The Selective Reduction of Benzene to Cyclohexene mediated by Platinum Metal Complexes: *X*-Ray Crystal Structure of $[(\eta^5\text{-}C_5Me_5)Ir(\eta^5\text{-}C_6H_6CH_2NO_2)][BF_4]$ †

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The dicationic η^6-benzene complexes $[(C_nMe_n)M(C_6H_6)]^{2+}$ [M = Rh, n = 5 (2a); M = Ir, n = 5 (2b); M = Ru, n = 6 (2c)] are reduced by tetrahydroborate to the η^5-cyclohexadienyl complexes $[(C_nMe_n)M(C_6H_7)]^+$ (3) which are further reduced to the η^4-cyclohexadiene complexes $[(C_nMe_n)M(C_6H_8)]$ (4). Reaction of complexes (4) with acid gives cyclohexene with 100% selectivity; when the reaction is carried out with tetrafluoroboric acid in benzene, the initial benzene complexes (2) are regenerated. The overall reaction consists of addition of two hydrides followed by two protons to co-ordinated benzene, and a cycle catalytic in the platinum metal can be constructed. The efficiency of the overall reduction of benzene to cyclohexene decreases in the order Ir > Ru > Rh. The reaction is compared to the reduction of benzene to cyclohex*a*ne mediated by rhodium, iridium, and ruthenium trichloride hydrates and tetrahydroborate in ethanol. Other nucleophiles also attack the benzene ring in (2b): these include methyl-lithium (which gives two dimethylcyclohexadiene complexes from which isomeric dimethylcyclohexenes can be obtained with acid), methoxide (which gives the methoxycyclohexadienyl and, with an excess, two dimethoxycyclohexa-1,3-diene complexes), and nitromethane which in the presence of base gives the nitromethylcyclohexadienyl complex $[(C_5Me_5)Ir(C_6H_6CH_2NO_2)][BF_4]$ (9). The single-crystal *X*-ray structure determination of (9) shows the C_5Me_5 and the C_6 ring both to be η^5-bonded, and the CH_2NO_2 substituent to be in the *exo* position on the η^5-cyclohexadienyl ring. Analysis of the high-field ^{1}H n.m.r. spectra of the complexes showed that *exo* attack on the C_6 ring occurred with all the nucleophiles. In the presence of base, (9) reacted further with (2b) to give $[\{(C_5Me_5)Ir(C_6H_6)\}_2CHNO_2]^{2+}$. These reactions show the versatility of the reduction procedure.

There are now a number of catalyst systems, heterogeneous [1] and homogeneous,[2] as well as some that appear to proceed by a mixed regime,[3] for the complete hydrogenation of benzene to cyclohexane. Synthetically and industrially it would, however, be of much greater interest partially to reduce benzene to cyclohexene. Unfortunately, $\Delta G^{\ominus}$ (298 K) for benzene to cyclohexene (-23 kJ mol^{-1}) [4] is substantially smaller than for the through reaction, benzene to cyclohexane (-98 kJ mol^{-1}).[4] Hence there is a strong tendency for the reaction, once initiated, to proceed all the way to cyclohexane, rather than to stop at cyclohexene. Nevertheless, a number of heterogeneous catalyst systems (the best being ruthenium-based) have been reported for the partial hydrogenation of benzene to cyclohexene.[5] However, despite strenuous attempts to optimise the catalyst, reproducible selectivities of higher than 20% towards cyclohexene (the remainder being cyclohexane) have not been obtained.[6,7] The only other route to cyclohexene from benzene is by a Birch reduction under forcing conditions (alkali metal in liquid ammonia in an autoclave at higher temperatures or in an organic primary amine solvent) so that the intermediate cyclohexa-1,4-diene is further reduced.[8] These reactions are of course non-catalytic and, in view of the severity of conditions needed, they would not lend themselves to the partial reduction of many functionalised benzenes.

We have developed a different strategy for reduction of benzene to cyclohexene, involving the addition of two hydrides, followed by two protons, to a co-ordinated benzene in a dicationic metal complex. This was based on the observations (*i*) that the η^6-co-ordinated benzene complex $[(C_5Me_5)Ir(C_6H_6)][BF_4]_2$ (2b) added one hydride easily to give the η^5-cyclohexadienyl complex $[(C_5Me_5)Ir(C_6H_7)][BF_4]$ (3b),[9] which in turn reacted with further hydride {a reaction that would be anticipated to give the iridium(I) η^4-cyclohexa-1,3-diene complex $[(C_5Me_5)Ir(C_6H_8)]$ (4b) [10]}, and (*ii*) that related co-ordinated diene complexes reacted with acid (2 H$^+$) to give the free mono-olefin.[11]

We also focus attention on the wider possibilities of this reaction, namely that nucleophiles other than hydride and electrophiles other than proton may be used.

A Preliminary Communication on part of this work has been published.[12]

Results and Discussion

Iridium-mediated Synthesis of Cyclohexene.—A high-yield synthesis of the bis(tetrafluoroborate) salt of the η^6-benzene dication (2b) was developed. The hexafluorophosphate had previously been made but it was found that the tetrafluoroborate reacted more cleanly and without the complications often found for hexafluorophosphate salts.[13,14] Complex (2b) reacted with aqueous sodium tetrahydroborate to give the η^5-cyclohexadienyl complex (3b) (76%), the spectroscopic properties of which were very similar to those of the known hexafluorophosphate salt.[9]

The hexadeuteriobenzene complex [$^2H_6$]-(2b) was also made [ν(C–D) at 2 219 and 2 250 cm^{-1} corresponding to ν(C–H) in (2b) at 3 015 and 3 082 cm^{-1}; ν(C–H)/ν(C–D) = 1.35, in agreement with theory]. On reduction with sodium tetrahydroborate in water the cyclohexadienyl complex [$^2H_6$]-(3b) was formed in 52% yield; this showed only two singlets in the ^{1}H n.m.r. spectrum, one at δ 2.20 corresponding

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† (1—5-η-6-Nitromethylcyclohexadienyl)(1—5-η-pentamethylcyclopentadienyl)iridium(III) tetrafluoroborate.

Supplementary data available (No. SUP 23940, 33 pp.): H-atom co-ordinates, thermal parameters, structure factors, least-squares planes, full bond lengths and angles. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

Non-S.I. unit employed: mmHg ≈ 133 Pa.

Table 1. Microanalytical data (%)[a]

Compound	C	H	N
(2a) $[(C_5Me_5)Rh(C_6H_6)][PF_6]_2$	32.2	3.5	
	(31.7)	(3.5)	
(3a) $[(C_5Me_5)Rh(C_6H_7)][PF_6]$	38.2	4.6	
	(41.5)	(4.8)	
(2c) $[(C_6Me_6)Ru(C_6H_6)][BF_4]_2$	41.8	4.7	
	(41.9)	(4.7)	
(3c) $[(C_6Me_6)Ru(C_6H_7)][BF_4]$	50.4	5.6	
	(50.3)	(5.8)	
$[^2H_6]$-(2b) $[(C_5Me_5)Ir(C_6D_6)][BF_4]_2$	32.7	3.5[b]	
	(32.8)	(3.6)[b]	
$[^2H_6]$-(3b) $[(C_5Me_5)Ir(C_6D_6H)][BF_4]$	38.6	4.4[b]	
	(38.4)	(4.4)[b]	
(9) $[(C_5Me_5)Ir(C_6H_6CH_2NO_2)][BF_4]$	37.0	4.2	2.5
	(37.4)	(4.3)	(2.6)
(10) $[\{(C_5Me_5)Ir(C_6H_6)\}_2CHNO_2][BF_4]_2$	37.7	4.3	1.0
	(38.0)	(4.1)	(1.3)

[a] Calculated values are in parentheses. [b] Corrected for deuterium.

