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Studies on 2–6-η^5-cyclohexadienone-η^5-cyclopentadienyliron and some related systems

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Abstract

2–6-η^5-Cyclohexadienone-η^5-cyclopentadienyliron (Ia) and a number of related systems including the CpFe complexed 2-, 3- and 4-methylcyclohexadienones (Ib, Ic and Id), 2-, 3- and 4-chlorocyclohexadienones (Ie, If and Ig), and cyclohexadienethione (Ih) were prepared. The procedure used involved modifications of a previous method to ensure the purity of the products. The ^1H NMR spectra of these complexes in an aprotic solvent such as $CDCl_3$ or $(CD_3)_2CO$ gave broad, unresolved peaks for the cyclohexadienyl protons, while in a solvent system containing a protic component such as 4/1 $(CD_3)_2CO/D_2O$, the expected coupling patterns were observed. Changes in chemical shifts with different concentrations of D_2O in $(CD_3)_2CO$ were correlated with a model involving a 1/1 association of D_2O and a complexed cyclohexadienone. Probable explanations of these behaviors are proposed. It was also found that these complexed cyclohexadienones did not react with reagents that typically would react with ketones. A previously reported reaction between Ia, Ie or Ih and diazomethane to give a ring expansion was found to be in error since no such reaction took place.

Introduction

Cyclohexadienones are known to form η^5 complexes with various metal moieties, producing stable structures with the five non-carbonyl carbon atoms of the ring involved in bonding to the metal. Ruthenium [1], rhodium [1–5], iridium [2], chromium [6], cobalt [7], iron [8] and manganese [9] have been reported to be among the metals capable of forming such complexes. The cyclopentadienyliron (CpFe) complex of cyclohexadienone was reported first by Helling and Hendrickson [8] along with the sulfur and nitrogen analogs. In a preliminary communication [10] we reported that the CpFe complex of cyclohexadienone (Ia) gave a ring expansion upon treatment with diazomethane. Subsequent investigations, however, have shown that this conclusion was erroneous. The present paper describes the results from our studies on Ia and some related systems.

Results and discussion

When 2–6-η^5-cyclohexadienone-η^5-cyclopentadienyliron (Ia) was prepared from treatment of η^6-chlorobenzene-η^5-cyclopentadienyliron hexafluorophosphate with KOH in 50% aqueous acetone and worked up as described in the literature [8], the product obtained was difficult to purify, some residual water and inorganic hexafluorophosphate impurities being present even after treatment by column chromatography. Analytical results from such an impure product contributed significantly to our earlier erroneous conclusion of a ring expansion reaction [10]. A modification involving the use of $CHCl_3$ instead of CH_2Cl_2 as a solvent for the extraction of the product and further purifications after column chromatography as described in the Experimental section led to the recovery of pure Ia. In a similar way, the CpFe complexes of 2-, 3- or 4-methylcyclohexadienone (Ib, Ic or Id, respectively) and 2-, 3- or 4-chlorocyclohexadienone (Ie, If or Ig, respectively) were prepared from reactions of KOH with the CpFe complexes of *o*, *m*- or *p*-chlorotoluene and *o*, *m*- or *p*-dichlorobenzene. When the chlorobenzene complex was treated with NaSH instead of KOH and the product purified in the same way, 2-6-η^5-

