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DOUBLE NUCLEOPHILIC ATTACK ON η^6-ARENE(PENTAMETHYLCYCLOPENTADIENYL)IRIDIUM DICATIONS. ROUTES FROM SUBSTITUTED BENZENES TO SUBSTITUTED CYCLOHEXENES BY ADDITION OF TWO HYDRIDES AND TWO PROTONS *

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Summary

The complexes $[(C_5Me_5)Ir(\eta^6\text{-arene})][BF_4]_2$ (arene = toluene, toluene-d_8, t-butylbenzene, methoxybenzene, chlorobenzene, *o*-xylene, *p*-xylene, tetralin and phenol) were prepared from the arene and reduced with $NaBH_4$ to the η^5-cyclohexadienyl complexes. Attack was *exo* at the arene and, with one exception, never at the substituent. Toluene showed no site preference but t-butylbenzene was attacked preferentially *para*, and chlorobenzene, *ortho*. Methoxybenzene was attacked *ipso* as well as *ortho*, *meta* (predominant), and *para*, and phenol gave only the *meta*-isomer. *p*-Xylene gave one isomer and *o*-xylene and tetralin gave two. Further reduction occurred on reaction with stronger hydride reducers (e.g., sodium bis(methoxyethoxy)dihydroaluminate) to give mixtures of 1- and 2-substituted cyclohexa-1,3-diene complexes (t-Bu, 2- (> 95%); Me, 1- (25%), 2- (75%); Cl, 1- (> 95%); and OMe, 1- (33%), 2- (67%)). The *p*-xylene complex gave a mixture of the η^4-1,4-dimethylcyclohexa-1,3- and 1,4-diene complexes. Reaction of the cyclohexadiene complexes with HCl gas gave the free substituted cyclohexenes and $[(C_5Me_5Ir)_2Cl_4]$. The product from t-butylbenzene was predominantly (92%) the 3-substituted cyclohexene; that isomer (65%) and the 1-isomer (34%) were formed from toluene and the 1- (34%) and the 4-isomer (58%) were formed from chlorobenzene. Phenol gave only cyclohexanone. Overall these reactions yield the cyclohexene from the substituted benzene by addition of two hydrides and two protons and the iridium can be recycled.

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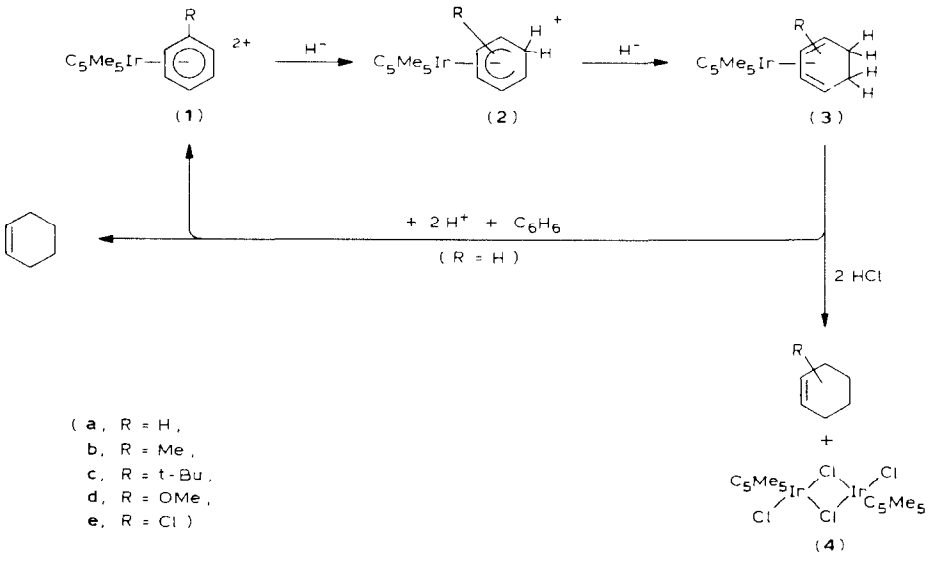
* With all good wishes to our dear friend, Sei Otsuka.

Introduction

We have recently reported the semi-catalytic reduction of benzene to cyclohexene by the addition of two hydrides followed by two protons [1,2]. This reaction relies for its success on the benzene being bound to a metal (Ir, Ru or Rh) in a complex which carries a high overall charge (2 +) and thus is susceptible to nucleophilic attack giving first, with one hydride, the η^5-cyclohexadienyl complex and then, with a second, the η^4-cyclohexadiene complex. This last complex has zero charge and is susceptible to attack by protons which release cyclohexene. In the presence of benzene and an acid such as tetrafluoroboric, which has a poorly coordinating anion, the initial benzene complex is regenerated, thus completing the cycle and making the reaction potentially catalytic in the platinum metal at least. The cycle is shown in Scheme 1.

There is, however, not only interest in making cyclohexene from benzene but also in the formation of substituted cyclohexenes from substituted benzenes. It is to this problem that this paper is addressed. We report on our exploration of the stoicheiometric reactions of a series of substituted benzene(pentamethylcyclopentadienyl)iridium dications (Table 1) first with two hydrides (or their equivalent) and then with two protons. Our chief concern at this point has been to establish the reactivity pattern and to show where the various additions occurred and, if possible, to ascertain in more detail the role played by the metal.

Since even the first step, the addition of one hydride giving the η^5-cyclohexadienyl complex, can give rise to four isomers (by attack *ipso*, *ortho*, *meta*, or *para* to the substituent on the benzene) the major problem was obviously going to be finding out which and how much of the various isomers were formed. As quantitative separation was really not practicable, we had to rely on ^{1}H NMR spectroscopy at high field, in most cases at 400.13 MHz. These studies were supplemented by ^{13}C NMR where



SCHEME 1

appropriate and by GC-MS investigations of the cyclohexenes formed at the end of the reactions.

Results

Reduction of toluene

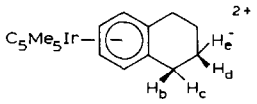
The general approach is illustrated for the reduction of toluene, in the η^6-toluene (pentamethylcyclopentadienyl)iridium dication (**1b**). When a suspension of this cation in water was reacted with an aqueous solution of sodium borohydride, reaction occurred readily to give a mixture of η^5-methylcyclohexadienyl complexes (**2b**). The proton NMR spectrum of this mixture showed the presence of three isomers (Tables 2–4). This was indicated by the appearance of three closely spaced C_5Me_5Ir resonances, at δ 2.135, 2.137 and 2.131 ppm with intensity ratio 46/37/17 (i.e. close to 2/2/1). These were also associated with three singlets (δ 1.41, 2.05 and 2.38 ppm) which, from their relative intensities, were due to the methyls on the cyclohexadienyl ligands. The fact that all three were singlets and not doublets indicated that all the methyls were on carbons not bearing a proton (i.e., sp^2) carbons). Thus the isomer where attack had occurred *ipso* (which would have given rise to a doublet, J ca. 8 Hz in the spectrum) was not formed.

