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ORGANOMETALLIC π-COMPLEXES
XVIII*. PROTON NUCLEAR MAGNETIC RESONANCE ANALYSIS OF SOME DEUTERATED FERROCENES**

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SUMMARY

A series of 2,5-dideuterated, monosubstituted ferrocene compounds has been prepared. A comparison of the proton NMR spectra of these deuterated products with the spectra of their non-deuterated derivatives has permitted the unequivocal assignment of proton resonance frequencies in the latter series.

INTRODUCTION

During the course of recent studies on vinylmetallocenes and metallocenyl acetylenes, it became necessary to make definitive assignments for resonances representing the 2,5- and the 3,4-protons in the proton NMR spectra of these and related metallocene derivatives. Such assignments have heretofore been postulated by analogy to the effects of substituents on the chemical shifts of protons on the benzene ring[2-7].

In general, the presence of electron-withdrawing substituents on ferrocene lead to pronounced differences in chemical shifts between the 2,5- and the 3,4-protons of the substituted cyclopentadienyl ring, and both resonances are usually*** shifted to lower field compared to the resonance for ferrocene itself. In certain cases, such as the haloferrocenes, one resonance appears at lower field and the other at slightly higher field compared to the resonance for ferrocene. Weakly electron-donating substituents such as alkyl groups generally do not exhibit this chemical shift difference between resonances representing the 2,5- and the 3,4-protons, whereas strongly electron-donating substituents such as $-NH_2$ and $-OCH_3$ result in substantially larger chemical shift differences between these resonances. The latter fall at higher field than does the resonance for ferrocene[6,7]. The resonances representing the 2,5- and 3,4-protons in nearly all monosubstituted ferrocenes except alkyl derivatives

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* For part XVII see ref. 1.

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*** Resonances due to ring protons in substituted vinylferrocenes are shifted significantly upfield when the vinyl group contains a phenyl substituent in the *cis*-position; see ref. 8.