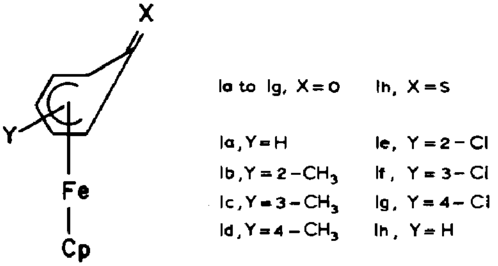


Table 1

Data for CpFe complexed cyclohexadienones Ia to Ig and cyclohexadienethione Ih

Complex [a]	Yield (%)	Physical state	MS [b] (*m/e*) (% base peak)	IR [c] (KBr) ν(CO) (cm^{-1})	Analysis (Found (calcd) (%))	
					C	H
Ia	43	Red crystals	214(20)	1535	61.60 (61.72)	4.90 (4.71)
Ib	22	Red crystals	228(100)	1530	63.34 (63.19)	5.47 (5.31)
Ic	24	Red powder	228(20)	1540	62.88 (63.19)	5.44 (5.31)
Id	30	Red powder	228(100)	1545	62.86 (63.19)	5.40 (5.31)
Ie	25	Dark red crystals	248(50)	1535	53.30 (53.17)	3.90 (3.65)
If	20	Dark red solid [d]	248(100)	1540	53.35 (53.17)	4.01 (3.65)
Ig	26	Dark red crystals	248(25)	1530	53.15 (53.17)	3.56 (3.65)
Ih	21	Orange powder	230(12)	1085 [e]	57.12 (57.41)	4.77 (4.38)

[a] Ia is the CpFe complexed cyclohexadienone; Ib, Ic and Id are the CpFe complexed 2-, 3- and 4-methylcyclohexadienones, respectively; Ie, If and Ig are the CpFe complexed 2-, 3- and 4-chlorocyclohexadienones, respectively; Ih is the CpFe complexed cyclohexadienethione. [b] Mass spectral peak for the molecular ion, relative abundance as % of base peak. [c] IR for carbonyl stretching in general agreement with similar cyclohexadienones complexed with other metals which showed ν(CO) in the 1550 cm^{-1} region [1,2,6,7]. For the originally prepared Ia [8], a strong peak at 1535 cm^{-1} was reported, but a medium peak at 1661 cm^{-1} was attributed to the CO absorption. The presently prepared Ia did not show this peak at 1661 cm^{-1}, which possibly could be due to the presence of residual water in the sample since neat H_2O would show a medium absorption at 1634.9 cm^{-1} [11]. [d] Solidified oil. [e] ν(CS).

Table 2

^{1}H NMR data for complexes Ia to Ih in different solvents

Complex	Solvent [a]	(ppm from TMS) [b] Cp	H2	H3	H4	H5	H6	CH_3
Ia	A	4.59	5.13	5.48	5.38	5.48	5.13	–
	B	4.61	4.79	5.53	5.53	5.53	4.79	–
	C	4.81	5.33(d,6.8)	5.81(dd,6.8,5.8)	5.66(t,5.6)	5.81(dd,6.8,5.8)	5.33(d,5.8)	–
Ib	A	4.45	–	5.49	5.32	5.25	5.14	2.16
	C	4.69	–	5.82(d,5.6)	5.55(t,5.6)	5.72(dd,6.7,5.6)	5.35(d,6.7)	2.17
Ic	A	4.50	5.13	–	5.28	5.45	5.13	2.22
	C	4.75	5.39(d,1.4)	–	5.62(d,6.6)	5.78(t,6.6)	5.31(dd,6.6,1.4)	2.32
Id	A	4.51	5.04	5.38	–	5.38	5.04	2.27
	B	4.54	4.70	5.47	–	5.47	4.70	2.29
	C	4.76	5.29(d,6.6)	5.74(d,6.6)	–	5.74(d,6.6)	5.29(d,6.6)	2.31
Ie	A	4.60	–	5.93	5.38	5.38	5.38	–
	C	4.72	–	6.10(dd,5.4,1.9)	5.54–5.71	(overlapping m)	5.30(dd,6.1,1.2)	–
If	A	4.64	5.47	–	5.65	5.47	5.01	–
	C	4.88	5.64(s)	–	6.05(d,4.9)	5.93(dd,6.7,4.9)	5.29(d,6.7)	–
Ig	A	4.66	5.04	5.80	–	5.80	5.04	–
	B	4.74	4.85	5.96	–	5.96	4.85	–
	C	4.88	5.28(d,7.0)	6.13(d,7.0)	–	6.13(d,7.0)	5.28(d,7.0)	–
Ih	B	5.03	6.31	6.43	6.31	6.43	6.31	–
	C [c]	5.06	6.34	6.47	6.34	6.47	6.34	

