Homoleptic Mesityls of Iridium(III,IV,V) and Ruthenium(IV,V)†

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The interaction of $IrCl_3(tht)_3$, tht = tetrahydrothiophene, and mesityl (2,4,6-trimethylphenyl, mes)-magnesium bromide in diethyl ether gives $Ir(mes)_3$ as a very air-sensitive crystalline solid. Interaction of partially dehydrated $IrCl_3$ with mesityllithium in Et_2O gives the air-stable, paramagnetic $Ir(mes)_4$. Interaction of $RuCl_3(tht)_3$ with $Mg(mes)_2(thf)_2$ (thf = tetrahydrofuran) gives $Ru(mes)_4$. The tetramesityls can be oxidised by AgO_3SCF_3 or $NOPF_6$ to give, respectively $[Ir^V(mes)_4]O_3SCF_3$ and $[Ru^V(mes)_4]PF_6$, the former being diamagnetic and the latter paramagnetic. Cyclic voltammetric and some chemical studies have been made and nuclear magnetic and electron paramagnetic resonance spectra recorded. The NMR spectra of the diamagnetic compounds show that there is synchronous rotation of mesityl groups about the M–C bond. The X-ray crystal structures of $Ir(mes)_3$, $[Ir(mes)_4]O_3SCF_3$ and $Ru(mes)_4$ have been determined; the tris(mesityl) is similar to that of $Rh(mes)_3$ described earlier while the tetramesityl compounds are tetrahedral or slightly distorted tetrahedral.

The synthesis, X-ray structure and some reactions of tris(mesityl)rhodium(III) (mesityl = 2,4,6-trimethylphenyl, mes) have been described.[1] We now report the synthesis of tris(mesityl)iridium, together with details of the synthesis and chemistry of $Ir(mes)_4$, whose X-ray crystal structure has been given;[2] an improved synthesis of $Ru(mes)_4$[3] from $RuCl_3(tht)_3$ (tht = tetrahydrothiophene) is reported, together with its X-ray crystal structure. Both $M(mes)_4$ compounds can be chemically oxidised to the respective M^V cations and the structure of the iridium(V) cation has been determined.

Analytical and physical data for the compounds are given in Table 1.

Table 1 Analytical and physical data[a]

Compound	Colour	M.p./°C	Analysis[b] (%) C	H
1 $Ir(mes)_3$	Brown-red	Decomp.	58.0	6.2
		>100	(59.0)	(6.1)
2 $Ir(mes)_4$	Brown-red	*ca.* 140	64.6	6.7
		(decomp.)	(64.6)	(6.6)
3 $Ru(mes)_4$	Green-black	Decomp.	74.3	8.1
		>300	(74.4)	(7.7)
4 $[Ir(mes)_4]$- O_3SCF_3	Green-brown	*ca.* 208	54.1	5.2
		(decomp.)	(54.3)	(5.4)
5 $[Ir(mes)_4]PF_6$	Green-brown	*ca.* 200	53.3	5.6
		(decomp.)	(53.1)	(5.5)
6 $[Ru(mes)_4]PF_6$	Blue-black	Decomp.	59.0	6.0
		>300	(59.8)	(6.1)

[a] For mass spectra see Experimental section. [b] Required values are given in parentheses.

Table 2 Selected bond lengths (Å) and angles (°) for $Ir(mes)_3$ 1

C(11)–Ir	1.980(9)	C(21)–Ir	2.051(10)
C(31)–Ir	1.972(10)		
C(21)–Ir–C(11)	109.9(4)	C(31)–Ir–C(11)	106.5(4)
C(31)–Ir–C(21)	106.1(4)	C(12)–C(11)–Ir	110.5(6)
C(16)–C(11)–Ir	130.9(6)	C(22)–C(21)–Ir	131.2(6)
C(26)–C(21)–Ir	109.0(7)	C(32)–C(31)–Ir	129.9(8)
C(36)–C(31)–Ir	109.6(7)		

Results and Discussion

Syntheses and X-Ray Crystal Structures.—Tris(mesityl)iridium 1 was obtained by interaction of mesitylmagnesium bromide with $IrCl_3(tht)_3$[4] in Et_2O, the procedure being essentially the same as that for $Rh(mes)_3$.[1b] The red-brown crystalline solid is readily soluble in hexane, toluene and hexamethyldisiloxane but the compound differs from its rhodium analogue in being exceedingly air-sensitive and reactive both in the solid state and in solution. It also differs in decomposing without melting on heating.

A diagram of the molecule of $Ir(mes)_3$ is shown in Fig. 1, with selected bond lengths and angles in Table 2. The structure is analogous to that previously found for tris(mesityl)rhodium.[1a] The $IrCl_3$ unit is pyramidal, with C–Ir–C angles of 106.1(4)–109.9(4)°. The planes of the three mesityls are oriented around the Ir–C bonds in a systematic, propeller-like manner, and the metal atom then makes very close contacts [2.28–2.40(5) Å] on the top side of the pyramid, with one hydrogen from an α-methyl group on each ligand, to complete a quasi *fac* (3C,3H), octahedral configuration. This arrangement is also correlated with an 'in-plane' tilt of the mesityl ring to give Ir–C–C_α angles of 129.9(8)–131.2(6)° at the 'underside' of the pyramid, and 109.0(6)–110.5(6)° on the side where the Ir··· H close contacts occur. This distortion could arise either through a pulling-in of the three hydrogens on 'top' of the pyramid due to genuine Ir··· H attractions or, more likely, in steric repulsions between the methyl groups on the underside of the pyramid. Magic-angle spinning NMR spectra of solid $Rh(mes)_3$ provided no evidence of agostic hydrogens.[1b]

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

Non-SI unit employed: G = 10^{-4} T.

