Journal of Organometallic Chemistry, 96 (1975) 283—287

AUTO-CONDENSATION OF ARYL- AND ARALKYLFERROCENES VIA LIGAND EXCHANGE

DIDIER ASTRUC and RENE DABARD

Laboratoire de Chimie des Organométalliques, U.E.R., Structure et Propriétés de la Matière, Equipe Associée au C.N.R.S. No. 477, Université de Rennes, 35031 Rennes Cédex (France)

(Received March 3rd, 1975)

Summary

An intermolecular exchange is described between two molecules of aryl- or aralkyl-ferrocene with $AlCl_3$ as catalyst. The cyclopentadienyl ring of one molecule is replaced by the phenyl nucleus of another similar molecule. In the case of a 1,1'-diaralkylferrocene, this auto-condensation reaction occurs exclusively to give a single salt containing the ferrocene moiety.

Introduction

Ligand exchange reactions between ferrocene and arenes readily provide cyclopentadienyl(arene)iron cations. These reactions were first reported by Nesmeyanov et al. [1] and applied to a variety of ferrocene and arene derivatives [2,3]. We report here the behaviour of mono- and 1,1'di-aralkylferrocenes in both aromatic and inert solvents.

Results and discussion

Behaviour of benzylferrocene with benzene

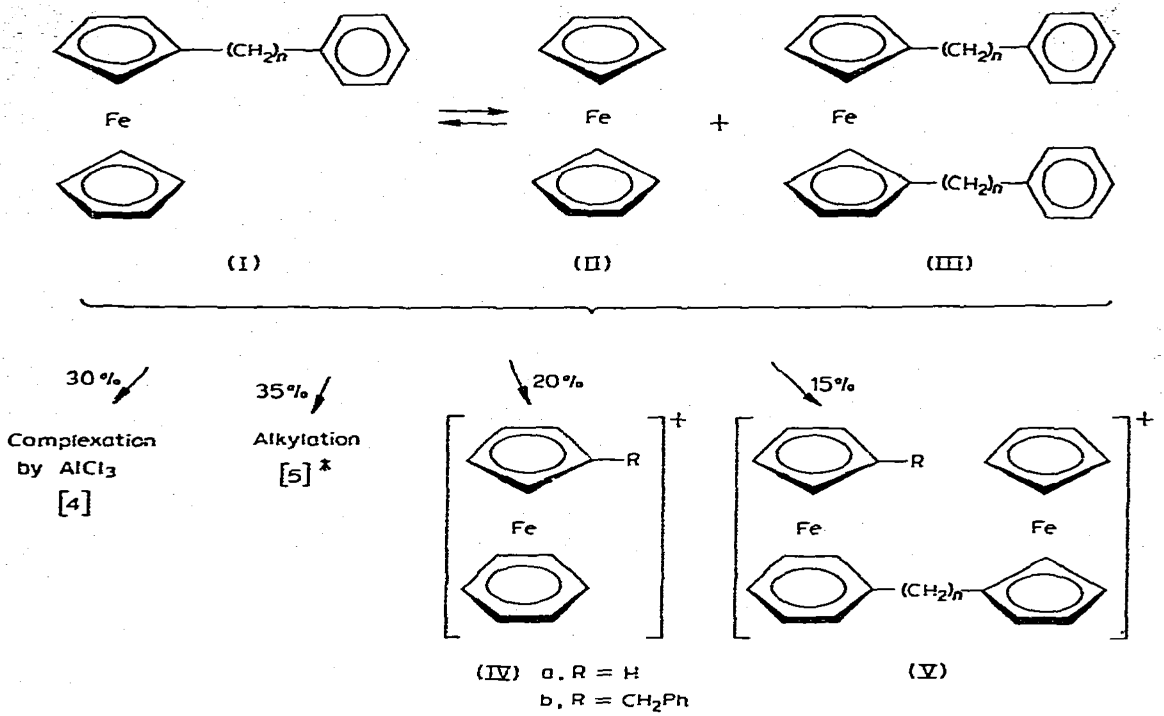
Refluxing a benzene solution of benzylferrocene brings about three types of ligand exchange in the one system (Scheme 1).

1. The replacement of one of the cyclopentadienyls which leads to two cations (n = 1) (IVa/IVb = 2). The ring bearing the benzyl substituent is preferentially replaced.

2. Disproportionation of benzylferrocene I (n = 1) (leading to II and III (n = 1) which is of the type observed by Bublitz [6] with alkylferrocenes in CH_2Cl_2.