[a] A, B and C represent chloroform-*d*, acetone-d_6 and 4/1 acetone-d_6/D_2O, respectively. [b] Cp and CH_3, respectively, are 5- and 3-proton singlets; absorptions in solvent A or B are broad, unresolved peaks, while in C, *J* values in Hz are given after descriptions of splitting patterns. [c] Splitting patterns not observed for Ih even in solvent C.

cyclohexadien-ethione-η^5-cyclopentadienyliron (Ih) was obtained. Summarized in Table 1 are some relevant data for complexes Ia to Ih.

Given in Table 2 are the ^{1}H NMR data for Ia to Ih in 2 or 3 different solvents. In the aprotic solvents $CDCl_3$ and $(CD_3)_2CO$, broad, unresolved peaks were observed for the cyclohexadienyl protons, while in 4/1 $(CD_3)_2CO/D_2O$, with a solvent component containing the hydroxyl group, the various absorptions showed good resolution with the expected coupling patterns. As an illustration, Fig. 1 shows the

Table 3

^{1}H NMR data for 2–6-η^5-chlorocyclohexadienone-η^5-cyclopentadienyliron (Ig) in various solvents

Solvent	δ (ppm from TMS) [a] Cp	H2,6	H3,5
$CDCl_3$ [b]	4.66	5.04	5.80
$(CD_3)_2CO$ [b]	4.74	4.85	5.96
$(CD_3)_2CO/D_2O$ (4/1) [b]	4.88	5.28(d,7.0)	6.13(d,7.0)
$(CD_3)_2CO/CH_3OD$ (4/1)	4.82	5.13(d,6.5)	6.11(d,6.5)
$CDCl_3/CH_3OD$ (4/1)	4.73	5.19(d,6.3)	5.89(d,6.3)
CD_3CN	4.65	4.76	5.85
$(CD_3)_2CO$/n-$BuND_2$ (4/1)	4.77	4.96(d,6.9)	5.98(d,6.9)

[a] *J* values in Hz given after descriptions of splitting patterns. [b] As given in Table 2.

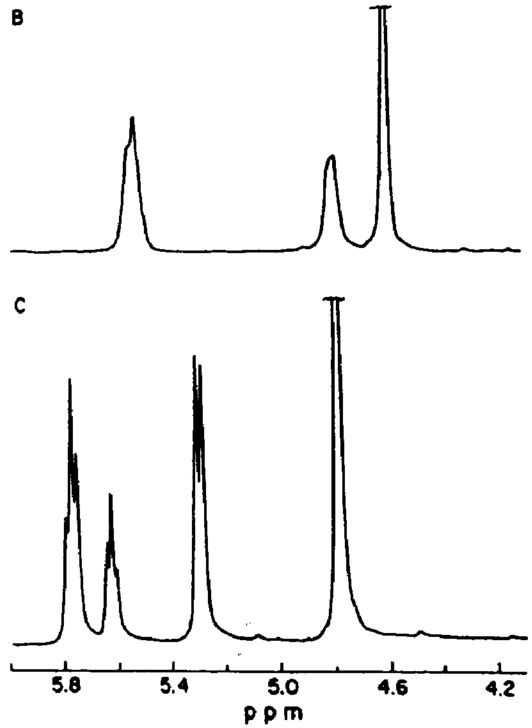


Fig. 1. ^{1}H NMR spectra of 2–6-η^5-cyclohexadienone-η^5-cyclopentadienyliron (Ia) in $(CD_3)_2CO$ (B) and 4/1 $(CD_3)_2CO/D_2O$ (C).

