Journal of Organometallic Chemistry, 56 (1973) 323–326

METALLOCENE POLYMERS

XXVIII*. *trans*-1,2-DIFERROCENYLETHENE AS A BY-PRODUCT IN THE FERROCENE RECOMBINATION REACTION

EBERHARD W. NEUSE

Department of Chemistry, University of the Witwatersrand, Johannesburg (South Africa)

(Received November 27th, 1972)

SUMMARY

A compound obtained as a low-yield by-product in the polyrecombination reaction of ferrocene, to which initially a terferrocenyl structure had been ascribed on a tentative basis, has been identified as *trans*-1,2-diferrocenylethene. This structural assignment is supported by IR, PMR and mass spectral evidence, and firmly established by comparison with authentic samples.

INTRODUCTION

The identity of a substance melting in the range 260–265°, isolated from the polyrecombination reaction of ferrocene[1,2] as a low-yield by-product along with other oligo- and polynuclear ferrocene derivatives, has up to now remained in doubt[3]. Initially[1,2], a terferrocenyl structure was tentatively ascribed to the product. Both 1,3- and 1,1'-terferrocenyl were known at that time, and so only the 1,2-terferrocenyl structure seemed to fit in with this assignment. Spectroscopic evidence, on the other hand, was opposed to such an assignment[1]. The 1,2-terferrocenyl would almost certainly exhibit electronic absorption maxima shifted towards the blue (and attenuated) relative to those of the remaining two terferrocenyl isomers because of steric crowding of the outer two ferrocenyl groups and resultant lack of coplanarity, whereas the substance in question had, in contrast, been found to show maxima batho- and hyperchromically shifted relative to both 1,3- and 1,1'-terferrocenyl.

Subsequently, moreover, an entirely different compound with m.p. 198–200°, separated from the products of ferrocene recombination, was identified as the 1,2-terferrocenyl[3] and did, indeed, show the expected lowering of wavelengths and intensities (see Table 1). A terferrocenyl structure for the compound with m.p. 260–265° had thus to be abandoned.

---

* For Part XXVII see ref. 6.

TABLE 1

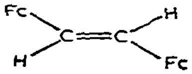
SOME ELECTRONIC ABSORPTION MAXIMA OF I AND ISOMERIC TERFERROCENYLS

Compound	*Solvent*	*λ_{max}, nm (ε in parentheses)*			*Ref.*
trans-1,2-Diferrocenyl-ethene (I)	ethanol, abs.	244 (19700)	313 (17000)	459 (1250)	this work
	chloroform	—[a]	314 (15500)	460 (1400)	4
	chloroform	246 (10200)	314 (10100)	—[a]	5
"Compound" m.p. 260–265°	ethanol, abs.	244[b] (17500)[c]	313 (16200)[c]	456 (1370)[c]	1,3
1,2-Terferrocenyl	ethanol, abs.	—	295 (9050)	449 (780)	3
1,3-Terferrocenyl	ethanol, abs.	—	301 (12500)	455 (1120)	3,6
1,1'-Terferrocenyl	ethanol, abs.	—	302 (15700)	454 (1290)	3

[a] Not reported. [b] Not reported in ref. 3. [c] ε corrected from previous work for mol. wt. of I.

RESULTS AND DISCUSSION

It has now been found that the compound in question in fact is *trans*-1,2-diferrocenylethene, I.



(I)

(Fc = ferrocenyl)