The assignment of these resonances to the *ortho-*, *meta-* and *para*-isomers, respectively, was shown by an analysis of the portion of the spectrum around δ 2.85 ppm where the three multiplets of H_{endo} were situated (Fig. 1). In each case the largest splitting (ca. 13 Hz) is a doublet due to $J(H_{endo}–H_{exo})$. For the isomer where attack has occurred *ortho* to the methyl there is only one hydrogen α to H_{endo} giving a further splitting of ca. 6 Hz into a double doublet. Long range couplings to the hydrogens β to H_{endo}, which are all ca. 1 Hz, allow one to distinguish the two isomers where hydride attack has occurred *meta* and *para* to the methyl. Thus, H_{endo}

TABLE 1

^{1}H NMR SPECTRA OF η^6-ARENE COMPLEXES (δ in ppm) [a]

	$\delta(C_5Me_5)$	$\delta(\eta^6$-Arene)	δ(Me)
$[C_5Me_5Ir(C_6H_5Me)][BF_4]_2$ (**1b**)	2.40	7.37	2.68
$[C_5Me_5Ir(C_6H_5CMe_3)][BF_4]_2$ (**1c**)	2.50	7.40	1.56
$[C_5Me_5Ir(C_6H_5OMe)][BF_4]_2$ (**1d**)	2.44	H(2,3) 7.30 H(4) 7.18 (J(4–3) = J(4–5) = 5 Hz)	4.22
$[C_5Me_5Ir(C_6H_6Cl)][BF_4]_2$ (**1e**)	2.47	7.59	–
$[C_5Me_5Ir$(*p*-xylene)$][BF_4]_2$ (**7**)	2.37	7.22	2.66
$[C_5Me_5Ir$(*o*-xylene)$][BF_4]_2$ (**11**)	2.33	7.25	2.55
$[C_5Me_5Ir$(tetralin)$][BF_4]_2$	2.49	7.26	b 2.85 c 3.31 d 2.1 e 1.9 (J(b–c) = 19; J(b–d) = J(b–e) = 5.5 Hz)

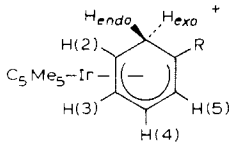


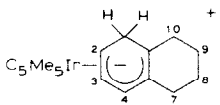
(13)

[a] In CF_3CO_2D solution.

TABLE 2

^{1}H NMR SPECTRA OF 6-SUBSTITUTED η^5-CYCLOHEXADIENYL COMPLEX (δ in ppm, in $CDCl_3$)



R	$\delta(C_5Me_5)$	$\delta(H_{exo})$	$\delta(H_{endo})$	δ(Me)	δ(H(2))	δ(H(3))	δ(H(4))	δ(H(5))
Me	2.135	4.41	2.77	1.41	3.54	5 22	6 43	5.15
	(J(*endo*–*exo*) 13; J(*endo*–3) = J(*endo*–5) = 1, J(*endo*–2) 6.5, J(2–4) 1, J(3–4) = J(4–5) = 5 Hz)							
CMe_3	2.142	4 27	2.93	1.03	3.47	5.14	6 52	5.32
	(J(*endo*–*exo*) 13; J(*endo*–2) 5; J(4–3) = J(4–5) = 6.5; J(2–3) 5; J(2–5) = J(2–4) = 1 Hz)							
OMe [a]	2.17	5.01	3.45	3 58	n.o.	n.o.	6.27	5.43
	(J(*endo*–*exo*) 13; J(4–3) = J(4–5) = 5; J(4–2) 1 Hz)							
Cl	2.16	4.78	3.24	–	4 04	5 47	6 73	5 70
	(J(*endo*–*exo*) 12, J(*endo*–2) 5; J(4–3) = J(4–5) = J(2–3) = 5 Hz)							
O-)2-H [a]	2.04	3.41	2.42	–	2 79	4.91	5.18	3.24
	(J(*endo*–*exo*) 17, J(*endo*–2) = J(2–3) = J(3–4) = 6, J(4–5) 5; J(*endo*–3) = J(*endo*–5) = J(2–4) = 1 Hz)							
3,6-Me_2	2.18	4.46	2.79	1.41 2 15	3 35	–	6.52	5.27
	(J(*endo*–*exo*) 13; J(*endo*–2) 7, (4–5) 5 Hz)							
5,6-Me_2	2.065	4.38	2 70	1.96 2.05	3 54	5.23	6 54	–
	(J(*endo*–*exo*) 13, J(*endo*–2) 6.5, J(2–3) 5.5, J(3–4) 5; J(*endo*–3) = J(2–4) = J(*exo*–2) = 1 Hz)							
	2.04	4.55	n.o.	H(7,10) ca 3 0 H(8,9) 1.64, 1 83	3 51	5.22	6 44	–
	(J(*endo*–*exo*) 13; J(*endo*–2) = J(2–3) = J(3–4) = 5 Hz)							

[a] In $(CD_3)_2CO$.

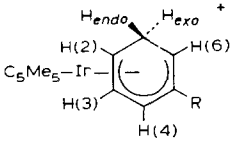
in the *ortho*-isomer shows long-range coupling to two β hydrogens as a triplet fine structure, confirming the assignment. H_{endo} in the *meta*-isomer is coupled to two α but to only one β hydrogen, while H_{endo} in the *para*-isomer is coupled to two α and two β hydrogens. As Fig. 1 shows, in each case the pattern calculated agrees well with that observed.

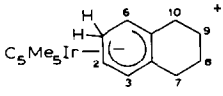
The relative intensities of the three sets of signals matched those of the C_5Me_5Ir protons and showed that the isomer ratio was indeed 46% *ortho*, 37% *meta* and 17% *para*. This is very close to a statistical distribution. However, when a different reducing agent, trimethylamine borane (Me_3NBH_3), was used, this changed to 17% *ortho*, 47% *meta* and 36% *para*. We ascribe the decrease in *ortho*- and the increase in *para*-substitution to arise from the use of a more bulky reagent in the second reaction. This presumably interacts with the methyl on the toluene in the transition state.

A separate series of reactions were carried out on the toluene-d_8 complex (**1b–1d**). The ^1H NMR spectrum of the product from reduction with $NaBH_4$ showed only the

TABLE 3

^1H NMR SPECTRA OF 5-SUBSTITUTED η^5-CYCLOHEXADIENYL COMPLEXES (δ in ppm) [a]

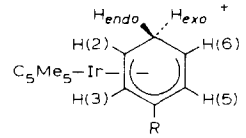


R	$\delta(C_5Me_5)$	$\delta(H_{exo})$	$\delta(H_{endo})$	δ(Me)	δ(H(2))	δ(H(3))	δ(H(4))	δH(6))
Me	2.137	4.24	2.91	2.05	3.54	5.22	6.63	3.38
	(J(*endo*–*exo*) 13; J(*endo*–2) = J(*endo*–6) = 6.5; J(*endo*–3) = J(2–6) = J(4–6) = 1; J(3–4) 5 Hz)							
CMe_3	2.156	4.27	2.96	1.19	3.57	5.26	6.81	3.57
	(J(*endo*–*exo*) 13; J(*endo*–2) = J(*endo*–6) = J(2–3) = 6.5; J(3–4) 5; J(endo–3) = J(2–4) = J(3–6) = J(4–6) = 1 Hz)							
OMe [b]	2.21	4.36	3.09	3.73	n.o.	n.o.	6.84	n.o.
	(J(*endo*–*exo*) 13; J(*endo*–2) = J(*endo*–6) = 6.5; J(*endo*–3) 1 Hz)							
Cl	2.16	4.37	n.o.	–	3.74	n.o.	6.94	5.60
	(J(*endo*–*exo*) 12; J(*endo*–2) = J(2–3) = J(3–4) = 5 Hz)							
O-)$_2$-H [b]	2.01	4.37	2.90	OH, 6.3	3.56	5.05	6.10	3.07
	(J(*endo*–*exo*) 12; J(*endo*–2) = J(*endo*–6) = J(2–3) = J(3–4) = 6; J(*endo*–3) = J(2–4) = J(2–6) = J(2–*exo*) = J(4–6) = 1 Hz)							
4,5-Me_2	2.055	4.25	2.86	2.13 2.32	3.56	5.19	–	3.34
	(J(*endo*–*exo*) 13; J(*endo*–2) 6.5; J(*endo*–6) = J(2–3) = 6; J(*endo*–3) = J(2–6) = 1 Hz)							
	2.05	4.32	n.o.	H(7,10) ca. 3.0 H(8,9) 1.64, 1.83	3.56	5.16	–	3.36
	(J(*endo*–*exo*) 13; J(*endo*–2) = J(*endo*–6) = J(2–3) = 5 Hz)							

