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Product distributions in the addition of the hydride ion to cyclopentadienyliron complexes of substituted benzenes

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Abstract

Fifteen $[C_6H_5(X)FeCp]^+$ cations with substituents X having different electron-donating or electron-withdrawing effects were treated with $NaBH_4$ in glyme or THF. The relative distributions of products from *o*-, *m*-, *p*- and *ipso*-additions of the hydride ion to the arene ring were determined by high resolution ^1H NMR. For the η^6-*N*,*N*-dimethylaniline-η^5-cyclopentadienyliron cation with the most electron-donating of the substituents studied, only *m*- and *p*-hydride addition products were obtained, while in the reaction with the η^6-nitrobenzene-η^5-cyclopentadienyliron cation, which contained the most electron-withdrawing of the substituents investigated, only the *o*-addition product was formed. For the other 13 cations, with $X = C_6H_5O$, CH_3O, p-$CH_3C_6H_4S$, $C_6H_5CH_2$, $(CH_3)_3C$, CH_3, CH_3CH_2, C_6H_5, Cl, $COOCH_3$, C_6H_5CO, CN and p-$CH_3C_6H_4SO_2$, *o*-, *m*- and *p*-hydride addition products were obtained in all cases, with a few instances also giving very minor amounts of *ipso*-adducts. The relative product distributions observed were interpreted by suggesting that while electronic effects played a major role, steric factors and free valency effects favoring *o*-addition as suggested by MO calculations [5] could also exert their influence in giving rise to the overall results.

Introduction

Watts and coworkers [1–4] have studied the nucleophilic addition of the hydride ion to a number of cyclopentadienyliron (CpFe) complexes of arenes including $[C_6H_5XFeCp]^+$ cations (I) with $X = CH_3$, CH_3O, Cl and $COOCH_3$. It was found that the addition took place exclusively at the arene ring, with the hydride ion adding from the *exo*-direction, the site of addition being dependent on the nature of substituent X. For the CpFe complexed toluene (I, $X = CH_3$), the ratio of hydride addition at the *o*-, *m*- and *p*-positions to the substituent was found to be about 1/1/1 after the statistical factor of 2 for additions to the *o*- and *m*-positions has been taken into account [1]. With the CpFe complex of anisole (I, $X = CH_3O$), the

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major product resulted from hydride addition to the *m*-position [3], while in similar reactions with the chlorobenzene or methyl benzoate complex (I, X = Cl or $COOCH_3$), the major product was derived from *o*-addition [2,4]. These results were explained by the inductive and resonance effects of substituent X, influencing the charge distributions at the *o*-, *m*- and *p*-positions, with an electron-donating substituent favoring hydride addition at the *m*-position, and an electron-withdrawing substituent favoring *o*-addition [1–4].

Clack and Kane-Maguire [5] have carried out molecular orbital calculations on the CpFe complexes of toluene, anisole and methyl benzoate (I, X = CH_3, CH_3O and $COOCH_3$) in order to test quantitatively the possible relationship between the sites of hydride addition and variations in positive charge values in the various arene carbon positions. The results indicated that for cation I with X = CH_3O, the positive charge, decreasing in the order of C(3) or $m >$ C(4) or $p >$ C(2) or *o*, correctly predicted the observed site preference for hydride addition. Similarly, the much smaller variation in arene carbon charges for cation I with X = CH_3 of $m > p > o$ would be consistent with the lack of regioselectivity in the hydride addition to the toluene complex. For cation I with X = $COOCH_3$, however, while the variation in positive charge of $o > p > m$ was in the order expected from the reported site preference for hydride addition, the magnitudes of the differences in charges were no larger than those calculated for I with X = CH_3. Thus the molecular orbital calculations would suggest that charge variations alone could not explain the very marked *o*-directing influence of the $COOCH_3$ substituent. In order to evaluate further the possible effects of various factors that may influence the site of hydride addition to η^6-substituted benzene-η^5-cyclopentadienyliron cations (I), we have examined the reaction of $NaBH_4$ with a series if 15 CpFe complexed monosubstituted benzenes.

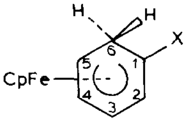
Results and discussion

Hydride addition reactions were carried out with η^6-substituted benzene-η^5-cyclopentadienyliron cations Ia to Io, all of which were prepared as their hexafluorophosphates using known procedures. Upon treatment with $NaBH_4$ in 1,2-dimethoxyethane (glyme) or tetrahydrofuran (THF), possible products could result from addition of the hydride ion at the *o*-, *m*- or *p*-position to give IIa to IIo, IIIa to IIIo, or IVa to IVo, respectively, with the designation of substituent X as a to o as given for Ia to Io. If hydride addition were to take place at the *ipso*-position, products Va to Vo could also be formed.

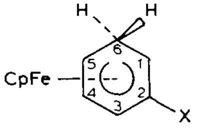
The results from the present studies are summarized in Table 1. As an indication of the electron-donating and electron-withdrawing power of the various substituents in the cations employed, known values of the Hammett σ constants [6] are also given in Table 1. It is of interest to note that, in general, longer reaction times were required for cations with electron-donating substituents and that the yields were generally better for cations with electron-withdrawing substituents. The relative product distributions were measured by high resolution ^1H NMR, similar to a method recently employed by Grundy and Maitlis [7] in their use of high resolution ^1H NMR in determining the product distributions obtained from the addition of one hydride ion to various η^6-arene-η^5-pentamethylcyclopentadienyliridium dications to give η^5-cyclohexadienyl complexes.

$C_6H_5XFeCp^+$
(I)

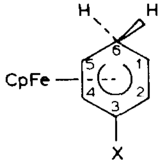
Ia : X = $(CH_3)_2N$
Ib : X = C_6H_5O
Ic : X = CH_3O
Id : X = p-$CH_3C_6H_4S$
Ie : X = $C_6H_5CH_2$
If : X = $(CH_3)_3C$
Ig : X = CH_3
Ih : X = CH_3CH_2
Ii : X = C_6H_5
Ij : X = Cl
Ik : X = $COOCH_3$
Il : X = C_6H_5CO
Im : X = CN
In : X = p-$CH_3C_6H_4SO_2$
Io : X = NO_2



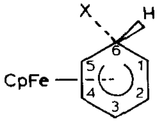
(IIa to IIo)



(IIIa to IIIo)



(IVa to IVo)



(Va to Vo)