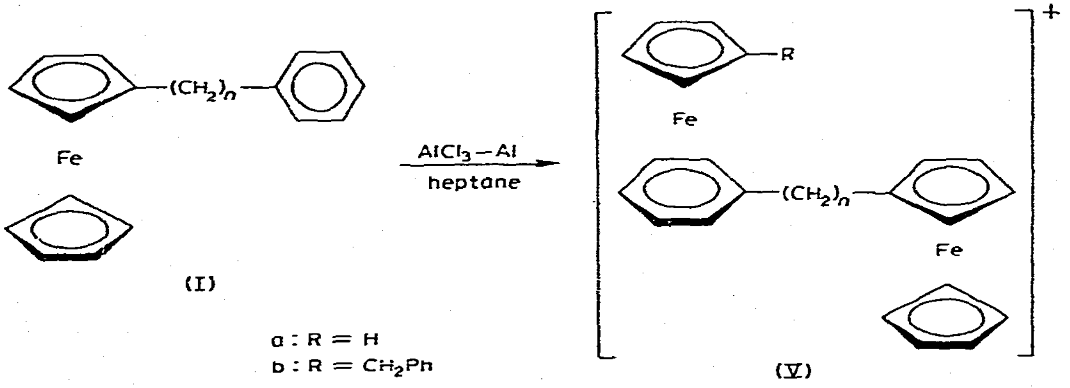
3. Auto-condensation which produces two cations V (n = 1) in the same proportions as in the first exchange (V i.e. Va/Vb = 2).

SCHEME 1



Behaviour of monoaryl- and aralkyl-ferrocenes in inert solvent

Use of an aromatic solvent, as in the previous example, leads to a complex mixture. In contrast, use of a non-aromatic solvent which does not participate in the exchange reaction, such as heptane, leads selectively to the salts resulting from auto-condensation** (eqn. 1). Thus the monoaryl- and aralkylferrocenes I



(1)

---

* As with alkylferrocenes, alkylation of aralkylferrocenes by protonated exchanged rings leads to ferrocenes bridged by cyclopentylene groups [5]. Their formation will be discussed, together with the overall mechanism of ligand exchange in alkylferrocenes, in a future publication [4].

** As with benzene as solvent, ferrocenes resulting from disproportionation and alkylation are formed, but as they remain in the organic layer after hydrolysis, they do not interfere with the isolation of the salts from the aqueous layer.

TABLE 1

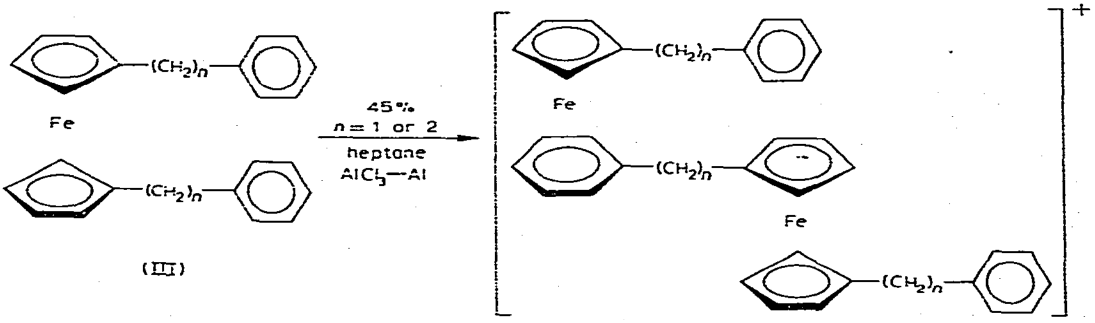
YIELDS OF SALTS Va AND Vb RESULTING FROM REACTION 1

n	Yield (%)	a/b
0	30	2/3
1	40	2
2	40	2

(n = 0, 1, 2) lead exclusively to mixtures of salts V, the composition of the mixture depending on the nature of the exchanged ring (Table 1). Table 1 shows that the yield is higher when the ferrocene and the phenyl rings carry electron-donating substituents: viz. $-(CH_2)_nPh$ and $-(CH_2)_nFc$ ($n \neq 0$, a/b > 1). In the case n = 0, the possibilities of exchange are slightly reduced as the phenyl substituent makes the substituted cyclopentadienyl ring less reactive towards cleavage (a/b < 1).

Behaviour of symmetrically disubstituted diaralkylferrocenes in inert solvent

Under similar conditions the symmetrically disubstituted diaralkylferrocenes give only one salt (eqn. 2).



(2)

Structure of the salts resulting from auto-condensation

The identification of the hexafluorophosphate salts was made by analysis and ^{1}H NMR spectroscopy (Table 2; solvent CD_3COCD_3, δ in ppm; TMS as internal reference).

