# Oxoaryls of Rhenium-(V) and -(VI) and Osmium(VI). *X*-Ray Crystal Structures of Dimesityldioxorhenium(VI), Tetramesityloxorhenium(VI), and Dimesityldioxo-osmium(VI) †

**Pericles Stravropoulos, Peter G. Edwards, Torsten Behling, and Geoffrey Wilkinson** *
*Chemistry Department, Imperial College of Science and Technology, London SW7 2AY*
**Majid Motevalli and Michael B. Hursthouse** *
*Chemistry Department, Queen Mary College, London E1 4NS*

The interaction of mesitylmagnesium bromide with $[Me_3NH][ReO_4]$ or $Re_2O_7$ leads to the isolation of the diamagnetic rhenium(V) complex $[(mes)_2ReO_2]_2Mg(thf)_2$ (mes = mesityl, thf = tetrahydrofuran), which can be oxidized to the paramagnetic compound $ReO_2(mes)_2$; $ReOCl_4$ gives, instead, the paramagnetic rhenium(V) complex $ReO(mes)_4$ along with minor amounts of $ReO_2(mes)_2$, upon oxidation of the reaction solutions. All three rhenium starting materials with *o*-tolylmagnesium bromide or *o*-methoxyphenylmagnesium bromide lead similarly to the paramagnetic complexes $ReO(o\text{-}MeC_6H_4)_4$ and $ReO(o\text{-}MeOC_6H_4)_4$, respectively. The diamagnetic compound $OsO_2(mes)_2$ has also been prepared by oxidizing solutions from the interaction of osmium tetraoxide with the appropriate Grignard reagent. The *X*-ray crystal structures of $ReO_2(mes)_2$, $OsO_2(mes)_2$, and $ReO(mes)_4$ have been determined to reveal tetrahedral, tetrahedral, and tetragonal pyramidal geometries respectively.

Although dirhenium heptoxide (combined with a tin alkylating reagent)[1] and osmium tetraoxide [possibly through an osmium(VIII) alkyl complex[2]] have been found, respectively, to metathesize and oxidize functionalized olefins, the chemistry of relevant, isolable, high oxidation state metal oxoalkyl and oxoalkylidene complexes has not yet been fully investigated.

In a previous paper[3] we have characterized a number of rhenium(V) complexes of the stoicheiometry $(R_4ReO)_2Mg(thf)_n$ [R = Me or *o*-$(CH_2)_2C_6H_4$, $n = 4$; R = $CH_2SiMe_3$, $n = 2$; thf = tetrahydrofuran], which can be oxidized to the $Re^{VI}$ paramagnetic compounds[4] $ReOR_4$ (R = Me or $CH_2SiMe_3$) and diamagnetic dimers $Re_2O_3R_6$ (R = $CH_2SiMe_3$); the complex $Re_2O_3Me_6$ has also been characterized.[3]

We now extend the studies to the rare class of high oxidation state metal oxoaryls. The best characterized members of this group are those of vanadium[5] and molybdenum[6] but there are no previously known rhenium and osmium compounds. Some reactions which could have led to rhenium(V) oxoaryls, by using the rhenium(V) starting materials $ReOCl_3(PR_3)_2$ or $ReO(OEt)Cl_2(PR_3)_2$ (R = aryl) with lithium alkylating agents, have been tried but yielded a number of reduced rhenium-(III) and -(II) aryls of the types $ReR_3(PR_3)_2$ and $[ReR_2(PR_3)_2]_n$ respectively.[7]

Trimethylammonium per-rhenate, dirhenium heptoxide, and osmium tetraoxide have been used to produce the oxoaryl complexes, the thermal and air stability of which is critically dependent, as demonstrated previously in other cases,[8-10] on the presence of one or two *ortho* substituents on the phenyl ligands. New compounds are listed in Table 1 together with analytical data.

## Results and Discussion

cis-*Dioxo Species of Rhenium*-(V) *and* -(VI).—The interaction of either trimethylammonium per-rhenate or dirhenium heptoxide with seven equivalents of mesitylmagnesium bromide per Re atom in thf leads to diamagnetic, air-sensitive, red-purple crystals of a complex of the stoicheiometry $[(mes)_2ReO_2]_2Mg(thf)_2$ (mes = mesityl), which can be crystallized in good yields from diethyl ether or toluene. The crystallinity of the compound depends on solvation and indeed efforts to recrystallize the complex several times may result in precipitation of a purple powder. The compound is soluble in aromatic hydrocarbons and ethers but exhibits slight solubility in light petroleum and rapid decomposition in halogenated solvents.

The formation of a $(mes)_2ReO_2^-$ unit as opposed to a $(mes)_4ReO^-$ one, as might have been expected by analogy with rhenium(V) oxoalkyls, may be a result of the steric demand of the mesityl group (see also the case of substitution reactions on $M(mes)_nX_{5-n}$;[11] M = Nb or Ta, X = Cl or Br, $n = 1$—3) though the binding of four mesityls to rhenium can be achieved by appropriate selection of the starting material (see below).

The $^1H$ n.m.r. spectrum at ambient temperature indicates restricted rotation about the metal–carbon bond and also non-equivalence of the mesityl ligands. Whereas two very close signals of equal intensity are observed for the *para* methyl groups at δ 2.147 and 2.145 p.p.m., a complicated pattern of four broad signals is observed for the *ortho* methyl groups at δ 3.039, 2.892 and δ 2.685, 2.562 p.p.m., each set being ascribed to the two *ortho* methyl groups of the mesityl ligand, whereas the smaller splitting within each set is due to the non-equivalence of the two mesityl groups. The compounds $TaCl_3(mes)_2$, $NbCl_3(mes)_2$, and $TaCl_2(mes)_2(CH_2CMe_3)$[11] show similar features, though the mesityl groups are equivalent here. In these niobium and tantalum species the phenomenon is attributed to restricted rotation of the mesityl ligand becauee the *ortho* methyl groups cannot pass by the axial chloride ligands or rotate past each other.

Apart from bands characteristic of the mesityl groups the i.r. spectrum shows bands at 1 032s br, 1 022(sh), 1 010s, 952s, 920s, 912(sh), and 870s br cm$^{-1}$ that can be assigned to skeletal vibrations of thf[12] and to Re–O stretches;[3] due to the presence of co-ordinated thf the Re–O stretches cannot be easily identified. Tentatively we assign the band at 1 032 cm$^{-1}$ to $\nu_{asym}$(COC) and that at 952 cm$^{-1}$ to one of the Re–O bands,[3,13]

† *Supplementary data available* (No. SUP 56652, 6 pp.): thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

**Table 1.** Physical and analytical data for rhenium oxoaryl compounds

| | | | Analysis (%)[a] | | |
|---|---|---|---|---|---|
| Compound | Colour | M.p. (°C) | C | H | O |
| $[(mes)_2ReO_2]_2Mg(thf)_2$ | Red-purple | *ca.* 200 (decomp.)[b] | 47.2 (48.8) | 5.7 (5.6) | 9.1 (8.9) |
| $ReO_2(mes)_2$ | Red | 161—163 | 47.3 (47.3) | 4.9 (4.9) | 7.0 (7.0) |
| $ReO(mes)_4$ | Green | 134—136 | 63.4 (63.7) | 6.5 (6.5) | 2.4 (2.4) |
| $ReO(o\text{-}MeC_6H_4)_4$ | Blue-green | 147—149 | 59.2 (59.3) | 5.0 (5.0) | |
| $ReO(o\text{-}MeOC_6H_4)_4$ | Green | 143—145 | 52.9 (53.3) | 4.5 (4.5) | |
| $OsO_2(mes)_2$ | Green | 178—179 | 47.0 (46.9) | 4.9 (4.8) | 6.6 (6.9) |

[a] Found (required). [b] Loses thf at *ca.* 130 °C; decomposition without melting.