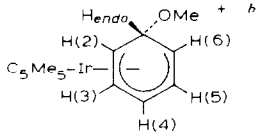
[a] In $CDCl_3$ solution. [b] In $(CD_3)_2CO$.

TABLE 4

^{1}H NMR SPECTRA OF OTHER SUBSTITUTED η^5-CYCLOHEXADIENYL COMPLEXES (δ in ppm) [a]



R	$\delta(C_5Me_5)$	$\delta(H_{exo})$	$\delta(H_{endo})$	δ(Me)	δ(H(2/6))	δ(H(3/5))
Me	2.131	4.26	2.87	2.38	3.54	5.15
	(J(*endo*–*exo*) 13; J(*endo*–2) = J(*endo*–6) = 6.5; J(*endo*–3) = J(*endo*–5) = 1 Hz)					
CMe_3	2.163	4.21	2.92	1.41	3.53	5.32
	(J(*endo*–*exo*) 13, J(*endo*–2) = J(*endo*–6) = 6.5; J(2–3) = J(5–6) = 5; J(3–6) = J(2–5) = J(*endo*–3) = J(*endo*–5) = 1 Hz)					
OMe [b]	2.22	4.23	2.98	3.91	n.o	5.57
	(J(*endo*–*exo*) 13; J(*endo*–2) = J(*endo*–6) = 6.5; J(*endo*–3) = J(*endo*–5) = 1 Hz)					



	$\delta(C_5Me_5)$	$\delta(H_{exo})$	δ(Me)	δ(H(4))	δ(H(2,3,5,6))
	2.26	5.82	3.39	6.79	n.o
	(J(4–5) = J(4–3) = 5; J(4–2) = J(4–6) = 1 Hz)				

[a] In $CDCl_3$ solution. [b] In $(CD_3)_2CO$

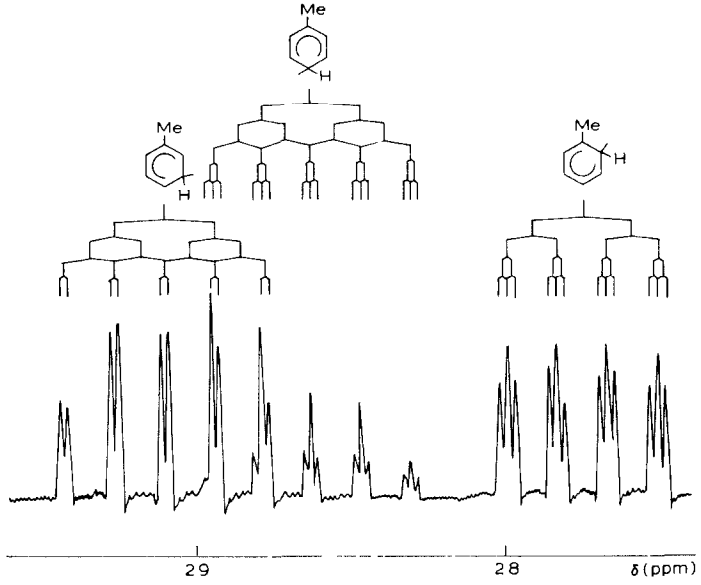


Fig. 1. Portion of the 400 MHz ^{1}H NMR spectrum of $[C_5Me_5Ir(C_6H_6Me)][BF_4]$ (**2b**), showing the typical patterns arising from H_{endo} *ortho*, *meta*, and *para* to the methyl substituent on the C_6 ring.

same C_5Me_5 resonances as for **2b** and two singlets (at δ 4.38 and 4.23 ppm) in the same places as the H_{exo} in the *ortho-* and *meta*-isomers of **2b**. The δ 4.23 resonance carried a small shoulder due to the *para*-isomer of **2b** (H_{exo} for which is at δ 4.24 ppm); the integrals of the two resonances, 47/53, compares with 46/54 found for *ortho/meta* plus *para* in **2b**. This shows that the same reaction has occurred in each case and that the only hydrogen on the C_6 ring, which came from the borohydride, is *exo*. We may conclude that borohydride attacks *exo* at the substituted benzene.

Pauson and coworkers [3] have shown that toluene in $[CpFe(C_6H_5Me)]^+$ is also attacked by borohydride; the proportions of *ortho-/meta-/para*-addition, 2/2/1, are again statistical and essentially the same as those found here. This suggests that the positions of attack found are really a property of η^6-bonded toluene, and depend little on the metal, the charge and the other ligands.

Stronger hydride reducers such as Red-Al (sodium bis(methoxyethoxy)dihydridoaluminate) reacted both with **1b** and with the isomer mix **2b** in the same way to give a mixture of η^4-methylcyclohexadiene isomers (**3b**). These were identified by mass spectrometry (molecular ion peaks at *m/e* 420 and 422 [4]).

NMR spectroscopy (Table 5) showed that two isomers were present, in the ratio of 27/73. These were ascribed to the isomers with the methyl at the 1- and at the 2-position respectively on the cyclohexadiene. Decoupling showed that the olefinic resonances at δ 2.71 and 4.31 ppm (overlapping) belonged to one isomer (associated with the methyl at δ 1.25 ppm) and that the resonances at δ 2.50, 2.61, and 4.38 ppm belonged to the other (associated with the methyl at 1.76 ppm). Again, as in **2b**, the C_6 ring methyls were both singlets showing that they were attached to non-proton-bearing (i.e., sp^2) carbons. On irradiation at δ 2.61 ppm the 4.38 resonance was simplified to a broad singlet, while irradiation at δ 2.50 ppm caused it to become a doublet (J 5 Hz), and irradiation at the methyl (δ 1.76 ppm) sharpened the 4.38 resonance into a double doublet (J 1 and 5 Hz). This showed that these resonances belonged to the 2-methylcyclohexadiene isomer and that they could be assigned as shown (Table 5).

Reaction of the toluene-d_8 complex with Red-Al gave a mixture of isomers, $[(C_5Me_5)Ir(C_6CD_3D_5H_2)]$, in the same ratios as found for the undeuteriated mixture. The ^1H NMR spectrum showed small peaks in the vinylic regions as well as in the aliphatic regions. This corresponded approximately to about 10% incorporation of H at C(2) and C(3) of the 1-methylcyclohexadiene complex, and about 10% at C(3) and 5% at both C(1) and C(4) of the 2-methylcyclohexadiene complex. We may conclude that in the step leading from **2b** to **3b** there participates a mechanism in which H/D scrambling can occur.