^{1}H NMR spectra for Ia in $(CD_3)_2CO$ and in 4/1 $(CD_3)_2CO/D_2O$. Another illustration of the effects of aprotic and protic solvents are given for the 4-chlorocyclohexadienone complex Ig in Table 3 and in Fig. 2. The presence or absence of a hydroxylic solvent also could influence the ^{13}C NMR spectra. For example, the ^{13}C NMR spectrum of Ia in $(CD_3)_2CO$ showed only one clearly defined peak for the Cp carbons, with the other carbons appearing as undefined smears over the background. In 4/1 $(CD_3)_2CO/D_2O$, however, well defined peaks for all carbons were observed. Summarized in Table 4 are the ^{13}C NMR data recorded in 4/1 $(CD_3)_2CO/D_2O$ for Ia to Ih.

In the previously reported isolation of a ruthenium complexed cyclohexadienone [1], it was pointed out that the species could also be formulated as a complexed phenoxide anion, together with a positive charge on the metal atom. The same is true here. In the case of the ruthenium complex, IR and crystal structure evidence suggested that the major contribution was from the keto structure; the complex was described as "2–6-η^5-cyclohexadienyl" or "2–6-η^5-oxacyclohexadienyl". However, this does not preclude some contribution from the phenoxide structure in solution. These two structures are not resonance forms, since conversion from one to the other requires physical movements of atoms. Further, due to the very stringent requirements for planarity in the "aromatic" form (eg. IIa), it seems probable that in fact these two forms are both present in an equilibrium mixture, rather than the system adopting some intermediate configuration.

Such a model readily explains the present observations. In an aprotic solvent such as $CDCl_3$ or $(CD_3)_2CO$, appreciable amounts of both forms are in equilibrium.

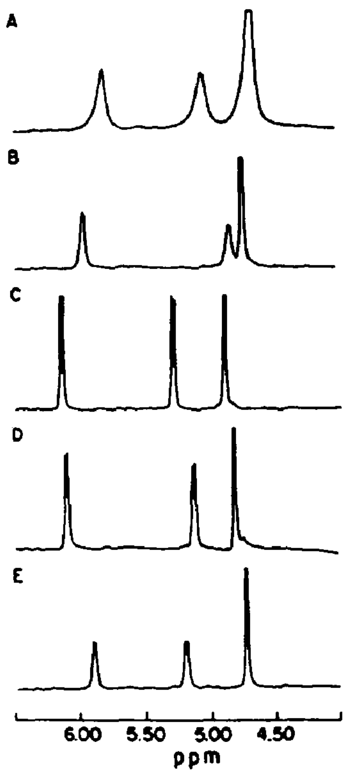


Fig. 2. ^{1}H NMR spectra of 2–6-η^5-4-chlorocyclohexadienone-η^5-cyclopentadienyliron (Ig) in $CDCl_3$ (A), $(CD_3)_2CO$ (B), 4/1 $(CD_3)_2CO/D_2O$ (C), 4/1 $(CD_3)_2CO/CH_3OD$ (D), and 4/1 $CDCl_3/CH_3OD$ (E).

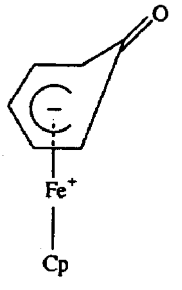
The observed proton NMR line-broadening is probably due to chemical exchange between these two environments. The lineshape data are not sufficient for a complete kinetic analysis; however, if plausible assumptions are made for the proton chemical shifts in the two forms, they do appear to be consistent with such an interpretation. The carbon lineshape data predict similar kinetics given analogous chemical shift assumptions, further supporting the idea. However, in the presence of a hydrogen-bonding solvent, the equilibrium is shifted almost entirely in favour of the form Ia, and the spectral lines are therefore sharp. Note that for the

Table 4

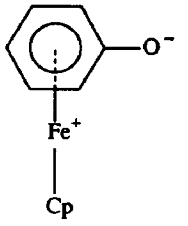
^{13}C NMR chemical shifts for Ia to Ih in 4/1 acetone-d_6/D_2O (δ, ppm from TMS)

