

CYCLOPENTADIENYL-RUTHENIUM AND -OSMIUM COMPLEXES

IV. SEPARATION AND IDENTIFICATION OF RUTHENOCENE-CARBOXYLIC AND -BORONIC ACIDS. USE AND EVALUATION OF THE CHROMATOGRAPHIC TEST FOR THE DETECTION OF COMPLEXING OF ALKALI METAL CATIONS

TADEUSZ WILCZEWSKI

Institute of Inorganic Chemistry and Technology, Technical University, 80-952 Gdańsk (Poland)

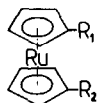
(Received November 7th, 1985)

Summary

Ruthenocene-mono- and -di-carboxylic acids have been separated and identified. The applicability range of the chromatographic test, previously used to detect the complexing phenomenon of alkali metal cations by crown ethers, has been determined. The performance of the test in the case of several new cyclopentadienyl ruthenium and osmium complexes, organic acids and compounds of the ionic-pair type containing a large BPh_4^- anion, has been investigated.

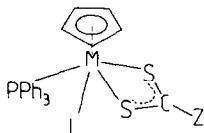
Results and discussion

Synthesis [1] of ruthenocenemonocarboxylic acid (Ia) and ruthenocenedicarboxylic acid (IIa) leads to a product consisting of a mixture of Ia, IIa and ruthenocene. The described [1] method of separation, consisting mainly of the washing out of compound Ia by ethyl ether and the crystallization of the residual compound IIa from glacial acetic acid, does not yield pure compounds. In addition, the mixture can be completely separated by chromatography, utilizing the elution technique.



	R ₁	R ₂
Ia	COOH	H
IIa	COOH	COOH
IIIa	B(OH) ₂	H

The field desorption mass spectra (FD/MS) of the separated compounds Ia and IIa show ion groups with maxima at m/e of 276 and 320, respectively. The ion intensity corresponds to the abundance of the natural ruthenium isotopes. In the mass spectrum (FD) of compound Ia, the molecular ions of compound IIa were not observed and vice versa.



	M	L	Z
I	Os	PPh ₃	OMe
II	Ru	—	OMe
III	Os	PPh ₃	OEt
IV	Os	PPh ₃	O-n-Pr
V	Os	PPh ₃	N(CH ₂) ₄
VI	Os	—	N(CH ₂) ₄

Fragmentation mass spectra (70 eV) of compounds Ia and IIa confirm the expected main fragmentation stages (Table 1).

The chromatographic behaviour of compounds Ia and IIa in the examined system (methanol) differs only slightly. However, it can be observed on plates covered with silicagel and partially impregnated with alkali metal salts, that considerable delays in the migration rates for compounds Ia and IIa occurred, in comparison to the unimpregnated part of the plate.

Until now, this type of behaviour of compounds (e.g. cyclopolyethers) in chromatographic tests [2] was seen as proof of complexing with alkali metal cations. The decrease in R_F values of the compounds on the salt-impregnated plates was interpreted as a result of the formation of a more polar complex with alkali metal cations. The relative values of the delay $B(\%)$ [2] were taken as an approximate measure of the stability of the given complex, for instance, the complex of cyclopolyethers with alkali metal cations.

However, a similar sort of migration behaviour is also shown by organic acids (Table 2). The dependence of the empiric parameter $B(\%)$ on alkali metal cation radii is characteristic for a given type of acid. Ruthenocenemonoboronic acid (IIIa) for example, shows a quite different dependence from compounds Ia and IIa. For *N*-phenylanthranilic acid, $B(\%)$ values were obtained: -21, +4, +27, +31 and

TABLE 1

THE MS/EI SPECTRA OF COMPOUNDS Ia AND IIa (¹⁰²Ru isotope)

Ion	II →	I →	RuCp ₂ →	RuCp →	RuC →	Ru
m/e	320	276	232	167	114	102
Relative intensity for IIa (%)	19.9	12.6	20.7	15.3	7.2	8.8
Relative intensity for Ia (%)	—	31.8	31.5	26.1	8.5	5.7

