

CHROM. 11,303

Note

High-performance liquid chromatography of some organometallic carborene π -complexes

ZBYNĚK PLZÁK, JAROMÍR PLEŠEK and BOHUMIL ŠTÍBR

Institute of Inorganic Chemistry, Czechoslovak Academy of Sciences, 250 68 Řež, near Prague (Czechoslovakia)

(Received June 28th, 1978)

Metallocene derivatives have been separated by high-performance liquid chromatography (HPLC)^{1,2} and even a few initial studies have demonstrated the potential of HPLC for preparative purposes and in kinetic studies relating to these compounds. Metalloborane chemistry is a relatively new area of organometallic chemistry in which many closely related species have been prepared. Several liquid chromatographic separations of metallocarboranes using silica gel of particle size 37–75 μm as adsorbent were described by Evans and Hawthorne³. In this study, the chromatographic conditions for the rapid separation of metallocarborane complexes by high-performance liquid–solid chromatography were determined.

EXPERIMENTAL

Home-built equipment with a UV detector operating at 254 nm was used⁴. The stainless-steel columns were packed as described earlier⁴ with silica gel prepared from Kieselgel H for thin-layer chromatography (TLC) (Merck, Darmstadt, G.F.R.) by sorting with an Alpine MZR air classifier.

A fraction with an average particle size of 13 μm (standard deviation 4.8 μm) was used. All measurements were carried out at room temperature. Sample sizes of 2–40 μl of fresh 0.5% solutions in the mobile phase were injected and the capacity factor (k') was calculated from the equation $k' = (t_r - t_0)/t_0$ in the usual way. Tetrachloroethylene was injected to determine the hold-up time (t_0) of the column. TLC was carried out in glass tanks well saturated with solvent vapour. Silufol plates (Kavalier, Sázava, Czechoslovakia) were used and for some experiments glass plates (12 \times 17.5 cm) were covered with 0.40-mm layers of Kieselgel H for TLC (Merck). After heating at 120°, these plates were conditioned for 48 h in a closed tank over saturated sodium bromide solution⁵.

The solvents used were of analytical-reagent grade, dried with a molecular sieve and distilled on a rotary evaporator before use.

All samples were obtained from laboratory stocks and their purities were checked by TLC and HPLC. The methods used to prepare the boron compounds are cited in the tables of results.

RESULTS AND DISCUSSION

The chromatographic results and a survey of the compounds chromatographed are given in Tables I–III. Results obtained with metalloborane complexes containing O, S, N, bridges between the carborane ligands are summarized in Table III.

All compounds studied exhibited UV absorption at 254 nm; for some complexes this value is very near the absorption maximum¹², and therefore spectrophotometric detectors operating at 254 nm can be used. The minimal detectable amount of

TABLE I
SANDWICH-LIKE METALLOCARBORANES CHROMATOGRAPHED

No.	Formula	Reference to the method of preparation
I	1-C ₅ H ₅ -Co-2,3-C ₂ B ₉ H ₁₁	6
II	1-Et-C ₅ H ₄ -Co-2,3-C ₂ B ₉ H ₁₁	7
III	1-C ₅ H ₅ -Co-2,3-C ₂ B ₉ H ₁₀ -8-F	7
IV	1-C ₅ H ₅ -Co-2,3-C ₂ B ₉ H ₁₀ -8-Cl	7
V	1-C ₅ H ₅ -Co-2,3-C ₂ B ₉ H ₁₀ -8-Br	7
VI	1-C ₅ H ₅ -Co-2,3-C ₂ B ₉ H ₁₀ -8-I	7
VII	1-C ₅ H ₅ -Co-2,4-C ₂ B ₉ H ₁₁	8
VIII	1-C ₅ H ₅ -Co-2,8-C ₂ B ₉ H ₁₁	8
IX	1-C ₅ H ₅ -Co-2-SB ₁₀ H ₁₀	9
X	1-C ₅ H ₅ -Fe-2,3-C ₂ B ₉ H ₁₁	6
XI	3,6-(C ₅ H ₅ Co) ₂ -1,2-C ₂ B ₈ H ₁₀	6
XII	2,4-(C ₅ H ₅ Co) ₂ -1-SB ₉ H ₉	10