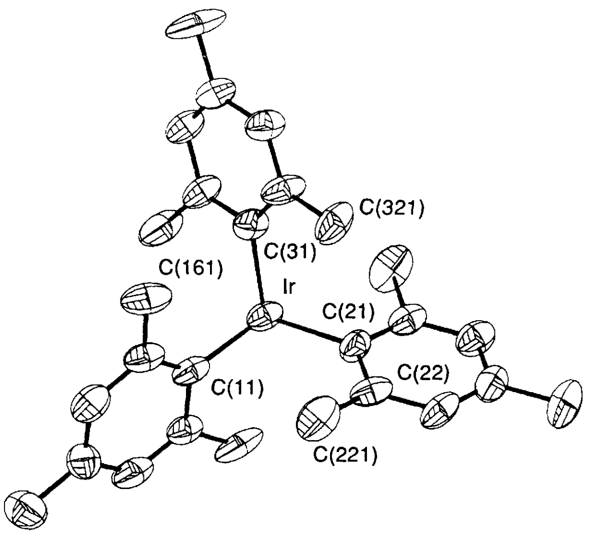

Fig. 1 The structure of tris(mesityl)iridium (30% probability ellipsoids)

Tetrakis(mesityl)iridium **2** has been obtained by the interaction of partially dehydrated $IrCl_3{\cdot}nH_2O$ (subsequently referred to as '$IrCl_3$') and mesityllithium at temperatures around 20 °C; no product is obtained using tetrahydrofuran (thf) as solvent although $Ir(mes)_4$ is stable in thf. The yields, which never exceed about 20%, also depend on the particular batch of $IrCl_3{\cdot}nH_2O$ and on the drying process; aged, '$IrCl_3$', especially if not kept moist with Et_2O, gives considerably reduced yields. The method of formation of $Ir(mes)_4$ is obscure, but could involve a disproportionation, $2Ir^{III} \longrightarrow Ir^{II} + Ir^{IV}$, or oxidation of an intermediate mesityl compound by '$IrCl_3$'; since '$IrCl_3$' is insoluble in Et_2O the reaction is heterogeneous. A possible intermediate could have been $Li[Ir(mes)_4]$ but, as noted later, $Ir(mes)_3$ does not react with Li(mes) in Et_2O and careful air-oxidation of the ether solution gives no $Ir(mes)_4$ but only a green solution (see later). There is always a dark intractable and insoluble residue after extraction of **2** by hexane.

Use of other starting materials in the reaction with Li(mes) gives no isolable product: $IrCl_3(tht)_3$,[4] K_2IrCl_6, $Li[IrI_4(dppe)]$ [dppe = 1,2-bis(diphenylphosphino)ethane],[5a] $IrCl_4(PR_3)_2$[5b] (R = Et or Ph) and the blue solid obtained after evaporation of the blue solution produced rapidly on ozonisation of glacial acetic acid containing $IrCl_3{\cdot}nH_2O$ and which is probably an oxo-centred bridged carboxylate[5c] of mixed $Ir^{III,IV}$ valence.

The tetramesityl forms dark brown-black crystals that are stable in air at room temperature: they are soluble in Et_2O, CH_2Cl_2, MeCN, toluene, *etc.*, giving pink-brown solutions. The compound is paramagnetic and its X-band EPR spectrum is shown in Fig. 2: the data are consistent with a tetrahedral, low-spin d^5 molecule having a single unpaired electron, $g_{\parallel} = 2.487$, $g_{\perp} = 2.005$. There is additional structure due to ^{191}Ir and ^{193}Ir isotopes (38 and 61% abundance, respectively). The EPR spectrum provides the best test for the presence of **2** in reaction solutions.

The X-ray crystal structure of $Ir(mes)_4$[2] showed a slight distortion from tetrahedral geometry with no evidence of any agostic hydrogen interactions. No other mononuclear tetrahedral compound of iridium(IV), either inorganic[6] or organometallic[7] is known. Iridium tetrafluoride is polymeric[8] while the structure of the other tetrahalides is unknown; they are doubtless polymeric with halide bridges.

Tetrakis(mesityl)ruthenium **3** was reported[3] as being obtained using diruthenium tetraacetate as starting material but this method is far from being reproducible. A much improved procedure uses $RuCl_3(tht)_3$[9] and $Mg(mes)_2(thf)_2$; the product is clean and X-ray quality crystals were obtained.