Characteristic ^1H NMR signals for the *o*-, *m*- and *p*-adducts from various hydride addition reactions were observed in each spectrum of a mixture of isomeric products, thus allowing for the integration of well-separated signals to give the relative product distribution. As a general description, besides the Cp singlets and the signals attributable to the various substituents, the *ortho*-adducts (IIb to IIo) show the presence of 6 complexed cyclohexadienyl protons (H(2), H(3), H(4), H(5), H(6-*exo*) and H(6-*endo*)) widely spread over the range of 1–7 ppm. The H(6-*exo*) protons appeared in the range of 0.95–2.00 ppm as a doublet due to splitting by H(6-*endo*) ($J \simeq 11$–13 Hz). No further splitting of this doublet by H(5) was observed, presumably because of the geometrical relationship between these 2 protons, the dihedral angle between the planes defined by H(6-*exo*), C(6), C(5) and by C(6), C(5), H(5) being about 90°, with $J \simeq 0$ Hz [8]. The H(6-*endo*) protons gave a complex set of absorption at 2.29–3.35 ppm owing to splitting by H(6-*exo*) into a doublet ($J \simeq 11$–13 Hz) which was further coupled to H(5) to give 4 lines ($J \simeq 6$–7 Hz). In some cases, these 4 lines were further split by H(4) ($J \simeq 0.8$–1.2 Hz) giving rise to 4 sets of doublets. The H(5) protons appeared in the range of 1.92–3.23 ppm as a triplet with broad lines. The signal should be a doublet of doublets due to coupling of H(5) to H(6-*endo*) ($J \simeq 6$–7 Hz) and to H(4) ($J \simeq 4.8$–6.5 Hz), but overlapping gave rise to a triplet. The H(4) protons also gave a broad line triplet in the range of 3.90–4.80 ppm owing to coupling of H(4) to H(5) and H(3) ($J \simeq 4.8$–6.4 Hz). In some cases, fine structures due to coupling to H(6-*endo*) and to H(2) were also observed. For the H(3) protons, the signals always appeared at the lowest field in the range of 5.75–6.47 ppm as a triplet due to splitting by H(2) and H(4) ($J \simeq 4.8$–5.8 Hz). Finally the H(2) protons generally appeared in the range of 3.90–5.90 ppm as a doublet due to splitting by H(3) ($J \simeq 4.8$–5.8 Hz). Again, in rare cases, fine structures were observed due to splitting by H(4) ($J \simeq 0.8$–1.2 Hz).

As an illustration, the spectrum of *o*-adduct IIo, namely, 1–5-η^5-1-nitrocyclohexadienyl-η^5-cyclopentadienyliron, is given in Fig. 1, and this adduct, IIo, was the

Table 1

Data from hydride addition to η^6-substituted benzene-η^5-cyclopentadienyliron cations

Cation[a]	X	σ[b] *para*	Reaction time (h)	Yield (%)[c]	Relative product distribution[d]			
					o-addition	*m*-addition	*p*-addition	*ipso*-addition
Ia	$(CH_3)_2N$	−0.83	18	20	0	1.0	0.47	0
Ib	C_6H_5O	−0.32	3	42	0.39	1.0	0.26	0.02
Ic	CH_3O	−0.27	3	41	0.15(0.2)	1.0(1)	0.50(0.6)	0
Id	*p*-$CH_3C_6H_4S$	–	3	40	0.88	1.0	0.63	0.14
Ie	$C_6H_5CH_2$	–	3	31	0.79	1.0	0.42	0
If	$(CH_3)_3C$	−0.20	3	39	0.67	1.0	1.7	0
Ig	CH_3	−0.17	3[e]	66	1.3(1)	1.0(1)	0.83(1)	0.07
Ih	CH_3CH_2	−0.15	3	52	1.2	1.0	0.91	0
Ii	C_6H_5	−0.01	3	58	2.8	1.0	1.2	0
Ij	Cl	0.23	0.5[e]	75	4.5(4)	1.0(1)	0.50(0)	0
Ik	$COOCH_3$	0.39	0.5	78	7.9(12.7)	1.0(1)	0.71(1.1)	0.28
Il	C_6H_5CO	0.46	5 min[f]	45	5.9	1.0	0.16	0
Im	CN	0.66	0.5	82	21	1.0	0.31	0
In	*p*-$CH_3C_6H_4SO_2$	–	0.5	88	21	1.0	0.18	0
Io	NO_2	0.78	0.5	80	1.0	0	0	0

[a] $C_6H_5XFeCp^+$ cation employed as its hexafluorophosphate in reaction with $NaBH_4$. [b] Hammett substituent constants from ref. 6; negative and positive values indicate electron-donating and electron-withdrawing effects, respectively. [c] Total yield of the mixture of isomeric addition products except in the case of cation Io which gave only one product. Elemental analyses for C, H and N on these mixtures of isomeric products showed good agreements with the calculated values. [d] Mean values from duplicate runs; values in parentheses are the previously reported results obtained by Watts and coworkers as summarized in ref. 4. [e] Increasing the reaction time up to 18 h with cation Ig or Ij did not significantly change the relative product distribution. [f] All reactions were carried out at room temperature except in the case of cation Il for which the reaction was carried out at −20 °C for 5 min in order to minimize reduction of the keto group to the alcohol.

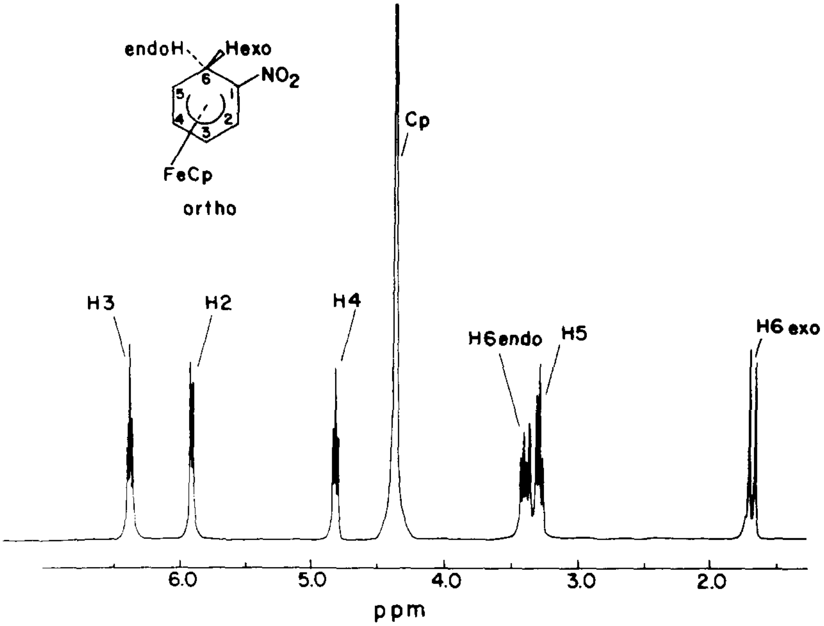


Fig. 1. ^{1}H NMR spectrum for 1–5-η^5-nitrocyclohexadienyl-η^5-cyclopentadienyliron (*o*-adduct-IIo) from the hydride addition to the nitrobenzene complex Io.

only product obtained from the hydride addition to the nitrobenzene complex Io, no *m*-, *p*-, or *ipso*-addition to give IIIo, IVo or Vo being observed in this reaction.

