with hexamethyldisiloxane (2 × 20 cm^3), and the combined extracts reduced to *ca.* 15 cm^3. Cooling at −20 °C overnight yielded dark blue-green crystals. Yield: 0.53 g, 35%.

An alternative crystallisation procedure involved initial extraction with hexane; the solvent was removed and the residue crystallised from diethyl ether. N.m.r.: ^1H, δ 1.51 (s, 12 H, CH_2SiMe_3) and 0.21 (s, 54 H, CH_2SiMe_3); ^{13}C-{^1H}, 15.86 (s, CH_2SiMe_3) and 1.03 p.p.m. (s, CH_2SiMe_3).

(*c*) *Di-μ-acetato-tetrakis(neopentyl)diruthenium*(III). As in (*a*) but using only 4 equivalents of alkylating agent; the reaction was stirred for only 1 h at room temperature. After removal of volatiles, extraction of the residue with hexane yielded a deep red solution; reduction in volume and cooling overnight to −20 °C gave dark red crystals. Yield *ca.* 26%. N.m.r.: ^1H, δ 2.69 (s, 8 H, CH_2CMe_3), 1.71 (s, 6 H, $MeCO_2$), and 1.28 (s, 36 H, CH_2CMe_3); ^{13}C-{^1H}, δ 185.7 (s, $MeCO_2$), 52.6 (s, CH_2CMe_3), 33.6 (s, CH_2CMe_3), 30.1 (s, CH_2CMe_3), and 23.2 p.p.m. (s, $MeCO_2$).

(*d*) *Di-μ-acetato-tetrakis(trimethylsilylmethyl)diruthenium*(III). As in (*b*) with 4 equivalents of Grignard, reaction time of 1 h, and evaporation of the reaction mixture to dryness at 0 °C. The residue was extracted with hexane (2 × 15 cm^3), the combined extracts reduced to *ca.* 5 cm^3 and cooled overnight at −20 °C to give red crystals. Yield: 25%. N.m.r.: ^1H, δ 1.85 (s, 6 H, $MeCO_2$), 1.31 (s, 8 H, CH_2SiMe_3), and 0.25 (s, 36 H, CH_2SiMe_3); ^{13}C-{^1H}, 180.1 (s, $MeCO_2$), 22.80 (s, $MeCO_2$), 13.4 (s, CH_2SiMe_3), and 0.8 p.p.m. (s, CH_2SiMe_3).

(*e*) *Dimethyltetrakis(neopentyl)diruthenium*(III). To a solution of $Ru_2(O_2CMe)_2(CH_2CMe_3)_4$ (0.7 g, 1.2 mmol) in hexane (30 cm^3) at −80 °C was added $MgMe_2$ (2.1 cm^3 of a 0.56 mol dm^{-3} solution in Et_2O, 1.2 mmol) and the solution allowed to warm. After stirring for 1 h at room temperature the solvent was removed and the residue extracted with hexane (2 × 20 cm^3). The combined extracts were filtered and reduced to *ca.* 10 cm^3; cooling at −20 °C gave a microcrystalline pinkish purple solid. Yield: 0.48 g, 78%. N.m.r.: ^1H, δ 2.75 (s, 8 H, CH_2CMe_3), 1.74 (s, 6 H, CH_3), and 1.05 (s, 36 H, CH_2CMe_3); ^{13}C, 52.3 (s, CH_2CMe_3), 35.8 (s, CH_2CMe_3), 27.4 (s, CH_2CMe_3), and 18.6 p.p.m. (s, CH_3).

(*f*) *Diethyltetrakis(neopentyl)diruthenium*(III). As in (*e*) but using $MgEt_2$. Crystallisation from hexane gave purple crystals in *ca.* 65% yield. N.m.r.: ^1H, δ 2.86 (s, CH_2CMe_3), 1.68 ('t', 6 H, CH_2CH_3, J = 4), 1.28 (s, 36 H, CH_2CMe_3), and 0.51 ('q', 4 H, CH_2CH_3, J = 4.7 Hz); ^{13}C-{^1H}, 41.4 (CH_2CMe_3), 26.3 (s, CH_2CMe_3), 18.0 (s, CH_2CH_3), and 10.3 p.p.m. (s, CH_2Me).

(*g*) *Dioxohexakis(trimethylsilylmethyl)diruthenium*(V). *Method* 1. To a solution of Ru_2R_6 (0.5 g, 0.69 mmol) in hexane (40 cm^3) at −30 °C was added dry oxygen (0.33 cm^3, 0.69 mmol) *via* a syringe. The solution immediately changed colour from blue-green to deep red. After warming to room temperature the solution was filtered from a black solid and evaporated; extraction with hexane (10 cm^3), reduction in volume to *ca.* 5 cm^3, and cooling to −20 °C gave deep red block crystals. Yield: 0.17 g, 30%.