The product melting in the range 255–270°, isolated from the ferrocene recombination experiment described previously[3] as the first chromatographic fraction (0.07 g; from 100 g of ferrocene starting material) after ferrocene and biferrocenyl*, was rigorously purified by fractional crystallization from benzene after 1,2-terferrocenyl (which is not readily separable by crystallization or chromatography) had been removed by sublimation *in vacuo*. The compound so obtained (0.025 g), orange needles melting at 269–271° (sealed evac. cap.) (Found: C, 66.80; H, 5.29. $C_{22}H_{20}Fe_2$ calcd.: C, 66.71, H, 5.10%) gave the same X-ray diffractogram and IR spectrum as shown by authentic I prepared by Schlögl *et al.*[7] and also by Rosenblum *et al.*[8]**. The IR spectrum (KBr) exhibits the bands at 1001, 1100, and 1410 cm^{-1} (unsubst. ferrocene rings) in similar intensities (relative to the 820 cm^{-1} doublet) found in the spectra of diferrocenylmethane and 1,2-diferrocenylethane, and also shows the medium-intensity band at 960 cm^{-1} (doublet) due to the CH out-of-plane deformation mode of the *trans*-1,2-ethene system (corresponding stretching band not observable). The PMR spectrum ($CDCl_3$, 60 MHz; δ rel. to TMS), essentially identical with that of Rosenblum's compound**, is characterized by two poorly resolved triplets near 4.33 (4 α-H) and 4.20 ppm (4 β-H), and a sharp singlet at 4.08 ppm (10 unsubst. ring-H); the olefinic proton signal (2 H) is at 6.36 ppm***. The electronic absorption spectrum,

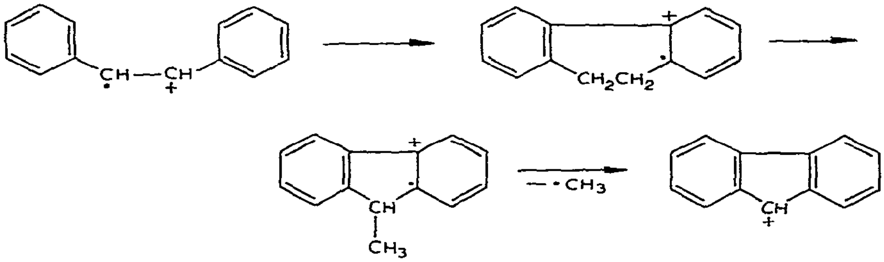
---

* This fraction was found by IR and X-ray diffractogram investigations to be identical in composition to the product melting at 260–265° obtained at the same stage of the work-up in the original study[1,2], and was used for the current investigation.

** A sample of I was furnished by Dr. Schlögl; Dr. Rosenblum provided IR and PMR spectra of both the *cis*- and the *trans*-compound. We are much obliged to them for their kind cooperation.

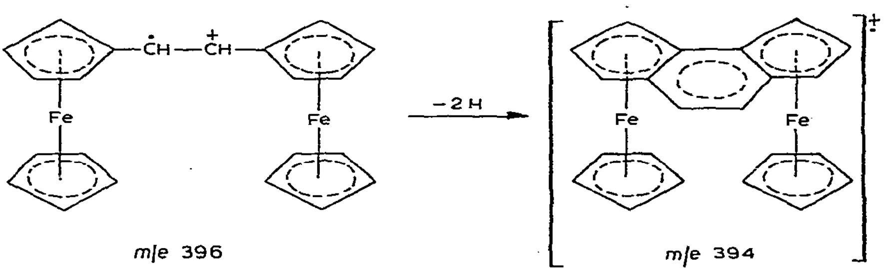
*** An up-field shift of this absorption would be expected for the *cis*-isomer because the olefinic protons are less exposed to the deshielding effect of both substituted cyclopentadienyl rings. In agreement with this, the spectrum of *cis*-1,2-diferrocenylethene (see preceding footnote) has the olefinic proton signal at 6.13 ppm.

similar to that recorded[3] for the crude material obtained in the initial work[1,2], features maxima at the positions reported by other workers[4,5] and expected for this compound (see Table 1; spectrum kindly recorded by Mr. P. Jwili of this Department). The mass spectrum (70 eV; 150° inlet) shows the parent-ion (base) peak (*m/e* 396; rel. abundance 100) and the $[M+1]^+$ peak (29) in the intensity ratio required for the isotopic composition of I. (Corresponding doubly-charged peaks at *m/e* 198 and 198.5 in same intensity ratio.) Other prominent peaks appear at *m/e* 394(14), 329(25), 274(9), 210(20), 186(18), 152(19) and 121(18). The spectrum shows no peak due to $[M-15]^+$ (expulsion of a methyl radical) such as is found in the case of the analogous *trans*-stilbene, for which such elimination (involving one bridging CH plus two *ortho*-H) constitutes the main fragmentation route[9]. In the stilbene case the driving force is the formation of the stable fluorenyl ion (eqn. 1).