**Table 2.** Selected bond lengths (Å) and angles (°) for $ReO_2(mes)_2$*

| | | | |
|---|---|---|---|
| O(1)–Re(1) | 1.688(5) | C(1)–Re(1) | 2.062(6) |
| C(1)–Re(1)–O(1) | 106.4(3) | O(1)–Re(1)–O(1′) | 121.5(4) |
| C(2)–C(1)–Re(1) | 122.9(4) | C(6)–C(1)–Re(1) | 118.3(4) |
| C(1)–Re(1)–C(1′) | 102.2(3) | | |

* Key to symmetry operation relating designated atoms to reference atom at *x, y, z*: (′) 2 − *x*, *y*, 0.5 − *z*.

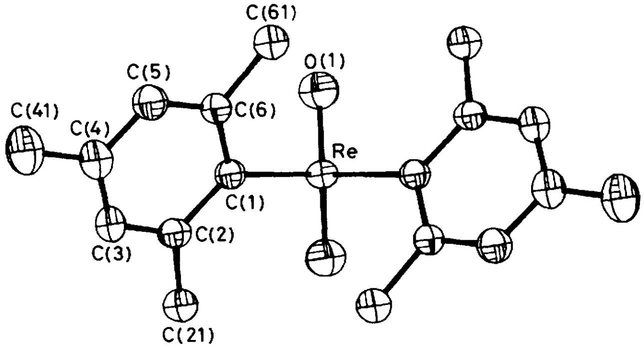


**Figure 1.** Molecular structure of $ReO_2(mes)_2$

probably the terminal one, while the bridging Re–O stretch is expected to appear at lower frequencies compared to the 972 and 930 $cm^{-1}$ stretches of 'free' $ReO_2(mes)_2$ and might be obscured by the broad bands of thf.

These spectroscopic data along with the diamagnetism and the chemical behaviour of the compound [it can be easily oxidized to $ReO_2(mes)_2$ as discussed below] suggest that tetrahedral $(mes)_2ReO_2^-$ units are co-ordinated to Mg centres probably *via* one of their oxygens only while the magnesium atom is solvated by two thf groups giving a tetrahedral environment resembling that of the complex $[(Me_3SiCH_2)_4ReO]_2Mg(thf)_2$.[3] The microcrystallinity of the compound prevented us from obtaining crystals of suitable size for an *X*-ray crystallographic investigation.

In thf the solvated magnesium complex is rapidly oxidized by dry oxygen or by addition of aqueous hydrogen peroxide to give bright red solutions from which the paramagnetic ($Re^{VI}$, $d^1$), deep red crystalline complex $ReO_2(mes)_2$ can be obtained in high yields. The compound is highly soluble in aromatic and halogenated hydrocarbons, ethers, and acetone but less soluble in light petroleum.

The formulation $ReO_2R_2$ is unique among the known oxo organorhenium species and to our knowledge is the only example of a tetrahedral co-ordination around a $Re^{VI}$ centre other than the ion $ReO_4^{2-}$[14] and perhaps the recently claimed $ReO_2Cl_2$.[15] The closest analogue is $MoO_2(mes)_2$[6] prepared by the action of the mesityl Grignard on $MoO_2Cl_2(thf)_2$. A number of other complexes, $MoO_2R_2(bipy)$ (R = Me,[16] $CH_2CMe_3$,[17] or $CH_2Ph$;[18] bipy = 2,2′-bipyridyl) are known but a supporting base was found indispensable for the stabilization of these alkyls.

The i.r. spectrum of the compound shows two strong bands at 972 and 930 $cm^{-1}$ for the Re=O stretches of the *cis*-$ReO_2$[19] unit.

The compound in the solid state shows high air and thermal stability, presumably due to the protection of co-ordinated sites by the *ortho* methyl groups of the mesityl ligands. However, solutions of the complex especially in aromatic hydrocarbons exhibit slow decomposition over a period of several days on exposure to air, turning from bright red to pale yellow.

The structure of the molecule, which has crystallographic $C_2$ symmetry, is shown in Figure 1; selected bond lengths and angles are given in Table 2. The geometry of the molecule is realistically described as tetrahedral, although not unexpectedly the O–Re–O angle is enlarged due to repulsion between the electron density in the Re=O multiple bonds, and the C–Re–C angle reduced from idealized values; however, the angle between the $O_2Re$ and $ReC_2$ planes is close to 90°, at 88°. The bonding of the mesityl ligand is not quite symmetrical, with Re–C–C angles differing by *ca.* 5°. This is probably due to the steric repulsion between the oxygens and the C(21) methyl groups, where the O···C(21) distance is 2.99 Å, compared with O···C(61), 3.14 Å, since the angle Re–C(1)–C(2) is greater than Re–C(1)–C(6). Although the stability of the compound may be ascribed, in part, to the shielding effect of the four *ortho* methyl groups, there are no unusually short Re···H contacts, the closest being 3.07 Å [H(212)].

*Mono-oxo Species of Rhenium*(VI).—The interaction of $ReOCl_4$ with five equivalents of mesitylmagnesium bromide in thf leads to the formation of a red-purple solution from which no pure product can be isolated. However, on treatment of these solutions with oxygen or with aqueous hydrogen peroxide the colour changes to green and polyhedra of the paramagnetic, air-stable, deep green complex $ReO(mes)_4$ can be crystallized in good yield from acetone or light petroleum along with a small amount of $ReO_2(mes)_2$.