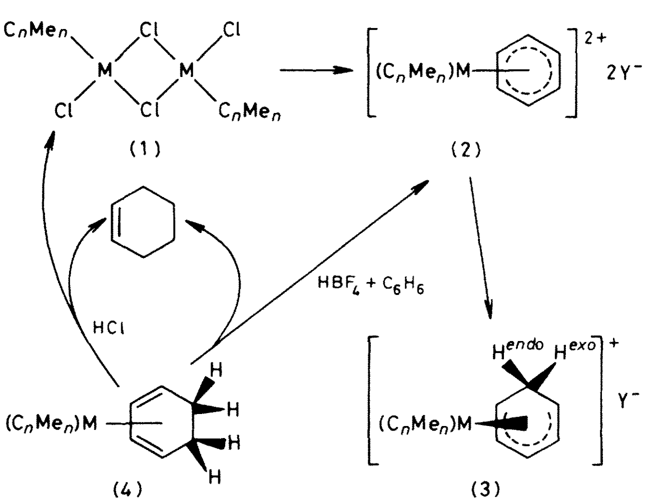
to the C_5Me_5 methyls (15 H) and the other at δ 4.22, due to H^{exo} (1 H), the coupling to H^{endo} having been removed. ν($C-H^{exo}$) was at 2 860 cm^{-1} by comparison with 2 843 cm^{-1} for the all-protio complex (3b).

Although (3b) did not react further with tetrahydroborate, both it and complex (2b) reacted rapidly with sodium dihydridobis(2-methoxyethoxy)aluminate ('Red-Al') in toluene to give the colourless air-sensitive neutral η^4-cyclohexadiene complex (4b) in good yield (83 and 79% respectively). This complex had previously been made directly from cyclohexa-1,3- or -1,4-diene and $[\{(C_5Me_5)Ir\}_2Cl_4]$ in ethanol with base.[15]

The hexadeuteriocyclohexadiene complex $[^2H_6]$-(4b) was formed analogously by Red-Al reduction of $[^2H_6]$-(3b). It showed a broadened singlet (due to H–D coupling) in the ^1H n.m.r. spectrum at δ 1.08, corresponding to the signal at δ 1.13 in (4b). The fact that the signal was a singlet indicates that the ligand must be symmetrical (dynamic processes can be ruled out here) and hence that the second hydride must also have attacked the molecule *exo* to the metal. Interestingly, the mass spectrum of $[^2H_6]$-(4b) showed the molecular ion at *m/e* 414 (relative intensity 80), corresponding to $C_{16}H_{17}D_6{}^{193}Ir$, a peak at *m/e* 412 (57) made up of $C_{16}H_{17}D_6{}^{191}Ir$ and $C_{16}H_{15}D_6{}^{193}Ir$, the base peak at *m/e* 410 made up of $C_{16}H_{15}D_6{}^{191}Ir$ and $C_{16}H_{17}D_4{}^{193}Ir$, and a peak at *m/e* 408 (65), $C_{16}H_{17}D_4{}^{191}Ir$. We take these data to imply that loss of D_2 is the predominant cracking mode in the mass spectrometer; this may mean that the D atoms that are *endo* to the metal move to the metal on electron impact before being lost.

A pentane solution of the cyclohexadiene complex (4b) reacted with gaseous hydrogen chloride to precipitate (1b) in 93% yield. Gas-chromatographic analysis of the organic materials dissolved in the pentane showed the presence of only cyclohexene, present in essentially quantitative amount. Under the conditions used the relative retention times were: pentane 30, cyclohexane 87, cyclohexene 114, cyclohexa-1,3-diene 127, and benzene 144 s.

When the reaction was carried out in benzene using concentrated tetrafluoroboric acid, the products were again cyclohexene, as the only detectable organic compound, together with the reformed η^6-benzene dication (2b) (94%). {The reaction was also carried out in toluene and gave again only cyclohexene and the η^6-toluene complex $[(C_5Me_5)Ir(C_6H_5Me)][BF_4]_2$}. The cycle can thus be completed with only minimum loss of iridium complex and is therefore potentially catalytic in iridium.



Scheme 1. Compounds a: M = Rh, *n* = 5, Y = PF_6. Compounds b: M = Ir, *n* = 5, Y = BF_4. Compounds c: M = Ru, *n* = 6, Y = BF_4

Rhodium- and Ruthenium-mediated Syntheses of Cyclohexene.—Although the η^6-benzene–rhodium complex $[(C_5Me_4Et)Rh(C_6H_6)]^{2+}$ has been reported to reduce cleanly to the corresponding cyclohexadienyl complex on reaction with lithium tris(t-butoxy)hydridoaluminate,[16] this reaction was very difficult for the newly synthesised rhodium complex (2a). Even under optimum conditions ($NaBH_4$ in butan-2-one!) the yield of the cyclohexadienyl complex (3a) was very low. By contrast, the further reduction of (3a) to the known [15] cyclohexadiene complex (4a) went smoothly in good yield. Again, reaction of (4a) with hydrogen chloride in toluene gave cyclohexene only (92%) together with complex (1a) (90%); when the reaction was carried out with tetrafluoroboric acid in benzene, only cyclohexene (95%) and the benzene complex (2a) were obtained.

The closely related and isostructural dication (η^6-benzene)(η^6-hexamethylbenzene)ruthenium(II) (2c) [17] was reduced cleanly and in high yield to the η^5-cyclohexadienyl monocation (3c). Further reduction again took place with Red-Al to give the air-sensitive η^4-cyclohexadiene–ruthenium(0) complex (4c) in 71% yield. In neither case was the hexamethylbenzene ligand attacked; this remained η^6-bonded in all the complexes. Again, as in the previous cases, the cyclohexadiene complex (4c) reacted with hydrogen chloride to give (1c), and with tetrafluoroboric acid in benzene to give (2c), both in high yield; the only organic product in either case was cyclohexene (98% and 75% yields respectively): see Scheme 1.

All the new rhodium and ruthenium complexes were characterised by microanalyses and spectroscopically.

Summary and Related Reactions.—In all three cases a three-step reduction of co-ordinated benzene to free cyclohexene takes place as indicated in Scheme 1. In the first two steps two hydrides add *exo* at adjacent sites, giving the cyclohexadiene complexes with the metal in the lower oxidation state. In the final step, which may well also proceed by a stepwise path,[18,19] two protons are added to liberate the free cyclohexene and to (effectively) reoxidise the metal. When the acid has a non-co-ordinating anion and the reaction is carried out in benzene then the initial benzene complex (2) is reformed. This completes the cycle and allows the reaction to be carried out in a manner which is catalytic in the platinum metal, even though it is stoicheiometric in hydride and acid. Although turnover numbers have not been measured, if they are calculated on the basis of yields of (2) recovered and of (4), they appear to be *ca.* 10 for the Ir, 5 for the Ru, and very low for the rhodium systems. However, it should be borne in mind that the various procedures have not yet been optimised. For example, the reaction cycle should lend itself well to being carried out using polymer-supported complexes, in which case metal losses would be minimised.

