Synthesis of Homoleptic Tetrahedral Aryls of Rhenium(IV) and Ruthenium(IV). *X*-Ray Crystal Structures of Tetrakis(*o*-methylphenyl)rhenium(IV), Tetrakis(*o*-methylphenyl)oxorhenium(VI), and Tetrakis(*o*-methylphenyl)-ruthenium(IV)†

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The reaction of ReCl$_4$(thf)$_2$ (thf = tetrahydrofuran) with *o*-methylphenylmagnesium bromide leads to the isolation of Re(*o*-MeC$_6$H$_4$)$_4$, which has been characterised by *X*-ray crystallography. Air oxidation of this compound allows the isolation of the previously reported paramagnetic ReO(*o*-MeC$_6$H$_4$)$_4$, which has also been characterised by *X*-ray crystallography. The interaction of aryl Grignard reagents with NEt$_4$[RuCl$_5$(solv)] (solv = acetonitrile or tetrahydrofuran) leads to the isolation of homoleptic, tetrahedral ruthenium(IV) species, Ru(aryl)$_4$, aryl = *o*-methylphenyl, 2,6-dimethylphenyl, and *p*-t-butylphenyl. Tetrakis(mesityl)ruthenium(IV), mesityl = 2,4,6-trimethylphenyl, and Ru(*o*-MeC$_6$H$_4$)$_4$ can be obtained from the interaction of diruthenium(II,II) tetra-acetate, Ru$_2$(μ-O$_2$CMe)$_4$, with the respective Grignard reagents. The *X*-ray crystal structure of Ru(*o*-MeC$_6$H$_4$)$_4$ has also been determined.

Neutral, homoleptic tetra-alkyls for various transition metals have been known for some time, being those of Ti, Zr, Th, V, Cr,[1] Mo,[2] W,[3] Mn,[4,5] Fe,[5] and Co.[5,6] However, homoleptic compounds of the platinum group metals have only recently been discovered.[7] The tetrahedral compounds, OsR$_4$, R = *o*-methylphenyl or phenyl, were isolated *via* the interaction of *o*-methylphenylmagnesium bromide or triphenylaluminium etherate with osmium tetraoxide. The tetrahedral cyclohexyls, M(cyclo-C$_6$H$_{11}$)$_4$, M = Os or Ru, were obtained *via* interaction of cyclohexylmagnesium bromide with Os$_2$(μ-O$_2$CMe)$_4$Cl$_2$ and Ru$_2$(μ-O$_2$CMe)$_4$Cl respectively.[8]

We now report the isolation of the first homoleptic tetra-aryl rhenium(IV) compound, tetrakis(*o*-methylphenyl)rhenium(IV), and the first examples of ruthenium(IV) compounds, RuR$_4$, R = *o*-methylphenyl, mesityl, 2,6-dimethylphenyl, or *p*-t-butylphenyl.

New compounds and their analyses are given in Table 1.

Results and Discussion

Tetrakis(o-methylphenyl)rhenium(IV).—The interaction of tetrachlorobis(tetrahydrofuran)rhenium(IV) with 2.4 equivalents of *o*-methylphenylmagnesium bromide in tetrahydrofuran under argon yields a deep red solution, from which dark red crystals of the paramagnetic compound tetrakis(*o*-methylphenyl)rhenium(IV) can be obtained in low yield after extraction into hexane and subsequent recrystallisation.

The i.r. spectrum shows only peaks characteristic of the *o*-methylphenyl ligand.

The mass spectrum shows two parent ions, *m/e* 551 (18%) for ^{187}Re and 549 (11%) for ^{185}Re, together with ions due to subsequent loss of *o*-methylphenyl ligands, with high intensities for both isotopes. The base peak is the tropylium ion, C$_7$H$_7$$^+$, *m/e* 91. No higher mass peaks were observed indicating that the compound is monomeric, and not the trimer, *i.e.*, dodeca(*o*-methylphenyl)-*triangulo*-trirhenium(IV). In the mass spectrum of Re$_3$(CH$_2$SiMe$_3$)$_{12}$ the *triangulo*-rhenium core was rigid and fragmentations due to the sequential loss of CH$_2$SiMe$_3$ groups were seen.[9]

Table 1. Analytical data for new compounds

Compound[a]	M.p./°C	Analysis (%)[b] C	Analysis (%)[b] H
Re(*o*-MeC$_6$H$_4$)$_4$	138—140	60.5 (61.0)	5.2 (5.1)
Ru(*o*-MeC$_6$H$_4$)$_4$	161—163	72.2 (72.2)	6.1 (6.1)
Ru(2,4,6-Me$_3$C$_6$H$_2$)$_4$	207 (decomp.)	74.4 (74.8)	7.3 (7.6)
Ru(2,6-Me$_2$C$_6$H$_3$)$_4$	182	73.4 (73.7)	6.9 (7.0)
Ru(*p*-Bu^{t}C$_6$H$_4$)$_4$	82—84 (decomp.)	75.7 (75.8)	8.1 (8.3)

[a] All compounds are dark red. [b] Found (required).