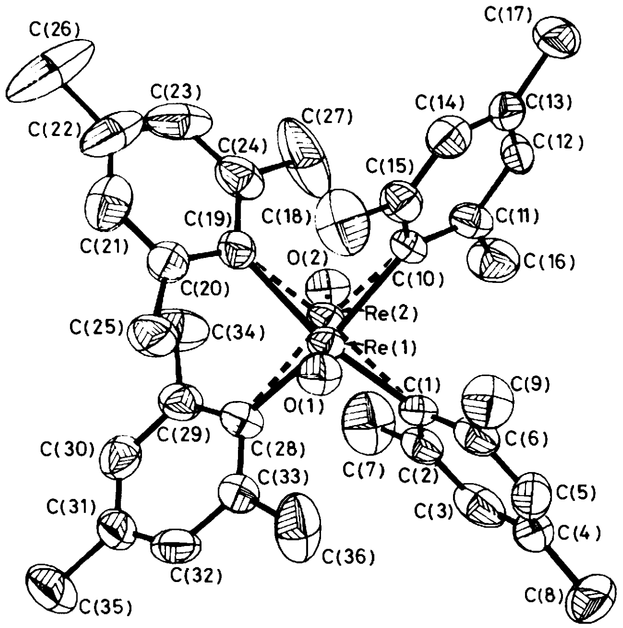


**Figure 2.** Molecular structure of $ReO(mes)_4$

**Table 3.** Selected bond lengths (Å) and angles (°) for $ReO(mes)_4$

| | | | |
|---|---|---|---|
| O(1)–Re(1) | 1.679(8) | C(1)–Re(1) | 2.141(8) |
| C(10)–Re(1) | 2.146(8) | C(19)–Re(1) | 2.191(8) |
| C(28)–Re(1) | 2.173(9) | O(2)–Re(2) | 1.646(15) |
| C(1)–Re(2) | 2.194(8) | C(10)–Re(2) | 2.197(8) |
| C(19)–Re(2) | 2.089(8) | C(28)–Re(2) | 2.216(8) |
| C(1)–Re(1)–O(1) | 108.3(3) | C(10)–Re(1)–O(1) | 105.0(4) |
| C(10)–Re(1)–C(1) | 87.2(3) | C(19)–Re(1)–O(1) | 106.5(4) |
| C(19)–Re(1)–C(1) | 145.2(2) | C(19)–Re(1)–C(10) | 83.6(3) |
| C(28)–Re(1)–O(1) | 102.8(4) | C(28)–Re(1)–C(1) | 86.7(3) |
| C(28)–Re(1)–C(10) | 152.1(2) | C(28)–Re(1)–C(19) | 86.0(3) |
| C(1)–Re(2)–O(2) | 107.0(6) | C(10)–Re(2)–O(2) | 108.8(6) |
| C(10)–Re(2)–C(1) | 84.7(3) | C(19)–Re(2)–O(2) | 103.3(6) |
| C(19)–Re(2)–C(1) | 149.6(2) | C(19)–Re(2)–C(10) | 84.8(3) |
| C(28)–Re(2)–O(2) | 107.6(6) | C(28)–Re(2)–C(1) | 84.3(3) |
| C(28)–Re(2)–C(10) | 143.6(2) | C(28)–Re(2)–C(19) | 87.4(3) |
| C(2)–C(1)–Re(1) | 131.6(4) | C(2)–C(1)–Re(2) | 105.2(5) |
| C(6)–C(1)–Re(1) | 110.7(5) | C(6)–C(1)–Re(2) | 138.5(5) |
| C(11)–C(10)–Re(1) | 133.3(4) | C(11)–C(10)–Re(2) | 107.3(5) |
| C(15)–C(10)–Re(1) | 111.0(5) | C(15)–C(10)–Re(2) | 133.8(4) |
| C(20)–C(19)–Re(1) | 112.1(5) | C(20)–C(19)–Re(2) | 137.3(5) |
| C(24)–C(19)–Re(1) | 131.0(5) | C(24)–C(19)–Re(2) | 104.2(6) |
| C(29)–C(28)–Re(1) | 131.2(5) | C(29)–C(28)–Re(2) | 105.3(5) |
| C(33)–C(28)–Re(1) | 110.1(6) | C(33)–C(28)–Re(2) | 137.2(5) |

$ReO(mes)_4$ is soluble in aromatic, aliphatic, and halogenated hydrocarbons and ethers, as well as in acetonitrile and acetone but is insoluble in and unaffected by water. The complex is air stable both in the solid state and in solutions presumably due to the protecting effect of the four bulky mesityl groups on the metal centre; slow decomposition, especially in aromatic hydrocarbons, occurs over a period of several days.

The i.r. spectrum shows a sharp band at 998 $cm^{-1}$ readily assigned as the ν(Re=O) stretch accompanied with a shoulder 988 $cm^{-1}$ probably due to strain effects in the crystal lattice. Such shoulders have been observed for related molecules in the solid state or Nujol mulls and disappear in solutions; $ReOCl_4$[20] has bands at 1 028 and 1 017 $cm^{-1}$ and $ReOMe_4$[4] at 1 016 and 1 004 $cm^{-1}$.

The molecule has a square-pyramidal structure, with the oxygen occupying the axial site. As described in the Experimental section, however (see below), the molecule is disordered such that the four mesityl groups form a common, well defined base, whilst the Re=O group lies either side, with an occupancy ratio of *ca.* 2:1. This is shown in Figure 2, where the most dominant Re=O position is shown with full bond connections. It is possible that this disorder may be the origin of the shoulder on the main Re=O i.r. band. Selected bond length and angle parameters are given in Table 3, and show that the mesityl connections to the metal and the Re–O distance are very similar for the two components.

The nature of the Re=O disorder implies a somewhat unsymmetrical mode of bonding of the mesityl ligands to the metal. The four aryl groups are arranged in an approximate propeller fashion around the square base, with their planes making angles of 53—57° with the basal plane, defined by the four metal-bonded carbon atoms. Moreover, the carbon σ-bonding orbitals, which, in each case, we might assume to lie in the plane of the aromatic ring and on the external bisector of the relevant C–C–C angle, all point approximately to the centre of the ring formed by the four metal-bonded carbons. As a result, these orbitals are not pointing directly at the metal, and we can therefore assume the C–Re interaction to involve a 'bent-bond,' which, again because of the two-way disorder, is rather flexible.

Although we were unable to isolate any well defined product from the initial red-purple reaction solutions prior to oxidation, it is reasonable to assume that these contain solvated magnesium adducts with $(mes)_4ReO^-$ units similar to others characterized.[3] The formation of the two compounds upon oxidation suggests at least two pathways for the oxygen attack since $ReO(mes)_4$ cannot be converted to $ReO_2(mes)_2$ by oxidation. A kinetically favoured electron-transfer reaction could account for the formation of $ReO(mes)_4$ whereas $ReO_2(mes)_2$ could result from a tendency to lower the steric strain at the metal centre. An analogous situation has been observed in the oxidation of the complex $[(Me_3SiCH_2)_4ReO]_2Mg(thf)_2$[3] to give mainly the paramagnetic, air-stable complex $ReO(CH_2SiMe_3)_4$ with small, variable amounts of the diamagnetic dimer $Re_2O_3(CH_2SiMe_3)_6$. Note that the oxidation of $(Me_4ReO)_2Mg(thf)_4$[3] gives only one product, namely $ReOMe_4$, though the dimer $Re_2O_3Me_6$ exists and can be prepared through other routes. The possibility that $ReO_2(mes)_2$ results from traces of higher oxo species in the starting material, especially of $ReO_3Cl$, cannot be totally excluded.

The interaction of $[Me_3NH][ReO_4]$, $Re_2O_7$, or $ReOCl_4$ with seven equivalents of *o*-tolylmagnesium bromide in thf gives orange-red solutions from which an extremely air sensitive, diamagnetic complex can be isolated. The i.r. spectrum of the compound shows similar features to other magnesium solvated rhenium oxoalkyls with peaks at 1 030s br, 1 020(sh), 954s, 920m, and 900s br $cm^{-1}$ which can be assigned to co-ordinated thf and ν(Re=O) stretches (probably the 954 $cm^{-1}$). Due to the extreme sensitivity of the complex reproducible analytical and spectroscopic data could not be obtained and further attempts to characterize the compound were not made.