Double hydride addition to an η^6-benzene complex has also recently been shown for the manganese system shown below[20] and in the earlier but more complex reduction of the

$$[(C_6H_6)Mn(CO)_3]^+ + BHEt_3^- \longrightarrow [(C_6H_8)Mn(CO)_3]^-$$

dibenzeneruthenium dication to give a mixture of the neutral bis(cyclohexadienyl)- and the (cyclohexadiene)(benzene)-ruthenium complexes.[21]

After the conclusion of this work Nishiki *et al.*[22] reported the use of a tetrahydroborate–rhodium system for reduction of substituted benzenes. We have shown that also the reduction of benzene to cyclohexane (0.5 mol per gram-atom of Rh) takes place under these conditions ($NaBH_4$ in aqueous ethanol was added to rhodium trichloride in ethanol–benzene at 30 °C). It also worked, but less well, when either ruthenium trichloride or iridium trichloride was substituted for the rhodium salt. However, in all cases metal (which was then inactive) was precipitated at the end of the reaction which was therefore stoicheiometric both in tetrahydroborate and in the platinum metal. Careful gas-chromatographic analyses of the organic components showed the absence of cyclohexene and cyclohexadiene.

Complexes (1a), (1b), or (1c) did not participate in this reaction but the tri-μ-hydroxo-complex $[\{(C_5Me_5)Rh\}_2(OH)_3]Cl$ yielded a trace (*ca.* 4%) of cyclohexane, possibly arising from a decomposition reaction. It is likely that all these reactions involve the hydrogenation of benzene on metal particles; in any case they are quite different from the processes involving complexes (1)–(4) described here.

Reactions of (2b) *with other Nucleophiles.*—The reactions described above should have wide applicability since both the nucleophiles adding to (2) and the electrophiles adding to (4) can readily be varied. This would afford a wide range of substituted cyclohexenes. In order to test this concept, other nucleophiles were initially reacted with the iridium complex (2b). This complex was chosen because of the convenience of handling and the efficiency of its reactions. We have shown elsewhere[19] that other sources of hydride will reduce η^6-arenes to the corresponding cyclohexadienyl and then to the cyclohexadiene complexes. We now report that (2b) also reacts with methyl-lithium and much weaker nucleophiles such as methoxide and the nitromethanide anion.

Two methyls were added to the benzene on reaction of (2b) with methyl-lithium giving two η^4-dimethylcyclohexadiene complexes identified by mass spectrometry (parent ions at *m/e* 434 and 436). The C_5Me_5 region of the ^1H n.m.r. spectrum showed the presence of the two isomers in the ratio 15 : 6, at δ 2.00 and 1.95. Two other methyl resonances were observed as doublets (J = 8 Hz) at δ 0.91 and 0.79 in the same relative ratios. These must arise from methyls attached to sp^3 carbons of the C_6 ring. If attack by the second methyl-lithium has occurred at the carbon vicinal to the first point of attack in both isomers (to give cyclohexa-1,3-diene complexes) then, since the two C_6-ring methyls are equivalent in both isomers, one must be the *endo* and the other the *exo* isomer of the 5,6-dimethylcyclohexa-1,3-diene complex (5a). This would imply *both* methyls being introduced by *exo* attack in one case and by *endo* attack in the other.

Table 2. Mass spectra of cyclohexadiene complexes

Compound	Molecular ion *m/e* *	Base peak (100%) *m/e*
(4a) $[(C_5Me_5)Rh(C_6H_8)]$	318 (37)	238
(4b) $[(C_5Me_5)Ir(C_6H_8)]$	408 (46) ^{193}Ir	406
$[^2H_6]$-(4b) $[(C_5Me_5)Ir(C_6D_6H_2)]$	414 (80) ^{193}Ir	410
(4c) $[(C_6Me_6)Ru(C_6H_8)]$	344 (42)	147
(5) $[(C_5Me_5)Ir(C_6H_6Me_2)]$	436 (84) ^{193}Ir	91
(7) $[(C_5Me_5)Ir\{C_6H_6(OMe)_2\}]$	468 (22) ^{193}Ir	78
(8) $[(C_5Me_5)Ir(C_6H_7OMe)]$	438 (27) ^{193}Ir	78

* Relative intensities (%) in parentheses.

An alternative explanation is that the 1,3-diene form is retained for only one of the isomers [which must then be the *exo*-5,6-dimethylcyclohexa-1,3-diene complex (5a)] and that the other has a 1,4-diene form and is thus the *exo*-3,6-dimethylcyclohexa-1,4-diene complex (5b) (Scheme 2). Again in both, the two C_6-ring methyls are equivalent and both isomers could result from addition of methyls *exo* to the metal. Although η^4-cyclohexadienes are uncommon, we have a well authenticated example in a related system from hydride attack on the *p*-xylene–iridium complex.[19]

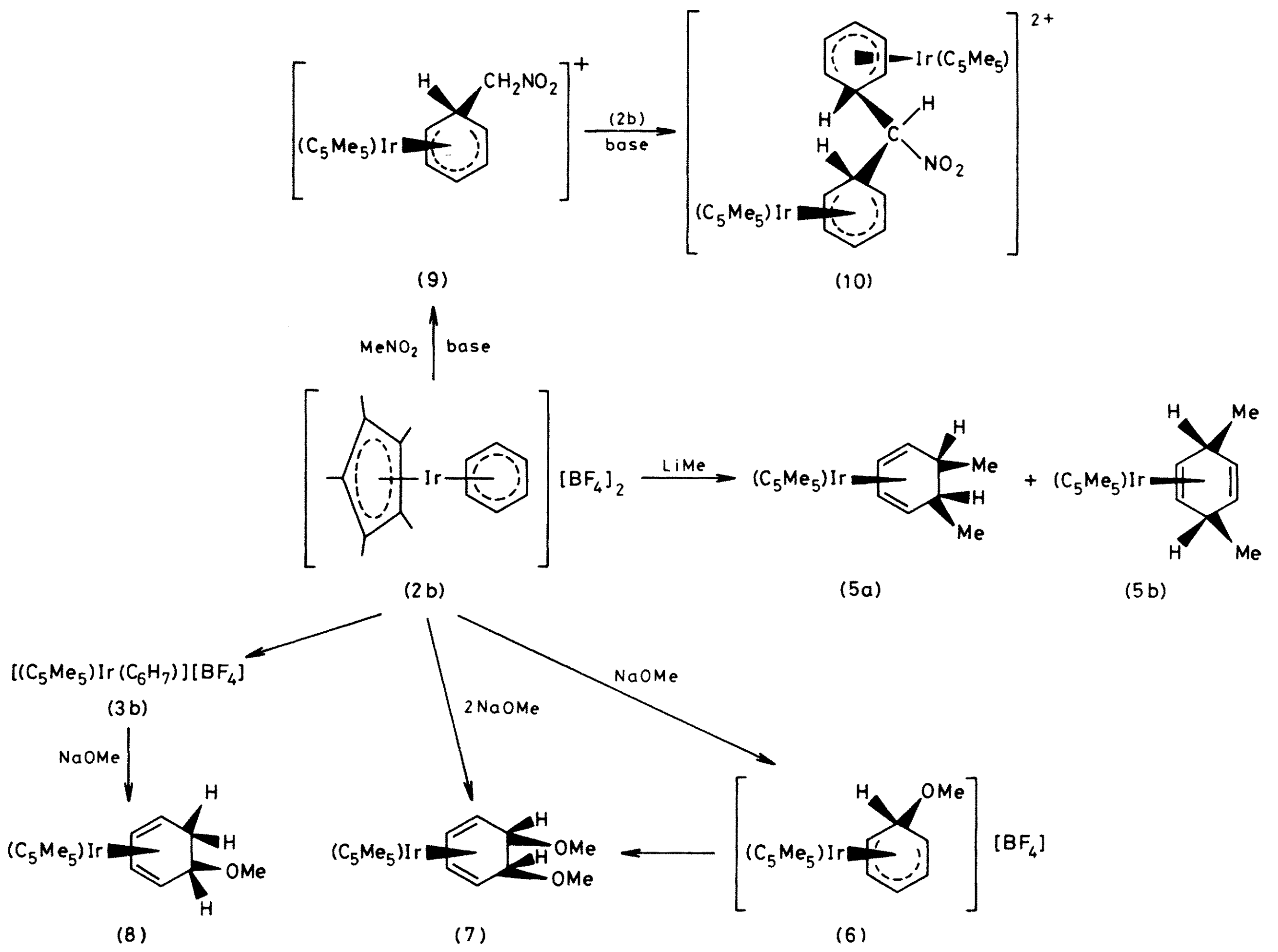
For this reason and because *exo* attack occurs elsewhere in preference to *endo* attack, we prefer the second proposal. Unfortunately, the low yield of product from this (unoptimised) reaction prevented us from carrying out further spectroscopic studies to establish the isomer structures.