A diagram of $Ru(mes)_4$ is shown in Fig. 3; selected bond lengths and angles are given in Table 3. The Ru–C bond lengths, 2.01(1)–2.02(1) Å, and C–Ru–C angles, 98.9(6)–117.4(6)° are very similar to those for $[Ir(mes)_4]^+$ described later. This is not surprising since the two species are isoelectronic. The range of values in both cases is smaller than that in the low-spin d^5 species $Ir(mes)_4$, 89.0(4)–123.9(5)°,[2] and this result now casts doubt on our earlier assumption[2] that single occupancy of a t_2 orbital in that complex would not contribute to the distortion of the IrC_4 tetrahedron. Nevertheless, steric factors are undoubtedly chiefly responsible for the distortion. In the d^4 diamagnetic molecule $OsPh_4$[10] the C–Os–C angles are 107.6(4)–110.4(4)°, but for the *o*-tolyl, $Os(C_6H_4Me\text{-}2)_4$,[10,11] the angle range widens to 106.9(3)–117(3)°. Interestingly, however, in $Os(C_6H_{11})_4$,[10,11] also d^4 low-spin, the C–Os–C angles are 105.3(3)–117.1(5)°, but in the paramagnetic d^2 $Cr(C_6H_{11})_4$ species[10] the C–Cr–C angles are 106.2(2)–114.5(2)°. The steric/electronic balance is clearly very delicate, and perhaps nowhere more so than in the tetramesityls.

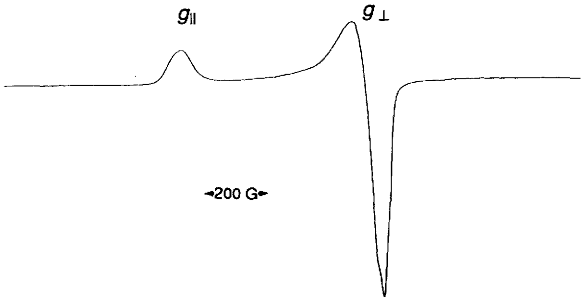

Fig. 2 The X-band EPR spectrum of tetrakis(mesityl)iridium in toluene at 77 K

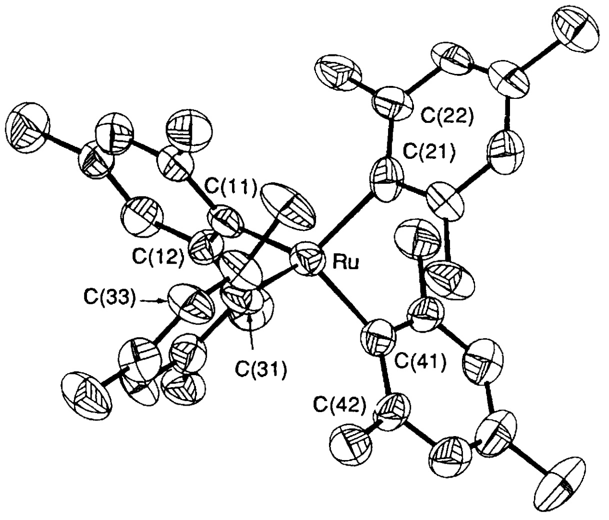

Fig. 3 The structure of tetrakis(mesityl)ruthenium (30% probability ellipsoids)

Redox and Other Chemistry.—The cyclic voltammetric data for **1**, **2** and **3** and of the $[M(mes)_4]^+$ cations discussed below are collected in Table 4; for the tetraaryls comparison can be made with values for the *o*-tolyls, $M(C_6H_4Me\text{-}2)_4$, M = Mo, Re, Ru or Os.[12]

For $Ir(mes)_3$ we have been unable to obtain any isolable product from either chemical reductions or oxidations. For **2** and **3** again no reduced species from either Na, Li or $Co(\eta\text{-}C_5H_5)_2$ reactions could be isolated (*cf.*, the similarity of *o*-tolyl compounds[12]). However, both **2** and **3** could be smoothly oxidised, **2** by AgX (X = CF_3SO_3 or PF_6) and **3** by $NOPF_6$ (but not by AgO_3SCF_3), to give the cations as crystalline salts. For these salts, under the same conditions as used for **2** and **3**, cyclic voltammetry showed two, one-electron reversible waves

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

C(11)–Ru	2.012(14)	C(21)–Ru	2.022(14)
C(31)–Ru	2.010(14)	C(41)–Ru	2.018(14)
C(21)–Ru–C(11)	113.3(6)	C(31)–Ru–C(11)	116.5(6)
C(31)–Ru–C(21)	98.9(6)	C(41)–Ru–C(11)	99.3(5)
C(41)–Ru–C(21)	117.4(6)	C(41)–Ru–C(31)	112.4(6)
C(12)–C(11)–Ru	115.3(11)	C(16)–C(11)–Ru	128.7(10)
C(22)–C(21)–Ru	116.3(10)	C(26)–C(21)–Ru	127.3(10)
C(32)–C(31)–Ru	127.8(10)	C(36)–C(31)–Ru	114.4(10)
C(42)–C(41)–Ru	126.3(10)	C(46)–C(41)–Ru	116.4(11)

Table 4 Cyclic voltammetry of homoleptic aryls[a]

	$E_{\frac{1}{2}}/V$[b]		
Compound	M^{III}–M^{IV}	M^{IV}–M^{V}	M^{IV}–M^{III}
$Rh(mes)_3$	+0.75[c]	—	—
$Ir(mes)_3$	+0.48	—	—
$Ir(mes)_4$	—	−0.44	−1.17
$Ru(mes)_4$	—	+0.32	−1.88
$[Ir(mes)_4]PF_6$	—	−0.44	−1.20
$[Ru(mes)_4]PF_6$	—	+0.35	−1.90

[a] In CH_2Cl_2 with 0.2 mol dm^{-3} $NBu^n{}_4PF_6$ as supporting electrolyte at 20 °C; scan rate 50 mV s^{-1}. [b] Potentials referenced to the redox couple $[Fe(\eta\text{-}C_5H_5)_2]$–$[Fe(\eta\text{-}C_5H_5)_2]^+$ at 0.00 V. [c] From ref. 1(*b*).