Interaction of solutions of this complex, probably $[(o\text{-}MeC_6H_4)_4ReO]_2Mg(thf)_n$, with dry oxygen or aqueous hydrogen peroxide gave immediately a deep green-blue colour and the isolated paramagnetic $ReO(o\text{-}MeC_6H_4)_4$ can be crystallized from acetone or light petroleum as fine blue-green needles, soluble in aromatic, aliphatic, and halogenated hydrocarbons, ethers, acetonitrile, and acetone but insoluble in and unaffected by water. It exhibits remarkable air stability both in the solid state and solutions.

The i.r. spectrum shows analogous features to those observed for $ReO(mes)_4$, having a ν(Re=O) stretch at 992 $cm^{-1}$ with a

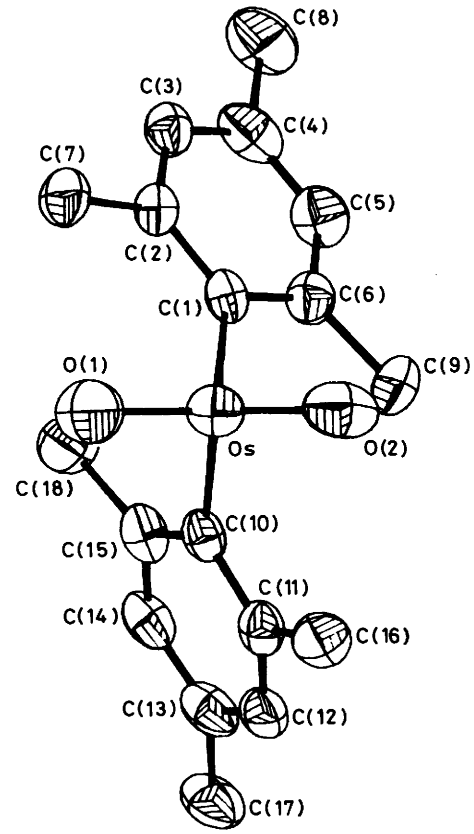


**Figure 3.** Molecular structure of $OsO_2(mes)_2$

shoulder at 982 $cm^{-1}$ probably due to aggregated species in the lattice.

The isolation of $ReO(o\text{-}MeC_6H_4)_4$ instead of the expected $ReO_2(o\text{-}MeC_6H_4)_2$ led us to study the effect of other groups in the *ortho* position. The interaction of $[Me_3NH][ReO_4]$, $Re_2O_7$, or $ReOCl_4$ with seven equivalents of $Mg(o\text{-}MeOC_6H_4)Br$ gave initially a deep red-purple solution which on oxidation led to the green, paramagnetic complex $ReO(o\text{-}MeOC_6H_4)_4$ which can be crystallized from acetone or light petroleum.

$ReO(o\text{-}MeOC_6H_4)_4$ shows high solubility in all common organic solvents and air stability similar to the other complexes of this series. The ν(Re=O) stretch in the i.r. spectrum is obscured by ligand vibrations but lies in the area 1 020—1 005 $cm^{-1}$ where a very strong peak appears at 1 010 $cm^{-1}$ which has a set of side shoulders.

Attempts to prepare phenyl or other *para*- and *meta*-substituted phenyl complexes by treating per-rhenate or dirhenium heptoxide with the appropriate Grignard reagent failed due to thermal decomposition. In these cases reactions were always observed at low temperatures (−78 °C) but decomposition was taking place evidently at even −30 °C. The stability of the mesityl group compared to the phenyl group has been shown in a number of cases (for example $TaCl_3Ph_2$ and $TaCl_2Ph_3$,[21] are thermally unstable whereas the mesityl analogues are comparatively stable) and can be attributed to suppression of decomposition pathways by the so-called '*ortho* effect'[8–10] of the *ortho*-methyl groups of the mesityl ligand. It should also be noted that in addition to the classical mode of decomposition of aryl ligands through biaryl formation,[22] *ortho*-hydrogen atom elimination from one phenyl ring to another has been observed[23] and benzyne (cyclohexa-1,3-dien-5-yne) complexes isolated.[24] The existence of an additional *ortho*-methyl group on the mesityl ligand seems to be also decisive for the stabilization of dioxo species. No analogous compounds were isolated upon using a mono *ortho*-substituted ligand; the only isolable products in this case are $ReOR_4$ complexes.

**Table 4.** Selected bond lengths (Å) and angles (°) for $OsO_2(mes)_2$

| | | | |
|---|---|---|---|
| O(1)–Os(1) | 1.700(7) | O(2)–Os(1) | 1.690(7) |
| C(1)–Os(1) | 2.053(8) | C(10)–Os(1) | 2.047(8) |
| O(2)–Os(1)–O(1) | 136.1(3) | C(1)–Os(1)–O(1) | 109.7(3) |
| C(1)–Os(1)–O(2) | 100.6(3) | C(10)–Os(1)–O(1) | 100.0(3) |
| C(10)–Os(1)–O(2) | 107.7(3) | C(10)–Os(1)–C(1) | 96.0(3) |
| C(2)–C(1)–Os(1) | 119.9(5) | C(6)–C(1)–Os(1) | 121.1(5) |
| C(11)–C(10)–Os(1) | 116.5(5) | C(15)–C(10)–Os(1) | 124.1(5) |

*Electron Spin Resonance Spectra of* $ReO_2R_2$ *and* $ReOR_4$ *Complexes.*—In toluene solution at 293 K the *X*-band spectrum of $ReO_2(mes)_2$ shows a simple pattern having a six-line hyperfine structure ($g_{iso} = 1.967$, $A_{iso} = -0.0196$). On lowering the temperature of the solution the spectrum resolved into a complicated pattern showing, at 98 K, more than two sets of six rhenium hyperfine lines with unequal spacing. The *Q*-band spectrum at 98 K showed two well separated sets of six lines for the *z*- and *x*-axes and a partially resolved multiplet for the *y*-axis at intermediate field, suggesting that the *g* tensor is strongly rhombic. The parameters for the *z* axis ($g_z = 2.095$, $A_z = -0.0355$) and the *x* axis ($g_x = 1.864$, $A_x = -0.0242$) were derived directly from the experimental fields of the *Q*-band spectrum whereas parameters for the *y* axis ($g_y = 1.942$, $A_y = 0.009$) were calculated from the isotropic and anisotropic values. The above parameters were checked with the computer program ESRS* which gave a good fit between the calculated and experimental field value for the *z*- and *x*-axes and predicted that most of the expected transitions for the *y* axis are due to $\Delta M_I = 1$ or 2.