The complexed cyclohexadienyl ring of *m*-adducts IIIa to IIIn also gave signals for 6 protons, H(1), H(3), H(4), H(5), H(6-*exo*) and H(6-*endo*). Similar to the *o*-adducts, the H(6-*exo*) protons appeared at the highest field in the range of 1.32–1.60 ppm as a doublet owing to coupling with H(6-*endo*) ($J \simeq$ 11–13 Hz). The H(6-*endo*) protons were observed in the range of 2.40–2.80 ppm as a five line multiplet arising from splitting by H(6-*exo*) ($J \simeq$ 11–13 Hz) into a doublet each line of which was splitted into a triplet by H(1) and H(5) ($J \simeq$ 6–7 Hz), with overlapping giving rise to five lines. In rare cases, fine structures were observed due to coupling to H(4) ($J \simeq 1$ Hz). The H(5) protons appeared in the range of 2.00–2.92 ppm as a broad line triplet due to splitting by H(6-*endo*) and H(4) ($J \simeq$ 5–7 Hz). The protons for H(3) gave a doublet from coupling with H(4) ($J \simeq$ 5–6 Hz) at the low field region of 5.73–6.93 ppm, while the H(1) protons appeared over a wide range of 1.97–4.33 ppm as a doublet due to splitting by H(6-*endo*) ($J \simeq$ 6–7 Hz). In some cases, fine structures for the H(3) or H(1) doublet were observed owing to long range coupling between H(3) and H(1) or H(3) and H(5) ($J \simeq 1$ Hz).

For the complexed cyclohexadienyl ring of the *p*-adducts, IVa to IVn, because of the symmetry of the molecule, only 4 signals were observed (H(1,5), H(2,4), H(6-*exo*) and H(6-*endo*)). The H(6-*exo*) protons gave a doublet in the range of 1.36–1.56 ppm owing to splitting by H(6-*endo*) ($J \simeq$ 11–13 Hz). The H(6-*endo*) protons gave a multiplet in the range of 1.90–2.60 ppm arising from coupling to H(6-*exo*) ($J \simeq$ 11–13 Hz) and to H(1) and H(5) ($J \simeq$ 6.0–6.5 Hz), but usually, these H(6-*endo*) signals would overlap with other signals in the spectrum and could not be

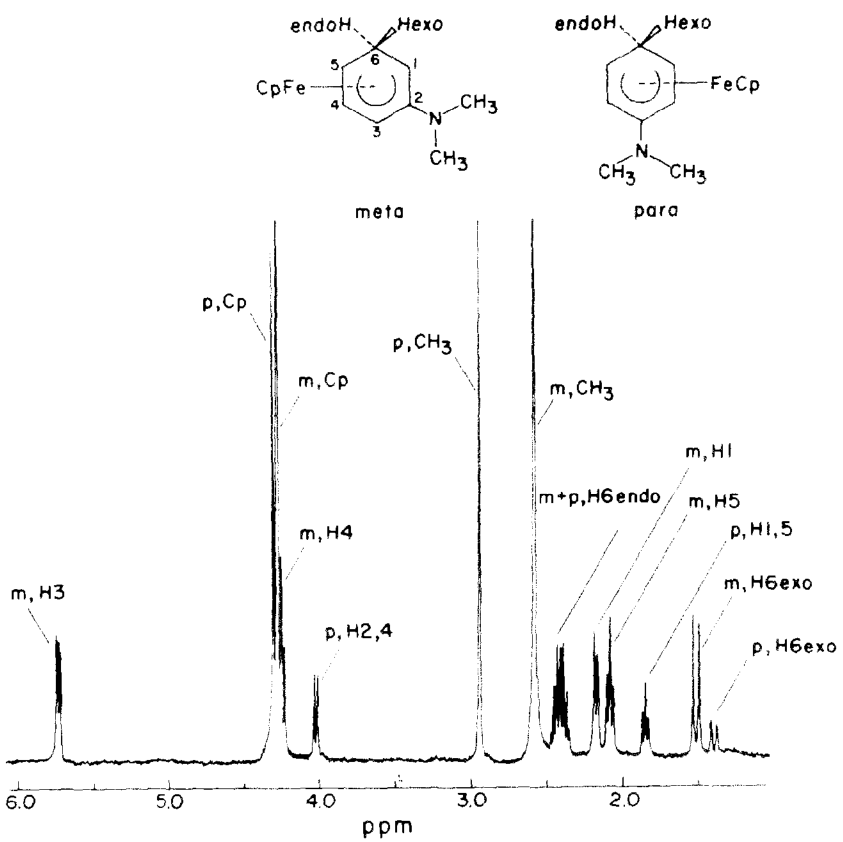


Fig. 2. ^1H NMR spectrum of a mixture of *m*- and *p*-adducts from the hydride addition to the *N*,*N*-dimethylaniline complex Ia.

clearly distinguished. The H(1,5) protons appeared as a triplet arising from overlapping doublets owing to coupling with H(6-*endo*) ($J \approx 6.0$–6.5 Hz) and with H(2,4) ($J \approx 5.5$–6.0 Hz). In some cases, fine structures were observed owing to a long range coupling such as between H(1) and H(4) or H(2) and H(5) ($J \approx 1$ Hz). Protons H(2,4) gave a doublet at 4.00–6.20 ppm owing to splitting by the neighboring H(1) and H(5) protons ($J \approx 6$–6.5 Hz), and again in some cases, long range couplings gave rise to fine structures.

Given in Fig. 2 is the spectrum of a mixture of *m*-adduct IIIa, 1–5-η^5-2-dimethylaminocyclohexadienyl-η^5-cyclopentadienyliron, and *p*-adduct IVa, 1–5-η^5-3-dimethylaminocyclohexadienyl-η^5-cyclopentadienyliron, this mixture being obtained from the hydride addition to the *N*,*N*-dimethylaniline complex Ia. No *o*-adduct IIa or *ipso*-adduct Va was formed in this reaction. Summarized in Table 2 are the 300 MHz ^1H NMR data for all the *o*-, *m*- and *p*-adducts obtained in the present studies on hydride additions to cations Ia to Io.

In the ^1H NMR spectra of a few of the product mixtures from the hydride addition reactions, extra lines other than those assigned to the *o*-, *m*- and *p*-adducts were observed, and these absorptions were attributed to the *ipso*-adduct. For example, in the reaction with the phenoxybenzene complex Ib, besides the *o*-, *m*-

and p-adducts IIb, IIIb and IVb, additional ^1H NMR signals attributable to *ipso*-adduct Vb were observed at δ 1.42 (s, H(6-*exo*)), 2.13 (d, H(1,5)), 4.24 (t, H(2,4)) and 6.08 (t, H(3)) ppm. The Cp and uncomplexed phenyl protons for Vb were not observable and were presumably hidden by overlapping with other signals.