The double addition of hydride (as Super Hydride or potassium tri-isopropoxyborohydride) to η^6-toluene(tricarbonyl)managanese cation to give the methylcyclohexadiene(tricarbonyl)manganese anion has been described by Brookhart [5]. However, as the system was highly dynamic no information on site preferences was obtained.

Reaction of the mixture of methylcyclohexadiene complexes with HCl gave $[(C_5Me_5Ir)_2Cl_4]$ and a mixture of isomeric methylcyclohexenes. GC-MS analysis and comparison with mass spectra of authentic samples showed that all three isomeric methylcyclohexenes were formed, in the ratio 30 (1-methyl)/65 (3-methyl)/5 (4-methyl). The mixture of methylcyclohexadiene-d_8 complexes reacted exactly analogously with HCl to give the same mixture of methylcyclohexenes-d_8.

In summary it appears that in this system hydride attack does not occur at a carbon bearing a methyl, either in the toluene or in the methylcyclohexadienyl complexes. However, protons (as HCl) do appear to be able to attack the η^4-cyclohexadiene complex both at coordinated carbons bearing a hydrogen and at those bearing a substituent.

Reduction of t-butylbenzene

The new η^6-t-butylbenzene complex (**1c**) was prepared by the standard route (87% yield). On reduction with borohydride a mixture of three isomeric η^5-t-butylcyclohexadienyl complexes was obtained in the ratio of 11 (*ortho*)/39 (*meta*)/ 50 (*para*). The assignments were made using similar arguments to those used for the isomeric methylcyclohexadienyl complexes. For example, the two lowest field resonances (δ 6.52 dt, and 6.81 dt ppm) must both arise from H(4) of two different isomers. The former is assigned to the *ortho*-isomer since it shows the larger splitting (6.5 Hz) as a triplet, due to coupling to H(3) and H(5), and the smaller one (1 Hz) as a doublet, due to coupling to H(2). The δ 6.81 resonance must by contrast belong to the *meta*-isomer since here the larger splitting is into a doublet (5 Hz) since it can only couple to H(3) directly, while the smaller, 1 Hz, splitting is a triplet due to coupling to H(2) and H(6).

The feature distinguishing this from the toluene reaction above is that much less *ortho*- and much more *para*-isomer is formed here. This again points to the importance of interactions between the reagent and the substituent in the transition state.

One single η^4-t-butylcyclohexadiene isomer was obtained when the t-butylbenzene complex was reduced with Red-Al. Although complicated by second order coupling the ^{1}H NMR spectrum showed that the t-butyl group was attached to C(2) of the cyclohexadiene. When the ^{13}C NMR spectrum of **3c** was compared with that of the unsubstituted η^4-cyclohexadiene complex (**3a**) it was found that C(2) had shifted by the largest amount (29.7 ppm), confirming that the substituent t-butyl was in that position.

Reaction of this complex with HCl gave $[(C_5Me_5Ir)_2Cl_4]$ (**4**) and a mixture of two isomeric t-butylcyclohexenes in the ratio of 92/8 by GC-MS. Comparison of the mass spectra with the Kratos Library spectrum of 1-t-butylcyclohexene showed that neither was that isomer. The ^{13}C NMR spectrum showed olefinic carbon resonances at δ 127.9 and 129.3 ppm, due to 3-t-butylcyclohexene [6], and the major component was assigned this structure. The minor component must therefore be 4-t-butylcyclohexene.

Reduction of anisole (methoxybenzene)

Reduction of the anisole complex **1d** [7] with sodium borohydride gave a mixture of methoxycyclohexadienyl complexes (**2d**). A careful analysis of the ^{1}H NMR spectrum showed the presence of four isomers. This implied that one of them must be the otherwise not observed *ipso*-isomer. This was confirmed by the observation of a singlet at δ 5.82 ppm, which we ascribe to H_{exo} of this isomer; the resonance is shifted ca. 1.6 ppm downfield from its normal position, entirely consistent with it being attached to a carbon also bearing a methoxy substituent. Associated with this was a signal at 6.79 ppm, which we assign to H(4) for this isomer since it is a triplet of triplets, indicating coupling to two adjacent hydrogens, H(3) and H(5), (J 5 Hz),

and to two further removed hydrogens, H(2) and H(6) (J 1 Hz). The other isomers were assigned by methods similar to those described above, and their relative amounts estimated to be 10 (*ipso*)/25 (*ortho*)/55 (*meta*)/10 (*para*).

Pauson and coworkers have also reported the attack of hydride on $[CpFe(C_6H_5OMe)]^+$ [8] and on $[Mn(C_6H_5OMe)(CO)_3]^+$ [9]. In the first case (attack by BH_4^-), the ratio of *ortho*-/*meta*-/*para*-attack observed was 13/67/20, while in the second (attack by AlH_4^-) it was 37/63/0. No *ipso*-attack was found in either but some loss of OMe (and formation of the ubsubstituted cyclohexadienyl complex) was observed. It is possible that substitution may proceed by initial *ipso*-attack, though other experiments (see below) suggest that the pathway may be more complicated.

The preponderance of *meta*-adduct found makes the iron, manganese, and iridium systems rather similar. However, the differences in the amounts of *ortho*- and *para*-isomers found suggest that this reaction is sensitive to other factors such as the attacking agent, the metal, the charge on the complex, and the other ligands present.

Further reduction to a mixture of η^4-cyclohexadiene complexes occurred on reaction of **1d** with Super Hydride; two isomers were identified and in addition evidence was obtained for the formation of some of the cyclohexadiene complex **3a**, by replacement of OMe by H. The isomers were identified as the 1-methoxy- (65%) and the 2-methoxy-cyclohexadiene (35%) complexes **3d** by the similarity of their ^1H NMR spectra to those of the **3b** isomers.

Reaction of the mixed methoxycyclohexadiene complexes with HCl gas gave **4** and a very complex mixture. GC-MS analysis showed the presence of cyclohexene, cyclohexanone, methoxycyclohexene, chlorocyclohexanone, and chlorocyclohexene. Clearly under these conditions a number of subsequent reactions occurred after the methoxycyclohexene was liberated. This is not unexpected since ethers are readily cleaved by HCl and one may anticipate that this problem can be overcome by using milder conditions.

Reduction of chlorobenzene

The chlorobenzene complex **1e**, prepared in 60% yield by a modification of the standard preparation, when reduced with borohydride gave a product showing low chlorine analyses for a mixture of chlorocyclohexadienyl complex isomers (**2e**). Indeed, increase of reaction time and the amount of borohydride gave a product with no chloride, which was identified as the cyclohexadienyl complex **2a**. This indicates that as well as nucleophilic addition, the hydride was effecting a nucleophilic substitution at the carbon bearing the chloride. This appeared to occur on the chlorocyclohexadienyl complexes **2e**, since low amounts of reagent and short reaction times gave two isomers where addition had occurred *ortho* and *meta* to the Cl. They were identified in the usual manner (Tables 2 and 3) and the ratio was 77/23.

Reduction of $[CpFe(C_6H_5Cl)]^+$ with borohydride gave a very similar result; only the *ortho*- and *meta*-positions were attacked and the ratio of the two was 83/17 [10], almost identical to that found here. Again in this case it appears as if the position of attack was predominantly determined by the η^6-chlorobenzene ligand.