TABLE II
CHROMATOGRAPHIC DATA FOR SOME SANDWICH-LIKE METALLOBORANES

HPLC system I: column, length 30 cm, I.D. 3.3 mm; sorbent, silica, 13 μm; guard column, length 60 mm, I.D. 3.3 mm; sorbent, Corasil II; eluent, 89.8% *n*-heptane–10% CH₂Cl₂–0.2% isopropanol; pressure drop, 5.0 MPa; flow-rate, 1.28 ml/min; detection, UV at 254 nm. System II: eluent, 79.8% *n*-heptane–20% CH₂Cl₂–0.2% isopropanol; other parameters as in system I. System III: eluent 69.8% *n*-heptane–30% CH₂Cl₂–0.2% isopropanol; other parameters as in system I. System IV: eluent, 59.8% *n*-heptane–40% CH₂Cl₂–0.2% isopropanol; other parameters as in system I.

TLC was carried out in glass tanks (8 × 18 × 17.5 cm). Silufol plates (15 × 15 cm) were developed in *n*-heptane–CH₂Cl₂ (1:1); visual detection after exposure to iodine vapour.

No.	<i>k'</i> (HPLC)				<i>R_F</i> (TLC)
	System I	System II	System III	System IV	
I	11.4	4.4	2.0	1.3	0.28
II	4.4	1.9	0.9		0.35
III		9.0	3.9	2.2	0.22
IV			4.6	2.7	0.16
V			5.2		0.16
VI			5.4	3.4	0.17
VII	3.1	1.5			0.35
VIII	0.5	0.2			0.51
IX	3.5	1.5			0.37
X	11.1		1.5		0.24
XI			2.8	1.7	0.13
XII			5.0	3.0	0.12

TABLE III

CHROMATOGRAPHIC DATA FOR SOME METALLOBORANES OF THE 8,8'-X(C₂B₉H₁₀)₂Co SERIES WITH A MONOATOMIC X BRIDGE BETWEEN CARBORANE LIGANDS

The method of preparation of these compounds was described in ref. 6; the structure, shown in Fig. 1, is in agreement with results of an X-ray diffraction study on 8,8'-CH₃O(C₂B₉H₁₀)₂Co¹¹.

HPLC system I: eluent 99.8% *n*-heptane-0.2% isopropanol. System II: eluent 89.8% *n*-heptane-10% CH₂Cl₂-0.2% isopropanol. System III: eluent 79.8% *n*-heptane-20% CH₂Cl₂-0.2% isopropanol. Other parameters as in Table II.

TLC: see Table II.

Compound	<i>k'</i> (HPLC)			<i>R_F</i> (TLC)
	System I	System II	System III	
MeO	7.7	1.9	1.0	0.41
EtO	6.5	1.6	0.9	0.42
MeS	10.5	2.4	1.4	0.40
EtS		2.2	0.9	0.41
BuS		2.1	1.0	0.40
Allyl-S		2.5	1.0	0.40
CH ₂ OCOCH ₂ S		5.0	2.8	0.30
H ₂ N		9.0		0.13
MeHN		2.8	1.3	0.30
Me ₂ N		1.3	0.5	0.41

sample that gives a response equal to twice the noise of the detector is routinely of the order of 10⁻⁸-10⁻⁹ g. The results in Tables II and III demonstrate the great sensitivity of the capacity factor to the composition of the mobile phase.

