On [(1,2,3,4,5-η)-6-(1-Ethoxyethyl)-3-mesityl-2,4,6-trimethylcyclohexa-2,4-dienyl]dimesityliridium(III)†

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The interaction of an aberrant batch of 'iridium trichloride hydrate' that had been treated with $SOCl_2$ in Et_2O gave, on interaction with mesityllithium, a cherry red, substituted cyclohexadienyl compound **1** of stoichiometry $Ir(mes)_2(C_{22}H_{31}O)$, mes = 2,4,6-trimethylphenyl, whereas previous arylations of hydrated iridium(III) chloride '$IrCl_3{\cdot}nH_2O$' gave $Ir(mes)_4$. Compound **1** has *exo* and *endo* isomers separable by column chromatography. The study of various treated iridium chlorides has given reproducible syntheses of **1**; a halide with water co-ordinated to iridium appears necessary. An X-ray crystal structure determination of the major isomer **1b** shows that the $C_{22}H_{31}O$ moiety bound to Ir comprises a cyclohexadienyl ring with a mesityl group at position 3, methyl groups at positions 2, 4 and 6 and an *exo* EtOC(H)Me group at position 6. Detailed variable-temperature ^1H and ^{13}C NMR studies have allowed almost complete assignments for both *exo* and *endo* isomers; additional diasteroisomers were detected in solution and activation parameters for dynamic processes were determined. Alternative syntheses of $Ir(mes)_3$ and $Ir(mes)_4$ as well as syntheses of **1** are discussed in relation to thermal and $SOCl_2$ treatments of $IrCl_3{\cdot}nH_2O$, $(H_3O)_2IrCl_6{\cdot}2H_2O$ and 'sodium hexachloroiridate hydrate'.

The interaction of $IrCl_3(tht)_3$, tht = tetrahydrothiophene, with mesitylmagnesium bromide in Et_2O leads to $Ir(mes)_3$ (mes = 2,4,6-trimethylphenyl), whereas interaction of $Li(mes){\cdot}OEt_2$ with commercial 'hydrated iridium trichloride,' partially dehydrated by treatment with thionyl chloride in Et_2O produces $Ir(mes)_4$.[1] On using up one batch (whose number was not recorded) of Johnson Matthey '$IrCl_3{\cdot}nH_2O$,' $Ir(mes)_4$ was not obtained after interaction with Li(mes) and work-up but instead a diamagnetic, cherry red product that had a complex ^1H NMR spectrum was obtained. Chromatography of the light petroleum soluble product $Ir(mes)_2(C_{22}H_{31}O)$ **1** on alumina allowed the separation of two isomers in a 1 : 3 ratio; the minor isomer **1a** was eluted first. Crystals of the major isomer **1b** as its diethyl etherate were obtained after cooling for *ca.* 2 weeks; crystals of **1a** could not be obtained. The minor isomer **1a** is the *endo* isomer as confirmed by NMR studies.

Although cationic cyclohexadienyls having methyl- and pentamethyl-cyclopentadienyl ligands of iridium(III) have been described,[2] structures were not determined nor were NMR spectra studied other than at room temperature.

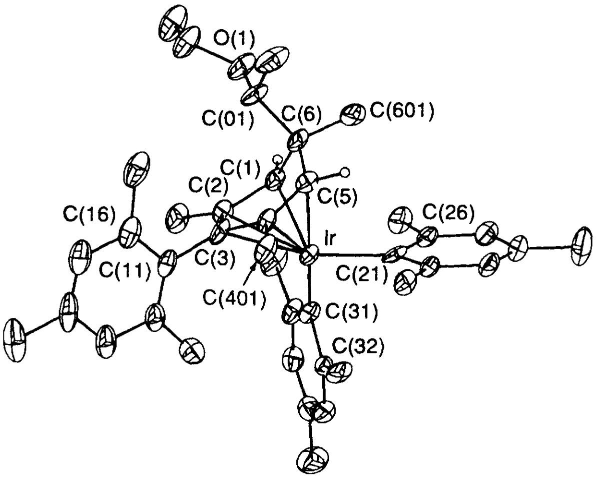
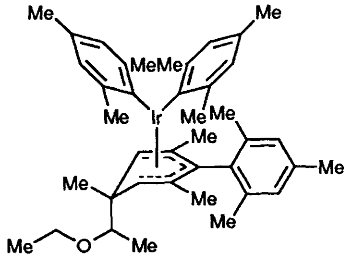


Fig. 1 The structure of the *exo* isomer **1b**

Results and Discussion

X-Ray Crystallography.—The structure of the molecule of **1b** is shown in Fig. 1. Selected bond lengths and angles are given in Table 1 with the numbering and important distances (Å) for the C_6 ring given in Fig. 2. The latter is bound to Ir in essentially the pentahapto mode with C(6) displaced from the plane of C(1)–C(5) to give an envelope conformation with a fold angle of 46.3(3)°. The 1-ethoxy group is *exo* and the carbon atom bound to C(6) is chiral. Since the space group is $P\bar{1}$ (see Experimental section) there are equal numbers of the two enantiomers in the crystal and, presumably, also in solution (see below).



1 (*exo* isomer **1b**)

The substitution pattern for the other substituents on the ring is 'mirror symmetrical' with methyls at C(2), C(4) and C(6) and a mesityl group at C(3). However, the distribution of bond

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Non-SI units employed: cal ≈ 4.184 J, eV ≈ 1.6 × 10^{-19} J.

Table 1 Selected bond lengths (Å) and angles (°) for compound **1b**

C(6)–Ir	2.793(14)	C(5)–Ir	2.267(14)
C(4)–Ir	2.227(12)	C(3)–Ir	2.373(12)
C(2)–Ir	2.290(15)	C(1)–Ir	2.076(15)
C(21)–Ir	2.021(13)	C(31)–Ir	2.072(13)
C(5)–C(6)	1.549(21)	C(1)–C(6)	1.518(19)
C(601)–C(6)	1.518(16)	C(01)–C(6)	1.514(18)
C(4)–C(5)	1.304(16)	C(3)–C(4)	1.412(21)
C(401)–C(4)	1.548(20)	C(2)–C(3)	1.373(18)
C(11)–C(3)	1.532(16)	C(1)–C(2)	1.487(14)
C(201)–C(2)	1.494(22)	C(12)–C(11)	1.362(18)
C(16)–C(11)	1.406(18)	C(13)–C(12)	1.386(17)
C(121)–C(12)	1.519(21)	C(14)–C(13)	1.357(23)
C(15)–C(14)	1.369(23)	C(141)–C(14)	1.541(20)
C(16)–C(15)	1.395(19)	C(161)–C(16)	1.555(21)
C(22)–C(21)	1.438(21)	C(26)–C(21)	1.455(14)
C(23)–C(22)	1.383(19)	C(221)–C(22)	1.508(17)
C(24)–C(23)	1.379(19)	C(25)–C(24)	1.411(26)
C(241)–C(24)	1.528(24)	C(26)–C(25)	1.383(20)
C(261)–C(26)	1.529(23)	C(32)–C(31)	1.428(17)
C(36)–C(31)	1.399(20)	C(33)–C(32)	1.344(18)
C(321)–C(32)	1.493(21)	C(34)–C(33)	1.385(25)
C(35)–C(34)	1.356(23)	C(341)–C(34)	1.541(22)
C(36)–C(35)	1.402(19)	C(361)–C(36)	1.520(22)
C(01)–O(1)	1.419(20)	C(03)–O(1)	1.452(20)
C(02)–C(01)	1.489(23)	C(04)–C(03)	1.473(27)
C(120)–O(100)	1.537(54)	C(130)–O(100)	1.571(48)
C(120)–C(110)	1.411(53)	C(140)–C(130)	1.529(45)
C(5)–Ir–C(6)	33.6(4)	C(4)–Ir–C(6)	59.0(4)
C(4)–Ir–C(5)	33.7(4)	C(3)–Ir–C(6)	68.0(4)
C(3)–Ir–C(5)	61.2(5)	C(3)–Ir–C(4)	35.6(5)
C(2)–Ir–C(6)	59.7(5)	C(2)–Ir–C(5)	74.0(6)
C(2)–Ir–C(4)	63.8(6)	C(2)–Ir–C(3)	34.2(4)
C(1)–Ir–C(6)	32.2(5)	C(1)–Ir–C(5)	63.2(6)
C(1)–Ir–C(4)	77.0(6)	C(1)–Ir–C(3)	65.5(5)
C(1)–Ir–C(2)	39.4(4)	C(21)–Ir–C(6)	96.1(5)
C(21)–Ir–C(5)	94.6(6)	C(21)–Ir–C(4)	119.5(6)
C(21)–Ir–C(3)	154.7(4)	C(21)–Ir–C(2)	151.1(4)
C(21)–Ir–C(1)	111.7(5)	C(31)–Ir–C(6)	140.3(4)
C(31)–Ir–C(5)	173.7(5)	C(31)–Ir–C(4)	147.7(4)
C(31)–Ir–C(3)	117.1(5)	C(31)–Ir–C(2)	101.2(6)
C(31)–Ir–C(1)	110.5(6)	C(31)–Ir–C(21)	87.8(5)

