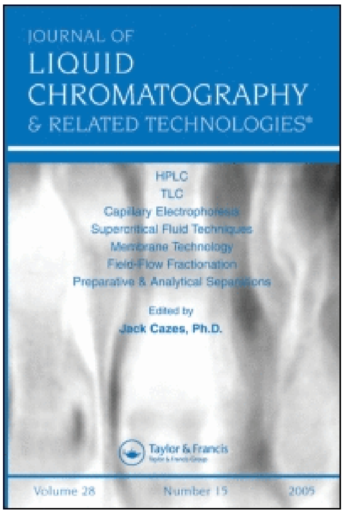

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A Study of the Retention Behaviour of Various Organometallic Complexes in HPLC Phase Systems

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A STUDY OF THE RETENTION BEHAVIOUR OF VARIOUS ORGANOMETALLIC COMPLEXES IN HPLC PHASE SYSTEMS

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ABSTRACT

The retention behaviour of various organometallic complexes in HPLC has been investigated. Three polar adsorbents (silica, a CN-bonded and a diol-bonded stationary phase) and a nonpolar adsorbent (C_{18}-bonded stationary phase) were used in this study for normal phase LC and reversed-phase LC respectively. The retention is influenced by the type of metal atom and the type of ligand in both types of LC. The study includes complexes of iron, ruthenium, cobalt, manganese, molybdenum and nickel with di-aza-butadiene and tetra-azadiene ligands. It was found that some ruthenium complexes are not eluted from bare and chemically modified silica.

INTRODUCTION

The development of high performance liquid chromatography (HPLC) has provided an analytical technique with outstanding possibilities. Due to the application of small particles modern HPLC is characterized by a high separation speed and a high column efficiency. The availability of different modes of LC (adsorption, partition, ion-exchange and exclusion) makes HPLC a versatile separation technique, which is widely used for organic and biochemical samples.

HPLC separations of metal chelates, with the purpose of metal-ion determination, have been published in a number of papers(1-8). However, HPLC, unlike classical LC and TLC, has less frequently been applied to problems associated with organometallic chemistry. Veening et.al. reported separations of arene tricarbonyl chromium complexes using normal phase adsorption chromatography(9,10). Lillya et.al. separated various tricarbonyl iron complexes by normal phase as well as by reversed phase liquid chromatography(11,12). Other examples of the use of normal phase liquid chromatography include metal complexes of cyclopentadienyl(13), triphenylphosphine(14), cycloheptatriene(15) and substituted hydrazones(16), and also metallocarboranes(17,18) and organomercury(19) and organopolymetallic compounds(20). Reversed phase LC has been applied for the separation of transition metal clusters(21), of iron carbonyl(22), organomercury(23,24) and organolead compounds(25). For the determination of diester, monoester-monocarboxylate and dicarboxylate derivatives of tris(2,2'-bypiridyl)ruthenium(II) ion-pair liquid chromatography has been applied(26).

This summary clearly demonstrates the potential of HPLC in the field of organometallic chemistry, especially for kinetic studies(15,20,26,27). Moreover, scaling up of HPLC(28,29) could extend its use to synthetic work also.

In the present paper the results of a study of the influence of the type of metal and ligand on the chromatographic behaviour of various organometallic complexes are reported. Bare and chemically bonded silica's were tested with a number of mobile phases.

EXPERIMENTAL

Apparatus

The chromatographic system consisted of commercially available elements. A microprocessor controlled pump module

(Series 3; Perkin Elmer, Norwalk, Conn., U.S.A.), a high pressure sampling valve (HPV-4; Chromatronix, Berkeley, Calif., U.S.A.), stainless steel columns (4,6 mm I.D., 150 mm length for reversed phase experiments and 3.0 mm I.D., 150 mm length for normal phase experiments), a variable wavelength detector (827 Spectrophotometer; Dupont, Wilmington, Del., U.S.A.) and a linear potentiometric recorder (Servogor RE 511; Goerz, Vienna, Austria) were used.

Chemicals en materials

In all experiments doubly distilled water and organic solvents of analytical grade were used. The packing materials applied were commercially available Zorbax ODS (7 μm) (Dupont, Wilmington, Del., U.S.A.), Lichrosorb Diol (10 μm) (Merck, Darmstadt, GFR), HPLC-Sorb Sil 60-D 5CN (5 μm) (Macherey-Nagel & Co., Düren, GFR) and porous silica (SI 60, Merck). The SI 60 material was ground and classified by means of an air-classifier to a particle size of 7-8 μm. The synthesis of the organometallic complexes used in this study has been described in the literature(30-34). $Ru_3(CO)_{12}$ was commercially available (Strem Chemicals Inc., Newburyport, Mass., U.S.A.).

