Unique Deuterium Exchange Reaction in Certain Substituted Ferrocenes

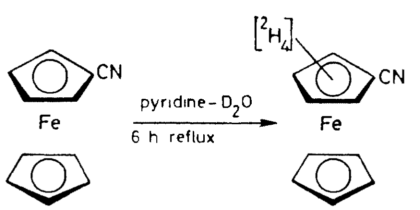
By D. W. Slocum, David L. Beach, Carl R. Ernst, Robert Fellows, Morek Moronski, Brian Conway,
and Joseph Bencini
(*Neckers Laboratories, Southern Illinois University, Carbondale, Illinois* 62901)

and Alan Siegel
(*Department of Chemistry, Indiana State University, Terre Haute, Indiana* 47801)

Summary Deuterium exchange of certain substituted ferrocenes (under very mild basic conditions) occurs in only the substituted cyclopentadienyl-ring in non-statistical pattern; a $\pi \rightarrow \sigma$ ($\eta^5 \rightarrow \eta^1$) rearrangement mechanism is proposed to account for the novel pattern of exchange.

ISOTOPIC exchange of deuterium for hydrogen in aromatic systems is a well known phenomenon found in certain organometallic complexes, *e.g.* several ferrocene systems. Most studies have involved acid-catalysed exchange,[1] although an example of an exchange effected by a strong base has been reported.[2] We report here that several substituted ferrocenes undergo not only a base-promoted exchange under very mild conditions, but also exhibit a unique deuterium distribution in the exchanged material.

Reflux of cyanoferrocene in the relatively weak base pyridine containing 9% D_2O (v/v) resulted in the incorporation of deuterium into the substituted ring of the ferrocene nucleus [equation (1)]. Furthermore, analysis by mass spectroscopy revealed that the distribution of incorporated deuterium was not statistical. Within experimental error (1—3%) and after deconvolution, the only species present in the molecular ion region were $[^2H_0]$- and $[^2H_4]$-substituted ferrocenes. No intervening nor more highly deuteriated species were found.



(1)

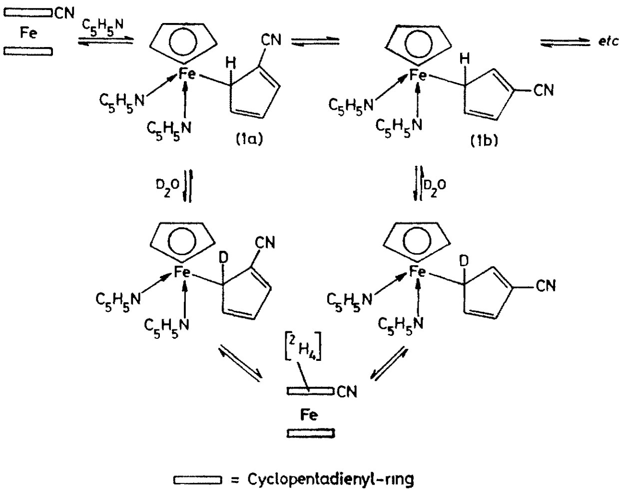
To examine this phenomenon in more detail, several mono- and di-substituted ferrocenes were each refluxed in pyridine–D_2O solution. These results, summarized in the Table, cannot be attributed to the acidity in the normal sense of the substituted cyclopentadienyl-ring protons in the π-complex. It is significant that only the electron-withdrawing substituents are capable of activating the ferrocenyl-group towards this protophilic exchange. However, not all electron-withdrawing substituents promoted exchange (*cf.* Table, footnote b).

In order to confirm that only the protons from the substituted ring are exchanged, the distribution of the peaks originating from some fragment ions was examined. In no case did the *m/e* 121 peak, attributed to the $[C_5H_5Fe]^+$ group, contain deuterium. In the spectrum of cyanoferrocene the peak at *m/e* 146, derived from the $[FeC_5H_4CN]^+$ fragment, exhibited also a prominent peak at *m/e* 150.

1,1′-Disubstituted ferrocenes also exhibited exchange under these conditions (*cf.* Table). However, the distribution of deuterium atoms was not as expected on the basis of the observations of the monosubstituted ferrocenes, *i.e.* that both rings would separately incorporate four deuterium atoms. Rather, no $[^2H_4]$ species were found in either case and significant quantities of the $[^2H_7]$ species, in addition to the predominant $[^2H_8]$ species, were observed for both molecules.†

Since cyanoferrocene proved to be the most reactive among the monosubstituted ferrocenes examined, it was chosen as a model for preliminary mechanistic investigation. The extent of exchange in cyanoferrocene exhibited a linear dependence of the percentage of $[^2H_4]$ species upon the reaction time. The addition of a base to the solution (NaOD) increased the rate of reaction by a factor of only *ca.* 2. These results suggest that abstraction of a proton cannot be the rate-determining step in the reaction and are in agreement with the above-mentioned statement that the acidity of the ring protons does not determine the rate of reaction.