A toluene solution of $ReOR_4$ (R = mes, *o*-tolyl, or *o*-methoxyphenyl) gave a set of six rhenium hyperfine lines at 293 K at *X*-band. At 98 K there is a well resolved spectrum with at least two sets of six hyperfine lines and an axially symmetric appearance. The parameters for the parallel orientation [$ReO(mes)_4$: $g_\parallel = 2.133$, $A_\parallel = -0.0360$; $ReO(o\text{-}MeC_6H_4)_4$: $g_\parallel = 2.160$, $A_\parallel = -0.0350$; $ReO(o\text{-}MeOC_6H_4)_4$: $g_\parallel = 2.138$, $A_\parallel = -0.0373$] were accurately derived with the aid of both *Q*- and *X*-band spectra (five or two isolated, low field peaks, respectively). Both the *X*- and the *Q*-band spectra are greatly complicated in the perpendicular region by off-axis transitions and by the presence of many small lines attributed to $\Delta M_I = 1$ or 2 as encountered in other rhenium(VI), $d^1$ complexes.[25] The parameters for this orientation [$ReO(mes)_4$: $g_\perp = 1.925$, $A_\perp = -0.0185$; $ReO(o\text{-}MeC_6H_4)_4$: $g_\perp = 1.955$, $A_\perp = -0.0165$; $ReO(o\text{-}MeOC_6H_4)_4$: $g_\perp = 1.935$, $A_\perp = -0.0181$] were calculated from the isotropic and anisotropic values and are in good agreement with observed field values in both the *X*- and *Q*-band spectra. However, computer simulation indicates a better fit if a slight rhombic component to $g_\perp$ (*ca.* 0.005) is inserted and some nuclear quadrupole interaction assumed to account for the slight uneven spacing of the perpendicular hyperfine lines.

*Oxoaryls of Osmium*(VI).—The interaction of osmium tetraoxide with seven equivalents of mesitylmagnesium bromide in thf and subsequent oxidation of the resulting deep red solution leads to the isolation of the diamagnetic, air stable $Os^{VI}$ compounds $OsO_2(mes)_2$, which can be crystallized as fine green

* ESRS is a development of the program described by R. D. Dowsing and J. F. Gibson, *J. Chem. Phys.*, 1969, **50**, 294.

**Table 5.** Crystal data, intensity data, collection parameters, and details of refinement

| Complex | $ReO_2(mes)_2$ | $ReO(mes)_4$ | $OsO_2(mes)_2$ |
|---|---|---|---|
| Crystal data: | | | |
| Formula | $C_{18}H_{22}O_2Re$ | $C_{36}H_{44}ORe$ | $C_{18}H_{22}O_2Os$ |
| $M$ | 456.574 | 678.912 | 460.56 |
| $a$/Å | 13.533(2) | 11.115(2) | 8.380(1) |
| $b$/Å | 9.317(3) | 16.634(7) | 15.515(7) |
| $c$/Å | 13.383 | 16.837(5) | 12.800(5) |
| $\alpha$/° | 90.00 | 90.00 | 90.00 |
| $\beta$/° | 103.04(2) | 94.68(2) | 99.22(2) |
| $\gamma$/° | 90.00 | 90.00 | 90.00 |
| $U$/Å$^3$ | 1 643.92 | 3 102.56 | 1 642.57 |
| System | Monoclinic | Monoclinic | Monoclinic |
| Space group | $C2/c$ | $P2_1/n$ | $P2_1/a$ |
| $D_c$/g cm$^{-3}$ | 1.84 | 1.45 | 1.86 |
| $Z$ | 4* | 4 | 4 |
| $F$(000) | 884 | 1 372 | 888 |
| $\mu$(Mo-$K_\alpha$)/cm$^{-1}$ | 74.66 | 39.67 | 74.44 |
| Data collection: | | | |
| Crystal size/mm | 0.25 × 0.2 × 0.225 | 0.25 × 0.125 × 0.5 | 0.125 × 0.5 × 0.075 |
| Total data measured | 1 652 | 6 088 | 3 206 |
| Total data unique | 1 442 | 5 854 | 2 879 |
| Total data observed | 1 372 | 3 490 | 2 050 |
| Significance test | $F_o > 4\sigma(F_o)$ | $F_o > 4\sigma(F_o)$ | $F_o > 3\sigma(F_o)$ |
| Refinement: | | | |
| No. of parameters | 140 | 429 | 274 |
| Min. transmission factor | 0.565 | 0.829 | 0.79 |
| Weighting scheme | $1/[\sigma^2(F_o) + 0.000\,01F_o^2]$ | $1/[\sigma^2(F_o) + 0.0001F_o^2]$ | $1/[\sigma^2(F_o) + 0.000\,05F_o^2]$ |
| Final $R[= \Sigma\Delta F/\Sigma\|F_o\|]$ | 0.0192 | 0.0382 | 0.0276 |
| Final $R'\{= [\Sigma w(\Delta F)^2/\Sigma wF_o^2]^{\frac{1}{2}}\}$ | 0.0191 | 0.0350 | 0.0269 |

* Molecule sited on a two-fold axis of symmetry.

needles from petroleum or sublimed onto a cold probe at 50 °C ($10^{-1}$ mmHg).

The compound is thermally and air stable both as a solid and in solutions and is soluble in aromatic, aliphatic, and halogenated hydrocarbons, ethers, acetone, and acetonitrile but is insoluble in and unaffected by water; it shows greater stability and solubility than $ReO_2(mes)_2$.

Additional to peaks ascribed to the mesityl group the i.r. spectrum shows two strong peaks at 950 and 918 cm$^{-1}$ both accompanied with shoulders at 955 and 920 cm$^{-1}$ respectively, due probably to lattice effects and are assigned to the ν(Os–O) stretches of the *cis*-$OsO_2$ unit.

The $^1H$ n.m.r. spectrum shows two sharp peaks at δ 2.34 and 2.26 p.p.m. (relative intensity 2:1) readily assigned to the *ortho*- and *para*-methyl groups respectively and a broader band at δ 6.73 p.p.m. due to the aromatic protons. The $^{13}C$-{$^1H$} spectrum shows the *ortho*-methyl groups at δ 28.70 p.p.m. and the *para* at 20.09 p.p.m. Of the four unique aromatic carbons three can be seen at δ 146.68, 140.88, and 123.54 p.p.m.

The structure of the molecule is shown in Figure 3; selected bond lengths and angles are given in Table 4. The surprising result that crystals of $OsO_2(mes)_2$ are not isostructural with those of $ReO_2(mes)_2$ (see Table 5), is also reflected in the molecular structure, which shows some very significant differences. Most noticeable are the O–M–O and C–M–C angles, which for $OsO_2(mes)_2$ show a much greater difference than the corresponding angles in the Re complex. This difference may be a reflection of the greater deforming effect of a filled non-bonding orbital in this diamagnetic $d^2$ $Os^{VI}$ complex when compared with a half-filled orbital, in the $d^1$ $Re^{VI}$ analogue. Further differences from the structure of $ReO_2(mes)_2$ are found in the angle between the $O_2Os$ and $OsC_2$ planes (84°) and in the orientation of the two aromatic rings, which make angles of 40 and 56° with the $OsC_2$ plane. In $ReO_2(mes)_2$ the one unique angle is 66°.