Only one isomer of the η^4-chlorocyclohexadiene complex **3e** was obtained when **1e** was treated with N-Selectride (sodium tri-sec-butylborohydride). This was identified as the isomer with the chloride in the 1-position from the ^1H NMR spectrum which showed three vinylic resonances, a doublet at δ 4.69 due to H(2), a double

doublet at 4.26 due to H(3) and a multiplet at 2.80 ppm, assigned to H(4). The ^{13}C spectrum could also be assigned.

Reaction of this isomer (**3e**) with HCl led to the formation of complex **4** and a solution which was shown to contain three isomeric chlorocyclohexenes by GC-MS. They were identified by comparison of their mass spectra with those of Kratos Library spectra as the 1-chloro- (34%), the 2-chloro- (8%), and the 3-chloro- (58%) cyclohexenes.

Reduction of phenol

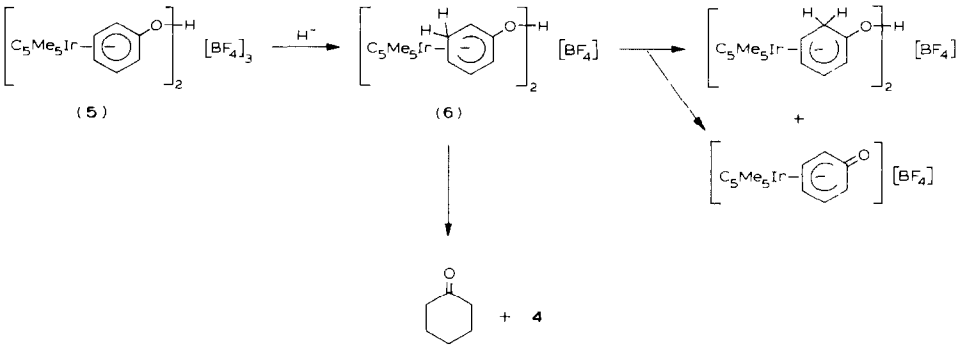
The dinuclear hydrogen-bonded phenol complex **5** [11] reacted with aqueous sodium borohydride to give a single material which was identified by microanalysis as another hydrogen-bonded dimer, and by ^1H NMR spectroscopy as containing the cyclohexadienyl complex **6** where attack by hydride had occurred *meta* to the oxygen (Scheme 2). Thus, for example, H_{endo} was coupled to H_{exo} (J 12.2 Hz), to H(2) 6 Hz, and to H(6) 6.5 Hz, but only showed a single 1 Hz coupling, to H(3) (Table 3).

No hydroxycyclohexadiene complex could be isolated when the phenol complex **5** was treated with the stronger reductants Super Hydride (lithium triethylborohydride) or N-Selectride (sodium tri-sec-butylborohydride). However in situ reaction of this reduced solution with HCl gave **4** and cyclohexanone as the only organic product. The cyclohexanone was easily identified by its characteristic mass spectrum which shows the base peak at m/e 55. By contrast, the cyclohexenols show base peaks at m/e 70 or 80.

A solution of the complex **6** in acetone slowly rearranged (4 weeks/20 °C). From the ^1H NMR spectrum (Table 2) it was deduced that the isomer **6** where attack had occurred *meta* to the OH had isomerised to the isomer where the OH was now *ortho* to the point of attack. Additionally, the η^5-oxocyclohexadienyl complex was formed to the extent of 25%; this was previously made by reaction of the η^6-phenol complex with sodium carbonate [11].

Reduction of disubstituted benzene complexes

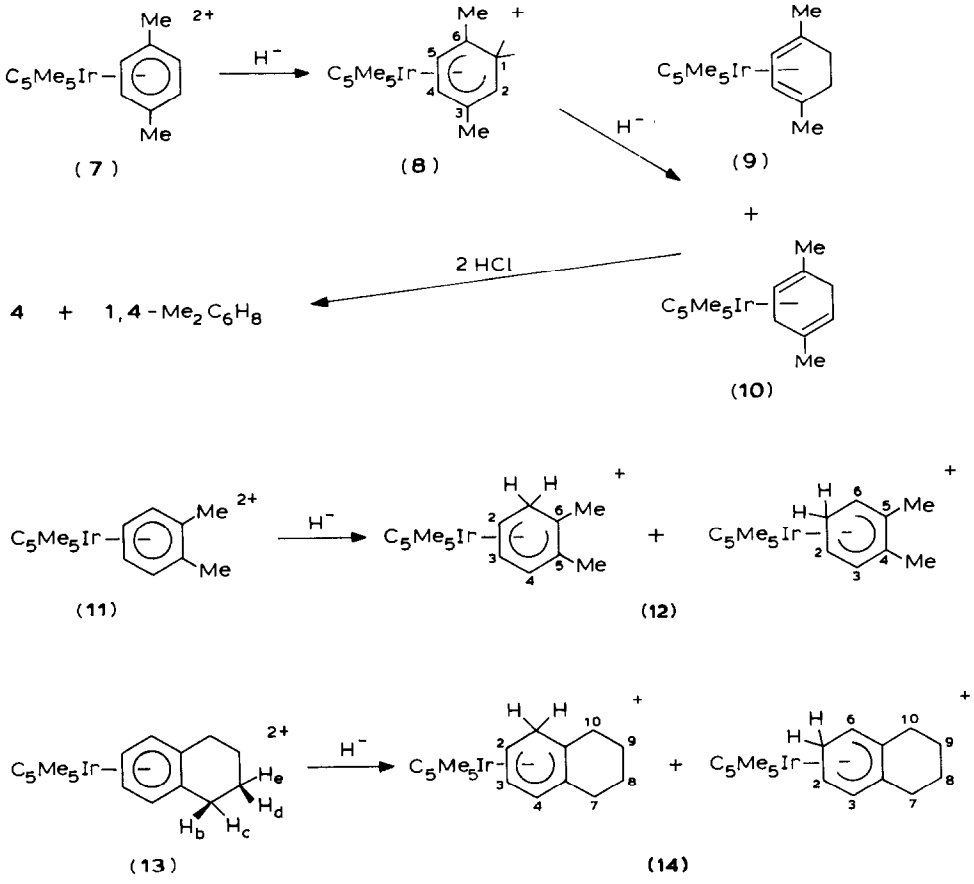
Although the entire sequences have not been completed here, even the preliminary stages of these reactions show some features which make them interesting. The complexes of *p*-xylene (**7**), *o*-xylene (**11**) and tetralin (**13**) were prepared and



SCHEME 2

treated with borohydride (Scheme 3). In all cases the expected products were formed. Reduction of **7** gave a single cyclohexadienyl complex **8** where attack had occurred adjacent to a methyl. On reduction **11** and **13** each gave two isomeric cyclohexadienyl complexes **12** and **14** where attack had occurred predominantly (ca. 55%) at the site adjacent (α) to the substituent and less (ca. 45%) at the site β to it.

