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HYDROGEN–DEUTERIUM EXCHANGE IN CYCLOHEXADIENYLIRON TRICARBONYL COMPLEXES

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SUMMARY

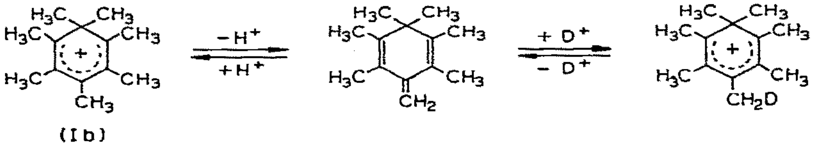
Methyl groups in positions 2 and 6 in the ring systems of (2,4,6-trimethylcyclohexadienyl)iron tricarbonyl and (heptamethylcyclohexadienyl)iron tricarbonyl cations have been shown to undergo hydrogen–deuterium exchange in diluted deuterioacids as well as in D_2O. This isotopic hydrogen–exchange reaction probably involves a proton–deuteron elimination–addition process with the formation of neutral intermediates, *i.e.* iron tricarbonyl complexes of 2-methylene-4,6-dimethyl-3,5-cyclohexadiene and 2-methylene-1,1,3,4,5,6-hexamethyl-3,5-cyclohexadiene, respectively. Such complexes have been obtained by the action of t-butylamine on the salts of the respective cations of these complexes.

The incorporation of benzenonium ions with iron tricarbonyl residues to give complexes apparently inhibits the degenerate rearrangement of these ions.

INTRODUCTION

As a part of a continuing programme to investigate the structure and reactivity of benzenonium ions combined with iron tricarbonyl residues to give iron tricarbonyl complexes (ITCs)*, we report a possible hydrogen–deuterium exchange reaction in ITCs of 2,4,6-trimethylbenzenonium (Ia) and heptamethylbenzenonium (Ib) ions [ITC (IIa) and (IIb) respectively].

It is known[3,4] that the methyl group in position 4 (apparently together with the methyl groups in positions 2 and 6) of the uncomplexed heptamethylbenzenonium ion undergoes a hydrogen–deuterium exchange with deuterioacids which proceeds by means of a proton elimination–addition mechanism [eqn. (1)].



(1)

The degenerate rearrangement of the ion (Ib) leads to a redistribution of the deuterated methyl groups and to an extension of the H–D exchange to groups initially located in non-exchangeable positions *i.e.* at the C-1, C-3 and C-5 atoms. The possi-

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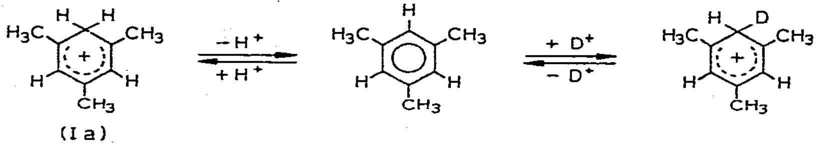
[*] See previous papers[1,2].

bility of selective H–D exchange in polyalkylated benzenonium ions containing no hydrogen atoms at C-1 has been employed for the detection of the degenerate rearrangement of these ions.

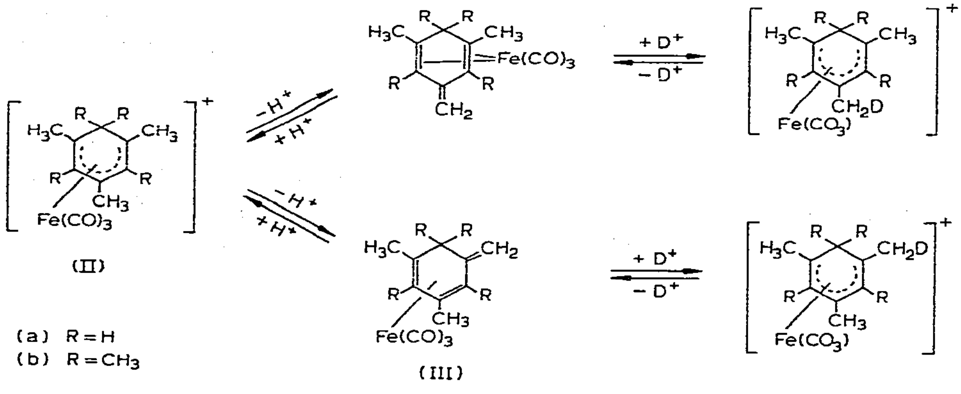
It has been shown[5] that only the ring hydrogens of the 2,4,6-trimethylbenzenonium ion (Ia) undergo deuterium exchange with DBr, apparently according to eqn. (2).