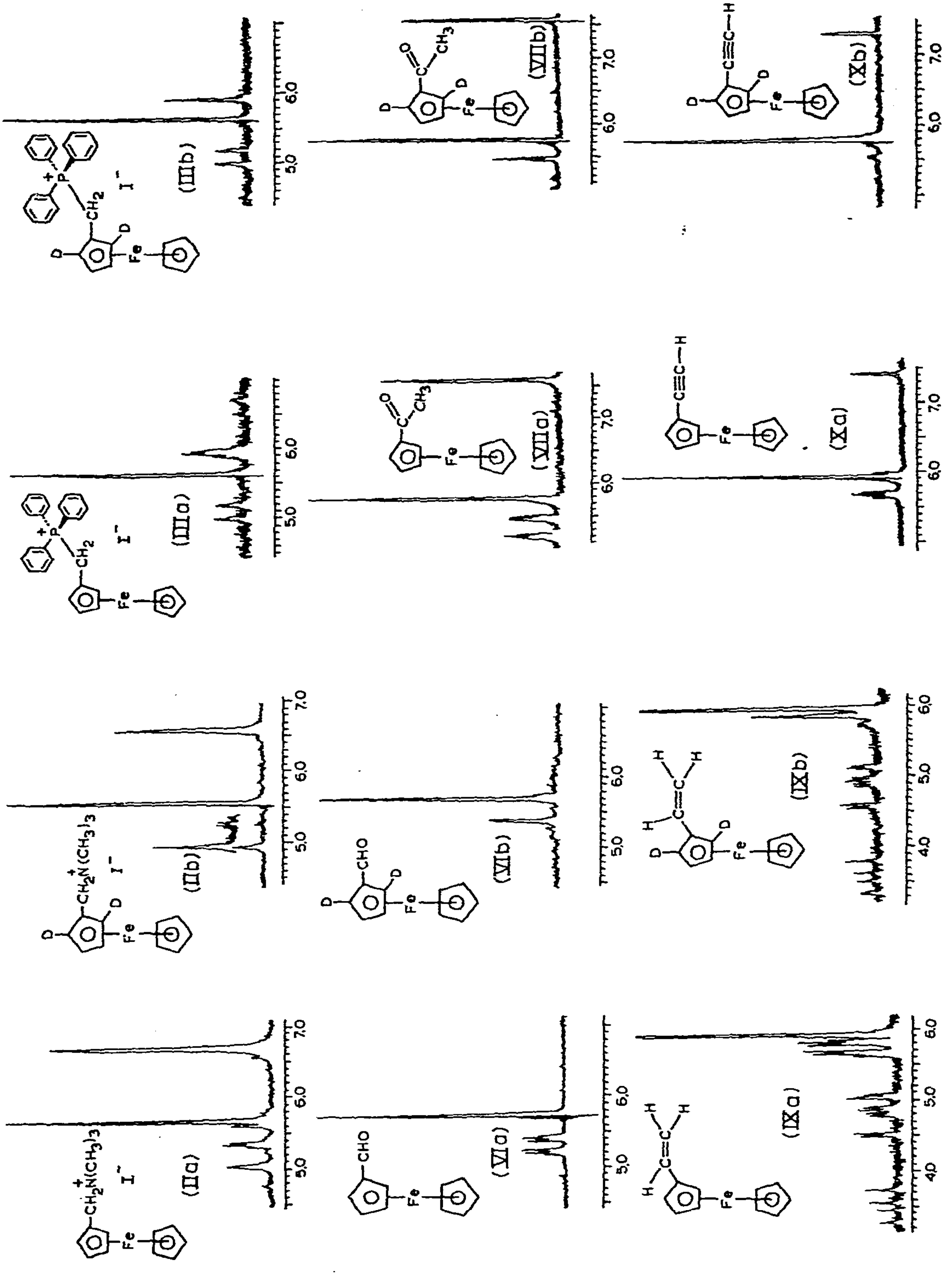


Fig. 1. Proton NMR spectra of some non-deuterated and 2,5-dideuterated ferrocene derivatives.

appear as a pair of apparent triplets (line separation *ca.* 2 Hz), corresponding to an A_2B_2 spin system.

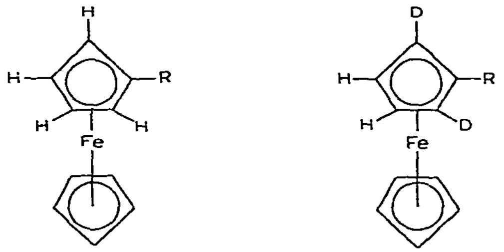
RESULTS AND DISCUSSION

The approach utilized in our study has been to prepare a series of selected 2,5-dideuterated, monosubstituted ferrocene derivatives, according to modifications and extensions of established literature procedures. The proton NMR spectra of these specifically deuterated derivatives were then compared with the spectra of analogous non-deuterated compounds. In this manner, resonances due to the substituted ring protons in the latter series could be unequivocally assigned. Chart 1 lists the ferrocene derivatives prepared in this study, and Fig. 1 presents comparative spectra for six typical sets of derivatives.

The starting material, [(dimethylamino)methyl]ferrocene (Ia) was prepared by a Mannich reaction involving ferrocene and bis[(dimethylamino)methyl]methane in acetic acid, according to the procedure of Hauser and Lednicer[9]. Hauser and coworkers[10] have recently reported that the metalation of amine (Ia) with n-butyllithium in ethyl ether/hexane solution under controlled conditions results in introduction of lithium at the 2-position. Treatment of the 2-lithio derivative with deuterium oxide was reported to produce a 70% yield of 2-deuterio[(dimethylamino)methyl]ferrocene. An alternate reaction of the 2-lithio derivative with benzophenone, followed by conversion of the resulting carbinol to the corresponding methiodide and cyclization with potassium amide, conclusively established that metalation had occurred in the 2-position.