Complex	Cp	C1	C2	C3	C4	C5	C6	CH_3
Ia [a]	74.8	149.7	75.8	87.1	77.4	87.1	75.8	–
Ib	74.7	148.9	89.2	85.4	76.4	88.2	74.3	17.3
Ic	74.9	148.3	73.8	102.0	78.4	85.8	77.4	20.4
Id	75.1	148.5	74.5	87.3	92.3	87.3	74.5	19.6
Ie [a]	76.5	147.9	95.4	86.4	76.6	87.2	74.4	–
If	76.6	149.1	73.9	107.3	77.9	85.3	76.9	–
Ig	77.1	149.5	73.8	87.4	99.1	87.4	73.9	–
Ih [a]	78.1	104.6	86.1	87.9	87.3	87.9	86.1	–

[a] As reported previously [10].



Ia



IIa

complexed cyclohexadienethione Ih/IIh, broad NMR signals are observed even in 4/1 $(CD_3)_2CO/D_2O$ (Table 2), reflecting the weaker ability of the sulfur analog to form hydrogen bonds.

In the present case, we were unable to grow crystals suitable for crystallographic examination. We therefore decided to examine further the possibility of H-bonding in the presence of a hydroxylic solvent. More ^1H NMR studies were carried out with the unsubstituted Ia, the 4-methyl substituted Id and the 4-chloro substituted Ig. These complexes were chosen since the symmetry of their structures gave rise to simpler spectra. It was found that the chemical shifts of various signals would remain almost unchanged in the temperature range 185–350 K but would change markedly with changing amounts of added D_2O in the $(CD_3)_2CO/D_2O$ mixture. Shown in Fig. 3 are the data for Ia, with the downfield shifts, $\Delta\delta_{obs}$, in Hz and relative to the δ value in pure $(CD_3)_2CO$ as zero. It is significant that these $\Delta\delta_{obs}$ values were largest for protons H2,6 smaller for H3,5 and smallest for H4. This trend was also observed for Id and Ig, and in Id, the D_2O-induced shift for the 4-methyl group was very small. This behavior would suggest that, rather than a non-specific medium effect, the shifts were due to some actual interaction of D_2O with the molecule under study. In such a case, it should be possible to apply the following treatment to the observed D_2O-induced shifts.

Assuming the existence of an "associated species" created by some interaction between one molecule each of D_2O and the compound in question (Ia, Id or Ig), and

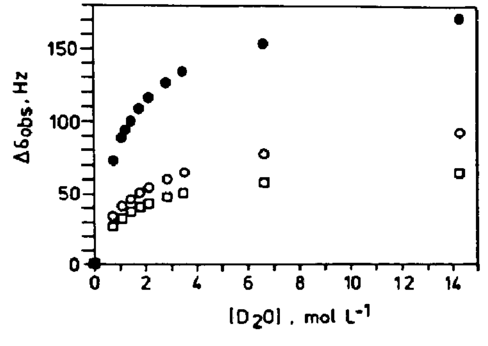


Fig. 3. D_2O-induced changes in chemical shifts for various protons of Ia; closed circles for H2,6, open circles for H3,5 and open squares for Cp.

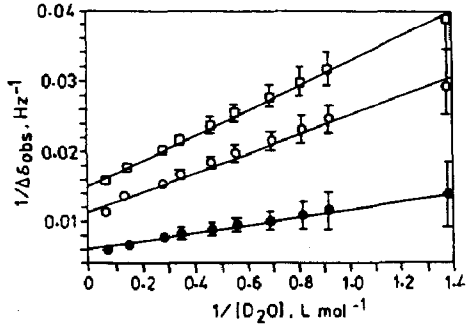


Fig. 4. Double reciprocal plot for data shown in Fig. 3.

assuming fast chemical exchange, for a given resonance the observed chemical shift, δ_{obs}, would be the weighted averaged of those in the "free" (f) and "associated" (as) forms, as given in eq. 1.