(2)

These data agree with the well known fact that mesitylene in deuterioacids usually exchanges with deuterium exclusively at the C_{Ar}–H positions[6]. Only under specially chosen conditions (in CF_3COOD, 150°, long exposure) does deuterium exchange with the methyl groups of mesitylene[7]. In this case the reaction probably follows a path similar to that depicted in eqn. (1).

Complexation with iron may result in a change in the exchange capabilities at certain ring positions in methylbenzenonium ions. Thus, in ITC (IIa) it is likely that the H–D exchange process depicted in eqn. (2) would be suppressed (*cf.* ref. 8). The participation of the methyl group in position 4 in ITCs (IIa) and (IIb) in such a H–D exchange reaction via eqn. (3) is hardly likely since it is well known[9,10] that in ITCs coordination involving conjugated dienes is preferred to similar coordination involving non-conjugated dienes. It follows, therefore, that the most probable mechanism for the H–D exchange reaction is that depicted in eqn. (4) which involves the methyl groups in positions 2 and 6 of ITCs (IIa) and (IIb). If this suggestion is correct it provides a method for obtaining ITCs (IIa) and (IIb) selectively labelled at the methyl groups in positions 2 and 6 and hence a suitable method for the detection of rearrangement processes in benzenonium ligands if such processes do occur.



(3)

(4)

RESULTS AND DISCUSSION

The experimental data obtained agree completely with the conclusions outlined above. From the PMR spectra of ITC (IIb) it is possible to deduce that this complex undergoes H–D exchange exclusively at methyl groups in positions 2 and 6 in deuterioacids (D_2SO_4, CD_3COOD) diluted with D_2O, as well as in D_2O. The mass spectrum of hexamethylbenzene obtained by the thermal decomposition of the hexafluorophosphate of deuterated ITC (IIb) shows the presence of up to six deuterium atoms in the molecule (*m/e* 163–168). The spectrum also exhibits a peak at *m/e* 169 but its intensity is less than 5% of the total intensity of all the parent peaks.

From the PMR spectra of ITC (IIa) it is also possible to deduce that only methyl groups in positions 2 and 6 in the benzenonium ligand are involved in H–D exchange.

Retention of the signal intensities associated with the methyl group in position 4, with the hydrogen atoms at positions 3 and 5 and of the characteristic absorption of the CH_2 fragment (AB system) shows that neither eqn. (3) nor any mechanism similar to eqn. (2) occurs in this system. The rate of H–D exchange in ITCs (IIa) and (IIb) decreases as the acidity of the medium increases (Table 1). All these observations agree with the proposed mechanism [eqn. (4)].

The PMR spectra also demonstrate that the heptamethylbenzenonium ligand in ITC (IIb) is not involved in any type of rearrangement which might lead to redistribution of the methyl groups under conditions leading to H–D exchange; in particular, 1,2 methyl group shifts characteristic of the free ligand[11-13] do not take place. Even after prolonged heating (127 h, 85°) in 63% H_2SO_4 of a 3% solution of ITC (IIb) hexafluorophosphate containing methyl groups in 2 and 6 positions labelled with deuterium, no methyl group redistribution was observed, whereas the frequency of 1,2-shifts involving methyl groups in the uncomplexed heptamethylbenzenonium ion (Ib) is about 10^3 s^{-1} at this temperature[11-13].

Comparison of the spectra reported for the uncomplexed benzenonium ion[14] with that for the ion complexed with iron in ITC (IV)[15,16] shows that degenerate

TABLE 1

HYDROGEN ISOTOPIC EXCHANGE REACTION OF (IIa) AND (IIb)

(Temperature, 65°)

Run No.	*ITC*	*Solvent*	*Time (h)*	*Deuterium content (%) of CH_3 groups in positions 2 and 6*[a]
1	(IIa)PF_6	32% D_2SO_4	22	40
2	(IIa)PF_6	11% D_2SO_4	22	70
3	(IIa)BF_4	50% CD_3COOD	11	80
4	(IIb)PF_6	32% D_2SO_4	22	5
5		11% D_2SO_4	11	20
6		11% D_2SO_4	22	40
7		CF_3COOD	22	0
8		50% CD_3COOD	22	70
9		D_2O/Acetone	2	30
10		(1/1)	11	60
11			22	90
12			65	90

[a] In all experiments the expected deuterium content at isotopic equilibrium was not less than 97% (as calculated for two exchangeable CH_3 groups, the isotopic effect being neglected).

