A New Preparation of Perdeuterated Ferrocene†

J. Chem. Research (S), 1999, 364–365†

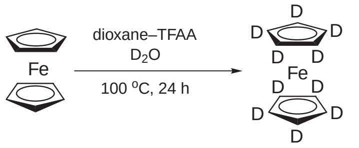
Elizabeth Shabanova,* Kjeld Schaumburg and Fadhil S. Kamounah

CISMI, University of Copenhagen, Fruebjergvej 3, DK-2100 Copenhagen, Denmark

A new synthesis of ferrocene-d_{10} using acid catalysed exchange is described.

Ferrocenes have in recent years gained increasing interest as building blocks for molecular magnets,[1] biosensors,[2] catalysts[3,4] and as diagnostic agents.[5] Ferrocene is attractive as a possible electron donor building block and shows a high molecular mobility at ambient temperatures.[6,7] It has been found that in complexes with other mobile molecules it shows interesting mobility properties.[8] Perdeuterated ferrocene **2** (ferrocene-d_{10}) is an interesting molecule, since comparison with the parent ferrocene **1** (ferrocene-h_{10}) can help to separate various contributions to molecular interactions and therefore, more clearly explain properties of materials. The indirect synthesis of **2** by metalation of pentadeuteriocyclopentadienyl salts has been reported.[9,10] The first report on the direct deuterium exchange[11] involved a base catalysed exchange with $Ca(OD)_2$ at 320 °C. This leads to high ferrocene loss and a poor yield. Later, a method using an acid catalysed exchange by D_3PO_4 at 110–120 °C was reported in compound **2** after several exchanges.[12–14] In the corresponding references the method gave conflicting results. In our hand, using this method[12] it was not possible to achieve the postulated results. The yield obtained was poor and the deuteration was slow. The poor yield is due to substantial formation of black tarry material during the exchange process. The limited solubility of ferrocene in D_3PO_4 makes the reaction a two-phase process. This will clearly cause a substantially longer reaction time.

Here, we report a new and efficient acid catalysed deuterium exchange of ferrocene as presented in Scheme 1. The reaction involves direct exchange with D_2O–trifluoroacetic anhydride (TFAA) in dry 1,4-dioxane at 100 °C. D_2O was slowly added to a solution of ferrocene in 1,4-dioxane–TFAA at 10 °C. Afterwards, the mixture was sealed in a glass tube and kept at 100 °C for 24 h. The enrichment obtained during the exchange, corresponds to equilibrium between the protons present in ferrocene and in the D_2O. The perdeuterated compound **2** was obtained after four exchanges with a yield of 90% per exchange (Fig. 1). From the mass spectrum of compound **2** [Fig. 1(*d*)] it can be calculated that 95% of the protons have been exchanged with deuterium in a statistical manner.



Scheme 1

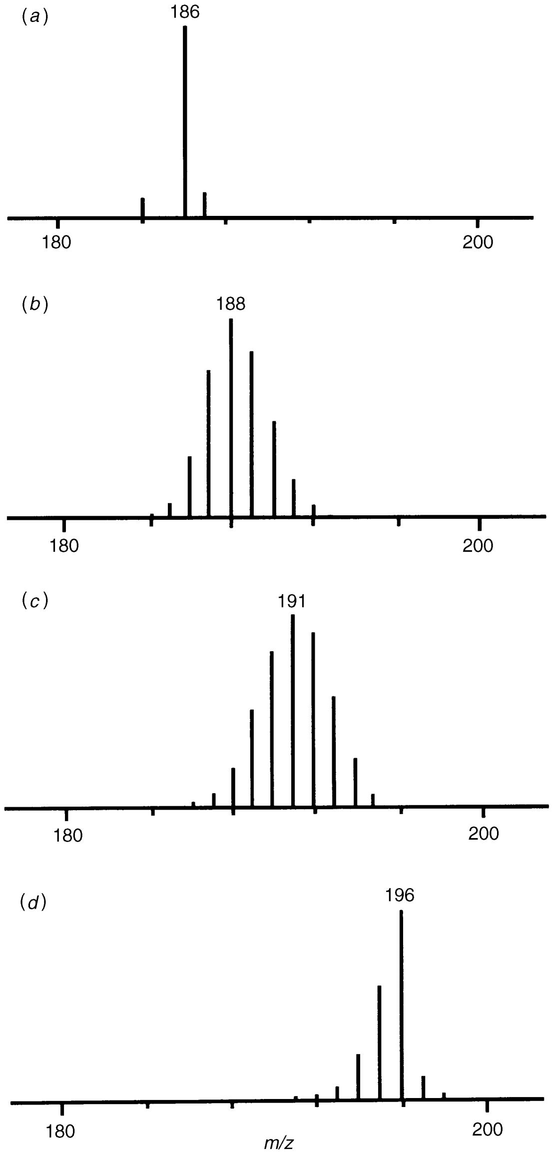
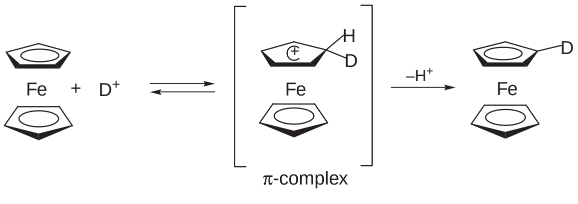


Fig. 1 High-mass part of GC–mass spectra of (a) ferrocene-h_{10} and deuterated ferrocene after (b) 1, (c) 2 and (d) 4 exchanges. The intensities are in arbitrary units.