Table 9. Fractional atomic co-ordinates (× 10^4) for $Ru_2O_2(CH_2SiMe_3)_6$

Atom	*x*	*y*	*z*
Ru(1)	3 856(0.5)	5 412(0.5)	4 385(0.5)
Si(1)	831(2)	4 604(1)	3 034(2)
Si(2)	3 520(1)	6 955(1)	6 086(1)
Si(3)	4 103(2)	5 975(1)	1 774(3)
O(1)	4 121(3)	4 365(2)	4 293(3)
C(1)	1 903(6)	5 519(4)	3 234(5)
C(2)	3 443(5)	5 818(4)	5 762(5)
C(3)	4 256(6)	6 236(4)	3 337(5)
C(11)	1 086(8)	4 115(5)	4 514(7)
C(12)	1 070(7)	3 791(5)	2 064(6)
C(13)	−877(7)	4 996(6)	2 253(8)
C(21)	5 076(7)	7 427(4)	6 253(6)
C(22)	3 392(7)	7 045(5)	7 557(6)
C(23)	2 138(7)	7 516(4)	4 886(6)
C(31)	3 548(8)	4 909(5)	1 258(6)
C(32)	2 917(9)	6 695(5)	655(6)
C(33)	5 738(9)	6 108(7)	1 811(8)

Method 2. To Ru_2R_6 (0.5 g, 0.69 mmol) in toluene (30 cm^3) at −78 °C was added nitrosobenzene (0.2 g, 1.8 mmol) in toluene (20 cm^3). The solution was stirred at room temperature for 2 h, filtered, reduced to *ca.* 15 cm^3 and cooled at −20 °C. Yield: 0.63 g, 78%. N.m.r.: ^1H, δ 1.78 (s, 12 H, CH_2SiMe_3) and 0.46 (s, 54 H, CH_2SiMe_3); ^{13}C-{^1H}, 35.8 (s, CH_2SiMe_3) and 8.43 p.p.m. (s, CH_2SiMe_3).

(*h*) *Hexakis(neopentyl)dioxodiruthenium*(V). As in (*g*), method 2, but using $Ru_2(CH_2CMe_3)_6$ to give red block crystals in 45% yield. N.m.r.: ^1H, δ 2.94 (s, 12 H, CH_2CMe_3) and 1.24 (s, 54 H, CH_2CMe_3); ^{13}C-{^1H}, 67.27 (s, CH_2CMe_3), 39.54 (s, CH_2CMe_3), and 34.08 p.p.m. (s, CH_2CMe_3).

(*i*) *Bis(phenylimido)hexakis(trimethylsilylmethyl)diruthenium*(V). To a solution of $Ru_2O_2R_6$ (0.1 g, 0.13 mmol) in hexane (40 cm^3) at −30 °C was added excess of PhNCO (0.1 cm^3, 1 mmol). The solution was stirred at room temperature for 2 h and the red-brown precipitate collected, extracted with toluene (3 × 20 cm^3), and the combined extracts filtered and reduced to *ca.* 20 cm^3. Addition of hexane (5 cm^3) and cooling to −20 °C for 2 d gave a brown microcrystalline solid. Yield: 0.06 g, 56%. N.m.r.: ^1H, δ 7.37, 7.14 (m, C_6H_5), 1.62 (s, 12 H, CH_2SiMe_3), and 0.38 p.p.m. (s, 54 H, CH_2SiMe_3).

(*j*) *Bis(trimethylsilylimido)hexakis(trimethylsilylmethyl)diruthenium*(V). To $Ru_2O_2R_6$ (0.3 g, 0.39 mmol) in hexane (40 cm^3) was added $Me_3P{=}NSiMe_3$ (0.2 cm^3, 0.8 mmol) and the solution stirred at room temperature for *ca.* 12 h. After removal of volatiles the residue was washed with hexane (2 × 10 cm^3), extracted with toluene (2 × 20 cm^3), and the extracts evaporated. Extraction into acetonitrile (2 × 10 cm^3), reduction to *ca.* 10 cm^3, and cooling to −20 °C for 3 d gave orange microcrystals. Yield 0.13 g, 38%. N.m.r.: ^1H, δ 1.58 (s, 12 H, CH_2SiMe_3), 0.39 (s, 54 H, CH_2SiMe_3), and −0.15 (s, 18 H, $NSiMe_3$); ^{13}C-{^1H}, 20.32 (s, CH_2SiMe_3), 4.58 (s, CH_2SiMe_3), and −4.8 p.p.m. (s, $NSiMe_3$).