Reaction of the mixture of isomeric dimethylcyclohexadiene complexes with hydrogen chloride gave no fewer than six isomeric dimethylcyclohexenes (by g.c.–m.s. analysis) and thus was able to shed no further light on the stereochemistry of the various processes.

Reaction of complex (2a) with methoxide proceeded in two stages. Very short reaction times and a stoicheiometric amount of methoxide gave the methoxycyclohexadienyl complex (6). The complex is assigned the structure shown, with the methoxy substituent *exo* to the metal, because the hydrogen on the C_6-ring sp^3 carbon resonated as a triplet [J(H–H) = 5 Hz] at δ 3.82. Both of these values are characteristic of H^{endo}; by contrast, a singlet at lower field would have been expected for H^{exo}. The complex also lacked the typical low-frequency ν(C–H) absorption around 2 800 cm^{-1} characteristic of complexes with H^{exo} present.

When complex (2a) was reacted with an excess of methoxide for longer times, a double addition occurred to give the neutral dimethoxycyclohexadiene complex (7). The ^1H n.m.r. spectrum was simple and consisted of singlets at δ 1.88 (15 H, C_5Me_5) and 3.39 (6 H, OMe), and three C_6-ring resonances at δ 2.92, 3.71, and 4.58 (each of intensity 2 H). This showed that only one isomer had been formed, and that it was a highly symmetrical one. By comparison to the spectra of other cyclohexadiene complexes in this series the multiplets at δ 2.92 and 4.58 are assigned to the pairs of equivalent hydrogens on the co-ordinated diene, and the triplet at 3.71 [J(H–H) = 1.5 Hz] to the *endo*-hydrogens on the sp^3 carbons. This assignment implies that *exo* attack by methoxide on the ring has again occurred. Had the attack been *endo*, the hydrogens on the sp^3 carbons would have been expected as a singlet since coupling to the hydrogens vicinal to H^{exo} is normally very small. Double methoxide attack on the related $[(C_5H_5)Co(C_6H_6)]^{2+}$ has also been shown to proceed by vicinal *exo* attack.[23]

Methoxide was also added to the η^5-cyclohexadienyl complex (3b) to give the η^4-methoxycyclohexadiene complex (8). The structure, with the methoxy group *exo*, is assigned on the



Scheme 2.

basis of a complete n.m.r. spectroscopic analysis (including decoupling to remove the degeneracy of the resonances at δ 2.15 and 4.73) as well as by comparison to that of the related complex $[(C_5H_5)Co(C_6H_7OMe)]$.[24] Owing to their sensitivity and volatility complexes (7) and (8) were not microanalysed; however, their mass spectra were in complete agreement with the structures proposed.

It was also found that, when the benzene-iridium dication (2b) was reacted with base in nitromethane solution, the resultant nitromethanide anion was a powerful enough nucleophile to attack the ring. This gave the *exo*-nitromethylcyclohexadienyl complex (9), which was again characterised by a detailed analysis of the 400-MHz ^1H n.m.r. spectrum (Table 3).

Confirmation of the structure and of the *exo* attack on the ring by the nitromethanide anion was provided by a single-crystal *X*-ray structure determination. This showed (Figure and Table 5) the C_5Me_5 ring carbons at an average distance of 2.179 Å from the metal, confirming the η^5 bonding of the C_5Me_5 ring; this distance is within the range quoted for C_5Me_5–Rh^{III} and C_5Me_5–Ir^{III} complexes (2.109—2.207 Å).[25] Five of the six carbons of the cyclohexadienyl ring are also, as expected, bonded to the metal and the average distance to the metal is virtually the same as for the C_5Me_5 carbons (2.180 Å). These carbons are essentially coplanar and this plane is virtually parallel to that of the C_5Me_5 ring. However, because the C_6 ring is more splayed out, the iridium is actually much closer to the C_6 ring than it is to the C_5Me_5 ring (perpendicular distances 1.70 and 1.81 Å respectively). The nitromethyl substituent is attached through its carbon to the ring sp^3 carbon, which is out of bonding range of the Ir, in the position *exo* to the metal. The ring carbon to which this group is attached is 0.67 Å out of the plane of the other five and this geometry causes a fold of 46° in the C_6 ring. Very similar geometries have been established for a range of other η^5-cyclohexadienyl complexes.[26]

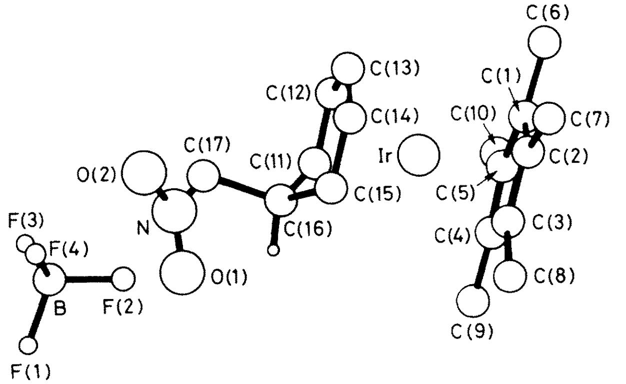
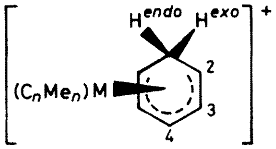


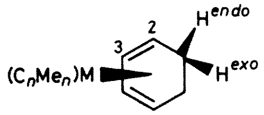
Figure. View of the structure of $[(\eta^5\text{-}C_5Me_5)Ir(\eta^5\text{-}C_6H_6CH_2NO_2)][BF_4]$ (9) (hydrogens omitted)

The very high reactivity of the dicationic benzene complexes towards nucleophiles is shown by the fact that, in the presence

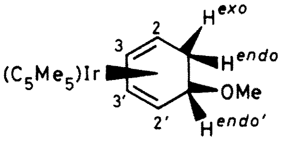
Table 3. Hydrogen-1 n.m.r. spectra



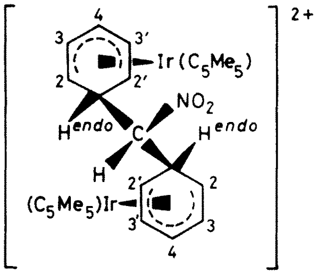
(3a), (3b), (3c)



(4a), (4b), (4c)



(8)