From the original deep red reaction solutions prior to oxidation some red needles can be crystallized from ether or toluene but isolation proved difficult and the resulting product, probably $[(mes)OsO_2]_2Mg(thf)_n$, impure.

The interaction of $OsO_4$ with *o*-tolylmagnesium bromide yields the diamagnetic, tetrahedral $Os(o\text{-}MeC_6H_4)_4$.[26] Once again, as in the case of rhenium, the use of a di-*ortho*-substituted ligand (mesityl) as opposed to a mono-*ortho* one (*o*-tolyl) has a significant influence on the formation of the isolable products ($OsO_2R_2$ and $OsR_4$ respectively). The only other similar compound is $OsO(CH_2SiMe_3)_4$[27] but nitrido-osmium(VI) alkyl complexes are known.[28]

## Experimental

Microanalyses were by Pascher, Bonn, and Imperial College Microanalytical Laboratories. Spectrometers were as follows: i.r., Perkin-Elmer 683 (spectra in Nujol mulls, values in cm$^{-1}$); n.m.r., JEOL FX-90Q and Bruker WM-250 (data in p.p.m. relative to $SiMe_4$); e.s.r., Varian E-12 ($X$-band) and Bruker ER 200D-SRS ($Q$-band), spectra in toluene ($A$ values in cm$^{-1}$). Melting points were determined in sealed tubes and are uncorrected.

Trimethylammonium per-rhenate[3] and tetrachlorooxo-rhenium[29] were prepared as before. Osmium tetraoxide was from Johnson Matthey PLC. Solvents were refluxed over sodium or sodium-benzophenone under argon and distilled before use. The light petroleum used had b.p. 40—60 °C. All operations were performed *in vacuo* or under purified argon.

1. *Bis(tetrahydrofuran)magnesium bis[dimesityldioxo-rhenate*(V)].—To a cooled (−78 °C) suspension of $[Me_3NH][ReO_4]$ (0.72 g, 2.32 mmol) in thf (30 cm$^3$) was added mesitylmagnesium bromide (17.5 cm$^3$ of a 0.93 mol dm$^{-3}$ solution in $Et_2O$, 16.27 mmol). The mixture was allowed to

**Table 6.** Fractional atomic co-ordinates ( × $10^4$) for $ReO_2(mes)_2$

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Re(1) | 10 000* | 5 242(0.5) | 2 500* |
| O(1) | 8 890(2) | 4 357(4) | 2 123(2) |
| C(1) | 9 819(3) | 6 632(4) | 3 644(3) |
| C(2) | 10 492(3) | 6 663(5) | 4 632(3) |
| C(3) | 10 245(4) | 7 535(5) | 5 380(4) |
| C(4) | 9 364(4) | 8 336(5) | 5 239(3) |
| C(5) | 8 718(4) | 8 275(5) | 4 281(3) |
| C(6) | 8 920(3) | 7 449(5) | 3 489(3) |
| C(21) | 11 460(4) | 5 815(7) | 4 916(4) |
| C(41) | 9 117(5) | 9 218(8) | 6 090(4) |
| C(61) | 8 161(4) | 7 469(7) | 2 484(4) |

* Invariant parameter.

**Table 7.** Fractional atomic co-ordinates ( × $10^4$) for $ReO(mes)_4$

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Re(1) | 4 139(0.5) | 2 166(0.5) | 8 892(0.5) |
| Re(2) | 3 682(1) | 2 786(1) | 9 094(0.5) |
| O(1) | 4 876(5) | 1 328(3) | 8 657(4) |
| O(2) | 3 022(11) | 3 617(8) | 9 366(8) |
| C(1) | 2 252(5) | 1 983(3) | 8 588(4) |
| C(2) | 1 239(6) | 2 170(4) | 8 994(4) |
| C(3) | 123(6) | 1 790(5) | 8 779(5) |
| C(4) | −33(6) | 1 231(4) | 8 185(5) |
| C(5) | 938(7) | 1 057(4) | 7 779(4) |
| C(6) | 2 063(6) | 1 417(4) | 7 947(4) |
| C(7) | 1 285(8) | 2 794(5) | 9 635(5) |
| C(8) | −1 234(7) | 822(5) | 8 016(6) |
| C(9) | 3 009(8) | 1 160(5) | 7 410(5) |
| C(10) | 4 136(5) | 2 918(4) | 7 856(3) |
| C(11) | 3 257(5) | 3 441(4) | 7 463(4) |
| C(12) | 3 523(6) | 3 854(4) | 6 774(4) |
| C(13) | 4 576(6) | 3 767(4) | 6 428(4) |
| C(14) | 5 417(6) | 3 232(4) | 6 778(4) |
| C(15) | 5 220(6) | 2 815(4) | 7 468(4) |
| C(16) | 2 012(7) | 3 572(4) | 7 719(5) |
| C(17) | 4 861(7) | 4 235(5) | 5 698(4) |
| C(18) | 6 225(7) | 2 234(5) | 7 744(5) |
| C(19) | 5 512(6) | 3 014(4) | 9 386(4) |
| C(20) | 6 504(6) | 2 616(4) | 9 800(4) |
| C(21) | 7 528(7) | 3 049(7) | 10 081(5) |
| C(22) | 7 643(9) | 3 848(7) | 9 969(7) |
| C(23) | 6 697(11) | 4 238(6) | 9 567(6) |
| C(24) | 5 623(8) | 3 844(4) | 9 288(4) |
| C(25) | 6 569(10) | 1 724(6) | 9 970(8) |
| C(26) | 8 778(16) | 4 298(14) | 10 280(15) |
| C(27) | 4 552(17) | 4 343(7) | 8 945(8) |
| C(28) | 3 761(6) | 1 946(4) | 10 119(4) |
| C(29) | 3 911(6) | 2 445(4) | 10 810(4) |
| C(30) | 3 906(6) | 2 100(5) | 11 566(4) |
| C(31) | 3 756(6) | 1 293(5) | 11 688(5) |
| C(32) | 3 604(7) | 823(5) | 11 018(6) |
| C(33) | 3 593(6) | 1 127(4) | 10 241(4) |
| C(34) | 4 032(13) | 3 327(5) | 10 817(8) |
| C(35) | 3 767(13) | 897(11) | 12 492(8) |
| C(36) | 3 363(13) | 477(6) | 9 630(7) |

warm slowly and was held at room temperature for *ca.* 1 h with stirring. The resulting red-purple solution was evaporated and the residue extracted with diethyl ether (3 × 20 $cm^3$), filtered and concentrated (to *ca.* 50 $cm^3$) to afford on cooling (0 °C) red-purple crystals. The product can be recrystallized by dissolution in thf, evaporation of the solvent, and extraction with toluene. Yield: 0.48 g, 38%. I.r.: 3 020m, 1 620m, 1 340s, 1 292m, 1 232m, 1 175m, 1 032s br, 1 022(sh), 1 010s, 952s, 920s, 912(sh), 870s br, 845s, 680m, 590w, 470w, and 320m br.