Table 5 Selected bond lengths (Å) and angles (°) for $[Ir(mes)_4]O_3SCF_3\cdot MeCN$ **4**

C(11)–Ir	2.019(8)	C(21)–Ir	2.037(6)
C(31)–Ir	2.004(8)	C(41)–Ir	2.009(8)
C(21)–Ir–C(11)	114.8(3)	C(31)–Ir–C(11)	117.0(3)
C(31)–Ir–C(21)	95.5(3)	C(41)–Ir–C(11)	96.4(3)
C(41)–Ir–C(21)	116.8(3)	C(41)–Ir–C(31)	117.8(4)
C(12)–C(11)–Ir	115.3(5)	C(16)–C(11)–Ir	124.0(6)
C(22)–C(21)–Ir	114.3(5)	C(26)–C(21)–Ir	123.4(4)
C(32)–C(31)–Ir	124.3(5)	C(36)–C(31)–Ir	115.8(6)
C(42)–C(41)–Ir	124.3(5)	C(46)–C(41)–Ir	116.0(5)

as expected and hence we appear to have the redox sequences, M^{III}–M^{IV}–M^{V} for both [equation (1), M = Ir or Ru].

$$[M(mes)_4]^- \underset{}{\overset{-e}{\rightleftharpoons}} M(mes)_4 \overset{-e}{\rightleftharpoons} [M(mes)_4]^+ \qquad (1)$$

Crystals of $[Ir(mes)_4]O_3SCF_3$ **4** suitable for X-ray study were obtained by crystallisation from Et_2O–MeCN. These readily lose MeCN on evacuation or on drying so that for the X-ray study crystals were mounted in solvent as $[Ir(mes)_4]O_3SCF_3\cdot MeCN$ which is found in the asymmetric unit. A diagram of the packing in the crystal structure is shown in Fig. 4, selected bond lengths and angles in Table 5.

The geometry of the diamagnetic, d^4 $[Ir(mes)_4]^+$ ion is very similar to, but less distorted than, that of the d^5 neutral parent molecule.[2] The Ir–C distances in the cation are 2.004(8)–2.037(6) Å compared with 1.99(1)–2.04(1) in the neutral molecule. The tilts of the aryl rings relative to the Ir–C bonds are similar in both. The slight narrowing in the range of C–Ir–C angles in the cation, for very similar bond lengths, again indicates that our original assertion,[2] that the distortions in the $Ir(mes)_4$ molecules were entirely steric in origin, may not be correct (see also above).

Iridium(V) compounds are rare[13] and no homoleptic, four-co-ordinate species are known. The only other similar homoleptic cations are the *o*-tolyl, $[Os(C_6H_4Me\text{-}2)_4]^+$, which was structurally characterised in the trifluoromethanesulfonate salt,[14a] $[Mo(mes)_4]X_3$ (X = Br or I) where the cation has distorted tetrahedral geometry according to spectroscopic evidence,[14b] and $[Ru(mes)_4]^+$.