$$\delta_{obs} = \delta_{as}\alpha_{as} + \delta_f \alpha_f \tag{1}$$

where α refers to the mole fraction of each form. If we consider only shifts relative to δ_f, then eq. 1 reduces to eq. 2.

$$\Delta\delta_{obs} = \Delta\delta_{as}\alpha_{as} \tag{2}$$

where $\Delta\delta$ refers to a change in shift relative to δ_f. If a formation constant K for the "associated species" is defined by eq. 3,

$$K = [\text{associated}]/([\text{free}][D_2O]) \tag{3}$$

then it can be shown that

$$\alpha_{as} = K[D_2O]/(1 + K[D_2O]) \tag{4}$$

Substituting 4 into 2 and taking reciprocals for both sides of the equation gives eq. 5.

$$1/\Delta\delta_{obs} = (1/[D_2O])(1/K\ \Delta\delta_{as}) + 1/\Delta\delta_{as} \tag{5}$$

A double reciprocal plot of $1/\Delta\delta_{obs}$ versus $1/[D_2O]$ would yield a straight line with a slope of $1/(K\ \Delta\delta_{as})$ and an intercept of $1/\Delta\delta_{as}$.

Such plots are shown in Fig. 4 for the data from Ia given in Fig. 3. The correlation coefficients from all such plots were above 0.99, except where the actual changes in chemical shifts were very small such as for H4 of Ia. In such cases, the precision of the data was too poor to permit numerical analysis. The estimated values of K obtained by simple unweighted linear regression are 0.95, 0.82 and 0.87, respectively, for the H2,6, H3,5 and Cp resonances. Since the same "associated species" from Ia and D_2O was being investigated, in principle, the K values for the three sets of proton resonances should be identical. The agreements of the K values obtained, however, might be judged as being reasonable.

The reciprocal plots, while convenient for demonstrations of the trend, severely bias the experimental errors in the data. The non-linear least-squares routine KINET [12] was used to fit simultaneously the original H2,6, H3,5 and Cp chemical shift data to the original (nonlinear) model, yielding values of $\Delta\delta_{as}$ in each case and a common value of K. This treatment gave the data summarized in Table 5. Attempts

Table 5

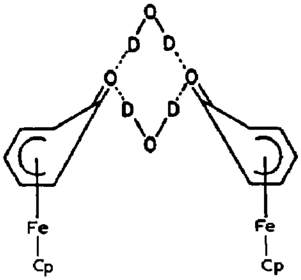
Values of $\Delta\delta_{as}$ and K for 1/1 "associated species" formed between Ia, Id or Ig with D_2O

Complex	$\Delta\delta_{as}$ (Hz) [a]				K [b]
	H2,6	H3,5	Cp	H4	
Ia	198	105	73	50	0.47
Id	202	80	73	–	0.54
Ig	188	79	62	–	0.53

[a] Standard deviation is typically 10 Hz. [b] Standard deviation is typically 0.04.

at fitting the data to a model involving association of two molecules of D_2O with one of Ia, Id or Ig were unsuccessful.

The above studies on the D_2O-induced changes in chemical shifts thus showed that there appeared to be a 1/1 interaction between D_2O and Ia, Id or Ig. Such an interaction likely would involve H- or D-bonding. If the complexed cyclohexadienone, such as Ia, and the complexed phenoxide ion, such as IIa, were in equilibrium in an aprotic solvent, in the presence of added D_2O, it would be difficult to assign definitively whether D-bonding would occur with Ia or IIa. A differentiation by IR, for example, was not possible since the CpFe complexed phenol, which could arise from H-bonding with IIa, gave a strong absorption at 1548 cm^{-1} [8] in the same region as the carbonyl absorption of Ia. In the work on the Ru-complexed cyclohexadienone [1], H-bonding to 2 phenol molecules per complexed ketone was reported, and this was in agreement with expectation that H-bonding could occur involving both unshared electron pairs in the keto oxygen [13]. For a phenoxide ion with 3 unshared electron pairs, H-bonding to 3 molecules of H_2O would be possible [13]. By analogy with the Ru complexed ketone [1], two molecules of D_2O could be D-bonded with 2 molecules of a complexed cyclohexadienone such as Ia as shown in IIIa, and the 2/2 ratio of Ia to D_2O would give rise to the 1/1 ratio of association as observed. The formation of a species such as IIIa would eliminate any possible equilibrations such as between Ia and IIa, and spin-spin coupling in the ^1H NMR spectrum would be observed.