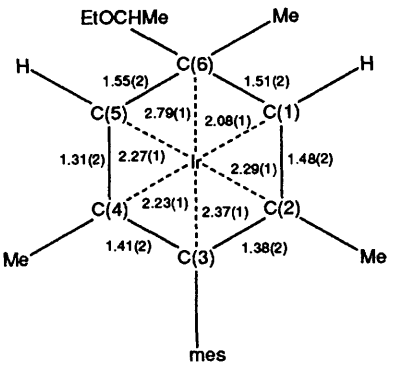


Fig. 2 The Ir–C and C–C distances in **1b**

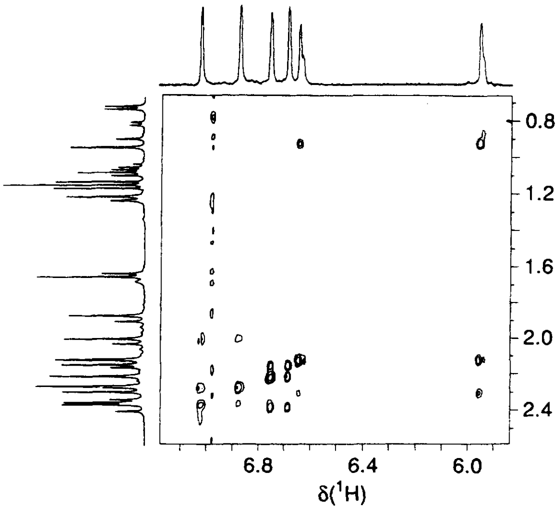
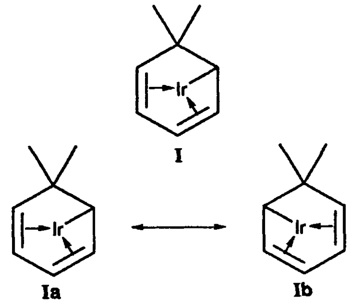


Fig. 3 The 400.13 MHz long-range COSY ¹H NMR spectrum of **1b** showing the correlation between the aromatic and methyl protons of the three mesityl rings, two on Ir and one on C(3) of the C_6 ring



I

Ia **Ib**

lengths within the ring and the metal, plus the disposition of the two iridium–mesityl linkages does not correlate with this symmetry. On the basis of data in Fig. 2 it is tempting to propose a localised canonical structure **I** as a significant contribution to the overall electronic structure. The fluxional behaviour identified in the NMR study discussed below, could then involve an oscillation between two mirror related forms **Ia** and **Ib**. Definition of the metal geometry in a structure of this kind is difficult due to the restricting geometry of the cyclohexadienyl ligand, but the best approximation seems to be a square pyramid with C(1) axial and the two double bonds *cis* basal. The two Ir–mes groups then occupy the remaining basal site.

Nuclear Magnetic Resonance Studies.—The ¹H NMR spectrum of the *exo* isomer **1b** (400.13 MHz, 20 °C, CD_2Cl_2) shows the presence of two isomers in the ratio of 1 : 0.45. Most of the ¹H NMR signals of the major isomer are resolved. The ¹H NMR spectrum consists of eight singlets due to the six CH protons of the three mesityl rings and the two CH protons of the dienyl ring, 12 singlets due to the nine CH_3 groups of the three mesityl rings, and three CH_3 groups of the dienyl, and the appropriate multiplets due to the EtOC(H)Me group. In addition there are a second set of resonances due to the minor isomer, but a number of these signals are obscured by the signals due to the major isomer. The observation of separate signals for each methyl group and CH proton shows that at room temperature, rotation of the mesityl groups is slow on the NMR time-scale. Attempts to assign the signals using nuclear Overhauser effect (NOE) measurements at room temperature showed that exchange was occurring both within the isomers and between the isomers, so the assignment of the signals was carried out at −30 °C, so that exchange effects did not confuse the assignments.

A long-range correlation COSY-90 spectrum, Fig. 3, was measured at −30 °C to detect coupling within each mesityl and the dienyl ring. These measurements clearly showed for the major isomer that the following groups of signals were connected through *J*-coupling and belong to separate rings: group 1 δ 6.63, 5.95, 2.31, 2.12, 0.92; group 2 δ 6.68, 6.75, 2.37, 2.21, 2.14; group 3 δ 7.02, 6.88, 2.36, 2.27, 1.99; group 4 δ 4.57, 4.32, 1.87, 1.65 (not shown in Fig. 3).

For each mesityl group, each CH group correlates with all three methyl groups and the other CH groups in the ring. Thus the long-range COSY-90 experiment permitted the assignment of signals to a ring, but not their relative assignments. The protons at δ 4.57 and 4.32 can be assigned to the dienyl CH groups. Only two methyl groups correlate with these protons. It is probable that the *endo* methyl group does not show a sufficiently large coupling constant to these protons to correlate; since the only methyl signal not accounted for is at δ 1.19, this is presumably the *endo* methyl group.

The relative positions of the CH and methyl groups were determined by NOE measurements at −30 °C. These measurements permitted the positioning of the CH groups between methyl groups as shown in Fig. 4(*a*). The signals are somewhat temperature dependent. The spectra were measured at intervals of 10 °C, and by 20 °C, they have moved as shown in Fig. 4(*b*).

A selective 180° pulse was applied to each signal in turn at 20 °C, and the transfer of magnetisation to other signals in the spectrum was monitored as a function of delay time between the selective 180° pulse and the general 90° observing pulse. These experiments permitted the rate of exchange for many pairs of signals in the major and minor isomers, and the identification of which signal in the major isomer exchanges with which signal in the minor isomer. The data were analysed as described previously.[3] The signals in the minor isomer assigned from the major isomer are as in Fig. 5.

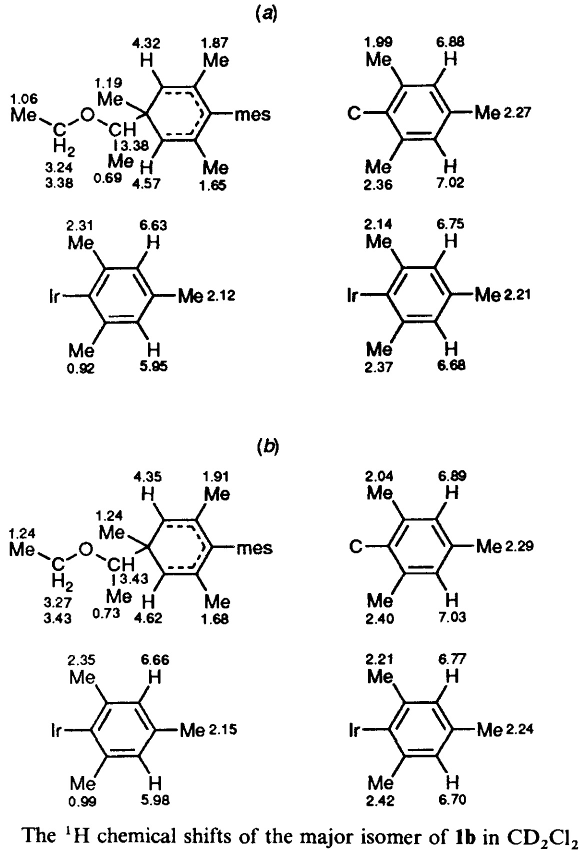


Fig. 4 The ^1H chemical shifts of the major isomer of **1b** in CD_2Cl_2: (*a*) at −30 °C; (*b*) at +20 °C

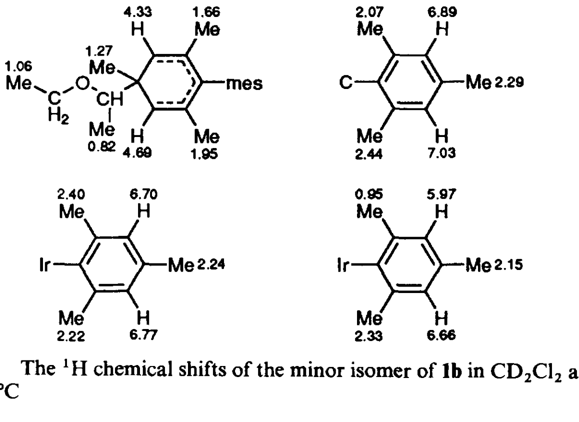


Fig. 5 The ^1H chemical shifts of the minor isomer of **1b** in CD_2Cl_2 at +20 °C

Further assignment of ^1H NMR signals of the mesityl groups has not proven to be possible. The observation for one Ir(mes) group in both isomers of signals moved to low frequency, δ 0.99/5.98 for the major isomer and δ 0.95/5.97 for the minor isomer compared with the other signals suggests that these protons are above a phenyl ring, but examination of the X-ray crystal structure does not give any suitable candidates. It would therefore appear that the solution conformation differs significantly from the solid-state conformation.