The magnetic moment of Re(*o*-MeC$_6$H$_4$)$_4$, $\mu_{\text{eff.}}$ = 1.31, accords with low-spin Re$^{\text{IV}}$, d^3, with one unpaired electron. The e.s.r. spectrum in frozen solution (98 K) shows a poorly resolved extremely broad signal over the range 150—380 mT, on which is superimposed the spectrum of ReO(*o*-MeC$_6$H$_4$)$_4$ [10] formed by oxidation; we have been unable to obtain a spectrum without this impurity due to the extreme air sensitivity of Re(*o*-MeC$_6$H$_4$)$_4$.

The structure of the compound has been determined by *X*-ray crystallography and a diagram of the molecular structure is shown in Figure 1; selected bond lengths and angles are given in Table 2. The rhenium co-ordination is slightly distorted tetrahedral, and, although the molecule lies in a general position in the unit cell, the molecular symmetry is quite close to $\bar{4}$. A similar structure was found for the osmium(IV) complex[8] (and the ruthenium analogue, see below) the molecules of which, however, occupy a special position in the cell. The main difference between the rhenium and osmium structures is that whereas there is a small degree of flattening of the tetrahedron in the direction of the $\bar{4}$ axis (C–Os–C′ angles ≈ 114, 117°), in the rhenium complex there is essentially no distortion of this type, but a slight twist of the two C–Re–C planes, which make a dihedral angle of 86.75°.

As noted above, Re(*o*-MeC$_6$H$_4$)$_4$ on air oxidation gives tetrakis(*o*-methylphenyl)oxorhenium(VI)[10] as air-stable, para-

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

Table 2. Selected bond lengths (Å) and angles (°) for Re(*o*-MeC$_6$H$_4$)$_4$

C(1)–Re	2.020(9)	C(8)–Re	2.038(9)
C(15)–Re	2.033(8)	C(22)–Re	2.028(9)
C(7)–C(6)	1.509(13)	C(21)–C(20)	1.511(14)
C(14)–C(13)	1.431(12)	C(28)–C(27)	1.491(12)
C(8)–Re–C(1)	108.9(4)	C(15)–Re–C(1)	105.6(4)
C(15)–Re–C(8)	113.4(4)	C(22)–Re–C(1)	112.4(4)
C(22)–Re–C(8)	107.4(4)	C(22)–Re–C(15)	109.3(4)
C(2)–C(1)–Re	119.9(6)	C(6)–C(1)–Re	122.1(6)
C(9)–C(8)–Re	118.0(6)	C(13)–C(8)–Re	123.7(7)
C(16)–C(15)–Re	120.0(6)	C(20)–C(15)–Re	122.5(7)
C(23)–C(22)–Re	119.1(6)	C(27)–C(22)–Re	122.9(6)

Table 3. Selected bond lengths (Å) and angles (°) for ReO(*o*-MeC$_6$H$_4$)$_4$

O–Re	1.822(8)	C(1)–Re	2.063(6)
C(7)–C(6)	1.543(13)		
C(1)–Re–O	106.0(2)	C(1)–Re–C(1a)	85.6(1)
C(1)–Re–C(1b)	148.0(3)	C(2)–C(1)–Re	118.5(4)
C(6)–C(1)–Re	124.0(5)		

Symmetry operations relating designated atoms to reference atoms at (*x*,*y*,*z*): (a) *y*, −*x*,*z*; (b) −*x*, −*y*,*z*.