Reaction of $Ru_2(CH_2SiMe_3)_6$ *with* PMe_3. To $Ru_2(CH_2SiMe_3)_6$ (0.3 g, 0.4 mmol) in hexane (40 cm^3) at −30 °C was added PMe_3 (0.5 cm^3, 5 mmol). The solution, which changed from green to red-brown, was stirred, filtered, reduced to *ca.* 10 cm^3, and cooled to −20 °C. The brown crystals were recrystallised from hexane to give $\overline{Ru(CH_2SiMe_2CH_2})(PMe_3)_4$,

Table 10. Fractional atomic co-ordinates (× 10^4) for $Os_2(\eta^3\text{-}C_3H_5)_2(CH_2CMe_3)_4$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Os(1)	419(1)	4 867(0.5)	7 991(0.5)	C(20)	4 889(18)	3 753(10)	9 000(10)
Os(2)	2 205(1)	5 093(0.5)	8 666(0.5)	C(21)	−2 137(16)	3 840(9)	7 818(11)
C(1)	−46(14)	4 045(7)	8 601(8)	C(22)	−1 521(18)	3 256(9)	8 925(11)
C(2)	−741(15)	5 459(8)	8 456(8)	C(23)	−641(17)	2 913(7)	7 979(10)
C(3)	2 643(14)	5 944(7)	8 041(8)	C(24)	−1 811(22)	6 438(10)	8 857(12)
C(4)	3 378(16)	4 501(8)	8 208(8)	C(25)	−2 279(20)	6 231(10)	7 617(12)
C(5)	2 201(16)	5 795(10)	9 554(9)	C(26)	−335(19)	6 735(9)	8 221(13)
C(6)	1 944(14)	5 078(9)	9 696(7)	Os(3)	5 541(1)	5 138(0.5)	4 640(0.5)
C(7)	2 865(18)	4 576(10)	9 695(8)	C(27)	6 619(13)	5 921(7)	5 272(7)
C(8)	−305(20)	5 368(11)	6 971(9)	C(28)	7 140(13)	4 520(7)	5 011(7)
C(9)	650(16)	4 867(10)	6 970(7)	C(29)	5 172(14)	4 714(8)	3 570(7)
C(10)	400(17)	4 135(9)	7 126(8)	C(30)	4 270(13)	5 209(8)	3 657(7)
C(11)	3 702(16)	6 450(8)	8 360(9)	C(31)	4 648(15)	5 918(8)	3 846(8)
C(12)	3 872(19)	3 733(8)	8 385(10)	C(32)	7 301(16)	6 472(8)	4 964(9)
C(13)	−1 071(16)	3 525(7)	8 306(10)	C(33)	7 479(15)	3 818(8)	4 769(8)
C(14)	−1 260(16)	6 230(9)	8 284(11)	C(34)	6 507(16)	7 113(8)	4 690(9)
C(15)	3 241(15)	7 039(8)	8 727(9)	C(35)	8 354(16)	6 738(8)	5 529(9)
C(16)	4 094(17)	6 776(9)	7 742(10)	C(36)	7 893(16)	6 183(9)	4 413(10)
C(17)	4 763(15)	6 093(9)	8 859(10)	C(37)	6 463(17)	3 269(8)	4 625(11)
C(18)	2 984(19)	3 217(9)	8 457(12)	C(38)	8 528(16)	3 531(9)	5 316(9)
C(19)	4 386(19)	3 523(10)	7 783(11)	C(39)	7 930(16)	3 898(8)	4 118(9)

analytically and spectroscopically identical with an authentic sample. Yield *ca.* 60%.

A similar reaction using dmpe gave yellow needles from hexamethyldisiloxane contaminated with a red oil which could be removed by repeated crystallisation. Yield: 36%.