A quantitative analysis of exchange using magnetisation transfer between the pairs of signals at δ 2.22/0.99, 2.20/0.95, 2.07/2.04, 1.94/1.68, 1.90/1.66, 2.42/2.32, 4.69/4.62 and 4.36/4.32 at 20 °C yielded the average rate of exchange 1.10 s^{-1} with values ranging from 0.97 to 1.24 s^{-1}. This corresponds to $\Delta G^{\ddagger}_{293}$ of 17.1 kcal mol^{-1}.

On warming to 32 °C, magnetisation transfer showed that a further dynamic process was beginning. It clearly showed that there was exchange between the pair of signals at δ 1.01/2.23 (at δ 0.99/2.21 at 20 °C) and the pair of signals at δ 2.36/2.41 (at δ 2.35/2.40 at 20 °C) and between the pair of signals at δ 2.44/2.34 (at δ 2.42/2.33 at 20 °C) and the pair of signals at δ 2.21/0.96 (at δ 2.21/0.95 at 20 °C). Equivalent exchanges were observed for the pairs of signals at δ 5.98/6.66 and δ 6.70/6.77, but due to overlap of signals, it is more difficult to be definitive about the pairs of hydrogens exchanging. These exchanges are consistent with rotation of two mesityl rings. It is improbable that the mesityl on C^3 of the cyclohexadienyl ring would be able to rotate at this temperature. It is well established that such crowded biphenyls have a high activation energy to rotation about the C–C bond.[4] It is therefore probable that this dynamic process is due to rotation about the Ir(mes) bonds.[1] This hypothesis also permits the assignment of these two mesityl rings to those attached to iridium.

The quantitative analysis of the higher energy dynamic process proved to be difficult, due to the much faster exchange between the major and minor isomers. The problem was compounded by the signal due to the minor isomer at δ 2.41, being obscured by a signal due to the major isomer. It proved impossible to obtain separate rates for ring rotation in both the major and minor isomers. If it is assumed that the rate is the same in the major and minor isomers, then the rate of rotation of the rings with methyl groups at δ 2.44/2.34/2.21/0.96 is 0.34 s^{-1} at 32 °C, corresponding to a $\Delta G^{\ddagger}_{305}$ of 18.5 kcal mol^{-1}, for the rings with methyl groups at δ 1.01/2.23/2.36/2.41 the rate is 0.31 s^{-1} at 32 °C, corresponding to $\Delta G^{\ddagger}_{305}$ of 18.6 kcal mol^{-1}.

The ^{13}C NMR spectrum was recorded at 0 °C, both as direct observation and using distortionless enhancement by polarisation transfer (DEPT) for CH only. The region of the spectrum for the non-proton bearing aromatic carbons proved to be confusing due to variable intensity and the presence of two isomers. The signals of the carbons bearing hydrogens were assigned using ^{13}C–^1H COSY. The part of the ^{13}C–^1H COSY for the methyl signals is shown in Fig. 6. In addition, signals were observed at δ 147.1, 146.7, 143.4, 143.4, 143.2, 143.0, 141.8, 141.8, 137.8, 137.6, 137.3, 135.4, 135.4, 135.3, 134.4, 132.5, 132.0, 130.7, 130.6 due to quaternary aromatic carbons. The dienyl CMe and C-mesityl carbons are at δ 117.2, 108.5 and 106.8 for the major isomer, and 117.0, 108.0 and 106.1 for the minor isomer. The dienyl CH carbons are at δ 26.2 and 77.9 for the minor isomer. The dienyl *C*Me[CHMe(OEt)] carbon is at δ 50.6 for the minor isomer. The *C*HMe(OEt) carbon is at δ 80.8 in the minor isomer and the Me*C*H_2OC(H)Me carbon is at δ 64.6 in both isomers. The remaining methyls that were not assigned for the minor isomer are at δ 25.2, 23.5, 23.4, 21.6, 21.3, 17.0, 16.0, 15.7 and 13.8. The $^1J(^{13}C^1H)$ coupling constants were measured by ^1H-coupled ^{13}C INEPT (insensitive nuclei exhanced by polarisation transfer) NMR

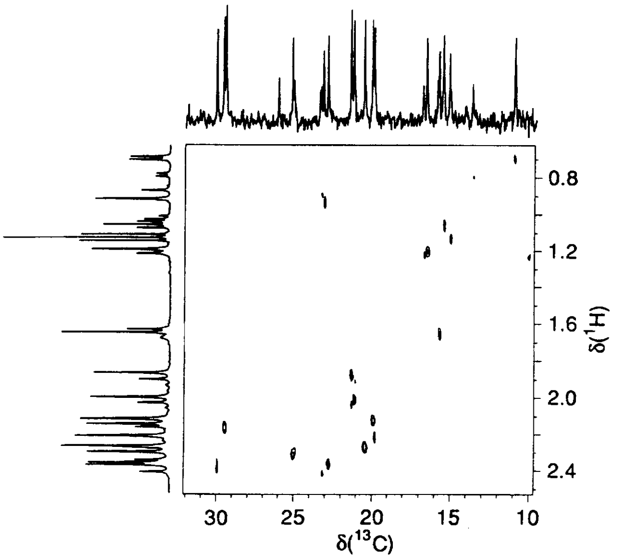


Fig. 6 The ^{13}C-{^{1}H} two-dimensional correlation spectrum showing the correlation of the methyl ^{1}H and ^{13}C chemical shifts of **1b**

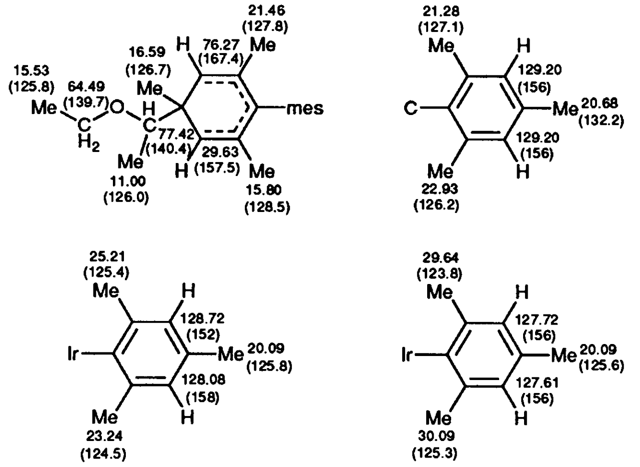


Fig. 7 The ^{13}C chemical shifts of the major isomer of **1b** in CD_2Cl_2 at 0 °C; $J(^{13}C^{1}H)$ values in parentheses

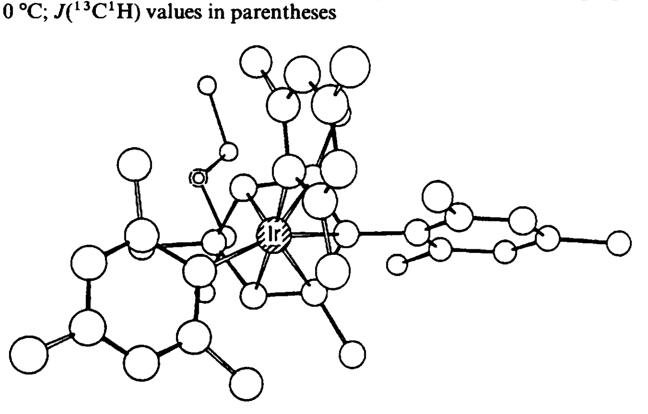


Fig. 8 The X-ray crystal structure of **1b** viewed so that the average plane of the dienyl ligand is in the plane of the paper

spectra and by the two-dimensional *J*-resolved spectra, and are given in Fig. 7 in parentheses, along with the ^{13}C chemical shifts.