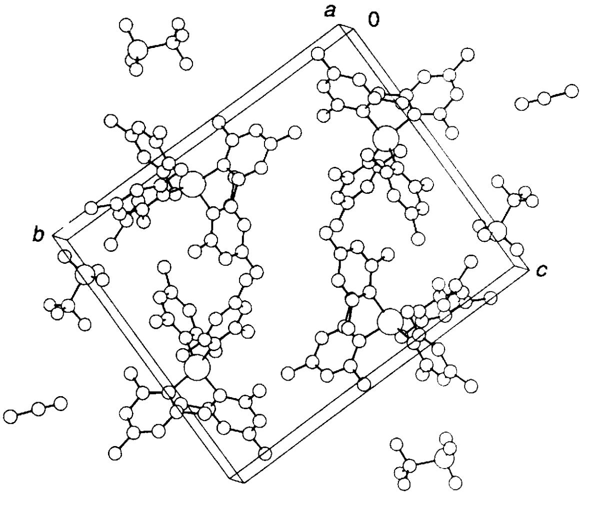

Fig. 4 The unit cell of $[Ir(mes)_4]O_3SCF_3\cdot MeCN$

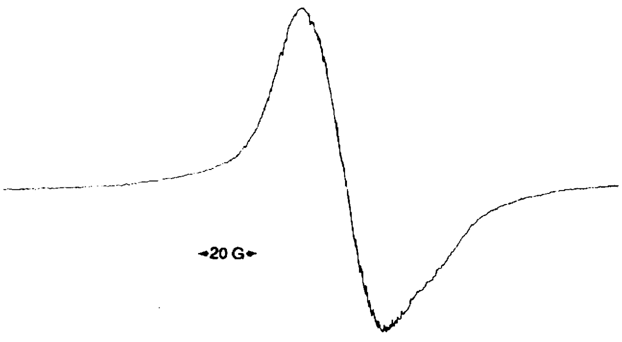

Fig. 5 The X-band EPR spectrum of $[Ru(mes)_4]PF_6$ in CH_2Cl_2 at 77 K

We have been unable to obtain X-ray quality crystals for $[Ru(mes)_4]PF_6$ **6**; the compound is paramagnetic and the X-band EPR spectrum has a singlet, $g = 2.035$, with linewidth 26 G (Fig. 5).

Despite the reactivity of $Ir(mes)_3$ we have so far been unable to isolate any well defined products; it does not react with water, tetramethylpiperidine or thf. In putative oxidative-addition reactions the products would presumably have initially been iridium(V) species that could well be unstable. Hydrogen gives a black solid soluble in MeCN but there is no Ir–H bond according to ^1H NMR spectra and no crystals could be obtained from the MeCN solution. Carbon monoxide reacts to give an amorphous solid that has broad mesityl band in the ^1H NMR and CO stretch at *ca.* 2000 cm^{-1}. Diphenylacetylene, CS_2, NH_2Bu^t and several tertiary phosphines gave no characterisable products; Bu^tNC and $NOPF_6$ gave intractable solids.

Similarly for $Ir(mes)_4$ there was no reaction with H_2, Bu^tNC, PMe_3 and CO under mild conditions and decomposition occurred on heating. The compound was not reduced by Li in thf in presence of *N,N,N′,N′*-tetramethylethylenediamine. At *ca.* 90 °C in hydrocarbons in air the solution becomes green and the green powder appears identical to the final oxidation product with O_2 of $Ir(mes)_3$. These oxygen-containing species and the reactions of **1** and **2** with NO will be discussed separately.

Nuclear Magnetic Resonance Spectra.—The ^1H and ^{13}C NMR spectra of $Rh(mes)_3$ were discussed at some length:[1] it was concluded that the solid-state structure was not retained in solution where the molecule appeared to be planar with the mesityl rings undergoing synchronous rotation about the Rh–C bond.

Table 6 Activation parameters for rotation of mesityl groups about the M–C bond[a]

Compound	$Rh(mes)_3$[b]	$Ir(mes)_3$	$Ru(mes)_4$	$[Ir(mes)_4]^+$[c]	
Solvent	$C_6D_5CD_3$	CD_2Cl_2	CD_2Cl_2	CD_3CN	CD_2Cl_2
$\Delta\nu$, 2-CH_3	80.02	78.5	108.5	78.3	75.6
T_c/K	308	285	253	283	295
$\Delta\nu$, 3,5-H	200.05	94.4	108.5	113.4	124.2
T_c/K	328	288	253	295	308[d]
$\Delta G^\ddagger$, 2-CH_3/kJ mol^{-1}	62.6	57.5	50.1	57.1	59.7
$\Delta G^\ddagger$ 3,5-H/kJ mol^{-1}	64.0	57.7	50.1	58.7	61.4
M–C_{av}/Å	1.967[e]	2.003	2.011	2.040	

[a] Using $\Delta G^\ddagger = -RT_c \ln \pi \Delta\nu h 2^{-\frac{1}{2}} (kT_c)^{-1}$ as in ref. 1(*a*); $\Delta\nu$ is the separation between resonances in Hz, T_c is the coalescence temperature. [b] Data from ref. 1. [c] As $O_3SCF_3^-$ salt. [d] Estimated. [e] From ref. 1(*a*).

Variable-temperature ^1H NMR spectra of **1**, **3** and **4** confirm similar rotational behaviour and the data are collected in Table 6 together with the corresponding M–C average bond lengths, from which it will be noted that the longer the M–C bond length, the lower is the value of $\Delta G^\ddagger$. It may be noted also that at 25 °C the ^1H NMR spectrum of $Ir(mes)_3$ differs from that of $Rh(mes)_3$ in having three sharp singlets assignable to the two aromatic hydrogen atoms, three hydrogens from the *p*-CH_3 groups and six hydrogens for the *o*-CH_3 groups, so that the spectrum is thus similar to that of $Rh(mes)_3$ [1a] at >50 °C.

Experimental

The general methods and instrumention used have been described.[1] Microanalyses by Pascher, Remagen, MEDAC, Brunel University, and Imperial College laboratories. ^1H NMR: δ values *vs.* $SiMe_4$ at 270 MHz. IR spectra (cm^{-1}) showed bands only due to mesityl groups.[1]

The hydrated iridium chloride was from Johnson Matthey; other chemicals were from Aldrich. Syntheses of $Mg(mes)_2(thf)_2$ [15] and $Li(mes)(OEt_2)$ [16] were standard. The $IrCl_3(tht)_3$, originally made[4] by interaction of Na_2IrCl_6 in acidic 2-methoxyethanol, is more conveniently made using $IrCl_3 \cdot nH_2O$ (2.6 g) in 2-methoxyethanol (*ca.* 150 cm^3) and tetrahydrothiophene (*ca.* 4 cm^3) and refluxing (1 h); on cooling yellow crystals are obtained in *ca.* 70% yield; a second crop can be obtained after concentration of the mother-liquor.