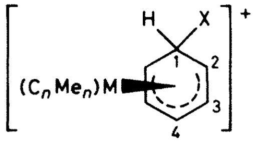


(10)

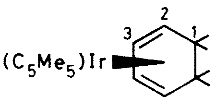
	Solvent	C_nMe_n(s)	H^{endo}	H^{exo}, X^{exo}	H^2	H^3	H^4
		Chemical shift (δ)					
(2a) $[(C_5Me_5)Rh(C_6H_6)][PF_6]_2$	CF_3CO_2D	2.45	—	—	7.56	—	—
(3a) $[(C_5Me_5)Rh(C_6H_7)][PF_6]$ [a]	$(CD_3)_2CO$	2.15	3.00(m)	2.55(d)	3.29(t)	5.45(t)	6.09(t)
(4a) $[(C_5Me_5)Rh(C_6H_8)]$	C_6D_6	1.94	1.62(m)	1.45(m)	2.86(m)	4.58(m)	—
(2b) $[(C_5Me_5)Ir(C_6H_6)][BF_4]_2$	CF_3CO_2D	2.05	—	—	7.03	—	—
(3b) $[(C_5Me_5)Ir(C_6H_7)][BF_4]$ [b]	$(CD_3)_2CO$	2.23	2.96(dt)	4.23(d)	3.69(t)	5.38(t)	6.77(t)
$[^2H_6]$-(3b) $[(C_5Me_5)Ir(C_6D_6H)]^+$	$CDCl_3$	2.20	—	4.22(s)	—	—	—
(4b) $[(C_5Me_5)Ir(C_6H_8)]$	$CDCl_3$	2.06	1.35(m)	1.13(m)	2.86(m)	4.64	—
$[^2H_6]$-(4b) $[(C_5Me_5)Ir(C_6D_6H_2)]$	$CDCl_3$	2.05	—	1.08(s)	—	—	—
(2c) $[(C_6Me_6)Ru(C_6H_6)][BF_4]_2$	CF_3CO_2D	2.21	—	—	6.79	—	—
(3c) $[(C_6Me_6)Ru(C_6H_7)][BF_4]$ [c]	$(CD_3)_2CO$	2.40	2.60(m)	—	3.00(t)	4.85(t)	6.25(t)
(4c) $[(C_6Me_6)Ru(C_6H_8)]$	$CDCl_3$	2.05	1.34(m)	1.12(m)	2.68(m)	4.54(m)	—
(6) $[(C_5Me_5)Ir(C_6H_6OMe)][BF_4]$ [d]	$CDCl_3$	2.26	3.82(t)	3.08(s) [e]	4.36(t)	5.48(t)	6.60(t)
(7) $[(C_5Me_5)Ir\{C_6H_6(OMe)_2\}]$	$CDCl_3$	1.88	3.71(t)	3.39(s) [e]	2.92(m)	4.58(m)	—
(9) $[(C_5Me_5)Ir(C_6H_6CH_2NO_2)][BF_4]$ [f]	$(CD_3)_2CO$	2.30	3.68(td)	3.90(d) [g]	4.05(t)	5.52(t)	6.88(t)
(10) $[\{(C_5Me_5)Ir(C_6H_6)\}_2CHNO_2][BF_4]_2$ [h]	$(CD_3)_2CO$	2.23	3.23(m)	—	3.55(tt, H^2) 4.28(tt, $H^{2'}$)	5.37(ddt, H^3) 5.46(t, $H^{3'}$)	6.82(tt)
(8) $[(C_5Me_5)Ir(C_6H_7OMe)]$ [i]	C_6D_6	1.98	2.15(m, H^{endo}) 3.81(dt, $H^{endo'}$)	2.15(m) 3.28 [e]	2.61(t, H^2) 3.07(t, $H^{2'}$)	4.73(m, H^3) 4.73(m, $H^{3'}$)	—

[a] $J(H^{exo}H^{endo})$ = 14, $J(H^{endo}H^2)$ = $J(H^2H^3)$ = $J(H^3H^4)$ = 6 Hz. [b] $J(H^{exo}H^{endo})$ = 12, $J(H^{endo}H^2)$ = $J(H^2H^3)$ = $J(H^3H^4)$ = 6 Hz. [c] $J(H^{endo}H^2)$ = $J(H^2H^3)$ = $J(H^3H^4)$ = 6 Hz. [d] $J(H^{endo}H^2)$ = $J(H^2H^3)$ = $J(H^3H^4)$ = 5 Hz. [e] X = O*Me*. [f] $J(CH_2H^{endo})$ = 6.6, $J(H^{endo}H^2)$ = $J(H^2H^3)$ = $J(H^3H^4)$ = 5.5 Hz. [g] X = CH_2NO_2. [h] $J(H^{endo}H^2)$ = $J(H^{endo}H^{2'})$ = $J(H^2H^3)$ = $J(H^{2'}H^{3'})$ = 6, $J(H^3H^4)$ = $J(H^{3'}H^4)$ = 5, $J(H^2H^4)$ = $J(H^4H^{2'})$ = 1 Hz. [i] $J(H^{endo}H^{endo'})$ = 9, $J(H^{endo'}H^{exo})$ = $J(H^{endo'}H^{2'})$ = 4; $J(H^{endo'}H^{3'})$ = $J(H^2H^{3'})$ = $J(H^{2'}H^3)$ = $J(H^{endo}H^3)$ = 5 Hz.

Table 4. Carbon-13 n.m.r. spectra



(3b; X = H)
(3c; X = H)
(9; X = CH_2NO_2)



(4b)

	Solvent	C_n*Me*$_n$	*C*$_n$Me$_n$	C^1	C^2	C^3	C^4	Other
(3b) $[(C_5Me_5)Ir(C_6H_7)][BF_4]$	$(CD_3)_2CO$	10.0	98.1	26.0	33.3	88.8	88.0	—
(4b) $[(C_5Me_5)Ir(C_6H_8)]$	$CDCl_3$	10.9	88.6	27.5	46.4	66.5	—	—
(3c) $[(C_6Me_6)Ru(C_6H_7)][BF_4]$	$CDCl_3$	17.0	102.9	26.8	40.3	87.3	89.8	—
(9) $[(C_5Me_5)Ir(C_6H_6CH_2NO_2)][BF_4]$	$(CD_3)_2CO$	10.0	98.9	35.5	37.1	87.7	89.4	86.8 (CH_2NO_2)
(10) $[\{(C_5Me_5)Ir(C_6H_6)\}_2CHNO_2][BF_4]_2$*	$(CD_3)_2CO$	9.9	99.1	33.6	36.7(C^2) 37.2($C^{2'}$)	87.2(C^3) 87.6($C^{3'}$)	89.8	106.6 ($CHNO_2$)

* For numbering, see Table 3.