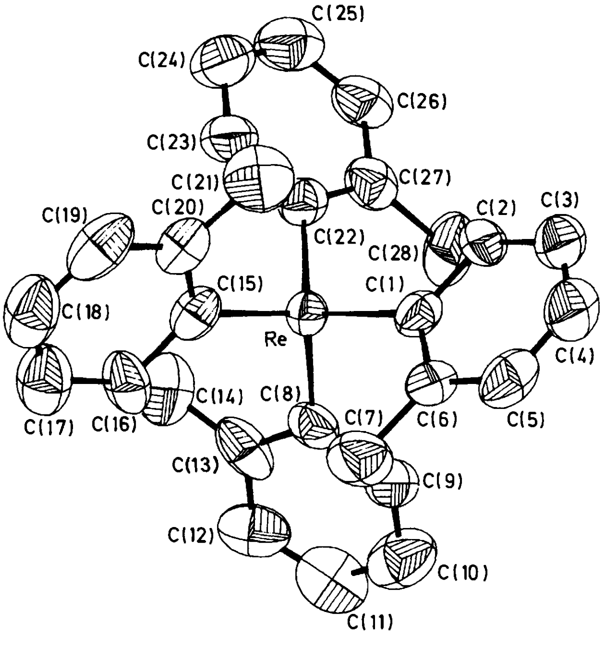

Figure 1. Molecular structure of Re(*o*-MeC$_6$H$_4$)$_4$

Table 4. Selected bond lengths (Å) and angles (°) for Ru(*o*-MeC$_6$H$_4$)$_4$

C(1)–Ru	2.047(9)	C(8)–Ru	1.943(9)
C(7)–C(6)	1.539(13)	C(14)–C(13)	1.471(14)
C(8)–Ru–C(1)	106.3(4)	C(1)–Ru–C(1a)	114.9(6)
C(8)–Ru–C(1a)	107.8(6)	C(8)–Ru–C(8a)	113.9(6)
C(2)–C(1)–Ru	117.4(7)	C(6)–C(1)–Ru	121.1(8)
C(9)–C(8)–Ru	118.5(7)	C(13)–C(8)–Ru	125.4(7)

Key to symmetry operation relating designated atoms to reference atoms at (*x*,*y*,*z*): (a) −*x*, −*y*,*z*.

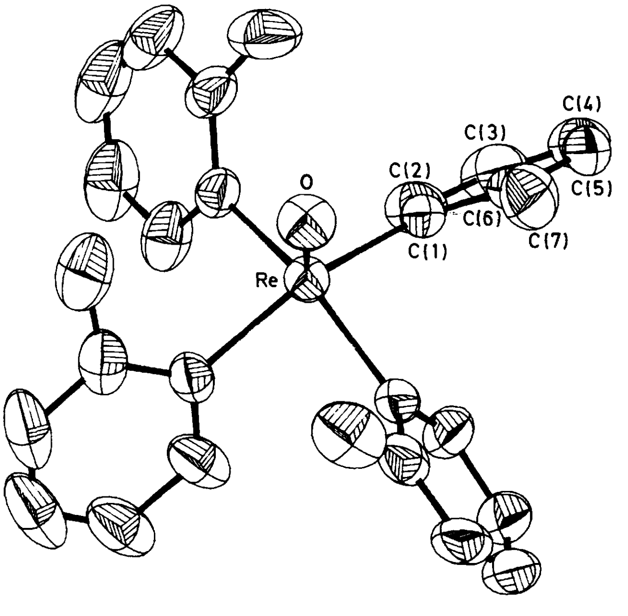

Figure 2. Molecular structure of ReO(*o*-MeC$_6$H$_4$)$_4$

magnetic dark green crystals: the structure has now been determined and is shown in Figure 2; selected bond lengths and angles are given in Table 3. The molecule lies on a four-fold axis in the unit cell and as a result all four *o*-methylphenyl rings have equivalent orientations, with the methyl groups on the same side as the oxo function. The contact distances between the oxo atom and the methyl carbon are 3.106 Å, and the CH$_3$ group is oriented so that one hydrogen is closer to the oxygen (2.633 Å) than the other two. It is possible that this is indicative of electrostatic interaction, although there is a clear indication that the ring is tilted slightly to relieve this close contact [*cf.* angles Re–C(1)–C(2) and Re–C(1)–C(6), Table 3]. It is also worth noting that the phenyl ring angle at the point of bonding to the metal [C(2)–C(1)–C(6)] is significantly less than 120°. The Re=O and Re–C distances are similar to those found in ReO(2,4,6-Me$_3$C$_6$H$_2$)$_4$.[10]

Reactions of Re(*o*-MeC$_6$H$_4$)$_4$ other than the oxidation noted above will be described later.

Tetra-aryls of Ruthenium(IV).—(*a*) o-*Methylphenyl*. The interaction of NEt$_4$[RuCl$_5$(solv)], solv = acetonitrile[11] or tetrahydrofuran (thf), with 5 equivalents of *o*-methylphenylmagnesium bromide in thf gives diamagnetic, air-stable tetrakis(*o*-methylphenyl)ruthenium(IV) which can be crystallised from hexane or acetonitrile as fine red needles. The compound can also be obtained from the interaction of Ru$_2$(μ-O$_2$CMe)$_4$[12] and 8 equivalents of *o*-methylphenylmagnesium bromide in thf.