For the determination of the relative product distributions, various regions of a spectrum containing distinctly separated peaks were expanded and integrated, and using the ratios of the integrated areas, the product distributions were calculated. As an illustration of the actual data, take, for example, the spectrum shown in Fig. 2 for the mixture of m-adduct IIIa and p-adduct IVa from the hydride addition to cation Ia. The integrated areas of the CH_3 singlets at 2.57 ppm for IIIa and 2.94 ppm for IVa were 116.4 and 27.6 units, respectively. Taking into account the statistical factor of 2 for m-addition over p-addition, the relative ratio of p-adduct/m-adduct would be $(27.6 \times 2)/116.4 = 0.47$. Similarly, the integrated areas for the absorptions of H(6-*exo*) at 1.38 ppm and H(1,5) at 1.84 ppm for the p-adduct were 4.2 and 8.4 units, while the corresponding areas for H(6-*exo*) at 1.50 ppm, H(1) at 2.17 ppm, and H(5) at 2.08 ppm for the m-adduct were 17.6, 17.9 and 17.7 units, giving a relative ratio for p-adduct/m-adduct of $2(4.2 + 8.4)/(17.6 + 17.9 + 17.7) = 0.47$. Moreover, in the lower field region, the integrated area for H(2,4) at 4.02 ppm for the p-adduct was 6.2, while the integrated area for H(3) at 5.73 ppm for the m-adduct was 13.2 units. As these integrals were due to 2 protons in both m- and p-adducts, the relative ratio of p-adduct/m-adduct $= 6.2/13.2 = 0.47$. These calculations thus showed remarkable agreements, giving a p-adduct/m-adduct ratio of 0.47 in the hydride addition to the *N*,*N*-dimethylaniline complex Ia. Results on the relative product distributions for all the hydride addition reactions studied are summarized in Table 1.

For comparison with the present results, the relative product distributions reported by Watts and coworkers [1–4] for the hydride addition to the CpFe complex of anisole (Ic), toluene (Ig), chlorobenzene (Ij) or methyl benzoate (Ik) are also given in Table 1. One obvious difference is the reported absence of any p-adduct in the hydride addition to the chlorobenzene complex Ij, although the authors stated that the formation of his adduct in a relatively minor amount was not excluded [2]. Similarly, in the addition of one hydride ion to the η^6-chlorobenzene-η^5-pentamethylcyclopentadienyliridium dication, Grundy and Maitlis [7] also reported the absence of the p-adduct, while with an increased reaction time and an increased amount of $NaBH_4$, some substitution of the chloride ion by the hydride ion was observed. In the present work, p-adduct IVj from cation Ij was definitely obtained, the ratio for *ortho/meta/para* addition being 4.5/1.0/0.50. The ^1H NMR spectrum for this mixture of products is given in Fig. 3, with the various assignments shown in the spectrum, and when necessary, these assignments were confirmed by homonuclear decoupling. When the time for the reaction of Ij with $NaBH_4$ was extended to 18 h, the spectrum of the product mixture was essentially the same indicating no significant change in the relative product distribution. However, after the removal of the hydride addition products by extraction with $CHCl_3$, a further extraction of the residual mixture with CH_2Cl_2 led to the recovery of about 10% of the CpFe complex of benzene, indicating that a prolonged reaction time did result in the formation of some substitution product as was observed by Grundy and Maitlis [7].

The relative $o/m/p$-adduct distribution in the hydride addition to the toluene

(Continued on p. 377)

Table 2

Chemical shifts and first order coupling constants from the 300 MHz ^{1}H NMR spectra of the *ortho, meta* and *para* adducts from hydride addition reactions with cations Ia to Io

Complex [a]	$\delta(CDCl_3)$ (ppm for TMS)								
	Cp	H(1)	H(2)	H(3)	H(4)	H(5)	H(6-*endo*)	H(6-*exo*)	Others
2-$C_6H_5(N(CH_3)_2)$FeCp	4.27	2.17	–	5.73	4.24	2.08	2.40	1.50	2.94 (s, CH_3)
(IIIa)	$J_{3,4} = J_{4,5} = 5.3$ Hz; $J_{1,6\text{-}endo} = J_{5,6\text{-}endo} = 6.8$ Hz; $J_{6\text{-}exo,6\text{-}endo} = 12.3$ Hz								
3-$C_6H_5(N(CH_3)_2)$FeCp	4.30	1.84	4.02	–	4.02	1.84	2.40 [b]	1.38	2.57 (s, CH_3)
(IVa)	$J_{1,2} = J_{4,5} = 6.5$ Hz; $J_{1,6\text{-}endo} = J_{5,6\text{-}endo} = 6.5$ Hz; $J_{6\text{-}exo,6\text{-}endo} = 12.3$ Hz								
1-$C_6H_5(OC_6H_5)$FeCp	4.38	–	4.44	5.83	4.14	1.92	2.78	2.00	6.8–7.4 (m, Ar)
(IIb)	$J_{2,3} = J_{3,4} = 5.0$ Hz; $J_{4,5} = 6.4$ Hz; $J_{5,6\text{-}endo} = 7.0$ Hz; $J_{6\text{-}exo,6\text{-}endo} = 12.2$ Hz								
2-$C_6H_5(OC_6H_5)$FeCp	4.36	2.42	–	6.26	4.31	2.05	2.53	1.67	6.8–7.4 (m, Ar)
(IIIb)	$J_{3,4} = 5.4$ Hz; $J_{4,5} = 6.2$ Hz; $J_{1,6\text{-}endo} = J_{5,6\text{-}endo} = 6.8$ Hz; $J_{6\text{-}exo,6\text{-}endo} = 12.6$ Hz								
3-$C_6H_5(OC_6H_5)$FeCp	4.35	2.62	4.58	–	4.58	2.62	2.43 [b]	1.55	6.8–7.4 (m, Ar)
(IVb)	$J_{1,2} = J_{4,5} = 6.4$ Hz; $J_{1,6\text{-}endo} = J_{5,6\text{-}endo} = 6.4$ Hz; $J_{6\text{-}exo,6\text{-}endo} = 13.0$ Hz								
1-$C_6H_5(OCH_3)$FeCp	4.25	–	4.11	5.75	4.03	2.34	2.97	1.94	3.93 (s, CH_3O)
(IIc)	$J_{2,3} = J_{3,4} = J_{4,5} = 5.4$ Hz; $J_{5,6\text{-}endo} = 6.4$ Hz; $J_{6\text{-}exo,6\text{-}endo} = 12.6$ Hz								
2-$C_6H_5(OCH_3)$FeCp	4.26	2.37	–	6.09	4.26 [b]	2.00	2.46	1.53	3.48 (s, CH_3O)
(IIIc)	$J_{3,4} = J_{4,5} = 5.2$ Hz; $J_{1,6\text{-}endo} = J_{5,6\text{-}endo} = 6.5$ Hz; $J_{6\text{-}exo,6\text{-}endo} = 12.1$ Hz								
3-$C_6H_5(OCH_3)$FeCp	4.29	1.79	4.40	–	4.40	1.79	2.40 [b]	1.36	3.93 (s, CHO_3)
(IVc)	$J_{1,2} = J_{4,5} = 6.4$ Hz; $J_{1,6\text{-}endo} = J_{5,6\text{-}endo} = 6.5$ Hz; $J_{6\text{-}exo,6\text{-}endo} = 12.5$ Hz								
1-$C_6H_5(SC_6H_4CH_3\text{-}p)$FeCp	4.38	–	4.69	6.06	4.33 [b]	2.53 [b]	2.42	1.54	2.28 (s, CHO_3);
(IId)	$J_{2,3} = J_{3,4} = 5.0$ Hz; $J_{5,6\text{-}endo} = 7.0$ Hz; $J_{6\text{-}exo,6\text{-}endo} = 12.4$ Hz								6.9–7.5 (m, Ar)
2-$C_6H_5(SC_6H_4CH_3\text{-}p)$FeCp	4.37	2.53 [b]	–	6.30	4.30 [b]	2.53 [b]	2.48 [b]	1.76	2.24 (s, CH_3);
(IIId)	$J_{3,4} = J_{4,5} = 5.0$ Hz; $J_{6\text{-}exo,6\text{-}endo} = 12.5$ Hz								6.9–7.5 (m, Ar)
3-$C_6H_5(SC_6H_4CH_3\text{-}p$-FeCp	4.32	2.24 [b]	4.58	–	4.58	2.24 [b]	2.55 [b]	1.63	2.33 (s, CH_3);
(IVd)	$J_{1,2} = J_{4,5} = 6.4$								6.9–7.5 (m, Ar)
1-$C_6H_5(CH_2C_6H_5)$FeCp	4.24		[b]	5.97	4.25	[b]	2.30	1.40	2.84, 3.32 (CH_2,
(IIe)	$J_{2,3} = J_{3,4} = 5.1$ Hz; $J_{5,6\text{-}endo} = 6.7$ Hz; $J_{6\text{-}exo,6\text{-}endo} = 12.2$ Hz								$J = 14.4$ Hz);
									7.1–7.5 (m, Ar)
2-$C_6H_5(CH_2C_6H_5)$FeCp	4.25	[b]	–	6.06	4.25 [b]	2.06	2.45	1.47	2.91, 3.53 (CH_2,
(IIIe)	$J_{3,4} = J_{4,5} = 5.0$ Hz; $J_{5,6\text{-}endo} = J_{1,6\text{-}endo} = 6.5$ Hz; $J_{6\text{-}exo,6\text{-}endo} = 12.4$ Hz								$J = 14.7$ Hz);
									7.1–7.5 (m, Ar)