rearrangement of the type exhibited by the former is also inhibited by complex formation. We have found that even heating a solution of cyclohexadienyliron tricarbonyl fluoroborate (10% concentration) in 63% H_2SO_4 up to 130° leads to no significant signal broadening in the PMR spectrum. The main reason for such inhibition of the degenerate rearrangement of the benzenonium and heptamethylbenzenonium ions complexed in ITCs (IV) and (IIb) respectively appears to be a dramatic decrease in the carbonium ion character of the ligand in the complex as has been suggested already by data obtained mainly by ^{13}C NMR spectroscopy[17]. Changes in the spatial arrangement of the benzenonium ligands due to complex formation (*cf.* refs. 14, 18 and 19) may also be important. Equation (4) suggests that addition of bases to solutions of ITCs (IIa) and (IIb) should result in a shift of the equilibria present towards neutral ITCs (IIIa) and (IIIb). In fact, the reaction of ITCs (IIa) and (IIb) with t-butylamine yields ITCs of 2-methylene-4,6-dimethyl-1,3,5-cyclohexadiene (IIIa), a non-aromatic cyclic isomer of mesitylene and 2-methylene-1,1,3,4,5,6-hexamethyl-1,3,5-cyclohexadiene (IIIb), respectively. The structures of these complexes have been established from their IR, UV and PMR spectral data. Strong absorptions corresponding to the *exo*-methylene group occur at 860–870 and 1610–1620 cm^{-1}, whilst very strong absorptions corresponding to the $Fe(CO)_3$ fragment occur at 1960–1980 and 2040 cm^{-1} in the IR spectra of (IIIa) and (IIIb). The UV spectra show an absorption at λ_{max} 240 nm characteristic of the neutral ITCs of conjugated dienes[20,21]. The PMR spectra of ITCs (IIIa) and (IIIb) show two signals in the region τ 5.3–5.8 ppm characteristic of the *exo*-methylene group protons. These signals are absent from the spectrum of ITC (IIIb) obtained by deuteration of the methyl groups in positions 2 and 6 in (IIb). The singlets corresponding to the "internal" (4 and 5) methyl groups are present in the region τ 7.8–7.9 ppm while those of the "external" groups (3 and 6) occur at τ 8.3–8.4 ppm (*cf.* refs. 20 and 22). The remaining two signals at τ 8.78 and 9.14 ppm observed in the PMR spectrum of ITC (IIIb) are related to the *endo*- and *exo*-methyl groups respectively (*cf.* ref. 23). The PMR spectrum of ITC (IIIa) also exhibits signals corresponding to the "internal" and "external" protons (τ 4.80 and 6.45 ppm) in addition to those corresponding to *exo*-methylene and methyl groups. The methylene protons at position C-1 in the ring appear as an AB system with J_{AB} 18 Hz. The above signal assignment is in complete agreement with the literature data on the ITCs of cyclohexadienyl systems[20,22]. The structure of ITCs (IIIa) and (IIIb) is also confirmed by the observation that protonation of (IIIa) with 75% sulphuric acid solution results in the formation of the cation (IIa) while treatment of (IIb) with 75% D_2SO_4 leads to the formation of cation (IIb), the PMR spectrum of the latter exhibiting a diminished intensity for the signals of the methyl groups in positions 2 and 6.

EXPERIMENTAL

General comments

The PMR spectra were recorded on Varian A 56/60A and HA-100 instruments (the concentration of the solutions being 3–5%). The spectra of the neutral compounds were obtained using hexamethyldisiloxane as an internal standard (τ 9.96 ppm) while the spectra of the ionic ITCs were measured relative to tetramethylammonium perchlorate (τ 6.80 ppm) as an internal standard. Mass spectra were measured on an MC-1303 mass spectrometer using 9 eV ionizing radiation. IR spectra were measured on UR-10 and UR-20 instruments, while UV spectra were measured using a Unicam SP 700 C spectrophotometer.

Deuteriosulphuric acid of the required concentration was prepared by diluting concentrated deuteriosulphuric acid (96 at. %*D*) with heavy water. A 50% solution of CD_3COOD was prepared by diluting the 99.5% acid (containing 95.5 at.% D) with D_2O. CF_3COOD was obtained by the method described previously[24], the deuterium content being 97 at.%.