The i.r. spectrum shows bands characteristic of the *o*-methylphenyl ligand and the ^{1}H n.m.r. spectrum has a singlet at δ 2.11 and multiplets at δ 6.85, 7.00, and 7.20 due to the aromatic hydrogens. The ^{13}C n.m.r. spectrum has seven sharp singlets as expected. The mass spectrum shows the parent ion, *m*/*e* 466 (84%), and subsequent losses of *o*-methylphenyl groups; the base mass is at *m*/*e* 282 corresponding to Ru(*o*-MeC$_6$H$_4$)$_2$$^+$.

A diagram of the molecular structure is shown in Figure 3; selected bond lengths and angles are given in Table 4. The complex is isostructural with the osmium(IV) complex previously characterised,[8] and has exact C_2 and $\bar{4}$ symmetry. Interestingly, we find that the two independent Ru–C distances

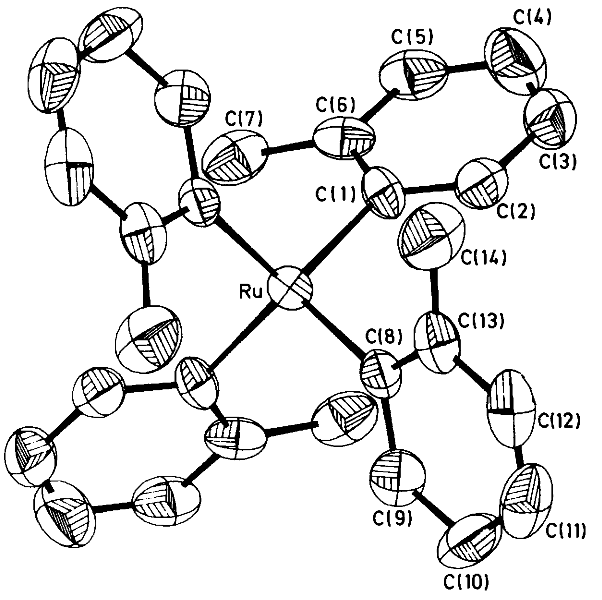

Figure 3. Molecular structure of $Ru(o\text{-}MeC_6H_4)_4$

show a slightly more pronounced difference than in the osmium complex (0.09 Å here, 0.04 Å in the osmium complex). Otherwise, the average value for the Ru–C bond is essentially identical to that for the Os–C bond.

The only other examples of tetrahedral *o*-methylphenyls are those of rhenium and osmium.[8]

The reactions of these ruthenium and osmium compounds will be reported separately but it may be noted that they are sufficiently resistant to survive electrophilic attacks and Friedel–Crafts acylation.

(*b*) *Mesityl.* The interaction of $Ru_2(\mu\text{-}O_2CMe)_4$ with 8 equivalents of mesitylmagnesium bromide in tetrahydrofuran leads to diamagnetic tetrakis(2,4,6-trimethylphenyl)ruthenium(IV) as a red powder. The reaction is clearly complicated, presumably involving a Ru–Ru bond cleavage and a disproportionation; possibly $2Ru^{II} \longrightarrow Ru^{IV} + Ru^0$.

The i.r. spectrum shows only mesityl bands while the ^1H n.m.r. spectrum has low-field phenyl resonances at δ 6.8 and two sharp singlets at δ 2.24 and 2.19 (relative intensities 3:6 H respectively). The mass spectrum at 70 eV (1.12×10^{-17} J) shows the parent ion, *m*/*e* 578 (4.1%), and subsequent loss of mesityl ligands, complicated further by the facile loss of methyl groups from the aromatic ring. The base peak, *m*/*e* 207, can be ascribed to $Ru(Me_2C_6H_2)^+$.

(*c*) *2,6-Dimethylphenyl.* The interaction of $NEt_4[RuCl_5(thf)]$ with 5 equivalents of 2,6-dimethylphenylmagnesium bromide in tetrahydrofuran gives diamagnetic tetrakis(2,6-dimethylphenyl)ruthenium(IV) as dark red crystals in a low yield. The i.r. spectrum exhibits peaks due to the 2,6-dimethylphenyl ligand and the ^1H n.m.r. spectrum shows peaks at δ 7.11 and 6.90 (intensity 2:1 H respectively) and at δ 2.13. The mass spectrum shows the parent ion *m*/*e* 522 (79%) and subsequent losses of the ligand, again complicated further by the facile loss of methyl groups.