TLC was used as a pilot technique to establish a suitable solvent system for HPLC and to predict the retention behaviour of the compounds separated by HPLC. In the last column, TLC *R_F* values are presented in order to make a comparison of the

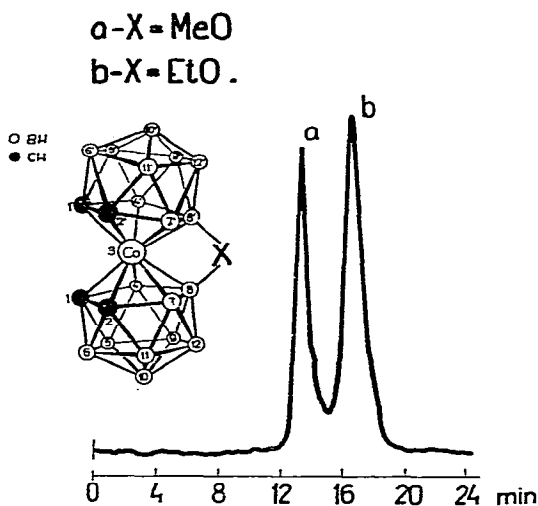


Fig. 1. Separation of metalloboranes 8,8'-X(-1,2-C₂B₉H₁₀)₂Co. Column: length 30 cm, I.D. 3.3 mm; sorbent, silica gel, 13 μ m; flow-rate, 1.28 ml/min; inlet pressure, 5.0 MPa; eluent, 99.8% *n*-heptane-;0.2% isopropanol; detection, UV; sensitivity, 0.25 absorbance unit.

resolving powers of TLC and HPLC possible. Using the relationship proposed by Soczewiński and Gotkiewicz¹³, good linear correlations of $\log k'$ versus R_M values were obtained, especially for plates covered with Kieselgel (correlation coefficient $r = 0.985$ for 6 values in the range of $1 < k' < 10$). A slightly polar solvent system was used in TLC to obtain R_F values in the optimal range. Fig. 1 shows a chromatogram obtained for a synthetic mixture of two bridged zwitterionic metallocarborane complexes differing by the methylene group in the aliphatic chain of the oxygen bridge. This separation demonstrates the unique selectivity of the silica adsorbent.

For the metallocarborane complexes separated, it appears that within groups of structurally related species (I and II; III, IV and V; and VII and VIII), the capacity factors or retention times are related to the polarity of these solutes.

The results obtained on the metalloborane complexes illustrate the potential of HPLC as a routine method for the separation of low-volatile and thermally unstable organometallic compounds without undue exposure to air or light.

ACKNOWLEDGEMENTS

The authors are grateful to Mrs. H. Čásenská for technical help and Dr. Tobola (Institute of Raw Materials, Kutná Hora, Czechoslovakia) for sorting the silica gel.

REFERENCES

- 1 R. Eberhardt, H. Lehner and K. Schögl, *Monatsh. Chem.*, 104 (1973) 1409.
- 2 D. T. Haworth and T. Liu, *J. Chromatogr. Sci.*, 14 (1976) 519.
- 3 W. J. Evans and M. F. Hawthorne, *J. Chromatogr.*, 88 (1974) 187.
- 4 Z. Plzák and B. Štíbr, *J. Chromatogr.*, 151 (1978) 363.
- 5 M. S. J. Dallas, *J. Chromatogr.*, 17 (1965) 267.
- 6 J. Plešek, B. Štíbr and S. Heřmánek, *Synth. Inorg. Met.-Org. Chem.*, 3 (1973) 291.
- 7 J. Plešek, K. Baše, S. Heřmánek, *Abstracts of Second International Meeting on Boron Chemistry, Leeds, March 25-29, 1974*, Abstract No. 46.
- 8 M. K. Kalousian, R. J. Wiersema and M. F. Hawthorne, *J. Amer. Chem. Soc.*, 94 (1972) 6679.
- 9 W. R. Hertler, F. Klanberg and E. L. Muettterties, *Inorg. Chem.*, 6 (1967) 1696.
- 10 J. Plešek, to be published.
- 11 V. Šubrtová, V. Petříček, A. Linek and J. Ječný, *Z. Kristallogr.*, 144 (1976) 139.
- 12 J. Plešek, S. Heřmánek, K. Baše, L. J. Todd and W. F. Wright, *Collect. Czech. Chem. Commun.*, 41 (1976) 3509.
- 13 E. Soczewiński and W. Gólkiewicz, *J. Chromatogr.*, 118 (1976) 91.