CHART 1

SOME NON-DEUTERATED AND 2,5-DIDEUTERATED FERROCENE DERIVATIVES



(Ia)	$R=CH_2N(CH_3)_2$	(Ib)	$R=CH_2N(CH_3)_2$
(IIa)	$R=CH_2N(CH_3)_3I$	(IIb)	$R=CH_2N(CH_3)_3I$
(IIIa)	$R=CH_2P(C_6H_5)_3I$	(IIIb)	$R=CH_2P(C_6H_5)_3I$
(IVa)	$R=CH{=}C(C_6H_5)_2$	(IVb)	$R=CH{=}C(C_6H_5)_2$
(Va)	$R=CH_3$	(Vb)	$R=CH_3$
(VIa)	$R=CHO$	(VIb)	$R=CHO$
(VIIa)	$R=C(O)CH_3$	(VIIb)	$R=C(O)CH_3$
(VIIIa)	$R=C(Cl){=}CHCHO$	(VIIIb)	$R=C(Cl){=}CHCHO$
(IXa)	$R=CH{=}CH_2$	(IXb)	$R=CH{=}CH_2$
(Xa)	$R=C{\equiv}CH$	(Xb)	$R=C{\equiv}CH$
(XIa)	$R=C{\equiv}CC_6H_5$	(XIb)	$R=C{\equiv}CC_6H_5$

In our studies, 2,5-dideuterio[(dimethylamino)methyl]ferrocene (Ib) was prepared by two successive metalations of (Ia) with n-butyllithium in ethyl ether/hexane, followed by respective reactions of the resulting lithioamines with deuterium oxide. The proton NMR spectrum of (Ia) exhibited overlapping singlets at τ 5.87 and 5.91 (ferrocenyl protons), τ 6.74 (methylene protons) and τ 7.89 (methyl protons) in a relative intensity ratio of 9/2/6. The proton NMR spectrum of (Ib) was identical to that of (Ia) except that integration indicated the ferrocenyl region had diminished in intensity by *ca.* 83% of two protons. A deuterium analysis by the combustion-falling drop method* indicated 9.98% atom-excess deuterium in the deuterated product, which corresponds to 85% incorporation of two deuterons [*e.g.*, *ca.* 85% of the product was (Ib) and *ca.* 15% was (Ia)]. The fact that the 2,5- and the 3,4-protons in (Ia) are essentially equivalent is in accord with the chemical shift differences observed in the *ortho*- and *meta*-protons of a benzene ring bearing a similar substituent[11].

Treatment of (Ib) with methyl iodide in methanol produced a nearly quantitative yield of [(2,5-dideuterioferrocenyl)methyl]trimethylammonium iodide (IIb). The NMR spectrum of (IIb) exhibited singlets at τ 5.00 (methylene protons), τ 5.62 (3,4- and C_5H_5-protons) and τ 6.65 (methyl protons) (Fig. 1). In contrast, the proton NMR spectrum of (ferrocenylmethyl)trimethylammonium iodide (IIa) consisted of a singlet at τ 5.00, a triplet at τ 5.30, a triplet superimposed on a singlet at τ 5.62, and a singlet at τ 6.65. As anticipated, all protons resonances of both methiodides (IIa) and (IIb) were deshielded relative to the corresponding resonances for amines (Ia) and (Ib). The triplet resonance at τ 5.30 in the spectrum of (IIa) can therefore be clearly assigned to the 2,5-protons in (IIa).