(*d*) p-*t-Butylphenyl.* The interaction of $NEt_4[RuCl_5(thf)]$ with 6 equivalents of *p*-t-butylphenylmagnesium bromide in tetrahydrofuran or diethyl ether gives diamagnetic tetrakis(*p*-t-butylphenyl)ruthenium(IV) as a dark red powder in low yield. The ^1H n.m.r. spectrum shows the unsymmetrical *p*-substitution pattern for the aromatic ring and a sharp singlet for the t-butyl protons. The $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum consists of six sharp singlets; those at 31.4 and 34.5 p.p.m. are due to the three methyl groups and the tertiary butyl group, respectively, while peaks at 125.6, 126.7, 138.3, and 149.9 are due to the four unique phenyl carbons. The mass spectrum is complicated by the facile losses of the methyl groups from the *p*-t-butyl groups. However, the spectrum shows all ruthenium aryl losses and peaks from the subsequent loss of methyl and butyl groups. The base mass, *m*/*e* 398, presumably corresponds to $Ru(Bu^tC_6H_4)(C_6H_4)(C_6H_4C)^+$ or an equivalent formulation.

Experimental

Microanalyses were by Pascher Laboratories. Spectrometers: i.r., Perkin-Elmer 683 (spectra in Nujol mulls or KBr discs); n.m.r., Bruker WM-250, AM 500 MHz, and JEOL FX 90Q (data in $CDCl_3$ or C_6D_6 in p.p.m. relative to $SiMe_4$); e.s.r., Varian E-12 (*X*-band); mass, Kratos MS 902 at 70 eV.

The compounds $ReCl_4(thf)_2$,[13] $Ru_2(\mu\text{-}O_2CMe)_4$,[12] and $NEt_4[RuCl_5(MeCN)]$[11] were prepared by literature methods. Solvents were refluxed over sodium or sodium–benzophenone under nitrogen and distilled before use. All operations were carried out under vacuum-purified argon.

Tetrakis(o-*methylphenyl*)*rhenium*(IV).—To a stirred suspension of $ReCl_4(thf)_2$ (0.54 g, 1.14 mmol) in thf (30 cm³) at −78 °C was added *o*-methylphenylmagnesium bromide (2.6 cm³ of a 1.0 mol dm⁻³ solution in Et_2O, 2.60 mmol) and the mixture warmed to room temperature and stirred overnight. The volatile material was removed under reduced pressure and the residue extracted with hexane (4 × 30 cm³). Concentration of the filtered extracts to *ca.* 30 cm³ and cooling overnight (−20 °C) afforded dark red crystals. Yield: 0.18 g, 29%.

Mass spectrum: *m*/*e* 551 (18), $^{187}Re(o\text{-}MeC_6H_4)_4^+$; 549 (11), $^{185}Re(o\text{-}MeC_6H_4)_4^+$; 459 (24), $^{187}Re(o\text{-}MeC_6H_4)_3^+$; 457 (21), $^{185}Re(o\text{-}MeC_6H_4)_3^+$; 369 (3), $^{187}Re(o\text{-}MeC_6H_4)_2^+$; 367 (8), $^{185}Re(o\text{-}MeC_6H_4)_2^+$; and 91 (100%), $C_7H_7^+$. I.r.: 3 050m, 1 564w, 1 440m, 1 281w, 1 247w, 1 190w, 1 110m, 1 052w, 1 028m, and 740s cm⁻¹.

Tetraethylammonium pentachloro(*tetrahydrofuran*)*ruthenate*(IV).—The salt $NEt_4[RuCl_5(MeCN)]$[11] (1.0 g, 2.2 mmol) was refluxed in thf (80 cm³) for *ca.* 1 d. The solid was collected and washed with thf (2 × 30 cm³) to yield a red-brown solid. Yield: 0.83 g, 79%. M.p. 156 °C (decomp.) (Found: C, 29.5; H, 5.6; N, 3.0. $C_{12}H_{28}Cl_5NORu$ requires C, 30.0; H, 5.9; N, 2.9%).

I.r.: 2 980s, 2 950(sh), 2 905(sh), 2 878(sh), 1 480s, 1 455s, 1 391s, 1 370m, 1 345w, 1 305w, 1 185s, 1 175s, 1 068m, 1 020s, 1 005s, 920m, 865vs, 790s, 690w, and 470m cm⁻¹.

Tetrakis(o-*methylphenyl*)*ruthenium*(IV).—*Method A.* To a stirred suspension of $NEt_4[RuCl_5(MeCN)]$ (0.43 g, 0.96 mmol) in thf (50 cm³) at −78 °C was added *o*-methylphenylmagnesium bromide (2.3 cm³ of a 1.6 mol dm⁻³ solution in Et_2O, 3.8 mmol) and the mixture warmed to room temperature then refluxed for 2 h. The volatile material was removed and the residue extracted in diethyl ether (3 × 30 cm³). Water (10 cm³, degassed for 1 h) was added to destroy any excess of Grignard, and the red ether solution filtered onto $MgSO_4$ (5 g) at −10 °C. Filtration and evaporation to dryness, extraction into hexane (10 cm³), and cooling overnight (−20 °C) yielded a dark red crystalline solid. Yield: 0.15 g, 34%.