The deuteration method presented shows promising results in comparison with the previous methods. The mechanism appears to be by direct formation of a π-complex (Scheme 2). The metal atom plays no role in the electrophilic deuterium substitution.[15,16]



Scheme 2

---

*To receive any correspondence (*e-mail:* E.Shabanova@symbion.ki.ku.dk).

†This is a **Short Paper** as defined in the Instructions for Authors, Section 5.0 [see *J. Chem. Research (S)*, 1999, Issue 1]; there is therefore no corresponding material in *J. Chem. Research (M)*.

Experimental

Ferrocene and TFAA (Fluka) were used as received. D_2O(99.9%) was supplied by CIL. HPLC 1,4-dioxane (Lab-Scan) was predried prior to use. Column chromotography was carried out using silica gel Kieselgel 60 type Merk (0.015–0.040 mm). Mass analyses were performed on VG MassLab 12-250 GC–mass spectrometer.

Ferrocene-d_{10}. A solution of ferrocene (2 g, 10.75 mmol) in dry 1,4-dioxane (35 ml) was treated with triflouroacetic anhydride (27 ml). Subsequently, D_2O (2.2 g, 110 mmol) was added dropwise at 10 °C. The brown mixture was sealed in an ampoule and kept at 100 °C for 24 h.

The brown mixture was cooled to ambient temperature, poured into a separating funnel containing ice water (100 ml) and extracted with diethyl ether (200 ml). The organic layer was separated and neutralized with aqueous K_2CO_3 solution, washed with water, and finally dried over anhydrous $MgSO_4$. The organic solvent was evaporated to dryness. The dark brown solid residue was purified by column chromatography over silica gel with *n*-hexane–ethyl acetate (10 : 1) to afford the partially deuteriated product. The deuterated ferrocene with a deuterium content of 95% was obtained as a result of four such exchanges. It is important that, after each exchange, the material should be dried before commencing the next exchange. All the exchanges were identified by GC–MS.

Received, 14th December 1998; Accepted 23rd February 1999
Paper E/8/09731C

References

1 J. S. Miller and A. J. Epstein, *Angew. Chem., Int. Ed. Engl.,* 1994, **33**, 385.
2 P. N. Bartlett, P. Tebbut and R. G. Whitaker, *Prog. React. Kinet.* 1991, **6**, 55.
3 K. S. Gan, T. S. A. Hor, T. Hayashi, Y. Butsugan, S. Araki and M. Watanabe, in *Ferrocenes,* ed. A. Togni and T. Hayashi, VCH, Weinheim, 1995, pp. 3–169.
4 J. C. Green, *Chem. Soc. Rev., 1998,* **27**, 263.
5 M. Weuzel, M. Langstaedtler and D. Preiss, *Appl. Radiat. Isot.,* 1988, **39**, 1023.
6 S. J. Heyes and C. M. Dobson, *Magn. Res. Chem.,* 1990, **28**, s37.
7 A. E. Aliev, K. D. M. Harris, I. J. Shannon, C. G. Glidewel, C. M. Zakaria and P. A. Schofield, *J. Phys. Chem.,* 1995, **99**, 12008.
8 E. Shabanova, K. Schaumburg and F. S. Kamounah, *Can. J. Analyt. Sci. Spect.,* 1998, **43**, 53.
9 V. P. Marin, O. N. Druzhkov, Yu. A. Andrianov, T. I. Arseneve and I. I. Grinvald, *Zh. Obshch. Khim.,* 1980, **50**, 1830 (*Chem. Abstr.,* 93:220924, 1980).
10 G. Wilkinson, *Org. Synth.,* 1956, **36**, 31.
11 E. R. Lippincottf and R. D. Nelson, *Spectrochim. Acta,* 1958, **10**, 307.
12 H. P. Fritz and L. Schäfer, *Chem. Ber.,* 1964, **97**, 1829.
13 R. T. Bailey, *Spectrochim. Acta.,* 1971, **27**, 199.
14 Y. Shiomi and H. Sorai, *Chem. Phys. Lett.,* 1983, **95**, 167.
15 M. Rosenblum and F. W. Abbate, *J. Am. Chem. Soc.,* 1966, **88**, 4178.
16 J. A. Mangravita and T. G. Traylor, *Tetrahedron Lett.,* 1967, 4461.