Examination of the X-ray crystal structure shows that the $Ir(mes)_2$ group is aligned at an angle close to 45° with respect to the approximate plane of symmetry through the dienyl group, see Fig. 8. There is also a propellor rotation of the two Ir-bonded mesityl groups relative to the plane defined by the Ir and the two bonded C atoms but the orientations are close to being orthogonal to this plane. Either of these two features which give rise to a chiral centre in the molecule, in addition to the one from the MeHCOEt group creating diasteroisomers could produce the two isomers which interconvert with an activation energy of 17.08 kcal mol^{-1}. It is probable that the barrier to remove the chirality is small in the case of the propellor arrangement. The more likely cause of the isomerism is the orientation of the $Ir(mes)_2$ group with respect to the dienyl ring which is locked into one extreme in the crystal structure as discussed above. The lower energy dynamic process is the oscillation of the $Ir(mes)_2$ group with respect to the dienyl (see Fig. 9 left). This is chosen in preference to the process shown in Fig. 9 (right).

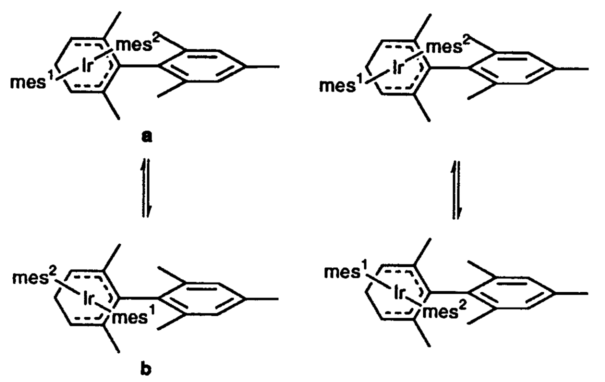


Fig. 9 The alignment of the $Ir(mes)_2$ group with respect to the dienyl group in **1b** and the proposed low energy dynamic process (left) and an alternative low energy dynamic process for **1b** (right)

In the dynamic process illustrated in Fig. 9 (left), the $Ir(mes)_2$ group has to pass the two dienyl methyl groups which are in the plane of the dienyl ring. This would appear to be easier than the process indicated in Fig. 9 (right), where the $Ir(mes)_2$ group has to pass the 6-methyl group and the very bulky mesityl group on the dienyl ring. This mesityl group is oriented at right angles to the dienyl ring.

Both the higher energy dynamic processes involve rotation of $Ir(mes)_2$ rings. As the rates are so similar, it is tempting to suggest that the rotations are correlated. However, there is an alternative interpretation. Examination of the X-ray crystal structure (Fig. 8) leads to the impression that in Fig. 9 (left) mesityl 2 in **a** is blocked from rotation by the dienyl-mesityl group, while the rotation of mesityl 1 is less restricted. However, in **b**, the reverse is true. Hence an alternative explanation is that the rotation of one mesityl ring occurs in the major isomer and the other in the minor isomer.

Endo isomer **1a**. The assignment of the signals due to the *endo* isomer followed the same procedure as with the *exo* isomer. The ^{1}H NMR signals were assigned for the major isomer at −20 °C in CD_2Cl_2 using long-range COSY-90 and NOE difference spectroscopy, see Fig. 10(*a*). The ^{13}C chemical shifts were then assigned using ^{13}C-{^{1}H} correlation, see Fig. 10(*b*). The doubt about the ^{1}H assignments is transmitted to the corresponding ^{13}C assignments. In addition, the protons at δ 2.27 and 2.28 were too close together for the ^{13}C–^{1}H correlation to differentiate between the attached ^{13}C nuclei. Values of $^{1}J(^{13}C^{1}H)$ are given in parentheses. They were obtained either by use of INEPT, or in the case of the crowded region of the spectrum between δ 35 and 12 by two-dimensional separation of δ(^{13}C) and $^{1}J(^{13}C^{1}H)$. This latter spectrum also assisted the assignment of the methyl signals as *ortho* methyls appeared with a small doublet splitting due to $^{2}J(^{13}C^{1}H)$, while the *para* methyls showed a corresponding triplet splitting.

In addition, there are quaternary ^{13}C NMR signals at δ 143.47, 143.02, 141.67, 137.40, 136.94, 135.67, 133.57, 132.51, 131.76, 127.50, 117.0, 108.13 and 106.12. In the X-ray crystal structure of **1b**, Fig. 1, there is a short Ir–H–C contact to a methyl group, suggestive of an agostic interaction. In the NMR spectrum, one methyl signal is moved to low frequency to δ 0.87

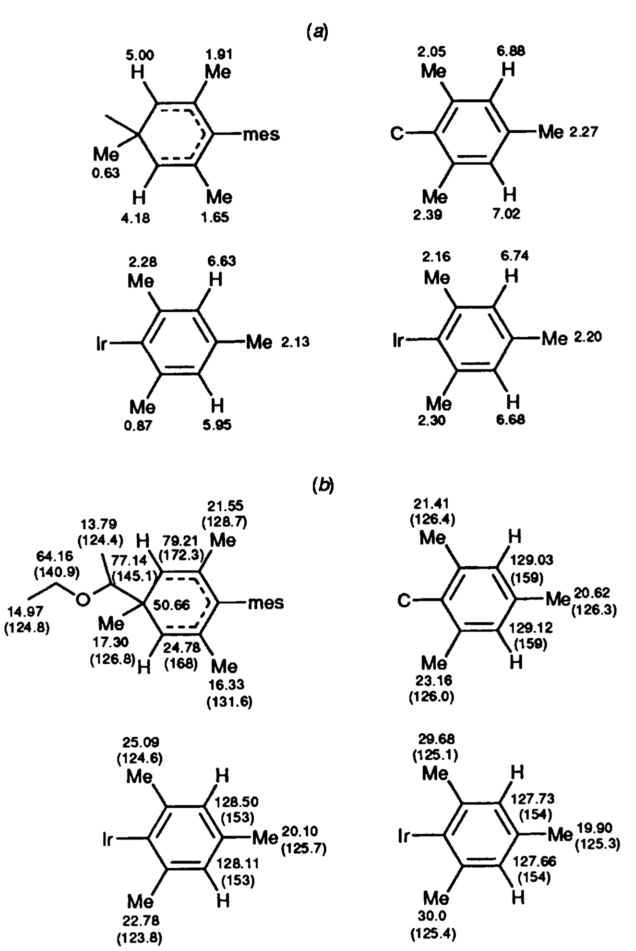


Fig. 10 (*a*) The ^1H chemical shifts of the major isomer in **1a** in CD_2Cl_2 at −20 °C; (*b*) the ^{13}C chemical shifts of the major isomer in **1a** at 0 °C, $^1J(^{13}C^1H)$ values in parentheses

and $^1J(^{13}C^1H)$ is a little smaller than the other values at 123.8 Hz rather than *ca.* 125 Hz. These NMR data would indicate that if there is an agostic interaction in solution, then it is small.[5] The major and minor isomers were correlated using NOESY and the assignments are given in Fig. 11.

Comparison of the ^1H chemical shifts of the dienyl ring protons of the *exo* and *endo* isomers shows a similarity in chemical shift between the major *exo* isomer and the minor *endo* isomer and a parallel similarity for the minor *exo* isomer and the major *endo* isomer. It is therefore probable that different isomers predominate for these two forms.

The dynamics of the *endo* isomer proved to be more difficult to analyse than those of the *exo* isomer due to greater proximity of signals. A quantitative analysis of exchange using magnetisation transfer between the pairs of signals at δ 2.31/2.38, 2.20/0.97 and 2.08/2.04 at 20 °C yielded the average rate of exchange 0.52 s^{-1} with values ranging from 0.44 to 0.59 s^{-1}. This corresponds to a $\Delta G^{\ddagger}_{293}$ of 17.5 ± 0.2 kcal mol^{-1}. A quantitative analysis of the rotation of the Ir–mes rings proved to be impossible, but NOE difference measurements at 38 °C clearly showed that this process was occurring, and the activation energy must be similar to that found for the *exo* isomer.

Synthetic Procedures: Comments on Starting Materials.—We noted previously[1] that Johnson Matthey (JM) hydrated iridium trichloride **2**, $IrCl_3{\cdot}nH_2O$, *n ca.* 3 can vary considerably; some batches are brown powders, others, sticky brown solids and, most commonly, black solids with a crystalline appearance. Only the latter were found to be suitable for synthesis of Ir(mes)$_4$; in the present work only black batches of **2** were used. Although the irreproducibility of syntheses of iridium complexes from **2** has long been known to those skilled in the art, the acrid, pungent odour, reminiscent to some extent of burnt sugar, of this material that ought to have no smell, appears not to have been remarked upon previously. That it contains organic matter is not surprising considering that it is made by addition of 'industrial methylated spirit' to aqueous hydrochloric acid solutions of chloroiridic acid, presumably $[H_3O]_2[IrCl_6]{\cdot}nH_2O$ ($n \approx 2$), followed by boiling, evaporation on steam-bath and steam-oven drying. Analyses (Table 2) show the carbon content to be around 0.5%. Headspace thermal desorption gas-liquid chromatography (GLC)–MS analysis at room temperature indicates that the aroma results from at least nineteen compounds assigned by matching spectra with standards (see Experimental section). In addition to HCl, these include many expected from the oxidation and/or chlorination of methanol and ethanol by $[IrCl_6]^{2-}$; the largest component was chloral, CCl_3CHO, or its hydrate which gives a similar mass spectrum.