(1)

In the ferrocene derivative the ethylene-bridged cyclopentadienyl rings apparently rearrange to the more stable *as*-indacene system through loss of two "*ortho*"-hydrogen atoms, *e.g.*



The stability of bis(*as*-indacenyliron) is well documented[10,11], as is that of the indacene cation, *m/e* 152, which occurs in the fragmentation of this metallocene[11]*.

A plausible but unproven (no metastables found) further fragmentation mechanism which would account for the prominent peaks listed would be one involving loss of a cyclopentadienyl ring from the π-indacenyl-bis(π-cyclopentadienyliron) cation, *m/e* 394, to form species *m/e* 329 and thence, through hydrogen capture and elimination of an iron atom, the radical ion *m/e* 274. Further loss of cyclopentadienylhydridoiron would then furnish the indacene cation, *m/e* 152. A second, perhaps simultaneous fragmentation path, favored by the inherent stability of ferrocene as a fragmentation product (expelled after hydrogen capture), could directly lead to ferro-

---

[*] The benzopentalene cation, isomeric with the indacene ion, also exhibits high stability in the spectrometer[12,13].

cenylacetylene. Both ferrocene and its acetylene derivative can exist as stable entities with or without the positive charge, and so could account for the two prominent peaks at *m/e* 186 and 210.

It is evident from the previous and current results that the "compound" as originally[1,2] separated and described (m.p. 260–265°) was actually I contaminated with some 1,2-terferrocenyl, the two compounds being so similar in solubility and adsorptive behavior as to prevent convenient separation by any technique based on fractional crystallization or chromatography. Indeed, the mass spectrum of a 7/1 mixture of I and 1,2-terferrocenyl turned out to be almost superimposable on that of the original product. This not only explains the broad melting range but also accounts for the mass peak at *m/e* 554 originally[1,2] observed.

The formation of the ethene I under the conditions of the ferrocene recombination reaction could conceivably proceed by pyrolytic scission of the (disubstituted) central cyclopentadienyl ring in 1,2-terferrocenyl. We were unable to verify such degradation in a control experiment employing 1,2-terferrocenyl (15 min at 210°). Moreover, no mass peaks corresponding to I and its fragmentation products were found in the mass spectrum of 1,2-terferrocenyl[3] even at an inlet temperature of 250°. A more plausible reaction path may involve a peroxide-assisted hydrogen elimination from 1,2-diferrocenylethane formed by recombination of intermediary ferrocyl free radicals, but this possibility needs further investigation.

REFERENCES

1 E. W. Neuse, K. Koda, E. Quo and R. K. Crossland, *Tech. Rept. AFML-TR*-158, *Part I*, AD 473 383 (1965).
2 H. Rosenberg and E. W. Neuse, *J. Organometal. Chem.*, 6 (1966) 76.
3 E. W. Neuse, *J. Organometal. Chem.*, 40 (1972) 387.
4 K. Schlögl and H. Egger, *Justus Liebigs Ann. Chem.*, 676 (1964) 88.
5 P. L. Pauson and W. E. Watts. *J. Chem. Soc.*, (1963) 2990.
6 E. W. Neuse and R. K. Crossland, *J. Organometal. Chem.*, 43 (1972) 385.
7 K. Schlögl and H. Egger, *Justus Liebigs Ann. Chem.*, 676 (1964) 76.
8 M. Rosenblum, S. J. N. Brawn and B. King, *Tetrahedron Lett.*, (1967) 4421.
9 R. A. W. Johnstone and B. J. Millard, *Z. Naturforsch. A*, 21 (1966) 604.
10 T. J. Katz and J. Schulman, *J. Amer. Chem. Soc.*, 86 (1964) 3169.
11 T. J. Katz, V. Balogh and J. Schulman, *J. Amer. Chem. Soc.*, 90 (1968) 734.
12 M. Cais, A. Modiano and A. Raveh, *J. Amer. Chem. Soc.*, 87 (1965) 5607.
13 I. J. Spilners and J. G. Larson, *Org. Mass Spectrom.*, 3 (1970) 915.