Method B. As above except using $NEt_4[RuCl_5(thf)]$. Yield: *ca.* 48%.

Method C. To a stirred suspension of $Ru_2(\mu\text{-}O_2CMe)_4$ (0.27 g, 0.62 mmol) in thf (50 cm³) at −78 °C was added *o*-methylphenylmagnesium bromide (3.0 cm³ of a 1.6 mol dm⁻³ solution in Et_2O, 4.9 mmol); work up as in method A. Yield: 0.07 g, 24%.

Mass spectrum: *m*/*e* 466 (84), Ru(*o*-MeC$_6$H$_4$)$_4{}^+$; 374 (12), Ru(*o*-MeC$_6$H$_4$)$_3{}^+$; 282 (100), Re(*o*-MeC$_6$H$_4$)$_2{}^+$; 192 (12), Ru(*o*-MeC$_6$H$_4$)$^+$; and 91 (55%), C$_7$H$_7{}^+$. I.r.: 1 565s, 1 435(sh), 1 255w, 1 190m, 1 160w, 1 050w, 1 025s, 979w, 865w, 860w, 740vs, 660m, 500w, and 445s cm^{-1}. N.m.r.: ^{1}H, 2.11 (3 H, s, *o*-Me), 6.85 (1 H, m, C$_6$H$_4$), 7.00 (2 H, m, C$_6$H$_4$), and 7.20 (1 H, m, C$_6$H$_4$); ^{13}C, 25.3 (s, *o*-Me), and 124.8, 127.3, 128.9, 133.4, 139.0, and 160.8 (s, C$_6$H$_4$).

Tetrakis(2,4,6-*trimethylphenyl*)*ruthenium*(IV).—To a stirred suspension of Ru$_2$(μ-O$_2$CMe)$_4$ (0.42 g, 0.96 mmol) in thf (40 cm^3) at −78 °C was added mesitylmagnesium bromide (12.8 cm^3 of a 0.6 mol dm^{-3} solution in Et$_2$O, 7.66 mmol). The mixture was warmed slowly and stirred at room temperature for 1 h. The resulting red solution was evaporated and the residue extracted into hexane (3 × 30 cm^3), and the solution filtered and evaporated. The residue was extracted with diethyl ether (2 × 30 cm^3) and water (20 cm^3) added, the mixture stirred for 0.5 h, cooled to −10 °C, and filtered onto MgSO$_4$ (5 g). The red solution was stirred for 1 h, filtered, concentrated, and the residue extracted with hexane (10 cm^3) and cooled overnight (−20 °C) to yield a red solid. Yield: 0.12 g, 21%.

Mass spectrum: *m*/*e* 578 (4.1), Ru(Me$_3$C$_6$H$_2$)$_4{}^+$; 341 (10), Ru(Me$_3$C$_6$H$_2$)$_2{}^+$; 221 (22), Ru(Me$_3$C$_6$H$_4$)$^+$; 207 (100), Ru(Me$_2$C$_6$H$_2$)$^+$; 119 (4), Me$_3$C$_6$H$_2{}^+$; 91 (29), C$_7$H$_7{}^+$; and 77 (15%), C$_6$H$_5{}^+$. I.r.: 1 582w, 1 305m, 1 260m, 1 085vbr, 1 030vbr, 805m, 608w, 540w, and 530w cm^{-1}. N.m.r.: ^{1}H, 2.19 (6 H, s, *o*-MeC$_6$H$_2$), 2.24 (3 H, s, *p*-MeC$_6$H$_2$), and 6.8 (2 H, s, phenyl).

Tetrakis(2,6-*dimethylphenyl*)*ruthenium*(IV).—*Method A*. To a stirred suspension of NEt$_4$[RuCl$_5$(thf)] (0.35 g, 0.73 mmol) in thf (40 cm^3) at −78 °C was added 2,6-dimethylphenylmagnesium bromide (11.6 cm^3 of a 0.5 mol dm^{-3} solution in Et$_2$O, 5.8 mmol) and the mixture was warmed to room temperature and stirred for *ca*. 1 d. The volatile material was removed under reduced pressure and the residue extracted in diethyl ether (3 × 30 cm^3). Water (20 cm^3, degassed for 1 h) was added, stirred for 1 h, and the dark red ether solution was filtered onto MgSO$_4$ (5 g) at −10 °C. Filtration and concentration to dryness, extraction into hexane (10 cm^3), and cooling overnight (−20 °C) yielded a dark red crystalline solid. Yield: 0.08 g, 21%.

Method B. As method A, except using NEt$_4$[RuCl$_5$(MeCN)] instead of the tetrahydrofuran adduct. Yield: 0.05 g, 13%.