Table 5. Significant bond lengths (Å) and bond angles (°) in complex (9)

Ir–C(1)	2.194(7)	Ir–C(11)	2.190(6)
Ir–C(2)	2.186(7)	Ir–C(12)	2.162(6)
Ir–C(3)	2.175(6)	Ir–C(13)	2.174(7)
Ir–C(4)	2.173(6)	Ir–C(14)	2.167(7)
Ir–C(5)	2.169(7)	Ir–C(15)	2.205(7)
Ir–C(mean)	2.179	Ir–C(mean)	2.180
Ir–C$_5$ plane	1.810	Ir–C$_5$ plane	1.699
C(1)–C(2)	1.423(11)	C(11)–C(12)	1.413(9)
C(2)–C(3)	1.422(10)	C(12)–C(13)	1.406(10)
C(3)–C(4)	1.418(10)	C(13)–C(14)	1.396(9)
C(4)–C(5)	1.436(9)	C(14)–C(15)	1.397(9)
C(5)–C(1)	1.433(10)	C(15)–C(16)	1.502(10)
C(17)–N	1.498(10)	C(16)–C(11)	1.460(10)
N–O(1)	1.193(8)	C(16)–C(17)	1.545(01)
N–O(2)	1.215(10)		
C(11)–C(12)–C(13)	117.4(6)	C(15)–C(16)–C(17)	114.1(6)
C(12)–C(13)–C(14)	118.9(6)	C(11)–C(16)–C(17)	113.2(5)
C(13)–C(14)–C(15)	118.9(6)	C(16)–C(17)–N	110.9(5)
C(14)–C(15)–C(16)	118.0(5)	C(17)–N–O(1)	118.0(7)
C(15)–C(16)–C(11)	101.6(5)	C(17)–N–O(2)	117.9(6)
C(16)–C(11)–C(12)	119.3(6)	O(1)–N–O(2)	124.1(7)

Angles of planes (°) to each other:
C(1)–C(2)–C(3)–C(4)–C(5) and C(11)–C(12)–C(13)–C(14)–C(15): 2
C(11)–C(12)–C(13)–C(14)–C(15) and C(11)–C(16)–C(15): 46
C(17)C–N–O(1)–O(2) and C(11)–C(16)–C(15): 79

of base, even the complex (9) acted as a nucleophile towards the benzene–iridium complex (2b). When they were reacted together in acetone in the presence of triethylamine, complex (10) was formed. This was characterised by microanalysis and n.m.r. spectroscopy, including complete decoupling of the 400-MHz ^{1}H spectrum (Tables 3 and 4). Both this and the ^{13}C spectrum showed a doubling of the signals arising from the *o*- and *m*-C–H groups of the ring but only single resonances from *p*-C–H and from C–H^{endo}. Both rings are therefore in equivalent environments but they lack the plane of symmetry through C(1)–H(1) shown for example by complexes (3), (6), or (9).

Experimental

All reactions were carried out routinely under a protective atmosphere of nitrogen. Microanalyses (Table 1) were carried out by the University of Sheffield Microanalytical Service; mass spectra (Table 2) were determined on Kratos MS-25 or MS-80 spectrometers coupled to a DS-55 data release system. Gas chromatographic analyses were performed on a Carlo-Erba 4200 or a Pye-Unicam 104 chromatograph, with flame ionisation detector, and g.c.–m.s. on a Carlo-Erba chromatograph connected to the above spectrometers. Hydrogen-1 n.m.r. spectra (Table 3) were measured on Perkin-Elmer R-12B (60 MHz) and R-34 (220 MHz), and Bruker WH-400 (400 MHz) spectrometers and ^{13}C spectra (Table 4) on JEOL PFT-100 (25 MHz) or Bruker WH-400 (100 MHz) spectrometers. 'Boron trifluoride dihydrate' (Fluka) was used as a convenient source of tetrafluoroboric acid. Representative experiments are detailed below.

(η^6-*Benzene*)(η^5-*pentamethylcyclopentadienyl*)*iridium*(III) *Bis*(*tetrafluoroborate*), (2b).—A solution of complex (1b) (1.00 g, 1.26 mmol) in acetone (10 cm^3) was treated with AgBF$_4$ (0.98 g, 5.0 mmol). The mixture was stirred (10 min, 20 °C) and the precipitated AgCl removed by filtering through 'Hyflo' cellulose filter aid. The filter cake was washed with acetone (2 × 10 cm^3) and the combined filtrates were evaporated to an oil under reduced pressure. Benzene (2 cm^3) and BF$_3$·2H$_2$O (1 cm^3) were added and the mixture stirred vigorously at 60 °C for 10 min. The benzene layer was decanted off and diethyl ether added to precipitate a white solid which was crystallised from nitromethane and ether to give complex (2b) (1.71 g, 91%). The same reaction using hexadeuteriobenzene gave complex [^{2}H$_6$]-(2b) (82%). The ruthenium complex (2c) was obtained in 73% yield.

(η^5-*Cyclohexadienyl*)(η^5-*pentamethylcyclopentadienyl*)-*iridium*(III) *Tetrafluoroborate*, (3b).—Complex (2b) (200 mg, 0.35 mmol) was suspended in water (20 cm^3) at 0 °C. A solution of NaBH$_4$ (20 mg, 0.53 mmol) in water (10 cm^3) was added dropwise (frothing occurred) to give a clear solution. Extraction with dichloromethane (3 × 10 cm^3), followed by filtration through a short alumina column (2 × 1 cm) gave a very pale yellow solution. Addition of ether gave colourless crystals of complex (3b) (129 mg, 76%).

The deuteriated complex [^{2}H$_6$]-(3b) (52%) and the ruthenium complex (3c) (86%) were prepared similarly.

(η^4-*Cyclohexa*-1,3-*diene*)(η^5-*pentamethylcyclopentadienyl*)-*iridium*(I), (4b).—*Method* (*a*). A suspension of complex (3b) (58 mg, 0.12 mmol) in toluene (5 cm^3) was treated with Red-Al in toluene (0.3 cm^3, 1.16 mmol) and the solution stirred for 5 min. The toluene was evaporated and the resulting oil extracted with dry ether. The ether was evaporated and the oil sublimed (30 °C and 10^{-3} mmHg) to give the white air-sensitive complex (4b) (40 mg, 83%).

The deuteriated compound [^{2}H$_6$]-(4b) (60%) and complexes (4a) and (4c) were prepared (81% and 71% respectively) in the same way.

Method (*b*). A suspension of complex (2b) (100 mg, 0.17 mmol) in ether (10 cm^3) was treated with Red-Al in toluene (0.5 cm^3, 1.7 mmol), evaporation followed by extraction with ether, and sublimation as in (*a*), yielded complex (4b) (56 mg, 79%).

Reactions of (η^4-*cyclohexa*-1,3-*diene*)(η^5-*pentamethylcyclopentadienyl*)*iridium*(I), (4b).—(*a*) *With hydrogen chloride*. HCl gas was bubbled through a solution of complex (4b) (30 mg, 0.07 mmol) in pentane (1 cm^3), giving an orange precipitate of complex (1b) (27 mg, 93%) and a colourless solution. Analysis of this solution by gas chromatography showed the presence of cyclohexene (7.2 µl, 0.07 mmol, 100%). No benzene, cyclohexane, or cyclohexadiene was detected. [A 2-m column at 50 °C (isothermal), packed with 10% P.M.P.E. on Chrome W was used for g.c. analysis. Relative retention times were: pentane 30, cyclohexane 87, cyclohexene 114, cyclohexa-1,3-diene 127, benzene 144, and toluene 300 s.] Complex (4a) gave (1a) (90%) and cyclohexene (92%), and (4c) gave (1c) (90%) and cyclohexene (98%) when reacted in this way.