The reaction of (IIb) with an excess of triphenylphosphine in refluxing ethanol, according to the procedure of Pauson and Watts[12], gave a 97% yield of [(2,5-dideuterioferrocenyl)methyl]triphenylphosphonium iodide (IIIb). Whereas the proton NMR spectrum of (ferrocenylmethyl)triphenylphosphonium iodide (IIIa) consisted of a doublet centered at τ 5.10 [methylene protons, $J(^1H-^{31}P)$ 12 Hz], a singlet at τ 5.61 (C_5H_5-protons), a broad multiplet centered at τ 5.93 (2,5- and 3,4-protons), and phenyl proton absorption between τ 2.0–2.5, the spectrum of the deuterated phosphonium salt (IIIb) was identical except that the resonance near τ 5.9 appeared as a singlet instead of a broad multiplet (Fig. 1). Integration indicated that the protons on the substituted cyclopentadienyl ring, as evidenced by the resonance near τ 5.9 in the spectra of (IIIa) and (IIIb), decreased in intensity by *ca.* 85% of two protons in the latter. It is of interest that the 2,5-protons and the 3,4-protons in (IIIa) are very nearly equivalent, and that both resonate at *higher* fields than do the unsubstituted ring protons. Molecular models indicate that the phenyl groups ride over the top of the substituted cyclopentadienyl ring, as is illustrated in Fig. 1. The 2,5-protons, and to a lesser extent, the 3,4-protons, lie in the shielding volume associated with the phenyl rings, resulting in a substantial upfield shift of the substituted ring protons relative to the corresponding protons in (IIa). Rosenblum[13] has attributed the marked upfield shifts of the 2,5- and the 3,4-protons in [*o*-(*p*-nitrophenyl)-*p*-methoxyphenyl]-ferrocene [relative to the *m*-(*p*-nitrophenyl) isomer] to a similar effect.

When (IIIb) was treated with an ethereal solution of n-butyllithium, a deep red solution resulted, indicating the formation of the corresponding ylide. A reaction

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* Performed by Mr. J. Nemeth, University of Illinois, Urbana, Illinois (U.S.A.).

between the latter and benzophenone afforded 1-(2,5-dideuterioferrocenyl)-2,2-diphenylethene (IVb). The proton NMR spectrum of (IVb) exhibited a multiplet centered at τ 2.53 (phenyl protons), a singlet at τ 3.16 (olefinic proton), and a singlet (broadened at the base) at τ 5.92 (3,4- and C_5H_5-protons). The proton NMR spectrum of 1-ferrocenyl-2,2-diphenylethene (IVa) was identical, except for the presence of an additional triplet at τ 6.14. Vinylferrocene derivatives of this type are of interest, since the factors responsible for the shifts to lower field of the 2,5- and the 3,4-protons, relative to ferrocene, are counterbalanced by apparent shielding effects of a phenyl group *cis* to a ferrocenyl group[8]. In (IVa), the 2,5-protons, and to a lesser extent, the 3,4-protons, lie in the shielding volume associated with the *cis*-phenyl ring, in a manner analogous to that described above for (IIIa). A comparison of the spectra of (IVa) and (IVb) conclusively demonstrates that the upfield triplet at τ 6.14 in the spectrum of (IVa) is assignable to the 2,5-protons.

Reduction of the phosphonium salt (IIIb) with lithium aluminum hydride in ethyl ether produced a 75% yield of 2,5-dideuteriomethylferrocene (Vb). In comparison with the proton NMR spectrum of methylferrocene (Va), which exhibited singlets at τ 5.92 (C_5H_5-protons), τ 5.97 (substituted ring protons) and τ 8.01 (methyl protons) in the ratio of 5/4/3, the spectrum of (Vb) was analogous except that the singlet at τ 5.97 was reduced in intensity by *ca.* 90% of two protons. Benkeser and coworkers[4,5] have suggested that the chemical shifts of the 2,5- and the 3,4-protons in the spectrum of (Va) are non-equivalent, on the basis of integration data. Such a conclusion is not in accord with our results. It should be mentioned, however, that Benkeser and coworkers[4,5] as well as others, have reported that the chemical shifts of the 2,5- and the 3,4-protons in ethylferrocene are equivalent. It seems unlikely that the effects of a methyl group *vis-à-vis* an ethyl group attached to a cyclopentadienyl ring would result in such distinct chemical shift differences. Were the original assignment for methylferrocene correct, the singlet resonance at τ 5.97 in (Vb) should have been virtually eliminated. Since a singlet is observed at τ 5.97 in the spectrum of (Vb) and since this peak is *ca.* $\frac{2}{3}$ the intensity of the methyl group resonance at τ 8.01, an equivalence in the chemical shifts of the 2,5- and 3,4-protons in methylferrocene is indicated.