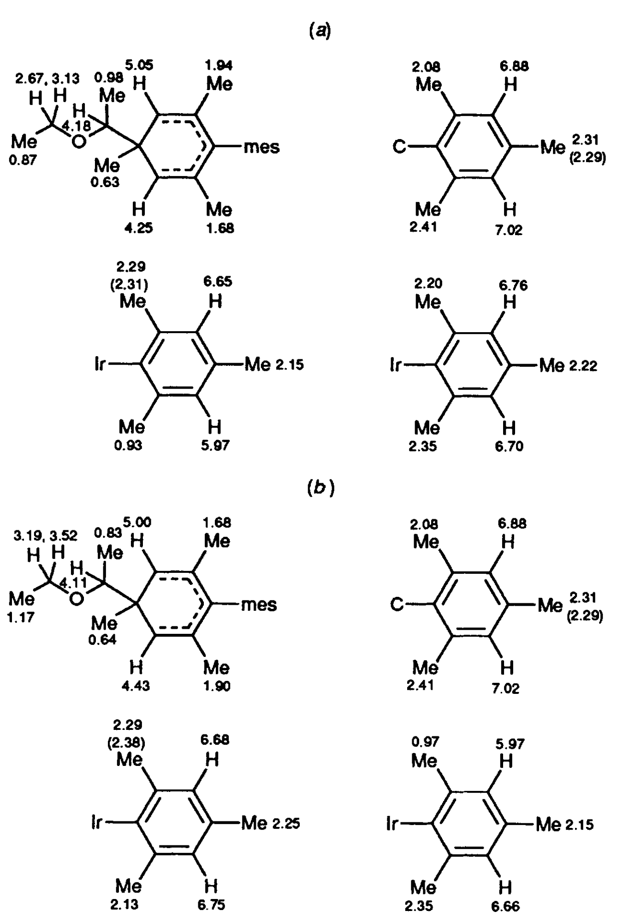


Fig. 11 The ^1H chemical shifts of the major (*a*) and minor (*b*) isomers of **1a** in CD_2Cl_2 at 20 °C

While we initially considered that the carbon content might have been a factor influencing the formation of **1** from the aberrant batch of **2**, this proved to be irrelevant except that it led us to a method of making an iridium starting material that gave **1** reproducibly. Since acetaldehyde and the acetal, $MeCH(OEt)_2$, could have been formed in the reduction in ethanolic HCl these substances were added to a hot solution of JM '$Na_2IrCl_6{\cdot}nH_2O$, $n \approx 6$' (see Experimental section) in aqueous ethanolic HCl. The green solution rapidly formed on boiling was evaporated over steam and the black residue dried in an oven that happened to be at 170 °C for *ca.* 30 min. The black product has the same acrid odour characteristic of **2** but, of course, contains sodium chloride. Extraction with CH_2Cl_2 to remove any soluble organic matter gave a brown solution,

Table 2 Representative analytical data for iridium halides

		Analysis[a] (%)					Atomic ratios			
Material	Batch/treatment	C	H	Cl	Ir	O	Ir	Cl	O	H
2[b]	051459	<0.3	1.2	35.3	51.6	(11.9)[c]	1	3.7	2.7	7.0
2[b]	EA0021	0.6	1.9	34.7	51.3	(11.5)[c]	1	3.7	2.7	7.1
2a[b]	EB0026	0.4	1.2	35.6	55.1	(7.7)[c]	1	3.5	1.7	4.3
3	*d*	0.3	0.9	31.5	57.0	(10.3)[c]	1	3.0	2.2	3.0
3	*e*	0.8	1.8	31.1			1			
4[f]	EB0038	—	0.8	40.5	54.2	5.8	1	4.0	1.3	2.8
5a[g]	*h*	—	1.1	38.3	53.7	6.9	1	3.9	1.5	3.9
5b[g]	*i*	—	1.0	34.1	59.8	5.1	1	3.1	1.0	3.1
6[g]	*j*	—	0.2	36.4	61.4	2.0	1	3.2	0.4	0.6

[a] Calculated values in parentheses. [b] $IrCl_3{\cdot}nH_2O$. [c] By difference; other O analysis by Pascher. [d] Obtained from **2a** upon heating at 170 °C for 30 min. [e] After suspension in Et_2O. [f] '$IrCl_4$'. [g] $H_2IrCl_6{\cdot}nH_2O$. [h] 120 °C, 3 h. [i] 120 °C, 20 h. [j] Refluxing of **5a** in $SOCl_2$; product shows absence of sulfur.

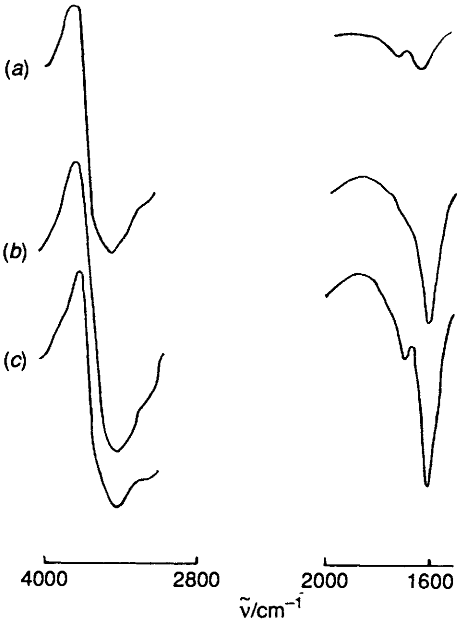


Fig. 12 Infrared spectra (Nujol bands omitted) in the 4000–2800 and 2000–1600 cm^{-1} regions. (*a*) JM $IrCl_3{\cdot}nH_2O$, (*b*) JM $RhCl_3{\cdot}3H_2O$ and (*c*) $IrCl_3{\cdot}nH_2O$ after *ca.* 20 min at 170 °C

which after evaporation and arylation in Et_2O as in ref. 1 gave no $Ir(mes)_4$ or **1**. However, the black, CH_2Cl_2 insoluble residue gave exclusively **1** in *ca.* 10% yield based on Ir. The standard procedure[1] used throughout was to treat the starting black materials with $SOCl_2$ in Et_2O at room temperature then, after decanting the liquid, washing the residue with Et_2O without allowing it to dry, and adding Li(mes) in Et_2O. The critical factor for obtaining **1** was the oven heating regime. After 1 h at 170 °C the yield of **1** was much reduced while 3 h heating gave complete inactivation of the halide. The optimum heating time was 15–30 min at 170 °C although longer times at, say, 130 °C, could be used. This suggested that the aberrant batch of **2** had either been heated at a temperature higher than normal or had been heated for a time longer than normal. It was then confirmed that any batch of black **2** when heated appropriately to give **3** will, after $SOCl_2$–Et_2O treatment and arylation, give **1**; the unheated **2** gave only $Ir(mes)_4$.[1]

Representative IR spectra in the H_2O/HO (which cannot be distinguished) regions are shown in Fig. 12 for **2**, for $RhCl_3{\cdot}3H_2O$ and for **2** heated at 170 °C for *ca.* 20 min. It may be noted that Fig. 12(*a*) and 12(*b*) are quite different, $RhCl_3{\cdot}3H_2O$ having the sharp δ(HOH) band(s) in the region around 1610 cm^{-1} that are characteristic for water co-ordinated to metal (for detailed discussion and references to co-ordinated and lattice water see ref. 6). All the bands in Fig. 12(*a*) > 3000 cm^{-1} and in the 1600–1700 cm^{-1} region shift when **2** is briefly suspended in D_2O in which it is insoluble. The major change in the heated samples **3** is the appearance of a sharp band around 1606 cm^{-1} indicating co-ordinated water. It may be noted that water co-ordinated to some ruthenium(IV) complexes has been found difficult to remove,[6b] also that subsequent treatment of the heated materials with $SOCl_2$ in Et_2O does not remove all the water: the bands > 3000 cm^{-1} may be altered and weakened but they and the δ(HOH) bands at *ca.* 1610 cm^{-1} remain. More drastic heating > 200 °C or longer times at 170 °C does remove more water but the halides are then unreactive.