TABLE 2

R_F^2 AND $B(\%)$ VALUES OF THE COMPOUNDS ON PLATES PARTIALLY IMPREGNATED WITH A 2% AQUEOUS SOLUTION OF ALKALI METAL CHLORIDES, (according to ref. 2)

Type of compounds	Compound	Mobile phase	R_F^2 (mean)	$B(\%)^a$				
				LiCl	NaCl	KCl	RbCl	CsCl
Organic acids	CpRu(η -C ₅ H ₄ COOH) (Ia)	Methanol	0.92	30	13	23	29	40
	Ru(η -C ₅ H ₄ COOH) ₂ (IIa)	Methanol	0.89	44	15	32	34	53
	CpRu[η -C ₅ H ₄ B(OH) ₂] (IIIa)	Ethanol	0.90	27	12	3	2	1
Ion pair	[CpRu(CO)(PPh ₃) ₂]BPh ₄	CH ₂ Cl ₂	0.83	19	8	39	81	79
		Ethyl acetate	0.95	5	2	5	5	6
Neutral compounds	CpRuCl(PPh ₃) ₂	CH ₂ Cl ₂	0.41	7	3	-7	-2	5
		Ethanol	0.65	32	13	17	11	18
	CpRuS ₂ COMePPh ₃ (II)	Benzene	0.87	3	4	6	5	5
		Benzene	0.88	1	2	3	3	4
	CpRuS ₂ COEtPPh ₃	Benzene	0.94	4	2	1	1	2
		Ethanol	0.55	27	25	22	-2	18
	CpRuS ₂ COMe(PPh ₃) ₂	CH ₂ Cl ₂	0.59	6	21	10	8	12
		Methanol	0.68	37	20	13	10	12
	CpOsS ₂ COMe(PPh ₃) ₂ (I)	CH ₂ Cl ₂	0.56	0	9	2	10	9
		Methanol	0.72	20	25	22	3	1
	CpOsS ₂ COEt(PPh ₃) ₂ (III)	CH ₂ Cl ₂	0.58	9	16	7	12	10
	CpOsS ₂ CO-n-Pr(PPh ₃) ₂ (IV)	CH ₂ Cl ₂	0.58	0	2	0	5	8
	CpOsS ₂ CN(CH ₂) ₄ (PPh ₃) ₂ (V)	Benzene	0.61	3	1	6	3	3

^a $R_F^1 = R_F$ values of the compounds on the impregnated half of the plate area.

$R_F^2 = R_F$ values of the compounds on the unimpregnated part of the plate.

$$B(\%) = \frac{R_F^2 - R_F^1}{R_F^2} 100\%$$

+42, for cations of Li⁺, Na⁺, K⁺, Rb⁺ and Cs⁺, respectively. This illustrates an almost linear dependence of $B(\%)$ and the alkali metal cation radii. Also, in the IR (Nujol) spectra of the alkali metal salts with *N*-phenylanthranilic acid, a practically linear decrease in the frequency ν (N-H) was observed in relation to the alkali metal cation radii [3].

The formation of sparingly soluble salts is assumed to be one of the reasons for the activity of the organic acids in the chromatographic test.

A similar mechanism can be postulated to explain the behaviour of complex compounds of the ionic-pair type, e.g. [CpRu(CO)(PPh₃)₂]BPh₄ (Table 2). The value of the parameter $B(\%)$ is reflected in the secondary reaction of the large BPh₄⁻ anion with alkali metal cations, leading to the formation of sparingly soluble tetraphenylborates of alkali metal cations. A certain correlation exists between the empiric parameter $B(\%)$ and the solubility of the alkali metal cation of the tetraphenylborates formed.