Treatment of (IIb) with refluxing aqueous sodium hydroxide readily afforded 2,5-dideuterio(hydroxymethyl)ferrocene, which on oxidation with activated manganese dioxide in chloroform, according to a modification of the procedure of Hauser *et al.*[14], produced a high yield of 2,5-dideuterioformylferrocene (VIb). The proton NMR spectrum of (VIb) exhibited singlets at τ 0.05, 5.40 and 5.71, due to formyl, 3,4- and C_5H_5-protons, respectively (Fig. 1). In contrast, the spectrum of formylferrocene (VIa) displayed singlets at τ 0.05 (formyl proton) and τ 5.71 (C_5H_5-protons), as well as a pair of triplets at τ 5.19 and 5.40. The *lower* field triplet in the spectrum of (VIa) is therefore unequivocally assignable to the 2,5-protons. Such a conclusion is in accord with a previously postulated assignment[7] based on known substituent effects for *ortho*-protons in aromatic carbonyl derivatives[15].

Addition of methyllithium to an ethereal solution of (VIb) produced 1-(2,5-dideuterioferrocenyl)ethanol, which was subsequently oxidized by activated manganese dioxide to afford 2,5-dideuterioacetylferrocene (VIIb). The proton NMR spectrum of acetylferrocene (VIIa) in the present study exhibited singlets at τ 5.79 (C_5H_5-protons) and τ 7.62 (methyl protons) as well as a pair of triplets at τ 5.48 and

5.21. The latter resonances have been previously attributed to the 3,4- and the 2,5-protons, respectively, on the basis of analogous chemical shifts in the benzene series[2-7]. Such an assignment is now definitely substantiated, since the spectrum of (VIIb) consists of singlets at τ 5.48, 5.79 and 7.62, and only a barely detectable triplet [due to a small amount of (VIa) in the sample being analyzed] at τ 5.21 (Fig. 1).

A reaction of (VIIb) with the Vilsmeier complex (dimethylformamide+phosphorus oxychloride), according to a modification of literature procedures[16,17], produced 2,5-dideuterio(2-formyl-1-chlorovinyl)ferrocene (VIIIb) in 81% yield. The proton NMR spectrum of (VIIIb) exhibited singlets at τ 5.71 and 5.41 (C_5H_5- and 3,4-protons, respectively), and two sets of doublets (J 7 Hz) at τ 2.53 and 0.03 (vinyl and formyl protons, respectively). The spectrum of (2-formyl-1-chlorovinyl)ferrocene (VIIIa) was very similar, except that the resonance at τ 5.41 was a triplet, and an additional triplet (assignable to the 2,5-protons) was present at τ 5.20. It is interesting to note that *all* the cyclopentadienyl ring protons in the spectra of (VIIIa) and (VIIIb) are substantially deshielded in comparison to similar resonances in vinylferrocene analogs (*vide infra*), and in fact fall at very nearly the same field as the resonances in the spectra of (VIa) and (VIb). This effect is believed to be due largely to the conjugated 2-formyl substituent, which is postulated to lie *cis* to the ferrocenyl group[18].

The dehydration of 1-(2,5-dideuterioferrocenyl)ethanol according to the method described by us previously[19] led to 2,5-dideuteriovinylferrocene (IXb) in 86% yield. The proton NMR spectrum of (IXb) was identical to that of (IXa) described earlier[19], except that the upfield triplet at τ 5.82 appeared as a singlet and the low field triplet at τ 5.66 was reduced in intensity by *ca.* 90% of two protons (Fig. 1). Our earlier assignment of the high and low field triplets as being due to the 3,4- and the 2,5-protons, respectively, is therefore substantiated. Incidentally, a deuterium analysis of the dehydration product by the combustion-falling drop method indicated 14.7% atom-excess deuterium incorporation, which corresponds to 88% incorporation of two deuterons. Isotopic purity was therefore maintained in the reaction scheme proceeding from (Ib) to (IXb).