Heating chloroiridic acid is said to give '$IrCl_4$'. The black solids obtained at 120 °C for 3–20 h (Table 2) also contain H and O by analysis but refluxing in neat $SOCl_2$ produces a material that has an Ir:Cl ratio of close to 1:3 with minimal amounts of O and H. The IR spectrum of the latter show only very weak bands > 3000 cm^{-1} and *ca.* 1615 cm^{-1} but in the heated products **5a** and **5b** there are bands at *ca.* 3445 and 1606 cm^{-1} that weaken with longer heating times.

The X-ray photoelectron spectra (XPS) (Table 3) showed the presence of iridium(III), chlorine and oxygen for all of the samples. The Ir $4f_{\frac{7}{2}}$ binding energies were in the range 62.6–63.0 eV characteristic for Ir^{III} with the Cl 2p and O 1s binding energies being *ca.* 199.4 and 532.7 eV respectively. The materials show no X-band EPR spectra in acetone in which they are slightly soluble. Chloroiridic acid and '$Na_2IrCl_6{\cdot}nH_2O$' have EPR spectra for Ir^{IV}, $g = 1.78$–1.79, but XPS data and analyses indicate that the sodium salt also contains Ir^{III} (see Experimental section).

As noted previously[1] it is essential that the halides be treated with $SOCl_2$ and Et_2O and not allowed to dry or age. The ether-saturated materials retain adsorbed Et_2O even after pumping in vacuum at 25 °C for *ca.* 30 min. The Et_2O can be detected by the IR band at 1154 cm^{-1} and, after heating the solids and collecting the volatiles in a cold trap, by ^1H NMR spectroscopy.

In summary, whether Ir^{III} or Ir^{IV} starting materials are used, the solids used in synthesis contain Ir^{III} and for **1**, co-ordinated water as well as adsorbed ether is required. A summary of the precursors used, their treatment together with arylation conditions and yields are given in Table 3. Note that to obtain good yields of $Ir(mes)_4$, the arylation reactions should proceed for no more than 1 h and the work-up must be done rapidly, otherwise an increasing amount of $Ir(mes)_3$ is formed (as detected by TLC, see Experimental section). Conversion of $Ir(mes)_4$ to $Ir(mes)_3$ in radical reactions has been noted.[8]

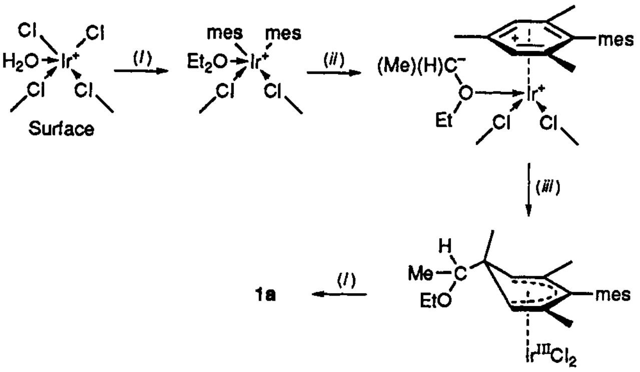
Product Formation.—As discussed previously[1] $Ir(mes)_4$ must be obtained from partially dehydrated $IrCl_3{\cdot}nH_2O$ by some type of disproportionation and $Ir(mes)_3$ seems not to be an intermediate. The formation of **1** presents more of a problem.

Interaction of organolithium compounds with Et_2O com-

Table 3 Precursors, treatment, XPS data, arylation, conditions and yields

Precursor	Pre-treatment	XPS/eV[a]	Arylation[b]	Product	Yield[c] (%)
$IrCl_3 \cdot nH_2O$	None[d]	62.6	4 equivalents, r.t. 2 h	$Ir(mes)_4$	17
$IrCl_3 \cdot nH_2O$	170 °C, 20 min[d]		8 equivalents, reflux 2.5 h then r.t. 24 h	**1a, 1b**	15
$H_2IrCl_6 \cdot nH_2O$	120 °C, 3–20 h[d]	62.6	4 equivalents, r.t. 1.5 h	$Ir(mes)_4$	25
or					
JM '$IrCl_4$'	None[d]	62.7	4 equivalents, r.t. 12 h	**1a, 1b**	15
			4 equivalents, r.t. 12 h then at 10 °C 24 h	$Ir(mes)_3$	23
$H_2IrCl_6 \cdot nH_2O$	Reflux $SOCl_2$	63.0	4 equivalents, r.t. 1 h	$Ir(mes)_4$	25
'$Na_2IrCl_6 \cdot nH_2O$'[e]	Reflux $SOCl_2$		6 equivalents, reflux 12 h	**1a, 1b**	18
			4 equivalents, r.t. 12 h	$Ir(mes)_4$	6
$[NBu_4]_2IrCl_6$[f]	None		6 equivalents, r.t. 12 h	$Ir(mes)_4$	Trace

[a] Binding energies for Ir $4f_{\frac{7}{2}}$. [b] Equivalents per Ir, $Li(mes) \cdot OEt_2$ in Et_2O. [c] Based on Ir content; yields are approximate and variable. [d] Samples stirred with $SOCl_2$ in Et_2O and then washed with Et_2O before arylation. [e] See Experimental section. [f] Made from the sodium salt in 1 mol dm^{-3} HCl saturated with chlorine followed by addition of NBu_4Cl, see ref. 7.



Scheme 1 Possible route to isomer **1a**. (*i*) Li(mes), Et_2O; (*ii*) σ–π reductive coupling and deprotonation of Et_2O; (*iii*) chlorine transfer to give Ir^{III}

monly leads to cleavage giving alkoxide doubtless *via* initial formation of short-lived EtOC(Li)(H)Me.[9] The unexpected incorporation of EtOC(H)(Me) groups from Et_2O has been observed in photochemical reactions, *e.g.*, of pentachloropyridine in Et_2O to give $C_5Cl_4[CHMe(OEt)]N$ but these are free radical in nature.[10]

The formation of **1** appears to be a heterogeneous reaction of the ether-insoluble activated hydrated halide with Li(mes). Presumably the initial reaction is arylation of a surface $IrCl_2(OH_2)^+$ group to give a *cis*-$Ir(mes)_2{}^+$ moiety which then undergoes the well known σ–π rearrangement involving coupling with reduction of Ir^{III} to Ir^{I} and retention of the biaryl on the metal.[11] There then arises the matter of a nucleophilic attack by an EtOC(H)Me$^-$ anion on the η^6-bimesityliridium(I) cationic entity that would generate both the *endo* and *exo* cyclohexadienyl $C_{22}H_{31}O$ ligand as in established attacks by external nucleophiles on cationic metal arene complexes [see ref. 11 (*b*), p. 1182]. The attack uniquely on the position *para* to the non-co-ordinated mesityl group can be attributed to the *para* directing electronic effect of the latter. While we have no evidence for or against a radical pathway, the attack only on the *para* position suggests that radicals are not involved. We then have to postulate transfer of Cl atoms from residual iridium(III) chloride (probably leading to reduction to metal) to the iridium(I) moiety $(C_{22}H_{31}O)Ir$, in effect an oxidative addition of chlorine, to give $(C_{21}H_{31}O)Ir^{III}Cl_2$ which then needs only arylation to give **1a**, **1b**.

The removal of co-ordinated water from $Ir(OH_2)$ by Li(mes), giving mesitylene which is always formed in these reactions, and LiOH, could generate a vacant site either on the Ir atom η^6-bound to bimesityl or on an adjacent $IrCl_n$ unit that would allow co-ordination of Et_2O to Ir, subsequent deprotonation by Li(mes) then giving an IrOC(H)(Me)Et group that is sufficiently stabilised towards the classical decomposition[9] to allow migration to the η^6 arene. A diagram of such a route leading to **1a** is shown in Scheme 1; the *exo* isomer could arise by transfer of EtOC(H)Me$^-$ from an adjacent iridium centre. The lifetime of the η^6-bimesityliridium(I) moiety must also be involved since elimination of bimesityl by the well established aryl coupling reaction [ref. 11 (*b*), p. 1137] occurs. Bimesityl is always formed in yields comparable to those of **1a**, **1b** (see Experimental section) and it is significant that this occurs only in reactions that give **1a**, **1b**. The formation of **1a**, **1b** is hence independent of the formation of homoleptic aryls and indeed, attempts to convert these or the Ir^{V} cation $[Ir(mes)_4]^+$ to **1a**, **1b** or to bimesityl *e.g.*, by treatment with iridium chlorides in Et_2O failed.

Attempts to make **1** by addition of MeCH(Cl)OEt[12] to partially dehydrated $IrCl_3$ prior to addition of Li(mes) or by interaction of LiBu^n and Et_2O at low temperature prior to addition of an Et_2O suspension of halide plus Li(mes) were unsuccessful. Also the substitution of Et_2O by $Pr^n{}_2O$, $Bu^n{}_2O$, PhOEt, tetrahydrofuran (thf) or 1,2-dimethoxyethane gave no isolable products.