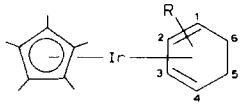
Reduction of the single cyclohexadienyl isomer **8** from *p*-xylene (with Red-Al) gave a simple 1/1 mixture of two η^4-cyclohexadiene complexes. A careful analysis of the ^{1}H NMR spectrum (Table 5) showed that one of these was the expected complex **9** containing the 1,4-dimethylcyclohexa-1,3-diene ligand; again attack by both first and second hydrides had occurred vicinally at carbons not bearing methyls. The other complex (**10**) was isomeric and had the 1,4-dimethylcyclohexa-1,4-diene as ligand. In this case attack was again at non-methyl-bearing carbons but the second hydride did not attack vicinally to the first. Although cyclohexa-1,4-diene complexes are rare, a number have been reported and one, (CpRh(η^4-3-methoxycarbonylcyclohexa-1,4-diene)), was crystallographically characterised [12]. The cyclohexa-1,4-diene there adopts a boat-shaped conformation on coordination.



SCHEME 3

TABLE 5

^{1}H NMR SPECTRA OF η^4-CYCLOHEXA-1,3-DIENE COMPLEXES [a]



δ

	δ(C_5Me_5)	δ(H(1))	δ(H(2))	δ(H(3))	δ(H(4))	δ(H5,6))	δ(Me)
[$C_5Me_5Ir(C_6H_7Me)$]							
1-isomer	1.983	–	4.31	4.31	2.71	0.98 1.32	1.25
2-isomer	1.986	2.50	–	4.38	2.61	0.98 1 32	1.76
	(J(3–4) 5; J(1–3) 1 Hz)						
[$C_5Me_5Ir(C_6H_7CMe_3)$]							
2-isomer	1.939	2.71	–	4 47	2.44	0 97 1.27	0.97
	(J(3–4) 6; J(1–3) 1.5 Hz)						
[$C_5Me_5Ir(C_6H_7OMe)$]							
1-isomer	2.10	–	4.56	4.56	3.00	1.3	3.26
2-isomer	2.08	2.80	–	4.56	2.80	1.3	3.33
[$C_5Me_5Ir(C_6H_7Cl)$]							
1-isomer	2.01	–	4.69	4.26	4.80	n.o.	–
[$C_5Me_5Ir(C_6H_6Me_2)$]							
1,4-dimethyl-cyclohexa-1,3-diene	1.84	–	4.23s	4.23s	–	1.20	1.17s
1,4-dimethyl-cyclohexa-1,4-diene	1.91	–	1.57	–	–	H_{endo} 3.03 H_{exo} 5.25	1.23s
	(J(*endo*–*exo*) 11; J(*endo*–2) 6 Hz)						

[a] In $CDCl_3$ solution.

On treatment with HCl the mixture of cyclohexadiene complexes (**9** and **10**) gave a 1/1 mixture of two isomeric dimethylcyclohexenes.

Discussion

The reactions involving toluene and toluene-d_8 show that the entering hydride becomes H_{exo} in the cyclohexadienyl complex, in agreement with our results on the reduction of benzene [2] and those of many other workers [13]. This implies that a metal hydride is not an intermediate and that the reaction proceeds by direct attack of the reagent on the C_6 ring.

Table 6 lists the site preferences for attack by hydride at substituted arenes in complexes of type **1** and compares them to data in the literature for the same arenes but complexed to $CpFe^+$ and $Mn(CO)_3^+$. (The site preference numbers take account of the fact that there are two *ortho*- and two *meta*-positions which can be attacked in each molecule, but only one *para*- and one *ipso*-position. The numbers are normalized to *meta* = 1.0 for each case.)

The agreement for toluene and chlorobenzene is very good. Toluene with borohydride shows an essentially statistical distribution, showing that no isomer is favoured, while chlorobenzene shows a strong preference for *ortho*-attack in both systems.

TABLE 6

SITE PREFERENCES FOR ATTACK AT MONOSUBSTITUTED BENZENES

$R-C_6H_5$---m [a]		*ipso*-	*ortho*-	*meta*-	*para*-	References
Me	Ir	0	1	1	1	this work
Me	Fe	0	1	1	1	[3]
t-Bu	Ir	0	0.3	1	2.5	this work
Cl	Ir	0	3	1	0	this work
Cl	Fe	0	4	1	0	[10]
OMe	Ir	0.4	0.5	1	0.4	this work
OMe	Fe	0	0.2	1	0.6	[8]
OMe	Mn	0	0.6	1	0	[9]
OH	Ir	0	0	1	0	this work
CO_2Me	Fe	0	12.7	1	1.1	[17]

[a] m = $IrC_5Me_5^{2+}$, $FeCp^+$ or $Mn(CO)_3^+$.

Increasing the bulk of the substituent (to t-butyl) or the bulk of the reagent (to Me_3NBH_3) shows a steric influence on the process. In both cases the site preferences *ortho/meta/para* are now closer to 0.3/1/2.5, showing a significant increase in attack at *para* at the expense of *ortho*. Presumably in the transition state for attack there is now substantial interference between the reagent and the substituent in both cases. Similar results have been reported for attack by C-centred nucleophiles on substituted benzene(tricarbonyl)chromium complexes [14].

This steric factor is not significant for chlorobenzene, implying that the *ortho*-attack is favoured for electronic reasons. This must be due to the strong $-I$ inductive effect of Cl. Our system and the iron one [10] have the further feature in common of loss of Cl; in our case long reaction times and high borohydride levels lead to **2a**. The mechanism of this transformation is not clear but our experiments suggest that the formation of **2a** proceeds via the chlorocyclohexadienyl complex **2e**, possibly by a substitution of chloride by hydride at the carbon. This again points to an electronic activation by the Cl of adjacent sites. (The formation of **2a** may also be more complex, involving addition of hydride to **2e** at the carbon bearing the Cl, followed by loss of HCl leading to formation of the benzene complex **1a**, which then reacts with hydride. This seems less likely since N-Selectride reacts with **1e** to give the chlorocyclohexadiene complex **3e** in reasonable yield.)

By contrast, phenol gives only *meta*-attack and anisole is attacked *ipso* as well as *ortho*, *meta* and *para* with approximate site preferences 0.4/0.5/1/0.4. *meta*-Attack is again favoured and the results are reasonably similar to those for the iron system [8]. Since Cl, OH, and OMe substituents are all classed as $-I$ in terms of their inductive effects on aromatic substitution reactions (in contrast with methyl or t-butyl which are $+I$), and since Cl is larger than O, the true reason for the differences between them must be sought elsewhere. One possibility is that resonance effects become significant here, though this has been discounted elsewhere [10]. However, Semmelhack et al. [14] have correlated the coefficients of the LUMO's of the uncomplexed substituted arenes [15] with the sites of nucleophilic attack in the complexes.

Alternatively, part of the reason for Cl activating the *ortho*-position so strongly may arise from a direct interaction between the entering reagent and the Cl substituent. Such a boron–chloride interaction in this process could also promote the

formation of the unsubstituted cyclohexadienyl complex **2a** on prolonged reaction.

Attack of the second hydride (at the η^5-cyclohexadienyl) again occurs at unsubstituted carbons to give the 1- or 2-substituted η^4-cyclohexadiene complexes *. With one exception all the products are complexes of cyclohexa-1,3-diene and we may therefore presume that attack occurs vicinally to the position which had already been attacked in going from **1** to **2** (or their equivalent).

However, only two cyclohexadiene isomers are formed and, this does not increase the difficulty of creating stereospecific reactions. Alkyl substituents favour the 2-isomer, and greater bulk favours it more (100% for t-butyl and 73% for methyl). Chloride by contrast only gives the 1-isomer; this may be a further example of Cl preferentially activating the site adjacent to it. Methoxy seems to have a dual effect since the major component is the 1-methoxycyclohexadiene but some 2- is also formed (65/35).