IIIa

In the earlier work with Ia [8], it was reported that treatment of the mother liquor from the crystallization of Ia with CH_3I resulted in methylation to give the CpFe complex of anisole. Since Ia could be in equilibrium with the complexed phenoxide ion IIa, presumably, a nucleophilic substitution reaction between the complexed phenoxide ion and CH_3I would account for the formation of the complexed anisole. Similarly, under acidic conditions, conversion of the phenoxide to the CpFe complex of phenol was reported [8]. Such conversions to various complexed phenols under acidic conditions have been confirmed in the present work.

The various CpFe complexed cyclohexadienones prepared in the present study have been found to fail to give any reaction with reagents that usually would react with a ketone. For example, there was no reaction with hydroxylamine, phenylhydrazine or semicarbazide. Nor was there any reduction of the carbonyl group upon treatment with $NaBH_4$, $LiAlH_4$ or lithium triethylborohydride, a so-called superhydride [14]. When these reagents were treated with typically Ia, Id or Ig, the complexed cyclohexadienone was recovered unchanged and in good yield. The phosphonium ylide from carbethoxymethylenetriphenylphosphorane has been shown to undergo the Wittig reaction with the CpFe complex of fluorenone [15], but this same ylide also failed to react with Ia, Id or Ig. Since these complexed cyclohexadienones could exist in equilibrium with the corresponding complexed phenoxide ions, these molecules would be highly electron rich. Their failure to show typical reactions as ketones probably could be explained on the basis that since reactions with ketones generally would involve a nucleophilic addition to the C end of the carbonyl, such a nucleophilic addition was not possible for a highly electron-rich system. Again because of their electron-rich nature, the chlorocyclohexadienone complexes Ie, If and Ig failed to show any nucleophilic displacement of the chloro group when treated with NaOH, $NaOC_2H_5$ or $NaSCH_3$.

In our previous study on a possible reaction with diazomethane [10], the starting material, Ia, Ie or Ih, was prepared without the rigorous purification as described in the present work. The analytical results of the recovered impure material as well as the ^{13}C NMR data (which have been reassigned in Table 4) were fortuitously interpreted as in agreement with a ring expansion product. Actually, there was no reaction between diazomethane and Ia, Ie or Ih.

Experimental

The CpFe complexes of chlorobenzene, *o*-, *m*- and *p*-chlorotoluenes, and *o*-, *m*- and *p*-dichlorobenzenes, utilized as starting materials in the preparation of the CpFe complexed cyclohexadienones, were prepared as described in the literature [16] from ligand exchange reactions and obtained as their hexafluorophosphates. The IR spectra were obtained on a Perkin–Elmer 781 spectrophotometer. The ^1H and ^{13}C NMR were recorded on a Bruker AM 300 instrument. In the work on the D_2O-induced changes in chemical shifts, numerical analyses of the data were carried out on a Dell Computer Corp. System 310 80386 microcomputer. The initial unweighted fitting of the results was accomplished using a linearization transformation then linear regression analysis by Lotus 1-2-3. The final weighted fitting was carried out using the general nonlinear least square routine KINET [12].