2,5-Dideuterioethynylferrocene (Xb) was prepared from (VIIIb) according to a modification of a literature procedure[17]. The proton NMR spectrum of (Xb) was comparatively simple, consisting of a singlet (broadened at the base) at τ 5.78, assignable to the C_5H_5- and the 3,4-protons, and a singlet at τ 7.28 (ethynyl proton) (Fig. 1). The spectrum of (Xa) was very similar, except for the presence of a triplet at τ 5.53 which can now definitely be assigned to the 3,4-protons, in accord with earlier assignments[17,20].

Treatment of the copper(I) salt of the deuterated acetylene (Xb) with iodobenzene in refluxing pyridine produced 2,5-dideuterio(phenylethynyl)ferrocene (XIb). A comparison of the proton NMR spectrum of (XIb) with that of (phenylethynyl)-ferrocene (XIa) described earlier[17,20] indicated that the triplet resonance appearing in the spectrum of (XIa) at τ 5.53 was virtually absent in the spectrum of (XIb). Thus, the higher field triplet at τ 5.82 and the lower field triplet at τ 5.53 in the spectrum of (XIa) can be respectively assigned to the 3,4- and the 2,5-protons, again in keeping with earlier conclusions[17,20].

The unequivocal proton NMR assignments presented in this paper should be generally applicable to many other substituted metallocene systems. Since most of the above-mentioned 2,5-dideuterated ferrocene derivatives can serve as important intermediates, extensions of this type of analysis to other more complicated systems can be visualized*. Studies on other specifically deuterated metallocenes are currently in progress and will be reported at a later date.

EXPERIMENTAL SECTION

Proton NMR spectra were recorded in CCl_3D solution on a Varian A-60 spectrometer. Non-deuterated ferrocene derivatives (A-series in Chart 1) were prepared by standard literature methods, and their reported melting points are compared with those of the 2,5-dideuterated derivatives as indicated below.

2,5-*Dideuterio*[(*dimethylamino*)*methyl*]*ferrocene* (*Ib*)

A magnetically stirred solution containing [(dimethylamino)methyl]ferrocene (81 g, 0.33 mole) in 400 ml anhydrous ethyl ether was treated dropwise over a period of 30 min with 0.50 mole of n-butyllithium in hexane under nitrogen. The solution was allowed to stir an additional 1 h, whereupon deuterium oxide (10.0 g, 0.50 mole) was added dropwise. The mixture was poured into 500 ml of water, the organic phase separated, and the latter dried over magnesium sulfate, Filtration of the ether solution and treatment again with n-butyllithium as described above, followed by reaction with deuterium oxide, afforded 78 g (97%) of (Ib). The product was purified by distillation, b.p. 96–98° (0.5 mm) [lit.[9] 91–92° (0.45 mm)].

[(2,5-*Dideuterioferrocenyl*)*methyl*]*trimethylammonium iodide* (*IIb*)

Treatment of 2,5-dideuterio[(dimethylamino)methyl]ferrocene in methanol with methyl iodide according to the method of Lednicer and Hauser[9] afforded (IIb) in 94% yield.

[(2,5-*Dideuterioferrocenyl*)*methyl*]*triphenylphosphonium iodide* (*IIIb*)

A reaction between [(2,5-dideuterioferrocenyl)methyl]trimethylammonium iodide and triphenylphosphine in ethanol[12] produced (IIIb), m.p. 258–259° decompn. (lit.[12] 254–256° decompn.) in 97% yield.

1-(2,5-*Dideuterioferrocenyl*)-2,2-*diphenylethene* (*IVb*)

[(2,5-Dideuterioferrocenyl)methyl]triphenylphosphonium iodide was treated with n-butyllithium in hexane[12], and the resulting phosphorane was allowed to react with benzophenone. Workup in the usual manner afforded (IVb), m.p. 76–77° (lit.[12] 77–79°) in 50% yield.

2,5-*Dideuteriomethylferrocene* (*Vb*)

Reduction of [(2,5-dideuterioferrocenyl)methyl]triphenylphosphonium iodide with lithium aluminum hydride in tetrahydrofuran[12] gave (Vb), m.p. 35–36° (lit.[12] 34–36°), in 75% yield.