(2,4,6-*Trimethylcyclohexadienyl*)*iron tricarbonyl hexafluorophosphate*

A solution consisting of 5.83 g (0.022 mole) of (1,3,5-trimethyl-1,3-cyclohexadiene)iron tricarbonyl[25] in 5 ml of CH_2Cl_2 was added to a solution of 7.30 g (0.022 mole) of triphenylmethylfluoroborate[26] in 50 ml of CH_2Cl_2. The mixture was kept for 24 h at ambient temperature then poured into 100 ml of dry ether. When filtered, it gave the fluoroborate of (IIa) which was purified by precipitation from its solution in acetone using dry ether. The fluoroborate (2.10 g, 28% yield) was obtained in the form of a yellow powder. (Found: C, 41.5; H, 3.59; F, 22,2. $C_{12}H_{13}BF_4FeO_3$ calcd.: C, 41.4; H, 3.76; F, 21.8%.) IR spectrum (in KBr): ν_{max}: 2050 and 2105 cm^{-1} (C≡O), 1060 cm^{-1} (BF_4^-).

The hexafluorophosphate of (IIa) was obtained via the exchange reaction with KPF_6 in aqueous solution. (Found: C, 35.2; H, 3.19; F, 27.4. $C_{12}H_{13}F_6FeO_3P$ calcd.: C, 35.5; H, 3.22; F, 28.0%.) IR spectrum (in KBr): ν_{max}: 2050 and 2105 cm^{-1} (C≡O), 850 cm^{-1} (PF_6^-). The PMR spectrum is given in Table 2.

(*Heptamethylcyclohexadienyl*)*iron tricarbonyl hexafluorophosphate*

This was prepared by the addition of a saturated aqueous solution of KPF_6 to an aqueous solution of the tetrachloroferrate of the complex cation (IIb)[1]. The yellow powder-like salt was purified by precipitation from its acetone solution using benzene or n-heptane. (Found: C, 41.4; H, 4.58; F, 24.4. $C_{16}H_{21}F_6FeO_3P$ calcd.:

TABLE 2

PMR DATA FOR CYCLOHEXADIENYLIRON TRICARBONYL COMPLEXES

Compound	*Chemical shifts, τ (ppm)*										*Solvent*
	H_4	$H_{3,5}$	$H_{2,6}$	H_{exo}	H_{endo}	$(CH_3)_4$	$(CH_3)_{3,5}$	$(CH_3)_{2,6}$	$(CH_3)_{exo}$	$(CH_3)_{endo}$	
(IV)BF_4	2.66	4.08	5.66	7.85 8.11 J(HH) 16 Hz	6.86 7.09						SO_2[a,b]
(IV)PF_6	2.70	4.13	5.67	7.88 J(HH) 16 Hz	6.93						85% H_2SO_4
(IIa)PF_6		4.40		7.46 J(HH) 16 Hz	7.02	7.21		8.12			85% H_2SO_4
(IIb)$FeCl_4$						7.34	7.76	8.22	9.39	8.52	20% HCl[c]
(IIb)PF_6						7.30	7.72	8.18	9.34	8.45	63% H_2SO_4

[a] See ref. 15. [b] See ref. 16. [c] See ref. 1.

C, 41.6; H, 4.58; F, 24.7%.) IR spectrum (in KBr): ν_{max}: 2023, 2045 and 2093 cm^{-1} (C≡O), 850 cm^{-1} (PF_6^-). The PMR spectrum is given in Table 2.

Cyclohexadienyliron tricarbonyl hexafluorophosphate (IV)

This was obtained via the exchange reaction of cyclohexadienyliron tricarbonyl fluoroborate[27] with KPF_6 in aqueous solution. IR spectrum (in KBr): ν_{max}: 2066 and 2120 cm^{-1} (C≡O), 850 cm^{-1} (PF_6^-). The PMR spectrum is given in Table 2.

Isotopic hydrogen exchange reactions (*Table* 1)

(a) *In deuterioacids.* The solutions of ITCs (IIa) and (IIb) (15–50 mg) in their respective deuterioacids (0.4–0.6 ml) were kept in sealed tubes at 65°. The position and extent of deuterium exchange in the benzenonium ligands was determined from the decrease in the signal intensities in the PMR spectra relative to those of the standard. For H–D exchange in 50% CD_3COOD, the change in intensity of the signal corresponding to methyl groups in positions 2 and 6 was determined from the ratio of this intensity to that of the methyl group in position 4. Recourse to this method was necessary since partial decomposition of ITCs (IIa) and (IIb) occurred during the course of the reaction.