**Table 8.** Fractional atomic co-ordinates ( × $10^4$) for $OsO_2(mes)_2$

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Os(1) | 5 586(0.5) | 4 768(0.5) | 2 540(0.5) |
| O(1) | 3 714(6) | 4 363(4) | 2 585(4) |
| O(2) | 6 439(7) | 5 758(3) | 2 594(3) |
| C(1) | 6 482(7) | 4 249(4) | 1 277(5) |
| C(2) | 5 408(7) | 3 925(4) | 399(5) |
| C(3) | 6 038(8) | 3 617(4) | −457(5) |
| C(4) | 7 683(9) | 3 624(4) | −508(5) |
| C(5) | 8 693(9) | 3 960(4) | 331(6) |
| C(6) | 8 162(7) | 4 262(4) | 1 233(5) |
| C(7) | 3 609(9) | 3 885(6) | 358(7) |
| C(8) | 8 260(14) | 3 305(8) | −1 495(8) |
| C(9) | 9 399(9) | 4 644(6) | 2 091(7) |
| C(10) | 6 933(7) | 4 020(4) | 3 670(5) |
| C(11) | 7 585(7) | 4 437(4) | 4 635(5) |
| C(12) | 8 601(8) | 3 969(4) | 5 390(5) |
| C(13) | 8 991(8) | 3 113(4) | 5 256(5) |
| C(14) | 8 262(8) | 2 714(4) | 4 349(5) |
| C(15) | 7 229(8) | 3 140(4) | 3 546(5) |
| C(16) | 7 206(11) | 5 354(6) | 4 868(6) |
| C(17) | 10 115(11) | 2 626(7) | 6 091(8) |
| C(18) | 6 448(13) | 2 597(5) | 2 625(7) |

2. *Dimesityldioxorhenium*(VI).—To a stirred suspension of $[Me_3NH][ReO_4]$ (0.6 g, 1.93 mmol) in thf (30 $cm^3$) at −78 °C was added mesitylmagnesium bromide (14.5 $cm^3$ of a 0.93 mol $dm^{-3}$ solution in $Et_2O$, 13.48 mmol) and the solution warmed slowly to room temperature and stirred for *ca.* 1 h. Oxygen was bubbled through the red-purple solution until the colour became bright red. The solvent was then removed *in vacuo* and the residue extracted with acetone (3 × 20 $cm^3$); concentration of the filtrate (to *ca.* 30 $cm^3$) and standing at room temperature overnight gave red crystals. The product can be recrystallized from toluene (30 $cm^3$) at −20 °C. Yield: 0.3 g, 34%. I.r.: 972s, 930s, ν(Re=O); other 3 000m, 1 580, 1 278s, 1 260(sh), 1 030m br, 1 000w, 952w, 915w, 850s, 700m, 595w, 550m, 545(sh), and 360w.

3. *Tetramesityloxorhenium*(VI).—To a thf (30 $cm^3$) solution of $ReOCl_4$ (0.56 g, 1.63 mmol) was added mesitylmagnesium bromide (8.7 $cm^3$ of a 0.93 mol $dm^{-3}$ solution in $Et_2O$, 8.1 mmol) at −78 °C. The solution was allowed to warm and stirred at room temperature for *ca.* 2 h. Oxygen was bubbled through the red-purple solution until the colour changed to green. The solvent was evaporated and the residue extracted with light petroleum (3 × 20 $cm^3$). The filtered extract was reduced to *ca.* 15 $cm^3$ and left at −20 °C overnight to give green polyhedra. Yield: 0.33 g, 30%. I.r.: 998s, [988(sh)] ν(Re=O); other 3 010m, 1 590s, 1 274s, 1 225w, 1 025m br, 945w, 910w, 848s, 708m, 590m, 550m, 545(sh), and 380w.

On cooling (−20 °C) the supernatant for several days a small amount of red crystals of $ReO_2(mes)_2$ can be obtained. Yield: 0.06 g, 8%.

4. *Oxotetrakis*(o-*tolyl*)*rhenium*(VI).—To a stirred suspension of $[Me_3NH][ReO_4]$ (0.5 g, 1.61 mmol) in thf (30 $cm^3$) was added *o*-tolylmagnesium bromide (10.3 $cm^3$ of a 1.1 mol $dm^3$ solution in $Et_2O$, 11.33 mmol). The mixture was allowed to warm and kept at room temperature for *ca.* 2 h. Oxygen was then bubbled through the filtered, orange-red solution until the colour became green-blue. The solvent was evaporated and the residue extracted with acetone (3 × 20 $cm^3$), the filtrate reduced to *ca.* 15 $cm^3$ and cooled to −20 °C to give green-blue needles. The product can be recrystallized from light petroleum. Yield: 0.24 g, 26%. I.r.: 992s [982(sh)] ν(Re=O); other 3 040m, 1 610m, 1 280m, 1 250m, 1 190s, 1 155m, 1 110s, 1 050m,

1 030w, 1 010w, 940w, 860m, 785m, 745(sh), 740s, 705m, 640w, 590w, 490w, 440s, and 415m.

5. *Tetrakis(o-methoxyphenyl)oxorhenium*(VI).—To a thf (30 $cm^3$) suspension of $[Me_3NH][ReO_4]$ (0.5 g, 1.61 mmol) was added *o*-methoxyphenylmagnesium bromide (17.4 $cm^3$ of a 0.65 mol $dm^{-3}$ solution in $Et_2O$, 11.33 mmol) at −78 °C. The solution was allowed to warm and stirred at room temperature for *ca.* 2 h. Oxygen was then passed through the purple solution until the colour changed to green. The solvent was evaporated, the residue extracted with acetone (3 × 20 $cm^3$), and the filtrate reduced to *ca.* 20 $cm^3$ and cooled to −20 °C to give green crystals. The product can be recrystallized from light petroleum. Yield: 0.24 g, 24%. I.r.: 1 010s ν(Re=O); other 3 040m, 1 560s, 1 550(sh), 1 280m, 1 265m, 1 240s, 1 230s, 1 175m, 1 155m, 1 120m, 1 050m, 1 020(sh), 1 015(sh), 1 008(sh), 1 005(sh), 925w, 855w, 785m, 750(sh), 740s, 640w, 570w, 530w, 450w, and 440(sh).

6. *Dimesityldioxoosmium*(VI).—To a stirred solution of $OsO_4$ (0.3 g, 1.18 mmol) in thf (40 $cm^3$) at −78 °C was added mesitylmagnesium bromide (8.9 $cm^3$ of a 0.93 mol $dm^{-3}$ solution in $Et_2O$, 8.28 mmol). The mixture was allowed to warm slowly to room temperature and stirring was continued for *ca.* 1 h. The solvent was removed *in vacuo* and oxygen saturated petroleum (70 $cm^3$) was added to the residue and the mixture stirred overnight. The green, filtered extract was concentrated to *ca.* 20 $cm^3$ and cooled to −20 °C to give green needles. Yield: 0.16 g, 29%. I.r.: 950s [955(sh)], 918s [920(sh)], ν(Os=O); other 3 020m, 1 590m, 1 285s, 1 260(sh), 1 030m, 1 010w, 1 002w, 980m, 850s, 700m, 582w, 555w, 550m, 518w, and 370w.