It is possible to rationalise the isomer distributions produced from toluene, t-butylbenzene, and chlorobenzene if we assume that the second hydride always attacks vicinal to the first site of attack but never vicinal to the substituent. In that case we may compare the expected ratios of 1- and 2-substituted cyclohexadiene complexes (based on the proportions of the *ortho*-, *meta*-, and *para*-isomers in **2**) with those actually found. Thus toluene gives a 2/3 ratio and 1/3 is expected based on the above premise; for t-butylbenzene it is (undetectable)/ > 95% compared to 1/9 expected; while for chlorobenzene it is > 95%/(undetectable) compared to an expected of 3/1. However for anisole the expected is ca. 1/3 and the found is 2/1.

Clearly other factors play a role in these systems. This is shown by the evidence of scrambling in the cyclohexadiene complex (**2b**-d_8) obtained from the toluene-d_8 complex (**1a**-d_8) and Super Hydride. This result indicates that the products observed are not entirely those formed under kinetic control but that other (hydrogen migration) reactions have occurred subsequent to the hydride addition. The degree to which this happens may be expected to vary for the different systems. Brookhart and his group have shown that the anionic cyclohexadienemanganese complexes formed by double reduction of $[(\text{arene})\text{Mn}(\text{CO})_3]^+$ exhibit very complex hydrogen migrations involving the metal [16]. Although our systems seem to be more inert, similar, though slower, processes may well occur here too.

Another potential complication is shown by production of two isomeric cyclohexadiene isomers from reduction of the single isomer of the dimethylcyclohexadienyl complex **8** from *p*-xylene. The isomer **10** in which a cyclohexa-1,4-diene is complexed to iridium is formed in addition to the expected isomer **9**. It is possible that attack to give 1,4-diene systems occurs more often initially but that a rearrangement to the more stable 1,3-isomer then takes place.

The last step, the liberation of the cyclohexene from the cyclohexadiene complex, seems to proceed well (except for anisole). It is not appropriate to rationalise the factors of significance here on the limited evidence of three systems (methyl-, t-butyl-, and chloro-benzene). However, the isomer distribution from the single

* We are indebted to a referee for drawing our attention to the fact that the 1-phenyl-2-methyl-5-methoxy-η^{2-6}-cyclohexadienyl(dicarbonylnitrosyl)manganese cation is attacked by borohydride both at the unsubstituted position (C(6)) and the substituted (C(2)) to give cyclohexadiene complexes. This reaction and other similar reactions also proceed by *endo*-attack at the ring carbon, Y.K. Chung, E.D. Honig, W.T. Robinson, D.A. Sweigart, N.G. Connelly, and S.D. Ittel, Organometallics, 2 (1983) 1479.

t-butylcyclohexadiene isomer **3c** (92% 3-t-butylcyclohexene) shows that, in contrast to hydride attack, protons preferentially attack the C(6) carbon bearing the substituent. This isomer also predominates in the product from the methylcyclohexadiene complex **3b**, and may be caused by an inductive effect (+*I*) making this carbon the most negative and hence the most easily attacked. The isomer distribution from the single chlorocyclohexadiene isomer **3e** cannot be explained so easily and this suggests that the products observed may arise from a number of different factors, both kinetic and thermodynamic.

An interesting and potentially very useful result was obtained from the phenol reaction since cyclohexanone was obtained as the only organic end-product. It is likely that cyclohexenols were also formed but that under the conditions of the reaction they were isomerised.

In summary it appears that quite usefully high selectivities can be obtained in such reactions with very bulky substituents (t-butyl); it should be reasonably easy to tune the other reactions to further improve their selectivities. Although in this exploratory study we have not investigated a very wide range of functionalities, it seems clear that a substantial number can be tolerated. There also seem to be no particular problems in reducing disubstituted benzenes.

Experimental

All reactions were carried out under a protective blanket of nitrogen; the η^6-arene and the η^5-cyclohexadienyl complexes were not appreciably affected by air. The η^4-cyclohexadiene complexes were very air-sensitive and were handled under vacuum line conditions. Experimental details of representative reactions are given below. Microanalytical data (from the University of Sheffield Microanalytical Service) are in Table 7. Since the cyclohexadiene complexes were oils or low melting solids only obtained in small amounts, they were characterised by their mass spectra (Table 7) [4] measured on a Kratos MS-25 or MS-80 mass spectrometer attached to a DS-55 Data Release System. Library spectra were obtained from the Kratos library. GC-MS analyses were carried out using a Carlo-Erba gas chromatograph attached to the MS-25 spectrometer. ^{1}H NMR spectra (Table 1–5) were measured on a Bruker WH-400 spectrometer at 400.13 MHz or on a Perkin–Elmer R-34 spectrometer at 220 MHz. $^{13}C\{^1H\}$ NMR spectra were measured on a JEOL PFT-100 spectrometer.

*Preparation of (η^5-pentamethylcyclopentadienyl)(η^6-arene)iridium(III) bis-tetrafluoroborates (**1b–1e**), (**5**), (**7**), (**11**) and (**13**)*

Method A. A solution of $[(C_5Me_5Ir)_2Cl_4]$ (**4**), (1.00 g, 1.25 mmol) in acetone (5 cm^3) was treated with silver tetrafluoroborate (0.98 g, 5.00 mmol) and stirred (10 min/20 °C). The precipitated silver chloride was removed by filtration through cellulose and the filtrate (I) was treated with excess arene (3 cm^3) (4 h/20 °C). This yielded a pale cream precipitate which was filtered off to give the complexes **1b** (1.21 g, 81%), **1d** (1.26 g, 82%), **7** (0.98 g, 64%), **11** (1.24 g, 81%), or **13** (1.40 g, 88%). Addition of phenol (0.5 g) to the acetone solution (I) gave the dinuclear H-bonded phenol complex **5** (1.15 g, 83%).

Method B. The acetone solution (I) (above, but using half quantities) was evaporated to an oil in vacuo. Boron trifluoride dihydrate (Fluka, 1 cm^3) and the arene (5 cm^3) were added and the mixture stirred (10 min/60 °C). Careful addition

of diethyl ether to the cooled solution gave a precipitate which was crystallised from nitromethane/diethyl ether to give **1c** (700 mg, 88%), **1e** (460 mg, 60%), or **1b**-d_8 (630 mg, 84%).