3-$C_6H_5(CH_2C_6H_5)$FeCp	4.22	2.11	4.21^{b}	–	4.21^{b}	2.11	2.37	1.43	3.98 (s, CH_2); 7.1–7.5 (m, Ar)
(IVe)	$J_{1,2} = J_{4,5} = 6.5$ Hz; $J_{1,6\text{-}endo} = J_{5,6\text{-}endo} = 6.2$ Hz; $J_{6\text{-}exo,6\text{-}endo} = 12.2$ Hz								
1-$C_6H_5(C(CH_3)_3)$FeCp	4.24.	–	4.20^{b}	6.01	4.20^{b}	2.00^{b}	2.48^{b}	1.26	1.02 (s, CH_3)
(IIf)	$J_{2,3} = J_{3,4} = 5.1$ Hz; $J_{6\text{-}exo,6\text{-}endo} = 12.3$ Hz								
2-$C_6H_5(C(CH_3)_3)$FeCp	4.25	2.19	–	6.08	4.20^{b}	2.04	2.15^{b}	1.39	1.14 (s, CH_3)
(IIIf)	$J_{3,4} = 5.2$ Hz; $J_{1,6\text{-}endo} = J_{5,6\text{-}endo} = 6.6$ Hz; $J_{6\text{-}exo,6\text{-}endo} = 12.4$ Hz								
3-$C_6H_5(C(CH_3)_3)$FeCp	4.23	2.04	2.48^{b}	–	2.48^{b}	2.04	2.15^{b}	1.39	1.54 (s, CH_3)
(IVf)	$J_{1,6\text{-}endo} = J_{5,6\text{-}endo} = 6.6$ Hz; $J_{6\text{-}exo,6\text{-}endo} = 12.5$ Hz								
1-$C_6H_5(CH_3)$FeCp	4.16	–	3.96	5.92	4.20^{b}	2.09^{b}	2.29	1.53	1.38 (s, CH_3)
(IIg)	$J_{2,3} = J_{3,4} = 5.0$ Hz; $J_{5,6\text{-}endo} = 6.4$ Hz; $J_{6\text{-}exo,6\text{-}endo} = 12.4$ Hz								
2-$C_6H_5(CH_3)$FeCp	4.17	1.97	–	6.00	4.20^{b}	2.07^{b}	2.33^{b}	1.38^{b}	1.76 (s, CH_3)
(IIIg)	$J_{3,4} = 5.0$ Hz; $J_{1,6\text{-}endo} = J_{5,6\text{-}endo} = 6.5$ Hz; $J_{6\text{-}exo,6\text{-}endo} = 12.5$ Hz								
3-$C_6H_5(CH_3)$FeCp	4.16	1.96^{b}	2.09^{b}	–	2.09^{b}	1.96^{b}	2.37^{b}	1.38^{b}	2.55 (s, CH_3)
(IVg)	$J_{1,6\text{-}endo} = J_{5,6\text{-}endo} = 6.5$ Hz; $J_{6\text{-}exo,6\text{-}endo} = 12.8$ Hz								
1-$C_6H_5(C_2H_5)$FeCp	4.18	–	3.99	5.93	4.20	2.10^{b}	2.30	1.58	0.85 (t, CH_3), 1.93 (q, CH_2) $J = 7.4$ Hz
(IIh)	$J_{2,3} = J_{3,4} = 5.0$ Hz; $J_{5,6\text{-}endo} = 6.7$ Hz; $J_{6\text{-}exo,6\text{-}endo} = 12.4$ Hz								
2-$C_6H_5(C_2H_5)$FeCp	4.17	2.12^{b}	–	6.02	4.20^{b}	2.12^{b}	2.05^{b}	1.44	1.12 (t, CH_3), 1.78 (q, CH_2) $J = 7.5$ Hz
(IIIh)	$J_{3,4} = 5.1$ Hz; $J_{6\text{-}exo,6\text{-}endo} = 12.8$ Hz								
3-$C_6H_5(C_2H_5)$FeCp	4.19	2.02^{b}	2.13^{b}	–	2.13^{b}	2.02^{b}	2.42	1.56	1.47 (t, CH_3), 2.87 (q, CH_2) $J = 7.5$ Hz
(IVh)	$J_{6\text{-}exo,6\text{-}endo} = 12.6$ Hz								
1-$C_6H_5(C_6H_5)$FeCp	4.11	–	4.80	6.29	4.48	2.53	3.03	1.74	7.1–7.9 (m, Ar)
(IIi)	$J_{2,3} = J_{3,4} = 5.6$ Hz, $J_{4,5} = 6.4$ Hz; $J_{5,6\text{-}endo} = 6.8$ Hz; $J_{6\text{-}exo,6\text{-}endo} = 12.4$ Hz								
2-$C_6H_5(C_6H_5)$FeCp	4.13	2.71	–	6.56	4.42	2.20	2.62	1.55	7.1–7.9 (m, Ar)
(IIIi)	$J_{3,4} = 5.5$ Hz; $J_{4,5} = 5.9$ Hz; $J_{1,6\text{-}endo} = J_{5,6\text{-}endo} = 6.6$ Hz; $J_{6\text{-}exo,6\text{-}endo} = 12.6$ Hz								
3-$C_6H_5(C_6H_5)$FeCp	4.17	2.32	4.78	–	4.78	2.32	2.49	1.56	7.1–7.9 (m, Ar)
(IVi)	$J_{1,2} = J_{4,5} = 6.0$ Hz; $J_{1,6\text{-}endo} = J_{5,6\text{-}endo} = 6.6$ Hz; $J_{6\text{-}exo,6\text{-}endo} = 12.0$ Hz								
1-C_6H_5ClFeCp	4.35	–	4.57	5.94	4.19	2.62	2.90	1.98	–
(IIj)	$J_{2,3} = J_{3,4} = 5.3$ Hz; $J_{4,5} = 5.8$ Hz; $J_{5,6\text{-}endo} = 7.0$ Hz; $J_{6\text{-}exo,6\text{-}endo} = 12.4$ Hz								
2-C_6H_5ClFeCp	4.34	2.57	–	6.34	4.30^{b}	2.07	2.48	1.56	–
(IIIj)	$J_{3,4} = J_{4,5} = 5.0$ Hz; $J_{1,6\text{-}endo} = J_{5,6\text{-}endo} = 6.5$ Hz; $J_{6\text{-}exo,6\text{-}endo} = 12.2$ Hz								