Anhydrous $IrCl_3$ was always freshly prepared by treating $IrCl_3 \cdot nH_2O$ with excess of $SOCl_2$ in Et_2O at room temperature. After 15 min the excess of liquid was decanted and the residue washed several times with peroxide-free Et_2O. The solid was *not allowed to dry* and was kept under nitrogen: the ether-moist product was suspended in Et_2O for immediate use.

Note that commercial $IrCl_3 \cdot nH_2O$ can vary from batch to batch; it may be a brown powder, a sticky brown solid or a black quasi-crystalline solid; only the black form gives reactive anhydrous $IrCl_3$. Further discussion of the nature of a particular sample of $IrCl_3 \cdot nH_2O$ that led, instead of $Ir(mes)_4$, on reaction with Li(mes) in Et_2O to a cherry red, diamagnetic compound characterised by X-ray crystallography of stoichiometry $Ir(mes)_2(C_{22}H_{31}O)$ will be given in a later paper.

Tris(mesityl)iridium(III) **1**.—To a suspension of $IrCl_3(tht)_3$ (1 g, 1.8 mmol) in Et_2O (100 cm^3) was added 8.2 cm^3 of 1.3 mol dm^{-3} mesitylmagnesium bromide in Et_2O. The mixture was refluxed (4 h) filtered, evaporated under vacuum and the brown-black residue extracted with hexane (2 × 20 cm^3). The combined extracts were reduced to *ca.* 10 cm^3, filtered and reduced again to *ca.* 5 cm^3. Filtration and cooling gave brown-red crystals. Yield 0.2 g, 20.5%, which after correction for $IrCl_3(tht)_3$ recovered from the first residue rises to 26% based on Ir.

Prolonged heating or longer reaction times at room temperature did not improve the yield and made the product more difficult to purify by crystallisation. ^1H NMR (C_6D_6, 25 °C): δ 2.07 (s, 6 H, *o*-Me), 2.2 (s, 3 H, *p*-Me) and 6.3 (s, 2 H, aromatic H).

The compound is exceedingly sensitive to oxygen as solid, turning green-black and in solutions in organic solvents, green.

Tetrakis(mesityl)iridium(IV) **2**.—To the moist, ether-washed $IrCl_3$, obtained from 1.5 g $IrCl_3 \cdot nH_2O$, suspended in 100 cm^3 degassed Et_2O, was added with rapid stirring a four-fold excess of $Li(mes)(OEt_2)$ (4.02 g): after stirring (4 h) the mixture was filtered and the solution evaporated. The residue was extracted with light petroleum (b.p. 40–60 °C, 2 × 30 cm^3) and the filtered extracts reduced to *ca.* 15 cm^3 and cooled (−20 °C) to give red-brown crystals. Yield 0.58 g, 17%. Positive-ion fast atom bombardment mass spectrum (+FAB): *m/z* 668.32 M^+, 549.23 $[Ir(mes)_3 - H]^+$. The solid is stable in air; solutions in common organic solvents are also air-stable for several hours.

Tetrakis(mesityl)ruthenium(IV) **3**.—To a suspension of $RuCl_3(tht)_3$ (2 g, 4.2 mmol) in Et_2O (60 cm^3) at −78 °C was added a solution of $Mg(mes)_2(thf)_2$ (3.4 g, 8.5 mmol) in thf (20 cm^3) with vigorous stirring. After warming and stirring at room temperature (*ca.* 20 h) the solution was evaporated under vacuum and the residue extracted with light petroleum (b.p. 40–60 °C, 3 × 30 cm^3). The extracts were reduced, filtered and cooled (−30 °C) to give feathery crystals. Yield 0.45 g, 18.4%. X-Ray quality crystals were grown by slow crystallisation from Et_2O. Mass spectrum (+FAB): *m/z* 578.21 M^+ with correct Ru isotope pattern. ^1H NMR (CD_2Cl_2, 20 °C): δ 1.94 (br s, 6 H, *o*-Me), 2.23 (s, 3 H, *p*-Me) and 6.54 (br s, 2 H, aromatic H).

Tetrakis(mesityl)iridium(V) *Trifluoromethanesulfonate* **4**.—A CH_2Cl_2 (20 cm^3) solution of **2** (0.13 g, 0.195 mmol) and AgO_3SCF_3 (0.06 g, 0.2 mmol) was stirred at room temperature (30 min) when the mixture was filtered from precipitated Ag and the solution evaporated under vacuum. The residue was dissolved in the minimum amount of MeCN and Et_2O was then added to precipitate the green-brown, air-stable product. Yield 0.12 g, 76%. ^1H NMR (CD_2Cl_2, 22 °C): δ 2.27 (br s, 6 H, *o*-Me), 2.50 (s, 3 H, *p*-Me), 6.55 (br s, 1 H, aromatic H) and 6.85 (br s, 1 H, aromatic H).