(*b*) *With boron trifluoride dihydrate*. A solution of complex (4b) (90 mg, 0.22 mmol) in benzene (1 cm^3) was treated with BF$_3$·2H$_2$O (0.5 cm^3), and stirred (20 °C, 12 h). The benzene layer was removed for analysis. Addition of more benzene (5 cm^3) followed by ether (20 cm^3) to the water layer precipitated the white complex (2b) (120 mg, 94%). G.c. analysis of the benzene layer showed the presence of cyclohexene (14.2 µl, 63%) only. The use of toluene in place of benzene gave the toluene complex [(η^5-C$_5$Me$_5$)Ir(η^6-C$_6$H$_5$CH$_3$)][BF$_4$]$_2$ (72%) and cyclohexene (46%) with 100% selectivity. Complex (4a)

Table 6. Atom co-ordinates ($\times 10^4$)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ir	2 167(1)	2 172(1)	318(1)	C(15)	1 329(5)	3 477(6)	1 149(4)
C(1)	3 360(5)	1 557(8)	−648(4)	C(16)	486(6)	2 589(7)	1 507(4)
C(2)	3 898(6)	2 582(7)	−203(5)	C(17)	−828(6)	3 067(7)	1 574(4)
C(3)	4 145(6)	2 311(7)	712(4)	N	−786(6)	4 143(6)	2 160(4)
C(4)	3 761(6)	1 122(6)	851(4)	O(1)	−138(6)	4 105(6)	2 849(4)
C(5)	3 268(6)	652(6)	5(5)	O(2)	−1 403(7)	5 005(6)	1 901(4)
C(6)	3 021(8)	1 432(11)	−1 609(5)	F(1)	−2 376(11)	1 517(13)	4 321(6)
C(7)	4 165(9)	3 740(9)	−639(7)	F(2)	−1 514(7)	1 159(7)	3 069(5)
C(8)	4 802(8)	3 130(9)	1 374(6)	F(3)	−3 449(8)	736(10)	3 139(6)
C(9)	3 921(8)	480(9)	1 702(5)	F(4)	−2 853(17)	2 642(10)	3 129(11)
C(10)	2 844(7)	−587(8)	−172(6)	B	−2 603(11)	1 596(11)	3 414(7)
C(11)	508(6)	1 606(6)	880(4)	F(11)	−3 863(20)	2 358(18)	3 420(14)
C(12)	219(6)	1 834(6)	−32(4)	F(12)	−1 990(27)	2 601(26)	3 472(19)
C(13)	488(6)	2 979(7)	−337(4)	F(13)	−2 713(45)	1 150(43)	2 734(29)
C(14)	1 083(6)	3 798(6)	260(4)	F(14)	−2 640(34)	1 140(33)	4 133(25)

gave (2a) (51%) and cyclohexene (95%), and (4c) gave (2c) (60%) and cyclohexene (75%) when reacted in this way.

(η^6-*Benzene*)(η^5-*pentamethylcyclopentadienyl*)*rhodium*(III) *Bis*(*hexafluorophosphate*), (2a).—A solution of complex (1a) (150 mg, 0.25 mmol) in acetone (5 cm^3) was treated with $AgPF_6$ (250 mg, 1.0 mmol). Precipitated silver chloride was filtered off and benzene (4 cm^3) added. The reaction was left to stand (2 h, 20 °C) and then the white precipitate of complex (2a) (230 mg, 77%) was collected.

(η^5-*Cyclohexadienyl*)(η^5-*pentamethylcyclopentadienyl*)-*rhodium*(III) *Hexafluorophosphate*, (3a).—A suspension of (2a) (100 mg, 0.16 mmol) in butan-2-one (50 cm^3) was treated with $NaBH_4$ (20 mg, 0.52 mmol) and stirred (6 h, 20 °C). The resulting deep red solution was evaporated to dryness under reduced pressure and the residue extracted with dichloromethane. From this solution the pale greenish complex (3a) (16 mg, 2%) was isolated.

Sodium Tetrahydroborate–Rhodium Trichloride Reduction of Benzene.—A solution of $RhCl_3\cdot3H_2O$ (519 mg, 1.93 mmol) and benzene (85 µl, 0.96 mmol) in ethanol (10 cm^3) was stirred (2 h, 30 °C). Sodium tetrahydroborate (370 mg, 9.74 mmol) in ethanol–water (5 : 1, 6 cm^3) was added dropwise over 30 min. The mixture was quenched with HCl (1 mol dm^{-3}, 20 cm^3) and extracted into pentane (2 × 1 cm^3). Analysis of the pentane extract by gas chromatography showed the presence of cyclohexane (98 µl, 95%) and benzene (44 µl, 4%). A 2-m column (packed with 10% P.M.P.E. on chrome W) was used at 80 °C isothermally. Relative retention times were: pentane 28, ethanol 37, cyclohexane 52, cyclohexene 67, cyclohexa-1,3-diene 75, and benzene 82 s.

Identical reactions using $IrCl_3\cdot3H_2O$ (1.44 mmol) or $RuCl_3\cdot3H_2O$ (0.96 mmol) gave cyclohexane [10.9 µl (10%) and 39.5 µl (37%) respectively].

Reactions of (η^6-*Benzene*)(η^5-*pentamethylcyclopentadienyl*)-*iridium*(III) *Bis*(*tetrafluoroborate*) *with Sodium Methoxide.*—(*a*) A suspension of complex (2b) (300 mg, 0.52 mmol) in methanol (5 cm^3) was treated with a methanolic solution of NaOMe [3.6 cm^3 of a solution freshly prepared from NaOMe (930 mg) dissolved in methanol (40 cm^3)]. The solution instantly cleared and the solvent was evaporated under reduced pressure. Extraction of the residue with dichloromethane and addition of ether to the extract yielded the white compound (6) (200 mg, 73%).

(*b*) A suspension of complex (2b) (200 mg, 0.35 mmol) in methanol (10 cm^3) was stirred with NaOMe (82 mg, 1.5 mmol) (20 °C, 18 h). The methanol was removed under vacuum and the residue extracted with ether. Removal of the ether followed by sublimation at 60 °C and 10^{-3} mmHg gave the colourless complex (7) (77 mg, 47%).

Reaction of (η^6-*Benzene*)(η^5-*pentamethylcyclopentadienyl*)-*iridium*(III) *Bis*(*tetrafluoroborate*) *with Methyl-lithium.*—A suspension of complex (2b) (100 mg, 0.17 mmol) in ether was treated with LiMe (0.27 cm^3 of a 1.60 mol dm^{-3} solution in ether, as purchased from Aldrich). The solution was stirred (18 h, 20 °C) to give a pale solution and a white solid (unreacted starting material and $LiBF_4$); the ether was removed and the residue sublimed (60 °C, 10^{-3} mmHg) and transferred to an n.m.r. tube under argon. Analysis by ^1H n.m.r. and mass spectroscopy showed that two isomers of complex (5) had been produced.

The solution produced above was treated with HCl gas to give complex (2b) and a solution containing six isomeric dimethylcyclohexenes, analysed by g.c.–m.s.

Reaction of (η^6-*Benzene*)(η^5-*pentamethylcyclopentadienyl*)-*iridium*(III) *Bis*(*tetrafluoroborate*) *with Nitromethane and Triethylamine to give Complex* (9).—A solution of complex (2b) (400 mg, 0.69 mmol) in nitromethane (20 cm^3) was treated with NEt_3 (0.5 cm^3, 1.7 mmol) and stirred (10 min, 20 °C). The nitromethane was evaporated under reduced pressure to leave 5 cm^3 of solution. This was treated with tetrachloromethane and diethyl ether to give an oily solid. The liquid was decanted off and the solid washed with ether and dried under high vacuum. Recrystallisation from acetone and diethyl ether gave colourless needles of complex (9) (300 mg, 79%).