Table 2 (continued)

Complex [a]	$\delta(CDCl_3)$ (ppm for TMS)								
	Cp	H(1)	H(2)	H(3)	H(4)	H(5)	H(6-*endo*)	H(6-*exo*)	Others
3-$C_6H_5ClFeCp$	4.32	1.98 [b]	4.69	–	4.69	1.98 [b]	2.35	1.42	–
(IVj)	$J_{1,2} = J_{4,5} = 6.2$ Hz; $J_{6\text{-}exo,6\text{-}endo} = 12.7$ Hz								
1-$C_6H_5(COOCH_3)FeCp$	4.26	–	5.28	6.33	4.61	2.68	2.85	1.29	3.72 (s, CH_3O)
(IIk)	$J_{2,3} = J_{3,4} = 5.2$ Hz; $J_{4,5} = 5.7$ Hz; $J_{5,6\text{-}endo} = 6.8$ Hz; $J_{6\text{-}exo,6\text{-}endo} = 12.9$ Hz								
2-$C_6H_5(COOCH_3)FeCp$	4.28	2.48	–	6.93	4.36 [b]	2.60 [b]	2.80 [b]	1.38	3.73 (s, CH_3O)
(IIIk)	$J_{3,4} = J_{4,5} = 5.5$ Hz; $J_{6\text{-}exo,6\text{-}endo} = 12.6$ Hz								
3-$C_6H_5(COOCH_3)FeCp$	4.25	2.25	5.15	–	5.15	2.25	1.98	1.43	3.97 (s, CH_3O)
(IVk)	$J_{1,2} = J_{4,5} = 6.4$ Hz; $J_{6\text{-}exo,6\text{-}endo} = 12.0$ Hz								
1-$C_6H_5(COC_6H_5)FeCp$	4.25	–	5.50	6.47	4.79	2.79	2.94	1.43	7.4–7.8 (m, Ar)
(IIl)	$J_{2,3} = J_{3,4} = 5.4$ Hz; $J_{4,5} = 5.8$ Hz; $J_{5,6\text{-}endo} = 6.9$ Hz; $J_{6\text{-}exo,6\text{-}endo} = 12.8$ Hz								
2-$C_6H_5(COC_6H_5)FeCp$	4.27	2.50	–	6.84	4.30 [b]	2.32	2.58 [b]	1.47	7.4–7.8 (m, Ar)
(IIIl)	$J_{3,4} = J_{4,5} = 5.0$ Hz; $J_{1,6\text{-}endo} = J_{5,6\text{-}endo} = 6.9$ Hz; $J_{6\text{-}exo,6\text{-}endo} = 12.4$ Hz								
3-$C_6H_5(COC_6H_5)FeCp$	4.22	2.24	4.54	–	4.54	2.24	2.48 [b]	1.50 [b]	7.4–7.8 (m, Ar)
(IVl)	$J_{1,2} = J_{4,5} = 6.2$ Hz								
1-$C_6H_5(CN)FeCp$	4.46	–	4.92	6.27	4.58	2.72	2.48	1.54	–
(IIm)	$J_{2,3} = J_{3,4} = 5.4$ Hz; $J_{4,5} = 5.8$ Hz; $J_{5,6\text{-}endo} = 6.8$ Hz; $J_{6\text{-}exo,6\text{-}endo} = 12.5$ Hz								
2-$C_6H_5(CN)FeCp$	4.47	2.32 [b]	–	6.49	6.05	2.92	2.52	1.40	–
(IIIm)	$J_{3,4} = 5.2$ Hz; $J_{4,5} = 6.4$ Hz; $J_{1,6\text{-}endo} = J_{5,6\text{-}endo} = 7.2$ Hz; $J_{6\text{-}exo,6\text{-}endo} = 12.2$ Hz								
3-$C_6H_5(CN)FeCp$	4.41	2.80 [b]	6.12	–	6.12	2.80 [b]	2.60 [b]	1.44	–
(IVm)	$J_{1,2} = J_{4,5} = 5.0$ Hz								
1-$C_6H_5(SO_2C_6H_4CH_3\text{-}p)FeCp$	4.64	–	5.13	6.16	4.61	2.82	2.67	0.95	2.33 (s, CH_3); 7.2–8.0 (m, Ar)
(IIn)	$J_{2,3} = J_{4,5} = 5.6$ Hz; $J_{4,5} = 5.8$ Hz; $J_{5,6\text{-}endo} = 7.2$ Hz; $J_{6\text{-}exo,6\text{-}endo} = 11.8$ Hz								
2-$C_6H_5(SO_2C_6H_4CH_3\text{-}p)FeCp$	4.64	4.33	–	6.73	4.38	[b]	2.50 [b]	1.32	2.39 (s, CH_3); 7.2–8.0 (m, Ar)
(IIIn)	$J_{3,4} = 5.0$ Hz; $J_{4,5} = 5.5$ Hz; $J_{6\text{-}exo,6\text{-}endo} = 13.3$ Hz								
3-$C_6H_5(SO_2C_6H_4CH_3\text{-}p)FeCp$	4.52	[b]	5.02	–	5.02	[b]	2.49 [b]	1.52	2.40 (s, CH_3); 7.2–8.0 (m, Ar)
(IVn)	$J_{1,2} = J_{4,5} = 6.5$ Hz; $J_{6\text{-}exo,6\text{-}endo} = 11.9$ Hz								
1-$C_6H_5(NO_2)FeCp$	4.35	–	5.90	6.37	4.80	3.23	3.35	1.64	–
(IIo)	$J_{2,3} = J_{3,4} = J_{4,5} = 5.4$ Hz; $J_{5,6\text{-}endo} = 7.2$ Hz; $J_{6\text{-}exo,6\text{-}endo} = 12.9$ Hz								