Mass spectrum: *m*/*e* 522 (79), Ru(2,6-Me$_2$C$_6$H$_3$)$_4{}^+$; 415 (27), Ru(2,6-Me$_2$C$_6$H$_3$)$_3{}^+$; 309 (100), Ru(2,6-Me$_2$C$_6$H$_3$)$_2{}^+$; 205 (34) Ru(2,6-Me$_2$C$_6$H$_3$)$^+$; 106 (43), 2,6-Me$_2$C$_6$H$_3{}^+$; 91 (70), C$_7$H$_7{}^+$; and 77 (30%) C$_6$H$_5{}^+$. I.r.: 1 556w, 1 375(sh), 1 305m, 1 265m, 1 161br, 1 153m, 1 020s, 978m, 897w, 802br, 768s, 605m, and 510m cm^{-1}. N.m.r.: ^{1}H, 2.13 (6 H, s, Me$_2$C$_6$H$_3$), 6.90 (1 H, m, *p*-Me$_2$C$_6$H$_3$), and 7.11 (2 H, m, *m*-Me$_2$C$_6$H$_3$).

Tetrakis(p-*t-butylphenyl*)*ruthenium*(IV).—To a stirred suspension of NEt$_4$[RuCl$_5$(thf)] (0.3 g, 0.63 mmol) in diethyl ether (40 cm^3) at −78 °C was added 2-t-butylphenylmagnesium bromide (4.8 cm^3 of a 0.78 mol dm^{-3} solution in Et$_2$O, 3.75 mmol) and the mixture warmed to room temperature and stirred for 8 h. The red solution was filtered and water (25 cm^3) added, stirred, and filtered onto MgSO$_4$ (8 g) at −10 °C. Filtration and concentration to dryness, extraction into hexane (25 cm^3), and cooling overnight at −20 °C yielded a dark red solid. Yield: 0.08 g, 20%.

Mass spectrum: *m*/*e* 634 (7), Ru(Bu^{t}C$_6$H$_4$)$_4{}^+$; 501 (8), Ru(Bu^{t}C$_6$H$_4$)$_3{}^+$; 368 (18), Ru(Bu^{t}C$_6$H$_4$)$_2{}^+$; 234 (4), Ru(Bu^{t}C$_6$H$_4$)$^+$; 90 (58), C$_7$H$_5{}^+$; and 57 (44%), CMe$_3{}^+$. I.r.: 2 964s, 2 904(sh), 2 872(sh), 1 601w, 1 494w, 1 461w, 1 400w, 1 362m, 1 297vbr, 1 262vs, 1 021vbr, 865(sh), 801vs, 702w, 664(sh), 557w, and 397s cm^{-1}. N.m.r.: ^{1}H, 1.41 (9 H, s, Bu^t) and 7.53 (4 H, m,

Table 5. Crystallographic data

(a) Crystal data			
Formula	C$_{28}$H$_{28}$Re	C$_{28}$H$_{28}$ORe	C$_{28}$H$_{28}$Ru
M	550.729	566.729	465.599
Crystal system	Monoclinic	Tetragonal	Orthorhombic
a/Å	18.311(2)	9.227(1)	8.054(1)
b/Å	10.936(2)	9.227(2)	16.241(1)
c/Å	11.598(1)	6.740(5)	8.551(2)
α/°	90	90	90
β/°	94.89(9)	90	90
γ/°	90	90	90
U/Å^3	2 314.04(62)	573.83(45)	1 118.51(30)
Space group	$P2_1/n$	$P4$	$Pba2$
D_c/g cm^{-3}	1.58	1.64	1.38
Z	4	1	2
F(000)	1 084	279	480
μ(Mo-K_α)/cm^{-1}	53.32	53.80	6.97
(b) Data collection			
$\theta_{\text{min., max.}}$/°	1.5, 25	1.5, 30	1.5, 25
Total data measured	4 682	1 958	1 186
Total data unique	4 062	903	1 054
Total data observed	2 843	900	787
Significance test	$F_o > 3\sigma(F_o)$	$F_o > 4\sigma(F_o)$	$F_o > 3\sigma(F_o)$
(c) Refinement			
No. of parameters	374	98	187
Weighting scheme parameter g[a]	0.0001	0.000 083	0.000 22
Final R[b]	0.0357	0.0155	0.0327
Final R'[c]	0.0303	0.0209	0.0394

[a] $w = 1/[\sigma^2(F_o) + gF_o{}^2]$. [b] $R = \Sigma\Delta F/\Sigma F_o$. [c] $R' = [\Sigma w(\Delta F)^2/\Sigma wF_o{}^2]^{\frac{1}{2}}$.