X-Ray quality crystals were obtained by slow crystallisation at −20 °C from Et_2O–MeCN mixture.

The *hexafluorophosphate* **5** used in cyclic voltammetric studies was made similarly. Interaction of $Ir(mes)_4$ with excess of iodine in light petroleum gives a black polyiodide.

Tetrakis(mesityl)ruthenium(V) *Hexafluorophosphate* **6**.—To **3** (0.14 0.24 mmol) in CH_2Cl_2 (15 cm^3) was added $NOPF_6$ (0.042 g, 0.24 mmol) in CH_2Cl_2 (15 cm^3) and the solution stirred for 0.5 h. Removal of solvent, dissolution of the residue in the

Table 7 Crystal data and details of refinement

Compound	**1**	**3**	**4**
Formula	$C_{27}H_{33}Ir$	$C_{36}H_{44}Ru$	$C_{37}H_{44}F_3IrO_3S{\cdot}CH_3CN$
M	549.78	577.82	859.09
Crystal system	Triclinic	Monoclinic	Monoclinic
a/Å	8.341(2)	16.539(5)	13.178(4)
b/Å	11.268(2)	24.158(2)	18.184(2)
c/Å	13.476(2)	15.136(4)	15.230(4)
α/°	98.60(1)	90	90
β/°	102.12(1)	93.43(3)	92.61(2)
γ/°	106.96(2)	90	90
U/Å^3	1184.97 (0.43)	6036.74 (2.48)	3645.76 (1.52)
Space group	$P\bar{1}$	$C2/c$	$P2_1/n$
Z	2	8	4
D_c/g cm^{-3}	1.541	1.272	1.565
$F(000)$	544	2432	1728
μ/cm^{-1}	56.20	5.29	37.53
Total data measured	4684	12 006	10 479
No. of unique reflections	4047	4730	5169
No. of observed reflections	2973	1955	4296
Significance test	$F_o > 3\sigma(F_o)$	$F_o > 3\sigma(F_o)$	$F_o > 3\sigma(F_o)$
No. of parameters	313	392	507
Minimum and maximum height in final difference map	−0.412, 0.323	−0.673, 0.369	−0.754, 0.631
Weighting scheme parameter g in $w = 1/[\sigma^2(F) + gF^2]$	0.0003	0	0
Final R	0.0416	0.0495	0.0314
Final R'	0.0371	0.0501	0.0331

Table 8 Fractional atomic coordinates (× 10^4) for $Ir(mes)_3$ **1**

Atom	x	y	z
Ir	150(1)	2956.8(3)	1712.4(3)
C(11)	1503(12)	4522(7)	2798(6)
C(12)	2176(12)	5522(8)	2342(6)
C(13)	3336(14)	6678(9)	2948(7)
C(14)	3837(13)	6894(8)	4011(7)
C(15)	3138(14)	5910(9)	4458(7)
C(16)	1978(13)	4726(8)	3887(6)
C(121)	1544(14)	5340(9)	1173(7)
C(141)	5059(17)	8164(10)	4671(8)
C(161)	1234(17)	3743(9)	4466(7)
C(21)	−2248(11)	2993(8)	1140(7)
C(22)	−3070(13)	3830(7)	1469(6)
C(23)	−4669(15)	3717(10)	826(8)
C(24)	−5497(13)	2815(9)	−81(7)
C(25)	−4671(14)	1996(9)	−381(8)
C(26)	−3043(13)	2062(8)	209(6)
C(221)	−2313(16)	4788(10)	2490(8)
C(241)	−7269(15)	2706(12)	−716(9)
C(261)	−2171(14)	1147(9)	−147(8)
C(31)	−112(12)	1528(8)	2420(6)
C(32)	−1520(13)	847(8)	2767(7)
C(33)	−1349(15)	−158(9)	3204(8)
C(34)	73(15)	−529(8)	3329(7)
C(35)	1420(16)	161(9)	2992(7)
C(36)	1360(13)	1183(8)	2551(6)
C(321)	−3164(14)	1189(10)	2692(9)
C(341)	203(19)	−1619(10)	3851(10)
C(361)	2908(14)	1961(10)	2264(9)