[a] Complexes IIb to IIo, IIIa to IIIn, and IVa to IVn, respectively, were derived from *o*-, *m*- and *p*-additions of the hydride ion to cations Ia to Io; no *o*-adduct IIa from cation Ia, nor *m*-adduct IIIo and *p*-adduct IVo from cation Io, were obtained. [b] Signals not clearly separated or hidden due to overlapping with other signals.

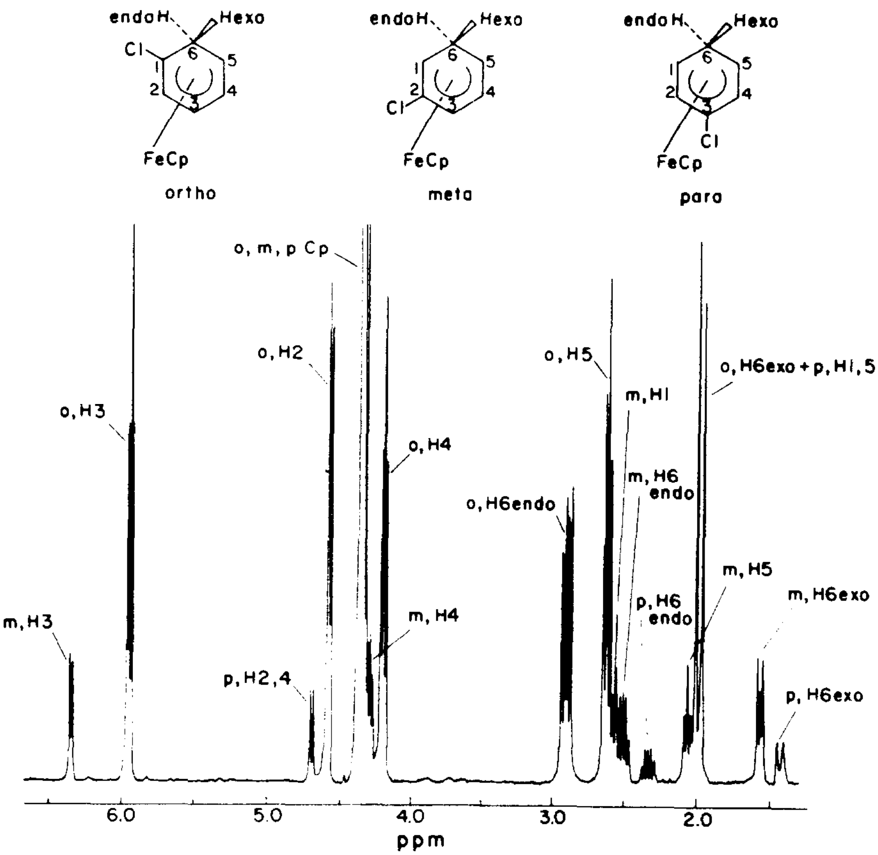


Fig. 3. ^{1}H NMR spectrum for the mixture of *o*-, *m*- and *p*-adducts from the hydride addition to the chlorobenzene complex Ij.

complex Ig was reported by Watts and coworkers to be 1/1/1 [1], while the analogous ratio obtained in the present work was 1.3/1.0/0.83. Although the difference is small, the present results may suggest a slight preference for *o*-addition. In the addition of one hydride ion to the $(CH_3)_5C_5Ir$ complex of toluene, the *o/m/p* adduct ratio was also reported to be about 1/1/1 [7]. This latter result was based on actual ^{1}H NMR integrals of 47/37/17 [7], which would correspond to an *o/m/p* ratio of $47/37/(2 \times 17) = 1.2/1.0/0.92$, and this ratio again suggested the possibility of a somewhat greater extent of *o*-addition. From the theoretical calculations of Clack and Kane-Maguire [5], it was concluded that charge variations alone could not explain the marked *o*-directing influence of the substituent in the hydride addition to the CpFe complexed methyl benzoate (Ib), and it was suggested that if one were to exclude addition at the *ipso*-position for steric reasons, the calculated C–C bond orders would indicate that the C(2) position would have the highest free valency, thus favoring *o*-addition. Such an effect may have played a role in giving rise to a somewhat greater amount of *o*-adduct in the hydride addition to toluene complex Ig. Clack and Kane-Maguire [5] also pointed out that if the products were not kinetically controlled, rearrangements could occur after the initial nucleophilic additions. When the reaction of toluene complex Ig with $NaBH_4$ was extended up to 18 h, no appreciable difference in the relative product distribution was observed, and this behavior, similar to that found for the chlorobenzene complex Ij, indicated no further equilibration among the *o*-, *m*- and *p*-adducts even with an extended reaction time.

Considering all the results summarized in Table 1, it is clear that electronic effects of substituent X in cations Ia to Io do play an important role in the addition of the hydride ion to these cations. For cation Ia, with $X = (CH_3)_2N$, the most electron-donating of all the substituents studied, the longest reaction time was required to give the lowest yield of 20% of *m*-adduct IIIa and *p*-adduct IVa, with no detectable amount of *o*-adduct IIa. These results are consistent with a nucleophilic addition of the hydride ion. For cations Ib to Ie, with $X = C_6H_5O$, CH_3O, p-$CH_3C_6H_4S$ and $C_6H_5CH_2$, respectively, the substituents are electron donating, but less powerfully than $(CH_3)_2N$ in Ia, all three *o*-, *m*-, and *p*-adducts were formed with the major product derived from *m*-addition. As suggested by Watts and coworkers [3] for the anisole complex Ic, with $X = CH_3O$, a major factor may be the electron-donating resonance effect ($+R$), which would render the *m*-position the most electron deficient, thus giving rise to the *m*-adduct as the major product. Superimposed on the electronic effect may be the effect of free valency favoring *o*-addition as suggested by the calculations of Clack and Kane-Maguire [5]; however with cations Ib to Ie, any extra *o*-addition due to free valency apparently could not reverse the $+R$ effect of the substituent and the *m*-adduct was found to be the major product.