X-*Ray Structure Determination of Complex* (9).—*Crystal data.* $[C_{17}H_{23}IrNO_2][BF_4]$, $M = 552.40$, monoclinic, $a = 10.913(10)$, $b = 11.194(12)$, $c = 15.260(12)$ Å, $\beta = 96.99(7)°$, $U = 1\,850$ Å^3, $Z = 4$, $D_c = 1.98$ g cm^{-3}, $F(000) = 1\,064$, space group $P2_1/c$ from absences, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, $\mu = 72.36$ cm^{-1}.

Unit-cell parameters were obtained from a least-squares fit of the setting angles of 18 well centred reflections. *X*-Ray data in the range $3.5 \leqslant 2\theta \leqslant 55°$ were collected on a Nicolet R3M four-circle automatic diffractometer from a single crystal measuring approximately 0.2 × 0.3 × 0.6 mm. 3 512 Independent reflections with $I \geqslant 3\sigma(I)$ were obtained and corrected for Lorentz and polarisation effects. An empirical absorption correction based on ψ-scans of 8 reflections (288 measurements) was also applied.

The structure was solved by Patterson and difference-Fourier methods and refined by cascade blocked-matrix least squares with weights $w_i = 1/[\sigma^2(F_i) + 0.00063F_i^2]$ to an R value of 0.035. All the non-hydrogen atoms were refined with independent positions and anisotropic vibrational parameters. Sufficient hydrogen atoms were observed on a low-angle difference map to define (approximately) the torsion angles of all the methyl groups. All the hydrogen atoms were constrained to ride upon the adjacent heavy atom at calculated bond lengths and angles, and the isotropic parameters set at 1.2 times U_{eq} for their adjacent atom.

Clear evidence for orientational disorder of the BF_4^- ion was obtained. The major component (71.9%) was refined normally. The minor component was represented by four isotropic fluorines sharing the same boron; consequently the B–F bond lengths show rather more than usual variations. The final Fourier map showed no peak higher than 1 e Å^{-3} and none which could be interpreted as an atom. The final analysis of variance against sin θ and against $|F|$ showed no unusual features; neither did the normal probability plot. The SHELXTL[27] suite of programs was used throughout.

Important bond lengths and angles are collected in Table 5, and atomic co-ordinates in Table 6; the numbering scheme used is shown in the Figure.

Reaction of (1—5-η-6-*Nitromethylcyclohexadienyl*)(η^5-*pentamethylcyclopentadienyl*)*iridium*(III) *Tetrafluoroborate*, (9), *with* (2b) *to give* (10).—A solution of complex (9) (60 mg, 0.11 mmol) in acetone (5 cm^3) was treated with complex (2b) (64 mg, 0.11 mmol) and triethylamine (0.1 cm^3) and stirred (20 °C, 18 h). Filtration followed by addition of ether gave colourless small crystals of complex (10) (73 mg, 64%).

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References

1 P. N. Rylander, 'Catalytic Hydrogenation over Platinum Metals,' Academic Press, New York, 1967, p. 309; R. B. Moyes and P. B. Wells, *Adv. Catal.*, 1973, **23**, 121; see also H. C. Foley, S. J. DeCanio, K. D. Tau, K. J. Chao, J. H. Onuferko, C. Dybowski, and B. C. Gates, *J. Am. Chem. Soc.*, 1983, **105**, 3074 and refs. therein.

2 E. L. Muetterties and J. R. Bleeke, *Acc. Chem. Res.*, 1979, **12**, 234; J. R. Bleeke and E. L. Muetterties, *J. Am. Chem. Soc.*, 1981, **103**, 556.

3 M. J. H. Russell, C. White, and P. M. Maitlis, *J. Chem. Soc., Chem. Commun.*, 1979, 427; A. Millan, Ph.D. Thesis, University of Sheffield, 1981.

4 R. C. Reid, J. M. Prausnitz, and T. K. Sherwood, 'Properties of Gases and Liquids,' McGraw-Hill, New York, 1977.

5 F. Hartog, Stamicarbon, U.S.P. 3 391 206/1966 (*Chem. Abstr.*, 1966, **64**, 1980g); W. C. Drinkard, Du Pont, U.S.P. 3 767 720/1973 (*Chem. Abstr.*, 1973, **78**, 42911p).

6 M. M. Johnson and G. P. Nowack, *J. Catal.*, 1975, **38**, 518; J. A. Don and J. F. Scholten, *Faraday Discuss. Chem. Soc.*, 1957, **72**, 145.

7 C. U. I. Odenbrand and S. T. Lundin, *J. Chem. Tech. Biotechnol.*, 1980, **30**, 677; 1981, **31**, 660.

8 Shell International, N.L.P. 6 516 994/1969 (*Chem. Abstr.*, 1969, **67**, 11271y) and 6 602 187/1968 (*Chem. Abstr.*, 1968, **66**, 10644w); R. A. Benkeser, R. E. Robinson, D. M. Sauve, and O. H. Thomas, *J. Am. Chem. Soc.*, 1955, **77**, 3230; see also G. P. Pez and I. L. Mador, Allied Corporation, U.S.P. 4 356 337/1982 (*Chem. Abstr.*, 1983, **98**, 88870r).

9 C. White and P. M. Maitlis, *J. Chem. Soc. A*, 1971, 3322.

10 C. White, personal communication.

11 H. B. Lee, K. Moseley, C. White, and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 1975, 2322.

12 S. L. Grundy and P. M. Maitlis, *J. Chem. Soc., Chem. Commun.*, 1982, 379.

13 C. White, S. J. Thompson, and P. M. Maitlis, *J. Organomet. Chem.*, 1977, **134**, 319.

14 M. A. Bennett, T. W. Matheson, G. B. Robertson, W. L. Steffen, and T. W. Turney, *J. Chem. Soc., Chem. Commun.*, 1979, 32.

15 K. Moseley and P. M. Maitlis, *J. Chem. Soc. A*, 1970, 2884.

16 N. A. Bailey, E. H. Blunt, G. Fairhurst, and C. White, *J. Chem. Soc., Dalton Trans.*, 1980, 829.

17 M. A. Bennett and T. W. Matheson, *J. Organomet. Chem.*, 1979, **175**, 87.

18 B. F. G. Johnson, J. Lewis, and D. J. Yarrow, *J. Chem. Soc., Dalton Trans.*, 1972, 2084.

19 S. L. Grundy, Ph.D. Thesis, University of Sheffield, 1983; S. Grundy and P. M. Maitlis, *J, Organomet, Chem.*, in the press.

20 W. Lamanna and M. Brookhart, *J. Am. Chem. Soc.*, 1981, **103**, 989.

21 G. Winkhaus, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 1971, 3807.

22 M. Nishiki, H. Miyataka, Y. Niino, N. Mitsuo, and T. Satoh, *Tetrahedron Lett.*, 1982, **23**, 193.

23 Y-H. Lai, W. Tam, and K. P. C. Vollhardt, *J. Organomet. Chem.*, 1981, **216**, 97.

24 G. E. Herberich and R. Michelbrink, *Chem. Ber.*, 1970, **103**, 3615.

25 P. M. Maitlis, *Chem. Soc. Rev.*, 1981, **10**, 1.

26 M. R. Churchill and F. R. Scholer, *Inorg. Chem.*, 1969, **8**, 1950; M. F. Semmelhack, H. T. Hall, R. Farina, M. Yoshifuji, G. Clark, T. Burgar, K. Hirotsu, and J. Clardy, *J. Am. Chem. Soc.*, 1979, **101**, 3535; P. H. Bird and M. R. Churchill, *Chem. Commun.*, 1967, 777.

27 G. M. Sheldrick, SHELXTL system of programs.

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