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* For example, conversion of the deuterated aldehyde (VIb) into the correspondingly deuterated 1,1'-(α-oxotrimethylene)- and 1,1'-(trimethylene)ferrocenes has enabled us to definitively assign resonances in the proton NMR spectra of these bridged ferrocenes[18].

2,5-*Dideuterioformylferrocene* (*VIb*)

[(2,5-Dideuterioferrocenyl)methyl]trimethylammonium iodide was converted by aqueous sodium hydroxide[14] to 2,5-dideuterio(hydroxymethyl)ferrocene, m.p. 79–81° (lit.[14] 81–82°) in 75% yield.

Oxidation of the carbinol by means of activated manganese dioxide[21] in chloroform afforded (VIb), m.p. 121–122° (lit.[22] 120–121°) in 82% yield.

2,5-*Dideuterioacetylferrocene* (*VIIb*)

Methyllithium in ethyl ether (0.05 mole) was added dropwise over a period of 10 min to a stirred solution of 2,5-dideuterioformylferrocene (8.1 g, 37 mmoles) in 150 ml of ethyl ether under nitrogen. The mixture was allowed to stir for 2 h during which time the color changed from red to yellow. The mixture was cooled to 0° and hydrolyzed cautiously by the dropwise addition of water. The ether portion was separated, washed with water, dried over magnesium sulfate, and evaporated to yield 7.1 g of crude product. Recrystallization of the material from hexane deposited 6.4 g (75%) of 1-(2,5-dideuterioferrocenyl)ethanol as yellow needles, m.p. 80–81° (lit.[23] 78–79°).

A mixture of the carbinol (6.0 g, 0.026 mole) and activated manganese dioxide[21] (23.4 g, 0.27 mole) was heated to reflux in 200 ml of chloroform for 6 h. After this period, TLC indicated the presence of only one component whose R_f value was the same as that of acetylferrocene. The mixture was filtered and the residue was washed with two 50 ml portions of ethyl ether. The combined organic portions were evaporated under reduced pressure to give 6.0 g of crude product. Recrystallization of the latter from hexane gave 5.6 g (93%) of (VIIb), m.p. 83–85° (lit.[24] 85–86°).

2,5-*Dideuterio*(2-*formyl*-1-*chlorovinyl*)*ferrocene* (*VIIIb*)

An improved modification of literature procedures[16,17] was employed. 2,5-Dideuterioacetylferrocene (4.6 g, 0.02 mole) was added in small portions to a preformed solution of the Vilsmeier complex [from 6.1 ml (60 mmoles) of phosphorus oxychloride and 50 ml of dimethylformamide] at 0°. The deep-blue reaction mixture was allowed to stir for 15 min at 0°, 2 h at 25°, and then carefully poured into cold saturated sodium sulfate solution. After an additional 2 h under stirring, the mixture was extracted with methylene chloride. The extracts were washed repeatedly with water to remove residual dimethylformamide, were dried over magnesium sulfate, and were evaporated. Recrystallization of the residue from hexane afforded 4.5 g (81%) of (VIIIb), m.p. 76–77° (lit.[16] 78–79°).

2,5-*Dideuteriovinylferrocene* (*IXb*)

1-(2,5-Dideuterioferrocenyl)ethanol was converted to (IXb), m.p. 51–52° (lit.[19] 51–52.5°), in 86% yield by means of the sublimation pyrolysis procedure of Rausch and Siegel[19].

2,5-*Dideuterioethynylferrocene* (*Xb*)

An improved modification of a literature procedure[17] was employed. 2,5-Dideuterio(2-formyl-1-chlorovinyl)ferrocene (2.75 g, 0.01 mole) was dissolved in 30 ml of dioxane and the solution was heated to reflux in a nitrogen atmosphere. To this solution was rapidly added 15 ml of hot 5 *N* sodium hydroxide solution, and reflux was continued for 30 min. The mixture was allowed to cool to room temperature and concentrated at 25° (15 mm) overnight. The residue was dissolved in a minimum of ethyl ether and chromatographed on an alumina column using pentane as eluent. The first yellow band gave 1.21 g (57%) of (Xb), m.p. 53–55° (lit.[25] 55–56°).