Osmium Compounds.—(*a*) *Di-μ-acetato-tetrakis(neopentyl)-diosmium*(III). To a suspension of $Os_2(O_2CMe)_4Cl_2$ (1 g, 1.45 mmol) in thf (50 cm^3) at −80 °C was added $Mg(CH_2CMe_3)Cl$ (25 cm^3 of a 0.35 mol dm^{-3} solution in Et_2O). The reaction mixture was allowed to warm slowly to room temperature, becoming deep red at about −20 °C. After stirring for 1 h at room temperature, the volatiles were removed and the residue extracted with hexane (2 × 30 cm^3). The combined extracts were reduced to *ca.* 15 cm^3 and cooled overnight at −20 °C to give dark green crystals. Yield: 0.3 g, 28%. N.m.r.: ^1H, δ 3.92 (s, 8 H, $C\mathit{H}_2CMe_3$), 2.08 (s, 6 H, $\mathit{Me}CO_2$), and 1.28 (s, 36 H, $CH_2C\mathit{Me}_3$); $^{13}C\text{-}\{^1H\}$, 193.97 (s, $Me\mathit{C}O_2$), 46.12 (s, $\mathit{C}H_2CMe_3$), 44.09 (s, $CH_2\mathit{C}Me_3$), 37.17 (s, $CH_2C\mathit{Me}_3$), and 28.10 p.p.m. (s, $\mathit{Me}CO_2$).

(*b*) *Di-μ-acetato-tetrakis(trimethylsilylmethyl)diosmium*(III). As in (*a*) but using $Mg(CH_2SiMe_3)Cl$ to give deep red crystals. Yield 24%. N.m.r.: ^1H, δ 2.10 (s, 6 H, $\mathit{Me}CO_2$), 1.42 (s, 8 H, $C\mathit{H}_2SiMe_3$), and 0.18 (s, 36 H, $CH_2Si\mathit{Me}_3$); $^{13}C\text{-}\{^1H\}$, 179.8 (s, $Me\mathit{C}O_2$), 28.4 (s, $\mathit{Me}CO_2$), 13.80 (s, $\mathit{C}H_2SiMe_3$), and 1.20 p.p.m. (s, $CH_2Si\mathit{Me}_3$).

(*c*) *Bis*(η^3-*allyl*)*tetrakis*(*neopentyl*)*diosmium*(III). To a solution of $Os_2(O_2CMe)_2(CH_2CMe_3)_4$ (0.5 g, 0.6 mmol) in hexane (40 cm^3) at −30 °C was added allylmagnesium bromide (3.4 cm^3 of a 0.35 mol dm^{-3} solution in Et_2O). Sufficient Et_2O was added to redissolve the Grignard which precipitated initially. The mixture was allowed to warm slowly to room temperature; after stirring for *ca.* 10 h the volatiles were removed, and the residue extracted with hexane (2 × 20 cm^3). The combined filtrates were reduced to *ca.* 10 cm^3; cooling to −20 °C overnight yielded orange crystals. Yield: 0.38 g, 85%. N.m.r.: ^1H, δ 3.99 (m, 2 H, $CH_2C\mathit{H}CH_2$), 3.4 (s, 8 H, $C\mathit{H}_2CMe_3$), 3.27 (d, 4 H, $C\mathit{H}_2CHC\mathit{H}_2$, J = 4), 1.50 (d, 4 H, $C\mathit{H}_2CHC\mathit{H}_2$, J = 4 Hz), and 1.14 (s, 36 H, $CH_2C\mathit{Me}_3$); $^{13}C\text{-}\{^1H\}$, 102.0 (2, $CH_2\mathit{C}HCH_2$), 46.6 (s, $\mathit{C}H_2CH\mathit{C}H_2$), 42.0 (s, $\mathit{C}H_2CMe_3$), 34.84 (s, $CH_2\mathit{C}Me_3$), and 24.37 p.p.m. (s, $CH_2C\mathit{Me}_3$).

X-*Ray Crystallography.*—Crystals of all four compounds studied were mounted under argon in glass capillaries. Following preliminary photography, unit-cell parameters were obtained by least-squares refinement of the setting angles for 25 reflections measured on a CAD4 diffractometer. Intensities were recorded in the ω-2θ scan mode with Mo-K_α radiation (λ = 0.710 69 Å) by following standard procedures.[30] Semiempirical absorption corrections[31] were applied to all data sets using ψ-scan values for three reflections in each case. Additional corrections were applied during refinement using DIFABS.[32] Further experimental details are given in Table 6.

The structures were solved using Patterson and difference electron-density syntheses and refined by full-matrix least-squares using SHELX 76.[33] For the final refinements, a weighting scheme of the form $w = 1/[\sigma^2(F_o) + gF_o^2]$ was used, with values of g chosen to give acceptable agreement analyses. For all structures, non-hydrogen atoms were refined with anisotropic thermal parameters whilst hydrogen atoms were included in calculated positions (AFIX[34]) and assigned refined, group isotropic thermal parameters. Refinement details are given in Table 6. Sources of scattering factor data were as given in ref. 34; all calculations were made on a VAX 11/750 computer. Final atomic positional parameters are given in Tables 7—10.

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