*Preparation of (η^5-pentamethylcyclopentadienyl)(η^5-substituted benzene)iridium tetrafluoroborates (**2b–2e**), (**6**), (**8**), (**12**) and (**14**)*

Method A. A solution of sodium borohydride (20 mg, 0.53 mmol) in water (10 cm^3) was added dropwise to a suspension of the η^6-arene complex $[(C_5Me_5Ir)(arene)][BF_4]_2$ (0.35 mmol) in water (20 cm^3) at 0 °C. Reaction occurred with frothing to give a clear solution; this was extracted with dichloromethane (3×10 cm^3). The combined dichloromethane extracts were filtered through a short

TABLE 7

MICROANALYSES AND MASS SPECTRA

		Found (calcd.)(%)		*m/e*
		C	H	
$[C_5Me_5Ir(C_6H_5Me)][BF_4]_2$	(**1b**)	34.4	3.6	
		(34.4)	(3.9)	
$[C_5Me_5Ir(C_6H_6Me)][BF_4]$	(**2b**)	40.5	4.8	
		(40.2)	(4.7)	
$[C_5Me_5Ir(C_6H_7Me)]$	(**3b**)			422, 420
$[C_5Me_5Ir(C_6H_2D_5CD_3)]$	(**1b**-d_8)			430, 428
$[C_5Me_5Ir(C_6H_5CMe_3)][BF_4]_2$	(**1c**)	37.5	4.5	
		(37.8)	(4.6)	
$[C_5Me_5Ir(C_6H_6CMe_3)][BF_4]$	(**2c**)	43.6	5.5	
		(43.7)	(5.4)	
$[C_5Me_5Ir(C_6H_5OMe)][BF_4]_2$	(**1d**)	33.3	3.9	
		(33.5)	(3 8)	
$[C_5Me_5Ir(C_6H_6OMe)][BF_4]$	(**2d**)	39.3	4.6	
		(39.0)	(4.6)	
$[C_5Me_5Ir(C_6H_7OMe)]$	(**3d**)			436, 438
$[C_5Me_5Ir(C_6H_5Cl)][BF_4]_2$	(**1e**)	31.3	3.3	
		(30.8)	(3.4)	
		Cl, 5.8		
		(5.9)		
$[C_5Me_5Ir(C_6H_7Cl)]$	(**3e**)			440, 442, 444
$[\{C_5Me_5Ir(C_6H_5O)\}_2H][BF_4]_3$	(**5**)	34.6	3.7	
		(34.9)	(3.7)	
$[\{C_5Me_5Ir(C_6H_6O)\}_2H][BF_4]$	(**6**)	42.0	5.0	
		(41.3)	(4.6)	
$[C_5Me_5Ir(p\text{-xylene})][BF_4]_2$	(**7**)	35.4	4.3	
		(35.6)	(4.1)	
$[C_5Me_5Ir(C_6H_5Me_2)][BF_4]$	(**8**)	41.5	5.0	
		(41.5)	(4.6)	
$[C_5Me_5Ir(o\text{-xylene})][BF_4]_2$	(**9**)	35.8	4.2	
		(35 6	(4 1)	
$[C_5Me_5Ir(C_6H_5Me_2)][BF_4]$	(**10**)	41.5	5.0	
		(41.5)	(5.0)	
$[C_5Me_5Ir(\text{tetralin})][BF_4]_2$	(**11**)	37.9	4.4	
		(37.9)	(4.3)	
$[C_5Me_5Ir(C_{10}H_{13})][BF_4]$	(**12**)	44.5	5.2	
		(43.9)	(5.1)	

alumina column (2 × 1 cm); addition of diethyl ether to the resultant very pale yellow solution gave colourless crystals of **2b**, (72%), **2b**-d_8 (87%), **2c** (58%), **2d** (50%), **6** (25%), **8** (81%), **12** (68%), and **14** (58%).

Method B. When the chlorobenzene complex **1e** was treated under conditions of method A a 90% yield of **1a** was isolated. Reaction of **1e** (140 mg, 0.23 mmol) in water (5 cm^3) with sodium borohydride (13 mg, 0.34 mmol) in water (2 cm^3) followed by a very rapid work-up gave **2e** in 17% yield.

Method C. The toluene complex **1b** (200 mg, 0.34 mmol) was treated with trimethylamine-borane (300 mg, 4.1 mmol) in dichloromethane (20 cm^3) (18 h/20 °C/argon atmosphere). The solvent was removed in vacuo; the excess trimethylamine borane removed by washing with diethyl ether and the residual solid crystallised from acetone/diethyl ether to give **2b** (70%).

*Preparation and reaction with HCl of (η^5-pentamethylcyclopentadienyl)(η^4-methylcyclohexa-1,3-diene)iridium(I) (**3b**), and related complexes*

A suspension of the toluene complex **1b** (200 mg, 0.39 mmol) in toluene (10 cm^3) was treated with Red-Al (sodium bis(methoxyethoxy)dihydridoaluminate, 195 mg, 0.43 mmol) (10 min/20 °C). The solvent was removed in vacuo and the residue extracted with pentane; the pentane was then removed and the residual solid sublimed (60 °C/10^{-3} mmHg) to give **3b** (66 mg, 40%). A similar reaction of 1b (400 mg, 0.68 mmol) in dry ether (10 cm^3) with Super Hydride (sodium triethylborohydride in ether solution, Aldrich, 0.3 cm^3, 6 mmol) gave, after a similar work-up, **3b** in 70% yield.

Reaction of the isomer mixture **3b** (100 mg, 0.24 mmol) in pentane (2 cm^3) with dry HCl gas gave an orange precipitate of **4** (82 mg, 86%). GC and GC-MS analysis (2m packed column of silver nitrate in ethylene glycol on Chromosorb P80-100; isothermally at 37 °C) of the pentane solution showed the presence of 1-, 3- and 4-methylcyclohexenes (retention times, 528, 1662, and 1518 s, respectively; c.f. pentane 132 s) in the ratios 30/65/5; combined yield 80%.

The toluene-d_8 complex was similarly reduced to **3b**-d_8 (53%), as was the t-butylbenzene complex **1c** to **3c** (41%, with Red-Al), the anisole complex **1d** to **3d** (60%, with Super Hydride), the chlorobenzene complex **1e** to **3e** (60%, with N-Selectride), and the *p*-xylene complex to a mixture of **9** and **10** (60%, with Red-Al). ^{13}C NMR spectra: (η^4-2-t-butylcyclohexa-1,3-diene)(pentamethylcyclopentadienyl)iridium (**3c**) ($CDCl_3$) δ (ppm): 11.0 ($C_5\mathit{Me}_5$), 88.4 (C_5Me_5), 29.3, 32.6 (t-Bu), 27.6, 27.8 (C(5,6)), 48.2 (C(1)), 95.3 (C(2)), 63.5 (C(3)), 41.3 (C(4)); (η^4-1-chlorocyclohexa-1,3-diene)(pentamethylcyclopentadienyl)iridium (**3e**) ($CDCl_3$) δ(ppm); 9.9, 89.8 (C_5Me_5), 27.6, 28.3 (C(5,6)), 38.3 (C(1)), 66.8 (C(2)), 66.1 (C(3)), 45.7 (C(4)).

The mixtures of isomeric cyclohexadiene complexes were analysed by NMR spectroscopy and then reacted with HCl in pentane to give complex **4** (usually greater than 90%) and the isomeric cyclohexenes. These were analysed by GC-MS, either using a packed column as described above or a 20 m OV101 capillary column (50 °C for 3 min, then programmed at 10 °C per min up to 120 °C).

*Reduction of the phenol complex **5** to cyclohexanone*

N-Selectride (Aldrich, 1 cm^3 of an ethereal solution, 1 mmol) was added to a suspension of the phenol complex **5** (200 mg, 0.18 mmol) in diethyl ether (10 cm^3).

When the suspension had cleared the solvent was removed in vacuo, and the residue extracted into pentane. Dry HCl gas was passed into this pentane solution and sodium carbonate (100 mg) was added. An orange precipitate was formed which, after washing with water to remove the excess inorganic salts, was shown to be complex **4** (71 mg, 51%). Analysis by GC-MS (capillary column, conditions as above) of the pentane solution showed the presence of only one organic compound, identified as cyclohexanone.

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