In addition, neutral complex compounds with an extended structure react in the chromatographic test (Table 2, Table 3 and Table 4). Because the possibilities of formation of complexes with alkali metal cations as well as the formation of sparingly soluble salts must be excluded, there remains only the phenomenon of distribution of the compound between a mobile phase and a carrier layer. This may occur in the use of a mobile polar phase (methanol, ethanol). This suggestion is

TABLE 3

YIELDS, MELTING POINTS AND MASS SPECTRAL DATA FOR NEW COMPOUNDS

Compound	Mol. wt.	MS/FD	Colour	Yield (%)	M.p. (°C)	Substrate used for syntheses with CpRuCl(PPh ₃) ₂ or CpOsBr(PPh ₃) ₂
	(calcd.)	Parent ion <i>m/e</i> ^a				
CpOsS ₂ COMe(PPh ₃) ₂ (I)	887.0	888	dark-yellow	90	164–165	MeOCS ₂ K
CpRuS ₂ COMePPh ₃ (II)	535.6	536	yellow-brown	72	141–142	MeOCS ₂ K
CpOsS ₂ COEt(PPh ₃) ₂ (III)	901.0	902	yellow	60	150–151	EtOCS ₂ K
CpOsS ₂ CO-n-Pr(PPh ₃) ₂ (IV)	915.0	916	yellow	60	141–142	n-PrOCS ₂ K
CpOsS ₂ CN(CH ₂) ₄ (PPh ₃) ₂ (V)	926.1	927	white-yellow	53	122–122.5	(CH ₂) ₄ NCS ₂ NH ₄
CpOsS ₂ CN(CH ₂) ₄ PPh ₃ (VI)	663.8	665	golden-yellow	81	211–213	(CH ₂) ₄ NCS ₂ NH ₄

^a Data for ¹⁰²Ru and ¹⁹²Os isotopes.

confirmed by the results given in Table 2. A differentiation of the values of parameter *B*(%) occurs due to a different solubility of alkali metal salts in the moving mobile phase, changing its polarity.

Because the halides of alkali metals are less polar than silicagel [2] one can expect only delays positive values of *B*(%) in the migration of spots on the impregnated part of the plate. This expectation is experimentally confirmed.

The dispersion of the values of the parameter *B*(%) against the values of *R*_F² has been investigated for two standard compounds: dibenzo-18-crown-6 obtained in 1967 by Pedersen [4] and hexaaxaferrocenophane obtained in 1980 by Biernat [5].

It was not possible to obtain polyoxaruthenocenophanes in a similar way. In the reaction of dilithium ruthenocene with B(O-n-Bu)₃ only ruthenocenemonoboronic acid was obtained (compound IIIa), already obtained in 1972 by Nesmeyanov [6,7].

The chromatographic plates were impregnated with NaCl and KCl over half of their width, according to ref. 2. The results are shown in Fig. 1 and Fig. 2

The value dispersion of *B*(%) is statistically significant and decreases clearly with the increase in *R*_F². An extrapolation to the value *R*_F² → 1 gives a value for *B*(%) of 85 with NaCl, and for KCl of 89, respectively, for the complex dibenzo-18-crown-6

TABLE 4

NMR DATA OF CYCLOPENTADIENYL RUTHENIUM AND OSMIUM COMPLEXES (Chemical shifts, δ (ppm))

Compound	¹ H NMR (TMS) Solvent CS ₂			³¹ P NMR (H ₃ PO ₄) Solvent CH ₂ Cl ₂
	P-C ₆ H ₅	Cp	Others	
CpOsS ₂ COMe(PPh ₃) ₂ (I)	7.00m	4.35s	OCH ₃ : 3.72s	-2.9 s
CpRuS ₂ COMePPh ₃ (II)	7.14m	4.21s	OCH ₃ : 3.40s	
CpOsS ₂ COEt(PPh ₃) ₂ (III)	7.01m	4.33s	OCH ₂ : 4.35q, <i>J</i> (HH) 7 Hz; CH ₃ : 1.21t	-3.0 s
CpOsS ₂ CO-n-Pr(PPh ₃) ₂ (IV)	7.02m	4.36s	OCH ₂ : 4.26t, <i>J</i> (HH) 7 Hz; CH ₂ : 1.61m; CH ₃ : 0.88t	-3.2 s
CpOsS ₂ CN(CH ₂) ₄ (PPh ₃) ₂ (V)	7.01m	4.56s	N(CH ₂): 3.4m and 1.7m	
CpOsS ₂ CN(CH ₂) ₄ PPh ₃ (VI)	7.11m	4.28s	N(CH ₂): 3.0m and 1.7m	