*Crystallography*.—All crystallographic measurements were made at room temperature (293 K) on crystals sealed under argon in glass capillaries, using a CAD4 diffractometer operating in the ω–2θ scan mode with graphite monochromated Mo-$K_\alpha$ radiation (λ = 0.710 69 Å) as previously described.[30] The structures were solved *via* standard heavy-atom procedures and refined using full-matrix least squares,[31] with scattering factors calculated using data from ref. 32. The successful structure solution for $ReO(mes)_4$ required that the Re atom be split between two neighbouring sites *ca.* 1.2 Å apart (all peaks corresponding to this splitting were present in the Patterson function), and the subsequent refinement indicated unequal occupancies of ~0.67(12), 0.33(12); atoms of the mesityl ligands were shown to occupy only one set of positions, and showed no disorder. For this structure all hydrogens bound to ring carbons were experimentally located and freely refined with isotropic thermal parameters. Those on the '*para*' methyl groups were located in difference syntheses and were included with idealized geometry and isotropic thermal parameters fixed at 1.2 times the $U_{equiv.}$ of the parent carbon, but location of hydrogen positions on the '*ortho*' methyls proved to be very difficult, and in the end, none was included. It is likely that the hydrogens adopt different positions, depending on whether, in a particular molecule, the methyl group is next to the axial oxygen or the lower empty space. In the dioxo structures all hydrogens were located and freely refined with isotropic thermal parameters. All non-hydrogen atoms were refined anisotropically. Details of crystal data, intensity measurements, and refinements are given in Table 5. Final atomic fractional co-ordinates are given in Tables 6—8.

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## References

1 J. C. Mol and E. F. G. Woerlee, *J. Chem. Soc., Chem. Commun.*, 1979, 330; R. H. A. Bosma, G. C. N. Van der Aardweg, and J. C. Mol, *J. Organomet. Chem.*, 1983, **255**, 159.
2 S. G. Hentges and K. B. Sharpless, *J. Am. Chem. Soc.*, 1980, **102**, 4263; M. Schroder and E. C. Constable, *J. Chem. Soc., Chem. Commun.*, 1982, 734; C. P. Casey, *ibid.*, 1983, 126.
3 P. Stavropoulos, P. G. Edwards, G. Wilkinson, M. Motevalli, K. M. Abdul Malik, and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1985, 2167.
4 K. Mertis, D. H. Williamson, and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1975, 607; K. Mertis and G. Wilkinson, *ibid.*, 1976, 1488.
5 W. Seidel and G. Kreisel, *Z. Chem.*, 1982, **22**, 113; 1981, **21**, 295; 1977, **17**, 73; R. Choukroun and S. Sabo, *J. Organomet. Chem.*, 1979, **182**, 221; K-H. Thiele, W. Schumann, S. Wagner, and W. Bruser, *Z. Anorg. Allg. Chem.*, 1972, **390**, 280.
6 B. Heyn and R. Hoffman, *Z. Chem.*, 1976, **16**, 195, 407.
7 J. Chatt, J. D. Garforth, and G. A. Rowe, *J. Chem. Soc. A*, 1966, 1834; W. E. Carroll and R. Bau, *J. Chem. Soc., Chem. Commun.*, 1978, 825.
8 J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 1960, 1718.
9 M. L. H. Green, 'Organometallic Compounds,' 3rd edn., Methuen, London, 1968, vol. 2, pp. 222—226.
10 D. R. Fahey, *Organomet. Chem. Rev.*, 1972, **7**, 245.
11 P. R. Sharp, D. Astruc, and R. R. Schrock, *J. Organomet. Chem.*, 1979, **182**, 477.
12 A. Palm and E. R. Bissell, *Spectrochim. Acta*, 1960, **16**, 459; J. M. Eyster and E. W. Prohotsky, *Spectrochim Acta, Ser. A*, 1974, **30**, 2041.
13 M. F. Lappert, C. L. Raston, G. L. Rowbottom, B. W. Skelton, and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1984, 883.
14 L. Astheimer, J. Hauck, H. J. Schenk, and K. Schwochau, *J. Chem. Phys.*, 1975, **63**, 1988; L. Astheimer and K. Schwochau, *J. Inorg. Nucl. Chem.*, 1976, **38**, 1131; J. J. Vajo, D. A. Aikens, L. Ashley, D. E. Poeltl, R. A. Bailey, H. M. Clark, and S. C. Bunce, *Inorg. Chem.*, 1981, **20**, 3328.
15 S. S. Eliseev, N. V. Gaidaenko, N. A. El'manova, and L. E. Malysheva, *Dokl. Akad. Nauk. Tadzh. SSR*, 1984, **27**, 145; *Chem. Abstr.*, 1985, 102: 55083j.
16 G. N. Schrauzer, L. A. Hughes, N. Strampach, P. Robinson, and E. O. Schlemper, *Organometallics*, 1982, **1**, 44.
17 G. N. Schrauzer, L. A. Hughes, N. Strampach, F. Ross, D. Ross, and E. O. Schlemper, *Organometallics*, 1983, **2**, 481.
18 G. N. Schrauzer, L. A. Hughes, E. O. Schlemper, F. Ross, and D. Ross, *Organometallics*, 1983, **2**, 11.
19 K. Nakamoto, 'Infrared and Raman Spectra of Inorganic and Coordination Compounds,' 3rd edn., Wiley-Interscience, New York, 1978, p. 115.
20 C. G. Barraclough and D. J. Kew, *Aust. J. Chem.*, 1972, **25**, 27.
21 R. R. Schrock, L. J. Guggenburger, and A. D. English, *J. Am. Chem. Soc.*, 1976, **98**, 903.
22 F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' 4th edn., Wiley-Interscience, New York, 1980, p. 1138.
23 G. Erker, *J. Organomet. Chem.*, 1977, **134**, 189 and refs. therein.
24 S. J. McLain, R. R. Schrock, P. R. Sharp, M. R. Churchill, and W. J. Youngs, *J. Am. Chem. Soc.*, 1979, **101**, 263.
25 J. F. Gibson, K. Mertis, and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1975, 1093.
26 R. P. Tooze, P. Stavropoulos, M. Motevalli, M. B. Hursthouse, and G. Wilkinson, *J. Chem. Soc., Chem. Commun.*, 1985, 1139.
27 A. S. Alves, D. S. Moore, R. A. Andersen, and G. Wilkinson, *Polyhedron*, 1982, **1**, 83.
28 P. A. Belmonte and Z-Y. Own, *J. Am. Chem. Soc.*, 1984, **106**, 7493.
29 P. G. Edwards, G. Wilkinson, M. B. Hursthouse, and K. M. Abdul Malik, *J. Chem. Soc., Dalton Trans.*, 1980, 2467.
30 M. B. Hursthouse, R. A. Jones, K. M. A. Malik, and G. Wilkinson, *J. Am. Chem. Soc.*, 1979, **101**, 4128.
31 SHELX 76, G. M. Sheldrick, University of Cambridge, 1976.
32 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.

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