Therefore, we deduce that although it has been stated that the metal atom plays no role in the electrophilic substitution reactions of ferrocene,[3] such involvement cannot be excluded in this case. A rate-determining $\pi\rightarrow\sigma$ ($\eta^5\rightarrow\eta^1$) rearrangement involving intermediates of the type (**1a**) and (**1b**) (Scheme), wherein all the ring protons are rendered exchangeable by a series of rapid 1,2-shifts, neatly accounts for the nonstatistical distribution of the incorporated deuterium.



SCHEME The proposed mechanism for deuterium exchange

TABLE Deconvoluted mass spectra of monosubstituted and 1,1′-disubstituted ferrocenes exchanged in D_2O–pyridine[a,b]

Substituent	$[^2H_0]$	$[^2H_1]$	$[^2H_2]$	$[^2H_3]$	$[^2H_4]$	$[^2H_5]$	$[^2H_6]$	$[^2H_7]$	$[^2H_8]$	$[^2H_9]$
Acetyl	84·0	3·5[c]	0·5	0·5	11·5	—				
Benzoyl	79·0	0·5	0·5	1·5	18·5	—				
Cyano	72·0	1·2	0·0	2·4	24·2	0·0				
1,1′-Diacetyl	54·0	1·5[c]	0·0	0·0	0·0	0·5	3·5	15·0	24·5	6·5[c]
1,1′-Dibenzoyl	66·0	0·0	1·5	0·0	0·0	0·5	3·5	10·5	18·5	0·0
Formyl	96·0	—	—	—	4·0					
$-SO_2NMe_2$	98·3	—	—	—	1·7					

[a] Run in 9% D_2O (v/v) for 6 h at reflux with 0·15 M substrate concentration, Hewlett-Packard Double Focusing Mass Spectrometer 59-30A, 70 eV, source 250 °C. [b] Also attempted with no exchange: monosubstituted ferrocenes containing $-NO_2$, $-CON(Me)_2$, $-CO_2R$, $-Cl$, $-CH{=}CH_2$, $-H$, and $-Me$ as substituents. [c] Thought to include some contribution of exchange at the methyl group(s).

---

† The presence of a $[^2H_7]$ species may reflect some contribution of back exchange.

Some precedents exist for the features of this mechanism. A σ→π rearrangement of cyclopentadienyl has been detected as an intermediate step in the formation of ferrocene,[4] although the reverse reaction has not, to our knowledge, yet been suggested. Moreover, in several transition-metal–cyclopentadienyl systems, a σ-cyclopentadienyl-ligand exhibits a singlet in its ^{1}H n.m.r. spectrum, a situation which has been interpreted in terms of a series of 1,2-shifts.[5] The $(C_5H_5)_3MoNO$ system also exhibits, in its ^{1}H n.m.r. spectrum, evidence for a reversible π→σ rearrangement, although none of the cyclopentadienyl-rings in this complex are true pentahapto-ligands.[6]‡

This research was supported by the Coal Extraction and Utilization Center and by the Research Administration at Southern Illinois University.

(*Received*, 20*th December* 1979; *Com.* 1325.)

---

‡ These solution results prompt us to propose a mechanism for the racemization of an optically active ferrocene. Originally we proposed a substituted ring-to-metal bond dissociation (D. W. Slocum, S. Tucker, and T. R. Engelmann, *Tetrahedron Lett.*, 1970, 621). Such a process would be *inter*molecular and was disproved by the paper of Falk *et al.*, where the *intra*molecularity of the racemization was demonstrated (H. Falk, H. Lehner, J. Paul, and U. Wagner, *J. Organomet. Chem.*, 1971, **28**, 115). A mechanism involving a π→σ→π rearrangement of the substituted ring of the chiral ferrocene in which the *ipso*-carbon of the σ-complex loses its configurational integrity through ionization accounts for all the observations to date. In essence, racemization is accomplished by turning the substituted ring over on the complex.

[1] (a) E. G. Perevalova and T. V. Nikitina in 'Organometallic Reactions,' Vol. 4, eds. E. I. Becker and M. Tsutsui, Wiley, New York, 1972, p. 163; (b) G. Gerichelli, G. Illuminati, and G. Orgaggi, *J. Organomet. Chem.*, 1977, **127**, 357.

[2] F. S. Yakushin, V. N. Setkina, E. A. Yakovleua, A. I. Shatenshtein, and D. N. Kursanov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1967, **1**, 206.

[3] M. Rosenblum and F. W. Abbate, *J. Am. Chem. Soc.*, 1966, **88**, 4178; J. A. Mangravite and T. G. Traylor, *Tetrahedron Lett.*, 1967, 4461.

[4] M. Tsutsui, M. Hancock, J. Ariyoshi, and M. N. Levy, *J. Am. Chem. Soc.*, 1969, **91**, 5233.

[5] F. A. Cotton, *Acc. Chem. Res.*, 1968, **1**, 257; K. Vrieze and P. W. N. M. van Leeuwen, *Prog. Inorg. Chem.*, 1971, **14**, 1.

[6] J. L. Calderon, F. A. Cotton, and P. Legzdins, *J. Am. Chem. Soc.*, 1969, **91**, 2528.