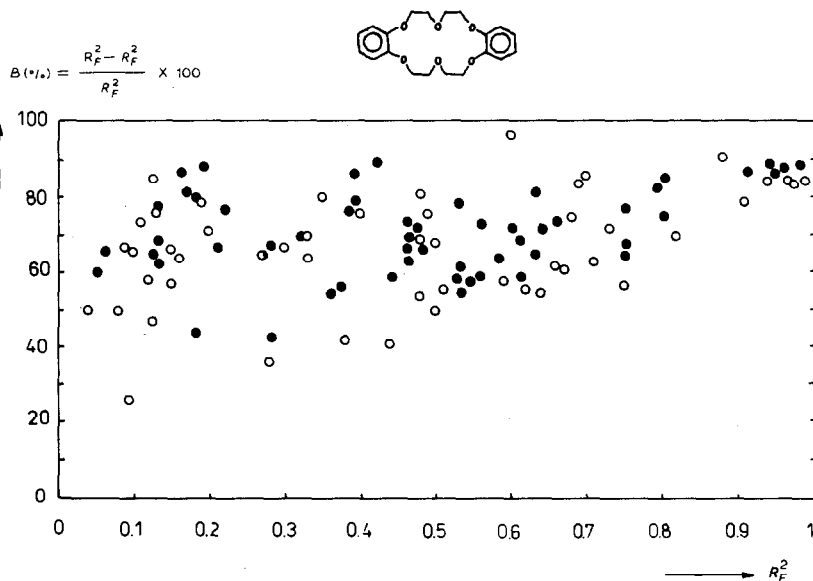


Fig. 1. Dependence of the $B(\%)$ parameter for dibenzo-18-crown-6 against the values of R_F^2 . \circ , half plates impregnated with a 2% aqueous solution of NaCl; \bullet , KCl.

Fig. 1. This is in good agreement with the known stability constants of the complexes of dibenzo-18-crown-6 with Na^+ and with K^+ (pK 4.5 and 5.1 in MeOH, respectively).

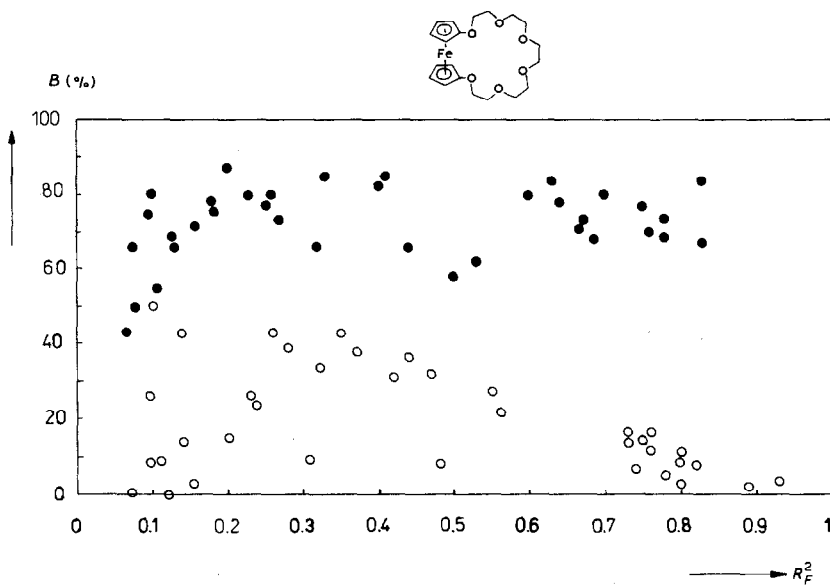


Fig. 2. Dependence of the $B(\%)$ parameter for hexaoxaferrocenophane against the values of R_F^2 . \circ , half plates impregnated with a 2% aqueous solution of NaCl; \bullet , KCl.

For hexaoxaferrocenophane (Fig. 2) the limiting values of the parameter $B(\%)$ differ considerably: 0 and approximately 75 for NaCl and KCl, respectively. A significant differentiation in the behaviour of hexaoxaferrocenophane occurred resulting in a polarity increase of the mobile phase ($R_F^2 \rightarrow 1$). The complex of hexaoxaferrocenophane with Na^+ is considerably less polar than that with K^+ .