Table 9 Fractional atomic coordinates (× 10^4) for $Ru(mes)_4$ **3**

Atom	x	y	z
Ru	2670(1)	4168.5(6)	3246(1)
C(11)	2847(7)	4967(5)	2934(6)
C(12)	2183(8)	5231(5)	2463(7)
C(13)	2232(8)	5778(5)	2189(7)
C(14)	2929(9)	6073(5)	2325(8)
C(15)	3585(7)	5829(5)	2749(6)
C(16)	3560(7)	5288(5)	3067(6)
C(121)	1384(7)	4938(5)	2255(7)
C(141)	2994(9)	6671(5)	2019(7)
C(161)	4340(7)	5079(5)	3530(7)
C(21)	1804(7)	4060(4)	4118(6)
C(22)	1631(7)	3510(5)	4345(6)
C(23)	1073(7)	3387(5)	4983(7)
C(24)	654(7)	3803(5)	5390(7)
C(25)	813(7)	4335(5)	5159(7)
C(26)	1367(7)	4482(5)	4555(7)
C(221)	2060(8)	3014(5)	3951(7)
C(241)	55(7)	3649(5)	6089(7)
C(261)	1510(8)	5090(4)	4447(7)
C(31)	3591(7)	3783(4)	3920(6)
C(32)	4017(8)	3308(5)	3665(7)
C(33)	4576(8)	3058(5)	4261(8)
C(34)	4747(9)	3259(6)	5104(9)
C(35)	4359(8)	3736(5)	5365(8)
C(36)	3776(8)	3997(4)	4781(7)
C(321)	3840(8)	3002(5)	2784(7)
C(341)	5345(8)	2957(5)	5735(8)
C(361)	3385(8)	4501(5)	5144(7)
C(41)	2455(7)	3857(5)	2017(7)
C(42)	1738(8)	3608(5)	1685(7)
C(43)	1673(7)	3397(5)	802(7)
C(44)	2292(8)	3459(5)	241(7)
C(45)	2988(8)	3716(5)	569(6)
C(46)	3085(8)	3918(5)	1428(7)
C(421)	973(7)	3526(5)	2176(7)
C(441)	2210(8)	3228(6)	−695(6)
C(461)	3883(6)	4200(5)	1715(6)

minimum of MeCN followed by addition of Et_2O and cooling (− 30 °C) gave air-stable crystals. Yield 0.12 g, 69%.

X-Ray Structure Determinations.—X-Ray data were recorded on crystals sealed under argon in thin-walled glass capillaries. Data for **1** were recorded using a CAD4 diffractometer[17] and for the tetramesityls **3** and **4** using a FAST TV area detector diffractometer,[18] with graphite-monochromated molybdenum radiation [λ(Mo-Kα) = 0.710 69 Å] , following previously described procedures. The CAD4 data were corrected for absorption first using psi-scan profiles and subsequently by application of the DIFABS procedure;[19] the FAST data were corrected for absorption by application of the DIFABS procedure.[20] The structures were solved and developed *via* the

Table 10 Fractional atomic coordinates (× 10^4) for $[Ir(mes)_4]O_3SCF_3\cdot MeCN$ **4**

Atom	*x*	*y*	*z*
Ir	2372.3(2)	1038.8(1)	3697.6(1)
C(11)	3031(5)	1078(3)	2527(4)
C(12)	3835(5)	582(3)	2430(4)
C(13)	4366(5)	600(3)	1654(4)
C(14)	4093(5)	1086(4)	974(4)
C(15)	3271(5)	1552(3)	1082(4)
C(16)	2726(5)	1557(3)	1840(4)
C(21)	3325(4)	1248(3)	4759(2)
C(22)	2871(4)	1160(3)	5588(2)
C(23)	3463(4)	1339(3)	6339(2)
C(24)	4419(5)	1644(4)	6305(4)
C(25)	4818(5)	1740(4)	5487(4)
C(26)	4297(5)	1530(4)	4694(4)
C(31)	1382(5)	1839(3)	3951(4)
C(32)	376(5)	1716(3)	4207(4)
C(33)	−175(5)	2321(4)	4518(4)
C(34)	218(5)	3021(4)	4576(4)
C(35)	1203(5)	3133(4)	4295(4)
C(36)	1785(5)	2568(4)	3977(4)
C(41)	1837(5)	8(3)	3571(4)
C(42)	2190(5)	−594(3)	4088(4)
C(43)	1834(5)	−1297(4)	3860(4)
C(44)	1108(5)	−1427(4)	3176(4)
C(45)	759(5)	−821(4)	2702(4)
C(46)	1114(5)	−114(4)	2868(4)
C(121)	4205(5)	29(4)	3119(4)
C(141)	4708(6)	1103(4)	159(4)
C(161)	1835(5)	2083(3)	1821(4)
C(221)	1799(5)	890(4)	5712(4)
C(241)	5005(6)	1891(4)	7140(4)
C(261)	4894(5)	1659(4)	3882(4)
C(321)	−164(5)	984(4)	4206(4)
C(341)	−364(6)	3653(4)	4944(5)
C(361)	2818(5)	2767(3)	3669(4)
C(421)	2932(5)	−569(4)	4872(4)
C(441)	728(6)	−2178(4)	2978(5)
C(461)	705(5)	501(4)	2252(4)
S	2504(1)	33(1)	8410(1)
C(1)	2637(6)	−873(4)	7919(5)
F(1)	3315(4)	−1283(2)	8334(3)
F(2)	1768(4)	−1225(3)	7894(4)
F(3)	2922(5)	−813(3)	7101(3)
O(1)	1707(4)	371(3)	7889(3)
O(2)	3482(4)	358(3)	8296(4)
O(3)	2268(5)	−118(3)	9292(3)
C(20)	3007(6)	8993(4)	1112(5)
C(10)	2935(5)	8246(5)	775(5)
N	2896(5)	7651(4)	482(5)

heavy-atom method, and refined by full-matrix least squares. Non-hydrogen atoms were refined anisotropically and hydrogens were included in idealised positions and refined with group U_{iso} values except the aryl hydrogens in the trimesityl, which were freely refined. Crystal data and experimental details are given in Table 7. Fractional atomic coordinates are given in Tables 8–10.

Additional data available from the Cambridge Crystallography Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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