TABLE 2

^{1}H NMR SPECTROSCOPIC DATA

	Cp—Fe—CpR	$\underline{\text{Cp}}$FePh	CpFeP$\underline{\text{h}}$	Ph non-ligand	CH_2
Va (n = 1)	4.24 3.95-4.15	5.17	6.43	7.34	3.95 [a]
Vb (n = 1)	3.95-4.20	5.19	6.43	7.32	3.95 [a]
Va (n = 0)	4.25 4.05-4.85	5.20	6.4	—	—
Vb (n = 0)	4.25 4.05-4.85	5.15	6.36	7.17-7.64	—
VI (n = 1)	4-4.15	5.08	6.38	7.27 and 7.30	3.71 and 3.90
VI (n = 2)	4-4.15	5.15	6.36	7.27	2.73-2.98

[a] Not separated from ferrocene multiplets.

The spectra are generally as expected for the CpFePh cations [7] and the ferrocene moiety. The spectra of Va ($n = 1$) and Vb ($n = 0$) do not contain the signal of the non-ligand phenyl ring, which do appear for the other salts as expected. For Va ($n = 1$) and VI ($n = 1$) the methylene groups are deshielded because of the proximity of $(CpFePh)^+$ and of the free phenyl group, which is not the case for VI ($n = 2$). In Vb ($n = 0$) the free phenyl has little influence upon the chemical shift of the Cp protons. On the other hand, in VIa ($n = 0$) and VIb ($n = 0$) th protons of the substituted ferrocene ring are strongly deshielded by the CpFePh cationic group.

It follows that, in all cases the auto-condensation of aryl- and aralkyl-ferrocenes is confined to one exchange. In particular, the formation of polycationic polymers is not observed. Thus, a suitable choice of substituents and solvent permits the synthesis of novel salts resulting from this selective auto-condensatio

Experimental

Action of $AlCl_3$ upon benzylferrocene in benzene

The method is similar to that used by Nesmeyanov with alkylferrocenes [1].

In 50 ml of benzene (distilled in an inert atmosphere), 2.75 g (10^{-2} mol) of benzylferrocene, 0.27 g (10^{-2} mol) of aluminium powder, and 2.67 g (2×10^{-2} mol) of $AlCl_3$ were introduced. The mixture was refluxed under nitrogen for 5 h, then cooled to 0°C and treated with 100 g of a mixture of ice and water. The aqueous layer was separated and washed several times with benzene. The Al^{3+} cations were removed by addition of concentrated ammonia and filtering off of the resulting alumina. Addition of an aqueous solution of a stoichiometric quantity of $NaPF_6$ precipitated the mixture of salts V. An excess of aqueo $NaPF_6$ was added and 0.33 g of salts IV were extracted with methylene chloride and precipitated by addition of ether. The composition of each mixture of two salts was determined by NMR spectroscopy (Varian EM 360, solvent CD_3COCD_3) using the protons of the non-ligand phenyl group. Finally, Va ($n = 1$) (0.44 g) and Vb ($n = 1$) (0.30 g) were separated by fractional reprecipitation from methylene chloride solutions by addition of ether.

The organic layer was washed with a solution of $NaHCO_3$, then with water and dried over $MgSO_4$. The benzene was removed and the yellow solid residue (2.2 g) dissolved in hexane and chromatographed on a column of silicic acid. The separation was completed by thick-layer chromatography on plates of silica gel (1 mm). It yielded FcH (0.1 g), $Fc(CH_2Ph)_2$ (0.15 g), $FcCH_2Ph$ (0.55 g) and a mixture of other alkylated ferrocenes (1.4 g).

Action of $AlCl_3$ upon monoaryl- or aralkyl-ferrocenes in heptane

The same method was used, except that benzene was replaced by heptane. The composition of the mixture of salts was determined by NMR spectroscopy, then a and b were separated as before (a always precipitates before b).

Action of $AlCl_3$ upon diaralkylferrocenes in heptane

The salts obtained from a similar procedure were purified by reprecipitation from their solution in CH_2Cl_2 by addition of ether. They are pink in the solid state and dark red in solution ($n = 0, 1$) or yellow ($n = 2$). They do not show sharp melting points, but progressively decompose between 150° and 200°C. The C and H analysis corresponds to the proposed structures within 0.3%.

References

1 A.N. Nesmeyanov, N.A. Vol'kenau and I.N. Bolesova, Dokl. Akad. Nauk SSSR, 61 (1963) 615.
2 Advan. Organometal. Chem. Vol. 10 (1972).
3 C.C. Lee, R.E. Sutherland and B.J. Thomson, Chem. Commun., (1972) 907.
4 D. Astruc and R. Dabard, unpublished data.
5 S.E. Cottis and H. Rosenberg, J. Polym. Sci., Part B, 2 (1964) 295.
6 D.E. Bublitz, Can. J. Chem., 42 (1964) 2381.
7 A.N. Nesmeyanov, I.F. Leshchova, Yu.A. Ustynyuk, Ye.I. Sirotkina, I.N. Bolesova, L.S. Isayeva and N.A. Vol'kenau, J. Organometal. Chem., 22 (1970) 689.