Table 6. Fractional atomic co-ordinates (× 10^4) for Re(*o*-MeC$_6$H$_4$)$_4$

Atom	x	y	z
Re	1 688(0.5)	2 322(0.5)	4 654(0.5)
C(1)	1 936(4)	563(6)	5 045(6)
C(2)	1 634(4)	−387(7)	4 328(6)
C(3)	1 806(6)	−1 596(7)	4 583(8)
C(4)	2 270(5)	−1 882(8)	5 529(8)
C(5)	2 576(5)	−978(8)	6 234(7)
C(6)	2 420(4)	237(6)	6 010(6)
C(7)	2 789(6)	1 213(9)	6 773(9)
C(9)	965(4)	2 261(8)	6 872(7)
C(10)	597(5)	2 663(10)	7 757(8)
C(11)	382(5)	3 875(10)	7 765(9)
C(12)	526(4)	4 682(10)	6 931(9)
C(13)	908(4)	4 264(7)	5 968(8)
C(8)	1 139(3)	3 051(6)	5 947(6)
C(14)	1 037(5)	5 112(9)	5 067(9)
C(15)	2 663(3)	3 156(7)	4 465(6)
C(16)	2 852(4)	4 220(8)	5 085(8)
C(17)	3 485(5)	4 886(8)	4 903(9)
C(18)	3 939(5)	4 451(11)	4 122(10)
C(19)	3 783(4)	3 372(10)	3 530(8)
C(20)	3 157(4)	2 726(7)	3 695(6)
C(21)	3 026(5)	1 541(9)	3 040(9)
C(22)	1 031(4)	2 486(6)	3 164(6)
C(23)	1 301(4)	3 108(8)	2 204(7)
C(24)	881(5)	3 264(9)	1 164(7)
C(25)	179(5)	2 805(9)	1 045(8)
C(26)	−93(5)	2 155(8)	1 933(8)
C(27)	313(4)	2 001(7)	3 023(7)
C(28)	−17(5)	1 366(9)	3 991(9)

Table 7. Fractional atomic co-ordinates ($\times 10^4$) for $ReO(o\text{-}MeC_6H_4)_4$

Atom	x	y	z
Re	0*	0*	0*
O	0*	0*	2 703(9)
C(1)	1 709(4)	1 304(4)	−844(7)
C(2)	1 611(6)	2 059(5)	−2 654(8)
C(3)	2 763(7)	2 878(6)	−3 376(10)
C(4)	4 009(7)	2 985(7)	−2 314(13)
C(5)	4 140(5)	2 255(6)	−510(11)
C(6)	3 014(4)	1 391(4)	179(14)
C(7)	3 291(6)	577(8)	2 143(10)

* Invariant parameter.

Table 8. Fractional atomic co-ordinates ($\times 10^4$) for $Ru(o\text{-}MeC_6H_4)_4$

Atom	x	y	z
Ru	0*	0*	0*
C(1)	1 635(8)	−687(5)	1 288(10)
C(2)	3 243(9)	−689(5)	827(9)
C(3)	4 398(10)	−1 150(6)	1 588(11)
C(4)	3 948(10)	−1 655(7)	2 804(12)
C(5)	2 281(10)	−1 607(5)	3 368(10)
C(6)	1 093(9)	−1 162(4)	2 611(8)
C(7)	−689(11)	−1 080(6)	3 241(10)
C(8)	1 334(8)	754(5)	−1 239(10)
C(9)	1 433(9)	1 598(5)	−760(10)
C(10)	2 458(10)	2 162(6)	−1 477(11)
C(11)	3 435(10)	1 845(6)	−2 735(11)
C(12)	3 344(9)	1 136(7)	−3 233(9)
C(13)	2 274(8)	538(5)	−2 548(9)
C(14)	2 333(11)	−308(6)	−3 159(11)

* Invariant parameter.

C_6H_4); ^{13}C, 31.4 (s, C*Me*$_3$), 34.5 (s, *C*Me$_3$), 125.6, 126.7, 138.3, and 149.9 (s, C_6H_4).

X-Ray Crystallography.—Crystals used for the *X*-ray work were sealed under argon in thin-walled glass capillaries. All crystallographic measurements were made at 293 K using a Nonius CAD4 diffractometer and graphite-monochromated Mo-K_α radiation (λ = 0.710 69 Å), following previously detailed procedures.[14] The structures were solved *via* the heavy-atom method and refined by full-matrix least squares. Non-hydrogen atoms were refined anisotropically and hydrogens, all of which were experimentally located on difference maps, isotropically. Details of the crystal data, data collection, and refinement are given in Table 5. Atomic co-ordinates are given in Tables 6—8. Computer programs and sources of scattering factor data were as previously indicated.[14]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond distances and angles.

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