The value of the parameter $B(\%)$ can measure the ratio of the polarity of the formed complex with alkali metal cations to the polarity of the carrier, modified by impregnation with salt used for covering the plates. An augmented sensitivity of the test, due to a change in the standardization conditions of the chromatographic plates was responsible for a considerable value dispersion of the parameter $B(\%)$ at lower R_F^2 values.

The chromatographic test was carried out within two ranges of R_F^2 , (i) near the value 1, and (ii) within the range 0.4–0.6. In the latter, it is also possible to obtain negative values of $B(\%)$. Negative values of the parameter $B(\%)$ may indicate either a lack of complexing, because the addition of alkali metal salts reduces the polarity of the silica-gel layer, or the formation of a stable complex with a tight coordination sphere around the alkali metal cation.

Experimental

Mass spectra were determined on a Varian MAT 711 apparatus. MS/EI and MS/FD 8 + 3 kV. Uncorrected melting points were measured in sealed capillaries. A glass column (S 0.85 cm²) was filled with a suspension of 10 g of silicagel (Macherey Nagel Kieselgel, 0.15–0.30 mm) in benzene. The effluent was colorimetrically detected (λ 380 nm). Absorbance changes were registered continuously. The effluent rate was 70–100 cm/h. Separation was carried out at room temperature.

In one case, the column charged with 0.1251 g of a mixture of Ia, IIa and ruthenocene, prepared as in ref. 1, was sequentially eluted with 150 cm³ portions of benzene, ethyl acetate and methanol. The obtained fractions were evaporated under vacuum. A 0.0730 g ruthenocene (benzene fraction), 0.0170 g of ruthenocenemonocarboxylic acid (Ia), m.p. 242–244°C (ethyl acetate fraction) and 0.0283 g of ruthenocenedicarboxylic acid (IIa) (methanol fraction) were obtained.

The chromatographic test was carried out according to ref. 2. 25 × 75 mm plates of aluminium foil, covered with a 0.2 mm layer of silicagel (DC-Alufohlen Kieselgel 60, Merck) were used. The R_F^2 values were changed using tetrachloromethane, benzene, chloroform, ethyl ether, dichloromethane, trichloroethylene, dioxane, ethyl acetate, acetone and their mixtures as the mobile phase.

Ruthenocenemonoboronic acid (IIIa) was obtained according to ref. 7 with a 19% yield (lit. [7] 15%). M.p. 177–178°C (crystallization from ethyl ether). IR (KBr) 3250bvs, 2266m, 1450bvs, 1200vs, 890w, 810vs, 652m, 550s. MS/FD: m/e 276 for ¹⁰²Ru.

The new compounds I–VI, shown in Tables 2, 3 and 4, were cited in a preliminary communication [8]. Due to its decomposition on the silica-gel layer it was not possible to carry out the chromatographic test with compound VI. The remaining compounds shown in Table 2, with the exception of Ia–IIIa, have already been described in refs. 9, 10.

Preparation of $\text{CpOsS}_2\text{COMe}(\text{PPh}_3)_2$ (I)

0.2404 g of $\text{CpOsBr}(\text{PPh}_3)_2$ (0.28 mmol), 2 cm³ of MeOH and 0.0955 g of

potassium methylxanthogenate MeOCS_2K (0.65 mmol) were refluxed for 1 h with stirring. The yellow crystalline precipitate was filtered off and washed with MeOH and n-hexane. 0.2228 g of I was obtained.

Preparation of $\text{CpRuS}_2\text{COMePPh}_3$ (II)

0.4358 g of $\text{CpRuCl}(\text{PPh}_3)_2$ (0.60 mmol), 30 cm³ of MeOH and 0.2648 g of potassium methylxanthogenate MeOCS_2K (1.81 mmol) were refluxed for 2 h. The warm solution was immediately filtered. A yellow needle-shaped compound crystallized from the filtrate. After storing overnight 0.2311 g of II was obtained.