In the hydride addition to the toluene complex Ig or ethylbenzene complex Ih, slightly more *o*-adduct than the *m*- or *p*-adduct was obtained. Since the methyl or ethyl substituent was only weakly electron-donating, probably, the free valency effect favoring *o*-addition [5] would be of relatively greater significance, resulting in the observed product distribution showing a small preference for *o*-addition. A similar trend could be invoked for cation Ii with $X = C_6H_5$, the still weaker overall electron-donating effect of the phenyl substituent giving a relative product distribution with a greater amount of *o*-adduct than in the case of cation Ig or Ih. For the t-butylbenzene complex If, however, the amount of *o*-adduct was the least among the *o*-, *m*- and *p*-isomers, suggesting that a steric hindrance effect could play a role in the hydride addition to If. As was pointed out by Clack and Kane-Maguire [5], the steric effect could also have been an important factor in accounting for the absence or only minor presence of *ipso*-adducts in these reactions.

For reactions with cations Ij to Io, with $X = Cl$, $COOCH_3$, C_6H_5CO, CN, p-$CH_3C_6H_4SO_2$ and NO_2, respectively, all of the substituents are electron-withdrawing and the reactions, carried out with a relatively short reaction time, generally gave much better yields than those obtained with cations Ia to Ii, which contain electron-donating substituents. These observations again are consistent with a nucleophilic addition. In the case of the benzophenone complex Il, however, since it is known that $NaBH_4$ could reduce the keto group to the alcohol [9], in order to minimize reduction, the hydride addition reaction was carried out at −20 °C for 5 min, giving a resulting yield of only 45%. We have also found that the cyclohexadienyl complexes obtained in the hydride addition reactions could be decomposed by treatment with dilute HCl, thereby regenerating the original CpFe complexed substituted benzene. A similar decomposition of a cyclohexadienyl adduct in order to regenerate the original complexed arene has been reported previously [10]. When the product mixture from the hydride addition to Il was treated with 5% HCl, cation Il was recovered as its hexafluorophosphate with less than 5% contamination by materials from reduction. This finding thus indicated that under the condition employed ($-20\,^{\circ}$C, 5 min), the *o*-, *m*- and *p*-adducts obtained were indeed derived from addition to the keto complex Il, and not from addition occurring subsequent to a reduction of the keto group.

The major product from the hydride addition to cations Ij to In was the *o*-adduct, and in the case of nitrobenzene complex Io, with the most electron-withdrawing of the substituents studied, the only product obtained was derived from *o*-addition. Again superimposed on the electronic effect could be the effect of free valency favoring *o*-addition [5], with the two factors reinforcing each other, giving rise to the observed predominant formation of the *o*-adduct, especially for cations with a substituent that would exert electron-withdrawing effects both inductively ($-I$) and by resonance ($-R$) [4]. Thus from the present work, it appears that electronic, steric and free valency effects all could play a role in influencing the hydride addition reactions, with the relative product distributions determined by the net overall effect of all of these factors.

Recently, we have reported that additions of carbanions derived from ketones to cations such as Il, Im, In and Io took place solely at the *o*-position to the substituent [11,12]. Similarly, addition of the cyanide ion to cations such as Ik, Il and Io also gave only the *o*-adduct [13]. In these nucleophilic addition reactions, as in the hydride addition, the relatively powerful electron-withdrawing effect of the substituent, possibly together with a reinforcing effect for *o*-addition due to free valency [5], may be the chief factors in influencing the observed result of a regiospecific addition of the nucleophile at a position *ortho* to the electron-withdrawing substituent.

Experimental

η^6-Substituted benzene-η^5-cyclopentadienyliron cations (Ia to Io)

Known methods were employed for the preparation of cations Ia to Io, all of which were isolated as their hexafluorophosphate salts. The *N,N*-dimethylaniline complex Ia was obtained as described by Helling and Hendrickson [14]. Cations Ib, Ic and Ie to Ij were prepared from ligand exchange reactions between ferrocene and an arene as summarized in a review by Sutherland [15]. The *p*-tolylthiobenzene complex Id was obtained via a nucleophilic substitution reaction between *p*-toluenethiol and the nitrobenzene complex Io [16], the latter complex, Io, being prepared by oxidation of the CpFe complex of aniline [17]. Conversion of Id to the sulfone complex In was effected by oxidation with *m*-chloroperbenzoic acid [10], while $KMnO_4$ oxidation of the diphenylmethane complex gave the benzophenone complex Il [18]. A nucleophilic substitution reaction between KCN and the chlorobenzene complex Ij gave the cyanobenzene complex Im [19], while the methyl benzoate complex Ik was prepared as described by McGreer and Watts [4].

Hydride addition reactions

As an illustration of the hydride addition reactions, a solution of 193 mg (0.5 mmol) of η^6-*N,N*-dimethylaniline-η^5-cyclopentadienyliron hexafluorophosphate (Ia-

PF_6) and 150 mg (4.0 mmol) of $NaBH_4$ in 10 ml of 1,2-dimethoxyethane (glyme) was stirred at room temperature for 18 h. The mixture was then filtered through a sintered glass filter, 15 ml of H_2O was added and the material was extracted with $CHCl_3$ (3 × 25 ml). The combined extract was washed with H_2O, dried over $MgSO_4$, and the solvent removed by a rotary evaporator. The residue was purified by passage through a short column (5 cm) packed with F-20 alumina (Alcoa Chemical Co.) which had been deactivated by exposure to air for 48 h. Any inpurities were first eluted with pentane and the hydride addition products were eluted with $CHCl_3$. Upon removal of the solvent from the eluate, 25 mg (20%) of a mixture of *m*-adduct IIIa and *p*-adduct IVa was recovered as a red solid.

Similarly, 0.5 to 1.0 mmol of the hexafluorophosphate salt of Ib to Ii and an excess of $NaBH_4$ in 10 ml of glyme was stirred at room temperature for 3 h and then worked up as described above to give the hydride addition products, with their yields and relative product distributions summarized in Table 1.

For reactions with cations Ij to Io, instead of glyme, the solvent employed was THF in which the hexafluorophosphate salts of Ij to Io were more readily soluble. Except for the benzophenone complex Il, the reaction time was 0.5 h. After the usual work-up, the results on yields and relative product distributions are summarized in Table 1.

With cation Il, in order to minimize the possible reduction of the keto group to the alcohol, the reaction with $NaBH_4$ was carried out at −20 °C for 5 min. After the usual work-up, the results obtained are also given in Table 1. In a similar treatment of Il-PF_6 with $NaBH_4$ at −20 °C for 5 min, instead of quenching the reaction by the addition of H_2O followed by extraction with $CHCl_3$, the reaction mixture was treated with 5% HCl, followed by the introduction of one molar equivalent of NH_4PF_6 and extraction with CH_2Cl_2. After drying the CH_2Cl_2 extract over $MgSO_4$, removal of the solvent gave an 85% recovery of the regenerated Il-PF_6, the NMR spectrum of which show less than 5% contamination by possible reduction products.

The ^1H NMR spectra of the hydride addition products were recorded in $CDCl_3$ with TMS as internal standard using a Bruker AM 300 spectrometer.

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