(b) *In a D_2O acetone mixture.* The hexafluorophosphate of (IIb) (60–90 mg) was dissolved in1 ml of acetone and 1 ml of D_2O was added to the resulting solution; the solution was then kept in a sealed tube at 65°. The salt obtained after evaporation of the solvent in vacuo and purification of the residue by precipitation from its acetone solution using n-hexane (yield 80%) was dissolved in CF_3COOH or 65%H_2SO_4 and the position and content of exchanged deuterium was determined from the PMR spectra.

Thermal decomposition of [1,1,3,4,5-*pentamethyl*-2,6-*bis*(*trideuteriomethyl*)*cyclohexadienyl*] *iron tricarbonyl hexafluorophosphate*

[1,1,3,4,5-Pentamethyl-2,6-bis(trideuteriomethyl)cyclohexadienyl]iron tricarbonyl hexafluorophosphate (27 mg) obtained in run 12 (Table 1) was kept at 200–220° for 1.5 h in a sealed tube. The reaction mixture after cooling was treated with chloroform, the residue after evaporation of the chloroform being dissolved in petroleum ether (b.p. 35–40°). The resulting solution was washed with concentrated HCl and water. The petroleum ether was evaporated and the residue sublimed *in vacuo* yielding 7 mg of deuterated hexamethylbenzene which was analyzed for deuterium content by low-voltage mass spectrometry.

(2-*Methylene*-1,1,3,4,5,6-*hexamethyl*-3,5-*cyclohexadiene*)*iron tricarbonyl* (*IIIb*)

The hexafluorophosphate of (IIb) (86 mg) was slowly added to a solution of 1.5 ml of t-butylamine in 6 ml of petroleum ether (b.p. 40–60°) with stirring under a nitrogen atmosphere. The mixture was stirred for a further 30 min and then filtered. Unreacted amine was extracted with water, the organic layer filtered through a column with silica gel and the solvent evaporated. 49 mg of a yellow-red oil was obtained and purified by vacuum distillation (3 mm) at 30–40° (bath temperature). The resulting oil was unstable in air and on heating. [Found: C, 61.9; H, 6.64. Mol. wt. (isothermal distillation), 312. $C_{16}H_{20}FeO_3$ calcd.: C, 60.8; H, 6.37%. Mol. wt., 316.] UV spectrum (solution in ethanol): λ_{max} 204 nm, log ε 4.41; 246 and 294 nm (sh). IR spectrum (film):

ν_{max}: 865 and 1612 cm^{-1} (=CH_2), 1962, 1975 and 2040 cm^{-1} (C≡O). PMR spectrum (in CS_2): τ 5.40 and 5.45 (*exo*-methylene protons), 7.80 and 7.84 (methyl group protons at C-4 and C-5 respectively), 8.34 and 8.44 (methyl group protons at C-3 and C-6 respectively), 8.78 and 9.14 ppm (*endo*- and *exo*-methyl groups respectively). The PMR spectrum of ITC (IIIb) prepared from the hexafluorophosphate of [1,1,3,4,5-pentamethyl-2,6-bis(trideuteriomethyl)cyclohexadienyl]iron tricarbonyl exhibits no signals corresponding to *exo*-methylene groups or to the methyl group in position 6.

(2-Methylene-3,5-dimethyl-3,5-cyclohexadiene)iron tricarbonyl (IIIa)

This was obtained from the hexafluorophosphate (IIa) in a similar manner to (IIIb). The yellow-red oil was purified by vacuum distillation (3 mm) with a bath temperature below 30°. The yellow oil obtained was unstable in air and on heating. [Found: C, 55.8; H, 5.27. Mol. wt. (isothermal distillation), 268. $C_{12}H_{12}FeO_3$ calcd.: C, 55.4; H, 4.65%; Mol. wt., 260.] UV spectrum (in ethanol): λ_{max} 204 nm, log ε 4.44; 244 and 294 nm (sh). IR spectrum (film): ν_{max} 862 and 1620 cm^{-1} (=CH_2), 1964, 1980 and 2044 cm^{-1} (C=O). PMR spectrum (in CS_2): τ 5.32 and 5.74 ppm (*exo*-methylene group protons coupled with each other and with the methylene group protons at C-1 with coupling constants of about 1.0–1.5 Hz as shown by a proton decoupling technique), 4.80 and 6.45 (protons at C-5 and C-3 ring atoms respectively, J(H-3, H-5) 1.5 Hz), 7.93 and 8.42 (methyl groups at C-4 and C-6 respectively) and 7.68 and 7.83 ppm (protons at C-1, AB system, J_{AB} 18 Hz).

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