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Note

Thin-layer chromatography of hetera[n](1,1')ferroceno- and -ruthenocenophanes

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Considerable interest has recently been shown in the synthesis and metal ion complexing properties of macrocyclic polyoxathia, polythia and polyoxa ethers containing the ferrocene subunit[1–6]. As an extension of our study on the application of chromatographic techniques in the separation and purification of ferrocene derivatives[7,8] we have undertaken a systematic investigation of a series of hetera[n](1,1')ferrocenophanes and -ruthenocenophanes.

This paper describes the partition thin-layer chromatographic (TLC) and high-performance thin-layer chromatographic (HPTLC) separation of some diastereomeric polyoxathiaferrocenophanes and -ruthenocenophanes.

EXPERIMENTAL

Materials

All compounds investigated are new and were synthesized from suitable ferrocene and ruthenocene diols and α, ω-dithiols in very dilute solution in methylene chloride, in the presence of trifluoroacetic acid as a catalyst. The detailed syntheses and full characterizations of the new compounds were published elsewhere[9]. All of the synthesized compounds were further purified by column liquid chromatography on a glass column (40 × 3 cm I.D.) filled with silica gel 60, 70–240 mesh (E. Merck, Darmstadt, F.R.G.), with *n*-hexane–acetone (4:1) as the mobile phase.

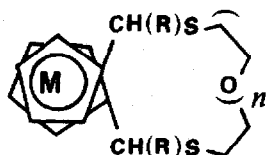The structural formula of the examined substances (for R and *n*, see Table I) is

TABLE I

CHEMICAL CONSTITUTION AND R_F VALUES OF METALLOCENOPHANE COMPOUNDS

Group	No.	Separated substances	Structural formula	R_F value TLC	R_F value HPTLC
Ferrocenophanes	1	2,14-Dithia-5,8,11-trioxa[15](1,1')-ferrocenophane	$n = 3$, R = H	0.29	0.40
	2	1,15-Dimethyl-2,14-dithia-5,8,11-trioxa[15](1,1')ferrocenophane	$n = 3$, R = CH$_3$: cis	0.35	0.46
			trans	0.40	0.52
	3	2,14-Dithia-5,8-dioxa[12](1,1')-ferrocenophane	$n = 2$, R = H	0.52	0.58
	4	1,12-Dimethyl-2,11-dithia-5,8-dioxa[12](1,1')ferrocenophane	$n = 2$, R = CH$_3$: cis	0.58	0.64
			trans	0.64	0.70
Ruthenocenophanes	5	1,15-Dimethyl-2,14-dithia-5,8,11-trioxa[15](1,1')ruthenocenophane	$n = 3$, R = CH$_3$: cis	0.38	0.49
			trans	0.43	0.54
	6	1,12-Dimethyl-2,11-dithia-5,8-dioxa[12](1,1')ruthenocenophane	$n = 2$, R = CH$_3$: cis	0.60	0.68
			trans	0.65	0.73
	7	1,9-Dimethyl-2,8-dithia-5-oxa-[9](1,1')ruthenocenophane	$n = 1$, R = CH$_3$: cis	0.70	0.76
			trans	0.76	0.80

Partition thin-layer chromatography

Separation was performed using pre-coated TLC glass plates covered with silanized silica gel 60 F_{254} (E. Merck) and impregnated with 20% formamide solution in acetone, using *n*-hexane–carbon tetrachloride–diethyl ether (12:1:1) as the solvent. Volumes of 5 μl of 2 mg/ml solutions of the metallocene derivatives in benzene were developed and the separated substances were detected under UV light at 254 nm.
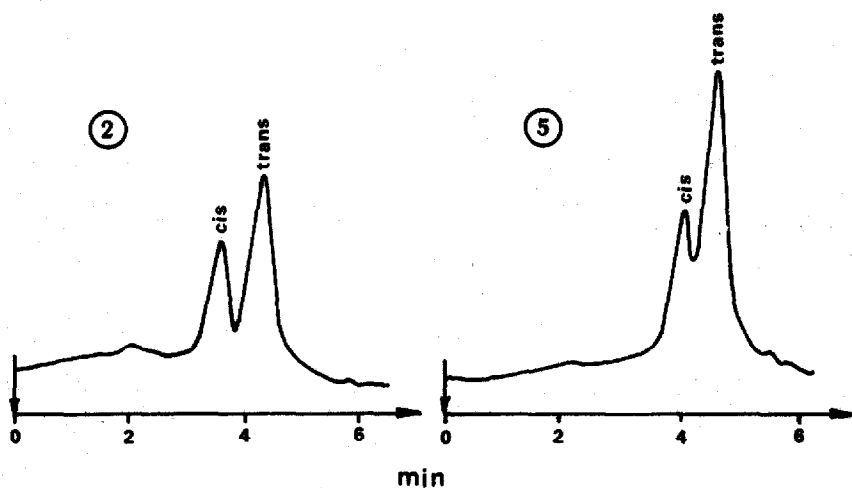

Fig. 1. HPTLC separation of diastereomeric mixtures of some metallocenophanes. 2 = *cis,trans*-1,15-Dimethyl-2,14-dithia-5,8,11-trioxa[15](1,1')ferrocenophane (*meso + rac.*); 5 = *cis,trans*-1,15-Dimethyl-2,14-dithia-5,8,11-trioxa[15](1,1')ruthenocenophane (*meso + rac.*).

High-performance thin-layer chromatography

HPTLC pre-coated 20 × 10 cm silica gel 60 plates for Nano TLC (E. Merck) were used, with *n*-hexane–benzene–acetone (3:2:1) as the mobile phase. The compounds were detected with 10% ammonium molybdate solution in 30% sulphuric acid. The samples were applied to the plate 10 mm apart, using a 200-nl capillary attached to a Nano-Applicator (Camag, Muttenz, Switzerland). The chromatograms were evaluated photometrically using a Model 42-B Varicord densitometer (Photovolt Corp., New York, NY, U.S.A.).

RESULTS AND DISCUSSION

The R_F values of the metallocenophanes are given in Table I. The conditions (non-reversed phase) used for partition macro-TLC give more satisfactory separations than adsorption macro-TLC. The results obtained by means of HPTLC are comparable to those by partition TLC.

Separations of metallocenophane diastereoisomers show higher R_F values for the *trans* than for the *cis* isomers, and ruthenocenophanes show higher R_F values than the corresponding homologous ferrocenophanes, in both partition TLC and HPTLC. The R_F values are also influenced by the number of oxygen atoms in the polyoxathio chain of the separated substances.

The example (Fig. 1) of the HPTLC separation of the diastereoisomeric ferrocenophane (2) and ruthenocenophane (5) mixtures shows the possibility of the application of densitometric to the quantitative evaluation of the results.

Densitometric detection is not more precise than spectrophotometry, but the results obtained, even if only treated semiquantitatively, allow one to control the course of the synthesis of the investigated substances.

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