Preparation of $\text{CpOsS}_2\text{COEt}(\text{PPh}_3)_2$ (III)

0.1033 g of $\text{CpOsBr}(\text{PPh}_3)_2$ (0.12 mmol), 14 cm³ of anhydrous EtOH and 0.2082 g of potassium ethylxanthogenate EtOCS_2K (1.30 mmol) were heated under reflux for 50 minutes. The warm solution was then immediately filtered. The filtrate was left to slowly crystallize, and after 5 h big prismatic crystals were collected, yielding 0.0658 g of III.

The use of MeOH instead of EtOH results in the formation of methyl derivatives as well (compound I). The yield of III also depends on the kind of ethylxanthogenate of alkali metals (Table 5). The procedure was that used for compound I.

Preparation of $\text{CpOsS}_2\text{CO-n-Pr}(\text{PPh}_3)_2$ (IV)

0.1097 g of $\text{CpOsBr}(\text{PPh}_3)_2$ (0.13 mmol), 4 cm³ of MeOH and 0.2335 g of potassium n-propylxanthogenate $\text{n-PrOCS}_2\text{K}$ (1.34 mmol) were refluxed for 1 h. Then the resultant yellow precipitate was filtered and washed. 0.0741 g of IV, containing 4% of I, were obtained.

Preparation of $\text{CpOsS}_2\text{CN}(\text{CH}_2)_4(\text{PPh}_3)_2$ (V)

0.0506 g of $\text{CpOsBr}(\text{PPh}_3)_2$ (0.059 mmol), 20 cm³ of MeOH and 0.2489 g of ammonium pyrrolidinedithiocarbamate (APDC) $(\text{CH}_2)_4\text{NCS}_2\text{NH}_4$ (1.52 mmol) were heated under reflux for 20 minutes. Then the warm solution was quickly filtered and the filtrate slowly cooled. After 1 day of storage, transparent, 0.0291 g of white-yellow crystals were collected (compound V).

Preparation of $\text{CpOsS}_2\text{CN}(\text{CH}_2)_4\text{PPh}_3$ (VI)

0.0724 g of $\text{CpOsBr}(\text{PPh}_3)_2$ (0.08 mmol), 5 cm³ of MeOH and 0.2017 g of ammonium pyrrolidinedithiocarbamate (APDC) $(\text{CH}_2)_4\text{NCS}_2\text{NH}_4$ (1.23 mmol)

TABLE 5

THE INFLUENCE OF THE KIND OF ALKALI METAL CATION IN ETHYLXANTHOGENATE SALTS ON THE YIELD OF COMPOUND III AND THE BY-PRODUCT (Medium MeOH)

Ethylxanthogenate used for syntheses	Yield (%)			M.p. of obtained mixture (°C)
	III	I	$\text{CpOsBr}(\text{PPh}_3)_2$ recovery	
EtOCS_2Li	13	19	48	148–151
EtOCS_2Na	58	26	8	150–151
EtOCS_2K	67	21	9	150–151

were refluxed for 8 h and then 0.0454 g of the crystalline compound VI were obtained after filtration.

References

- 1 M.D. Rausch, E.O. Fischer and H. Grubert, *J. Am. Chem. Soc.*, 82 (1960) 76.
- 2 J.F. Biernat and T. Wilczewski, *Polish J. Chem.*, 53 (1979) 513.
- 3 A. Bujewski and T. Wilczewski, *Polish J. Chem.*, in preparation.
- 4 C.J. Pedersen, *J. Am. Chem. Soc.*, 89 (1967) 7017.
- 5 J.F. Biernat and T. Wilczewski, *Tetrahedron*, 36 (1980) 2521.
- 6 A.N. Nesmeyanov, V.A. Sazonova and V.N. Drozd, *Chem. Ber.*, 93 (1960) 2717.
- 7 A.N. Nesmeyanov, A.A. Lubovich and S.P. Gubin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1972) 1823.
- 8 T. Wilczewski, *J. Organomet. Chem.*, 224 (1982) C1.
- 9 T. Wilczewski, M. Bocheńska and J.F. Biernat, *J. Organomet. Chem.*, 215 (1981) 87.
- 10 T. Wilczewski, *J. Organomet. Chem.*, in press.