2–6-η^5-Cyclohexadienone-η^5-cyclopentadienyliron (Ia) and related systems (Ib–Ih)

As a general procedure, a solution of 13 mmol of η^6-chloroarene-η^5-cyclopentadienyliron hexafluorophosphate in 60 ml of acetone was added to a solution of 78 mmol of KOH in 60 ml of H_2O. The mixture was then stirred under N_2 at room temperature for 18 h. Part of the acetone was then removed using a rotary evaporator. The residual solution was extracted with $CHCl_3$ (4 × 100 ml). The combined extract was dried over $MgSO_4$ and the $CHCl_3$ was then removed under reduced pressure. The remaining red oil was washed with ether (2 × 10 ml) and with *n*-hexane (2 × 10 ml). The residual material was redissolved in a small volume of $CHCl_3$ and passed 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. Some impurities were first removed by elution with ether and then with acetone. The product, which appeared as an orange band near the top of the column, was then eluted with dry methanol. Upon removal of the methanol from the eluate, the crude product was obtained either as a red oil or red solid. At this stage, the product still contained residual H_2O and inorganic hexafluorophosphates as impurities, and it was dissolved in 5–10 ml of dry acetone, filtered to remove any cloudiness, about 200 ml of additional dry acetone was added and all of the acetone was then evaporated off under reduced pressure at about 40 °C in order to remove the residual water. The process was repeated 3 more times and the residual product was dried in a vacuum desiccator over NaOH for 3 days. The resulting material was recrystallized from a solution in $CHCl_3$ upon addition of ether and then *n*-hexane. In some cases, such as Ic, Id and If, better results from recrystallization were obtained when the product was dissolved in 1/1 $CHCl_3$/ether, and dried over $MgSO_4$ before being recrystallized from $CHCl_3$–ether–*n*-hexane.

The thioketone complex Ih was obtained in the same way from reaction of the chlorobenzene complex with NaSH instead of KOH. The yields for Ia to Ih are given in Table 1.

η^6-p-Chlorophenol-η^5-cyclopentadienyliron hexafluorophosphate (IIg)

As an illustration of the formation of a complexed phenol from a complexed cyclohexadienone, to a solution of 248 mg (1.0 mmol) of 2–6-η^5-4-chlorocyclohexadienone-η^5-cyclopentadienyliron (Ig) in 20 ml of acetone, 10 ml of a 10% HCl solution and 500 mg of NH_4PF_6 were added. The mixture was stirred at room temperature for 1 h and then extracted with 4 × 50 ml of CH_2Cl_2. The combined extract was washed with H_2O, dried over $MgSO_4$, and after removal of the solvent, 276 mg (70%) of IIg was obtained as a yellow powder. ^{1}H NMR, δ(acetone-d_6) 5.23(s,5H,Cp); 6.33(br s,2H,H2,6); 6.67(br s,2H,H3,5); 8.90(s,1H,OH). (Found: C, 33.20; H, 2.65. $C_{11}H_{10}OClFePF_6$ calcd: C, 33.49; H, 2.56%).

Attempted reactions

The following are illustrations of attempted reactions that failed to yield any expected product.

To a solution of 350 mg (5.0 mmol) of $NH_2OH \cdot HCl$ and 1.64 g (20 mmol) of NaOAc in 10 ml of H_2O at about 40 °C, 500 mg (2.3 mmol) of Ia in 15 ml of THF was added. The mixture was stirred for 2 h and then extracted with $CHCl_3$ (4 × 25 ml). The combined extract was dried over $MgSO_4$ and after removal of the solvent, the residue was passed through a 5-cm alumina column. After the impurities were eluted with ether and with acetone, the orange band near the top of the column was eluted with dry methanol to give 380 mg (70%) of recovered Ia.

A mixture of 500 mg (2.0 mmol) of 2–6-η^5-2-chlorocyclohexadienone-η^5-cyclopentadienyliron (Ie) and 420 mg (6.0 mmol) of $NaSCH_3$ in 30 ml of THF was stirred under N_2 at 50 °C for 15 h. The resulting material was filtered through a sinter glass filter. The filtrate was evaporated to dryness, the residue redissolved in $CHCl_3$, dried over $MgSO_4$ and upon removal of the $CHCl_3$ and purification by passing through an alumina column, 350 mg (70%) of Ie was recovered.

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