Experimental

The general techniques and instrumentation are as given previously.[1] Microanalyses were by Imperial College, University College, London, and Pascher, Remagen, laboratories; iridium assays were by Johnson Matthey, Royston. General chemicals were from Aldrich: the light petroleum used had b.p. 40–60 °C. Mesityllithium diethyl etherate was made as described.[13]

For XPS, samples were analysed using Mo-Kα radiation at 130 W using 8/40/20 eV pass energies and 7 mm slits: data were referenced to C 1s at 284.8 eV.

NMR spectra of **1a**, **1b** were measured using a Bruker WH 400 spectrometer. Temperatures were measured by replacing the sample tube by a tube containing CH_2Cl_2 and a thermocouple attached to a Comark electronic thermometer. The magnetisation transfer measurements were performed by applying a selective π-pulse of 0.05 s to the required resonance and waiting various times for exchange to occur before applying a general observing $\frac{\pi}{2}$ pulse. The data were analysed as previously described.[3]

Iridium Trichloride Hydrate.—This was designated as '$IrCl_3 \cdot nH_2O$, $n \approx 3$, crystalline flakes' **2**. Most of this work was done using batch numbers 051459 and EA 0021. Batches vary in analyses and some samples show an additional weak peak at *ca.* 1615 cm^{-1} for co-ordinated water. The $IrCl_3 \cdot nH_2O$ is somewhat hygroscopic and is best kept out of moisture; all samples smell. The headspace/thermal desorption GLC–MS analysis of the vapours was carried out by M-Scan Ltd., Silwood Park, Ascot, by courtesy of Professor H. Morris of the Biochemistry Department, Imperial College. About 1 dm^3 of the headspace vapour over *ca.* 5 g of **2** at room temperature was drawn onto a Tenax tube and the material examined by thermal desorption GLC–MS. Major peaks were assigned by library matching and inspection of individual mass spectra and mass chromatograms. Identified compounds not present from the laboratory atmosphere were, in order of scan number: chloromethane, acetaldehyde, acetone, HCl, propan-2-ol, butanal, butanone, acetic acid, 1,2-dichloroethane, chloroacetone, 3-methylbutanone, 2,2,2-trichloroacetaldehyde, 4-methylpentan-2-one, hexan-2-one, hexanal, methyl dichloroacetate and several other unidentified species.

'Sodium Hexachloroiridate Hydrate'. While the material has an X-band EPR spectrum for Ir^{IV} in acetone, XPS data indicates the presence of both Ir^{III} (62.6 eV) and Ir^{IV} (63.7 eV). The analytical data on batch 051369 are not diagnostic (H, 1.5; Cl, 38.7; Ir, 37.1; Na, 7.6%; atomic ratios Ir:Cl:H:Na = 1:5.6:7.7:1.7), but suggest reduction, and anation (or hydrolysis) when a solution of chloroiridic acid containing NaCl is evaporated.

The spontaneous reduction of $[IrCl_6]^{2-}$ in neutral or weakly acidic aqueous solutions is well known,[14a–c] while the anation of $[IrCl_6]^{2-}$ has been studied in some detail[14c] and a procedure for making $Na_2IrCl_6 \cdot 6H_2O$ involving evaporation of HCl solutions and excess NaCl *in presence of chlorine* given, as well as a method for $Na_3IrCl_6 \cdot 2H_2O$.[14b] The inadvisability of the use of '$Na_2IrCl_6 \cdot 6H_2O$' from supply houses without purification (see *e.g.* ref. 14*d*) should be recognised.

Synthesis of 'Activated Iridium Chloride'.—(*a*) 'Hydrated sodium hexachloroiridate' (4 g) in 12 mol dm^{-3} HCl (30 cm^3) and ethanol (20 cm^3) was boiled with stirring for 10 min. Acetal (2 cm^3) followed by paraldehyde (1 cm^3) was added and the boiling continued for 10 min. Additional 12 mol dm^{-3} HCl (30 cm^3) and ethanol were added, the mixture boiled for 10 min when further quantities of acetal and paraldehyde were added. The green solution was boiled 20 min more, then evaporated on a steam-bath to dryness. The residue was heated at 170 °C for 15–20 min, then washed with CH_2Cl_2 (*ca.* 20 cm^3). The brown CH_2Cl_2 solution can be discarded as no identifiable compound could be isolated from it on arylation. The insoluble residue analyses as C, 1.7; H, 0.9; Cl, 41.3; Ir, 40.5; Na, 8.0%; it has the pungent odour of other samples of **2**.

(*b*) Up to 5 g of **2** was heated at 170° for *ca.* 20 min.

(*c*) Crystalline chloroiridic acid was dissolved in the minimum of water and heated in an oven at 120 °C for 3–20 h to give a black amorphous solid. The JM '$IrCl_4$' has similar properties including IR and XPS data and reactivity.

(*d*) Chloroiridic acid was refluxed with $SOCl_2$ (1 h) and pumped to dryness in vacuum.

Syntheses of **1a**, **1b**.—The detection of **1a**, **1b**, Ir(mes)$_3$ and Ir(mes)$_4$ in the light petroleum solution after extraction from the reaction mixture is readily made by thin layer chromatography on plastic sheets coated with silica gel (Merck) eluting with 10% Et_2O in petroleum. The elutions are in the order: brown Ir(mes)$_4$, green Ir(O)(mes)$_3$[8] [derived by air oxidation of Ir(mes)$_3$], and cherry red **1a**, **1b**.

(*a*) *From* $IrCl_3 \cdot nH_2O$. To the black solid after heating at 170 °C for *ca.* 20 min (0.5 g, 1.7 mmol) was added degassed Et_2O (*ca.* 10 cm^3) and $SOCl_2$ (*ca.* 2 cm) and the solution stirred for 15 min when the liquid was decanted and the solid washed 2–3 times with degassed Et_2O and left covered with Et_2O (20 cm^3). After addition of Li(mes)$\cdot$OEt$_2$ (1.34 g, 6.7 mmol) in Et_2O (*ca.* 30 cm^3) the mixture was stirred vigorously under N_2 for *ca.* 20 h. After filtration and removal of solvent in vacuum the residue was extracted with light petroleum (2 × 20 cm^3) which was evaporated to *ca.* 2 cm^3 and transferred to a chromatographic column of neutral alumina Grade 1. Elution using light petroleum containing 2% Et_2O by volume gave a single band which on evaporation left the isomeric mixture **1**. Yield: 0.1 g, 8.1% based on Ir; this could be increased to *ca.* 15% by using an 8-fold excess of Li(mes)$\cdot$OEt$_2$ with refluxing for 2.5 h followed by stirring for 12 h at room temperature.

Separation of exo *and* endo *Isomers*. The **1a**, **1b** mixture was dissolved in the mimimum of light petroleum and transferred to the alumina column. The elution was started using light petroleum to which Et_2O was added in 0.5% steps to 2%. This led to the two cherry red bands in a 1:3 ratio the first **1a** (*endo* isomer) and the second **1b** (*exo* isomer). The overall yield was essentially quantitative. The bands could be reprocessed to increase the purity. X-Ray quality crystals of **1b** were obtained on cooling a hexane solution at −30 °C for at least 2 weeks (Found: C, 65.2; H, 7.5. $C_{40}H_{53}IrO$ requires C, 64.7; H, 7.2%). Electron impact mass spectrum (EI) for both **1a** and **1b**: *m*/*z* 742 $(M + H)^+$, 622 $(M - C_9H_{11})^+$, 549 $(M - C_9H_{11}C_4H_9O)^+$ and 502 $(M - C_{18}H_{22})^+$.

Cyclic voltammetry of **1b** in CH_2Cl_2 using NBu_4PF_6 as supporting electrolyte at 20 °C shows two, reversible one-electron waves at +0.37 and −2.18 V *vs.* the ferrocene–ferrocenium standard (*cf.* ref. 1).

(*b*) *From* '$Na_2IrCl_6 \cdot nH_2O$'. The ground black solid (0.3 g, 0.5 mmol) was refluxed in neat $SOCl_2$ with stirring for 1 h; Et_2O (*ca.* 30 cm^3) was then added to the cooled solution. After stirring and decantation the residue was washed with Et_2O and left in Et_2O (*ca.* Et_2O). A solution of Li(mes)$\cdot$OEt$_2$ (0.64 g, 3.2 mmol) in Et_2O was added and the mixture refluxed for 5 h with continued stirring at room temperature for 12 h. Removal of solvent under vacuum and extraction with light petroleum followed by chromatography as above gave **1a**, **1b**. Yield: 0.072 g, 18%. Trace amounts of Ir(mes)$_4$ were detected in the solution before column chromatography by EPR spectra and by TLC.