2,5-Dideuterio(phenylethynyl)ferrocene (XIb)

Cuprous (2,5-dideuterioferrocenyl)acetylide was prepared from (Xb) in 80% yield according to the method of Stephens and Castro[26]. A mixture of this acetylide, iodobenzene and pyridine was converted in 77% yield to (XIb), m.p. 126–127° (lit.[20] 127–128°) by means of the procedure of Rausch, Siegel and Klemann[20].

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REFERENCES

1 M. D. Rausch, R. F. Kovar and C. M. Kraihanzel, *J. Amer. Chem. Soc.*, 91 (1969) 1259.
2 M. D. Rausch and V. Mark, *J. Org. Chem.*, 28 (1963) 3225.
3 V. Mark and M. D. Rausch, *Inorg. Chem.*, 3 (1964) 1067.
4 R. A. Benkeser, Y. Nagai and J. Hooz, *Bull. Chem. Soc. Jap.*, 36 (1963) 482.
5 Y. Nagai, J. Hooz and R. A. Benkeser, *Bull. Chem. Soc. Jap.*, 37 (1964) 53.
6 G. G. Dvoryantseva, S. L. Portnova, K. I. Grandberg, S. P. Gubin and Yu. N. Sheinker, *Dokl. Akad. Nauk SSSR*, 160 (1965) 1075.
7 D. W. Slocum, T. R. Engelmann, R. Lewis and R. J. Kurland, *J. Chem. Eng. Data*, 13 (1968) 378.
8 M. D. Rausch and D. L. Adams, *J. Org. Chem.*, 32 (1967) 4144.
9 D. Lednicer and C. R. Hauser, *Org. Synth.*, 40 (1960) 31.
10 D. Slocum, B. Rockett and C. R. Hauser, *J. Amer. Chem. Soc.*, 87 (1965) 2184.
11 N. S. Bhacca, L. F. Johnson and J. N. Shoolery, *NMR Spectra Catalog*, Varian Associates, Palo Alto, California (U.S.A.), 1962, spectrum No. 207.
12 P. L. Pauson and W. E. Watts, *J. Chem. Soc.*, (1963) 2990.
13 M. Rosenblum, *Chemistry of the Iron-Group Metallocenes*, Part I, Wiley, New York, 1965, p. 215.
14 J. K. Lindsay and C. R. Hauser, *J. Org. Chem.*, 22 (1957) 355.
15 L. M. Jackman, *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*, Pergamon, New York, 1959, p. 63.
16 K. Schlögl and W. Steyrer, *Monatsh. Chem.*, 96 (1965) 1520.
17 M. Rosenblum, N. Brawn, J. Papenmeier and M. Applebaum, *J. Organometal. Chem.*, 6 (1966) 173.
18 A. Siegel and M. D. Rausch, unpublished studies.
19 M. D. Rausch and A. Siegel, *J. Organometal. Chem.*, 11 (1968) 317.
20 M. D. Rausch, A. Siegel and L. P. Klemann, *J. Org. Chem.*, 31 (1966) 2703.
21 J. Attenburrow, A. F. B. Cameron, J. H. Chapman, R. M. Evans, B. A. Hems, A. B. A. Jansen and T. Walker, *J. Chem. Soc.*, (1952) 1094.
22 P. L. Pauson and W. E. Watts, *J. Chem. Soc.*, (1962) 3880.
23 C. R. Hauser and J. K. Lindsay, *J. Org. Chem.*, 22 (1957) 906.
24 V. Weinmayer, *J. Amer. Chem. Soc.*, 77 (1955) 3009.
25 R. A. Benkeser and W. P. Fitzgerald, *J. Org. Chem.*, 26 (1961) 4180.
26 C. E. Castro and R. D. Stephens, *J. Org. Chem.*, 28 (1963) 3313.