(*c*) *Isolation of Bimesityl*. On work-up and chromatography as in (*a*) the solution was collected before elution of **1**. Evaporation left a colourless product which was purified by chromatography on silica gel using light petroleum as eluent. Repeated crystallisation from methanol gave bimesityl, 2,2',-4,4',6,6'- hexamethylbiphenyl, m.p. 98–99 °C (lit.,[15] 98.5–99.5 °C). ^1H NMR ($CDCl_3$, 250 MHz): δ 6.86 (s, 4 H aromatic H), 2.26 (s, 6 H, *p*-Me) and 1.79 (s, 12 H, *o*-Me). Mass spectrum (EI): $m/z = 238$ M^+.

Products from Arylation of '$IrCl_4$' *from Chloroiridic Acid*.—The black residue from the heating (3 h, 120°) of chloroiridic acid (0.67 g, 2 mmol) was treated (15 min) with an excess of $SOCl_2$ and Et_2O at room temperature, ether washed as before and used immediately. To the solid was added Et_2O (5 cm^3) and Li(mes)$\cdot$OEt$_2$ (1.6 g, 8 mmol) in Et_2O (70 cm^3). The mixture was stirred vigorously for 1 h and worked-up in the following ways: (*a*) evaporation of the mixture then extraction with light petroleum (2 × 50 cm^3), filtration, reduction in volume and cooling to −30 °C gave brown crystalline *tetramesityliridium* (0.34 g, 25%) identified by EPR and TLC. This synthesis is preferred to that[1] starting with **2**.

(*b*) The mixture was kept at *ca.* 10 °C for 24 h when evaporation and work-up as in (*a*), with recrystallisation of the product from light petroleum gave brown crystalline *trimesityliridium* (0.25 g, 23%) identified by ^1H NMR and oxidation to green Ir(O)(mes)$_3$.

(*c*) Stirring the mixture at room temperature for 12 h followed by work-up as above and column chromatography gave **1a**, **1b** (0.22 g, 15%).

Note that (*i*) if the iridium(III) precursor is allowed to age under N_2 for *ca.* 3 weeks, Ir(mes)$_3$ is obtained; (*ii*) if the $SOCl_2$–Et_2O treatment is omitted the arylation reaction was very slow forming initially Ir(mes)$_4$ (by TLC) which slowly disappeared (12 h) with the appearance of **1a**, **1b**. There was no obvious difference between the reactions using chloroiridic acid heated over periods of 3–20 h. JM '$IrCl_4$' behaved similarly.

That Ir(mes)$_4$ is not an intermediate in the formation of **1a**, **1b** is suggested by the reaction of the pure compound in Et_2O with the iridium chloride—the brown colour of Ir(mes)$_4$ disappears and no identifiable product is isolated.

Table 4 Fractional atomic coordinates (× 10^4) for compound **1b**

Atom	*x*	*y*	*z*
Ir	187(1)	147(1)	2510(1)
C(6)	−2036(10)	1435(9)	2007(7)
C(5)	−1574(11)	1264(12)	2856(8)
C(4)	−1525(11)	295(10)	3504(7)
C(3)	−1628(10)	−737(10)	3399(7)
C(2)	−1479(10)	−741(9)	2562(7)
C(1)	−1276(10)	377(10)	1852(7)
C(11)	−1920(11)	−1812(10)	4196(7)
C(12)	−1065(14)	−2722(11)	4496(8)
C(13)	−1465(16)	−3619(12)	5245(9)
C(14)	−2661(17)	−3672(14)	5706(9)
C(15)	−3527(16)	−2774(15)	5384(10)
C(16)	−3181(13)	−1843(12)	4636(8)
C(21)	1279(9)	1445(10)	1939(7)
C(22)	1549(10)	2102(10)	2403(7)
C(23)	2240(12)	3030(11)	2019(9)
C(24)	2711(12)	3441(11)	1133(9)
C(25)	2443(12)	2860(12)	633(8)
C(26)	1775(10)	1916(10)	1006(7)
C(31)	1697(10)	−896(10)	2096(6)
C(32)	2617(10)	−1225(9)	2646(6)
C(33)	3639(13)	−1970(12)	2558(9)
C(34)	3900(12)	−2472(11)	1921(9)
C(35)	3014(14)	−2194(12)	1412(9)
C(36)	1908(10)	−1451(10)	1486(7)
C(121)	302(14)	−2771(13)	4032(10)
C(141)	−3039(19)	−4700(14)	6534(9)
C(161)	−4250(13)	−893(13)	4308(9)
C(221)	1070(12)	1823(10)	3372(7)
C(241)	3492(16)	4453(15)	687(11)
C(261)	1594(12)	1387(11)	363(7)
C(321)	2446(11)	−767(11)	3372(7)
C(341)	5127(14)	−3242(14)	1757(11)
C(361)	1036(11)	−1267(12)	853(8)
C(601)	−1612(12)	2492(11)	1251(7)
C(201)	−1595(13)	−1747(11)	2335(8)
C(401)	−1520(11)	251(11)	4440(7)
O(1)	−3709(8)	1305(8)	1398(5)
C(01)	−3447(11)	1410(12)	2153(8)
C(02)	−4259(13)	2346(13)	2421(11)
C(03)	−4843(14)	760(13)	1574(9)
C(04)	−4841(15)	463(15)	802(9)
O(100)	8327(37)	4878(19)	2828(25)
C(110)	9748(23)	5454(19)	1082(15)
C(120)	9037(49)	5469(31)	1900(29)
C(130)	7622(39)	4285(31)	3787(22)
C(140)	6593(23)	4212(25)	4596(19)

Chloroiridic acid (0.64 g, 1.3 mmol) was refluxed with neat $SOCl_2$ (8 cm^3) and stirring (1 h); the volatiles were removed under vacuum leaving a greenish black material. Diethyl ether (30 cm^3) was added followed by Li(mes)•OEt_2 (1.11 g, 5.6 mmol) in Et_2O (20 cm^3) and the mixture stirred at room temperature (1 h); filtration vacuum evaporation and extraction with light petroleum (2 × 30 cm^3) followed by reduction and cooling (−30 °C) gave crystalline $Ir(mes)_4$ (0.24 g, 27%).

X-Ray Crystallography of Complex **1b**.—The crystals of **1b** as its monoetherate were extremely thin, fragile cherry-pink flakes. The specimen used for X-ray work was a fragment of triangular shape, *ca.* 0.2 mm on edge and 0.01 mm thick. Cell dimensions and intensity data were recorded using a FAST TV area detector diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.7106 Å) following previously described procedures.[16] Slightly more than one hemisphere of data were recorded in the range $0 \leqslant \theta \leqslant 24.5°$ using a detector swing angle of −18° and a crystal-to-detector distance of 45 mm.

Crystal data. $C_{40}H_{53}IrO{\cdot}C_4H_{10}O$, $M_r = 816.55$, triclinic, space group $P\bar{1}$, $a = 16.748(2)$, $b = 12.681(4)$, $c = 16.648(2)$ Å, $\alpha = 68.14(1)$, $\beta = 76.25(1)$, $\gamma = 79.24(1)°$, $U = 2090.3$ Å^3, $Z = 2$, $D_c = 1.29$ g cm^{-3}, $F(000) = 840$, μ(Mo-Kα) = 31.0 cm^{-1}. A total of 11 126 reflections were processed to give 7000 unique ($R_{int} = 0.045$) of which 4430 were observed [$F_o > 3\sigma(F_o)$]. The structure was solved and developed by the heavy-atom method and refined by full-matrix least squares. Non-hydrogen atoms were refined anisotropically, methyl and methylene hydrogens included in idealised positions and refined with group U_{iso} values using AFIX routines in SHELX 76[17] and aryl hydrogens were freely refined isotropically. Use of the AFIX 35 facility to fix hydrogens on methyl groups attached to sp^2 carbons is open to question since orientations are not so clearly controlled by the geometry at the carbon, as for sp^3 carbons. However, the refinement of these groups proceeded smoothly and none of the refined group U_{iso} values adopted unusually high values, so we are fairly confident of the H positions. An absorption correction was applied during the refinement using the DIFABS[18] procedure. The *R* value was reduced by *ca.* 0.02 but, importantly, no geometry parameter changed by more than one e.s.d. The final *R*, *R′* values were 0.0496, 0.0481 for 527 parameters with weights $w = 1/\sigma(F)^2$. The highest residuals in the final difference map were two peaks of height +2.1 and +1.8 e A^{-3} at 1.0, 1.1 Å from the Ir atom. All other residuals were less than +1.0 e Å^{-3}.

Fractional atomic coordinates are given in Table 4.

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

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