Procedures

The chromatographic columns were packed by means of a stirred vessel(35). The column material was dispersed in n-hexane and columns were packed with the same solvent. All measurements were carried out at room temperature. Sample sizes of 5-20 μl of fresh solutions in the mobile phase (normal phase experiments) or in tetrahydrofuran or methanol (reversed phase experiments) were injected. The capacity ratio (κ_i) was calculated from the retention time of the solute (t_{Ri}) and that of an unretained solute (t_{Ro}) according to $\kappa_i = (t_{Ri} - t_{Ro})/t_{Ro}$.

RESULTS AND DISCUSSION

The retention behaviour of the selected organometallic complexes was investigated on three polar adsorbents (silica, diol-bonded and cyano-bonded silica) and a non-polar adsorbent (C-18 alkyl-bonded silica). Silica seems an obvious choice as it is frequently used for the isolation of organometallic complexes. A diol-bonded phase has been reported to be able to handle organometallic complexes which are unstable on bare silica(16). The cyano-bonded phase was chosen to investigate the possibility of special selectivity. The solvent strength of the mobile phase in the normal phase experiments was varied from heptane to tetrahydrofuran (THF). Solvents of intermediate strength were obtained by using hexane/THF and hexane/CH_2Cl_2 mixtures.

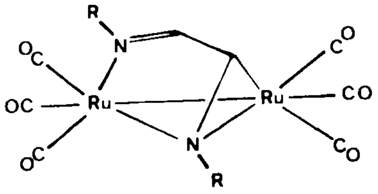
In reversed phase LC C_2, C_8 and C_{18} bonded phases are frequently applied. Although the magnitude of the retention may vary, usually no significant selectivity differences between these stationary phases are observed. Therefore mainly a C_{18} bonded phase was used in this study. Differences in selectivity can be obtained by the use of different organic solvents in reversed phase LC(36,37). This influence was investigated with methanol and THF.

The selection of organometallic complexes for this study was determined by: i) the objective to examine complexes of great interest in organometallic chemistry, ii) the objective to investigate the influence of ligands and metals, iii) the availability of pure substances. For the work described here several ruthenium carbonyl(30,31), iron carbonyl(31), molybdenum carbonyl(32) and cobalt-manganese carbonyl(33) complexes containing 1,4-diazabutadienes (DAB) (R-N=CH-CH=N-R) as ligands and tetra-aza-diene nickel complexes were studied.

$\underline{M_2(CO)_6(DAB)\ complexes}$

The compounds of the type $M_2(CO)_6(DAB)$ studied, are listed in table 1. The R-groups attached to the nitrogen atoms are

Table 1. $M_2(CO)_6(DAB)$ complexes

COMPOUNDS	NR.	STRUCTURE
$Ru_2(CO)_6$(iso-propyl DAB)	1	
$Ru_2(CO)_6$(tert.-butyl DAB)	2	
$Fe_2(CO)_6$(tert.-butyl DAB)	3	
$Fe_2(CO)_6$(cyclo-hexyl DAB)	4	
CoMn$(CO)_6$(iso-propyl DAB)	5	
CoMn$(CO)_6$(tert.-butyl DAB)	6	

iso-propyl, tert.-butyl or cyclohexyl groups. The retention behaviour of these substances for different adsorbents is given in table 2. The following mobile phases were used: heptane, 25% (v/v) CH_2Cl_2 in heptane, 50% (v/v) CH_2Cl_2 in heptane, CH_2Cl_2 and THF for normal phase experiments and 70% (v/v) THF in water and 95% (v/v) methanol in water for reversed phase experiments. The results obtained with those phase systems in which all six complexes were unretained, are not listed in table 2.

In the normal phase systems the retention on the CN- and diol-bonded phases is smaller compared to silica. No significant differences in selectivity between these stationary phases were observed. The complexes with similar metal atoms have corresponding capacity factors and the influence of the alkyl groups on the retention is small.

In the reversed phase systems the retention of $M_2(CO)_6(DAB)$ markedly depends on the nature of the hydrophobic parts (the alkyl groups) attached to the DAB unit(18), as can be seen in table 2. Differences in selectivity are observed for these complexes when methanol in the mobile phase is replaced by THF.

The $Ru_2(CO)_6(DAB)$ complexes were not eluted from silica when heptane was used as the mobile phase. Under the conditions that elution of these compounds from silica is observed their inter-

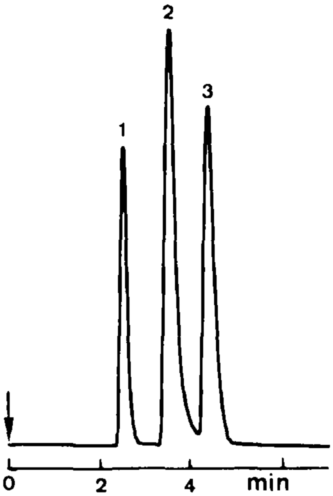


Figure 1. : Separation of a test mixture of $Ru_3(CO)_{12}$(=1), $Ru_2(CO)_6$(t.-butyl DAB)(=2) and $Fe_2(CO)_6$(t.-butyl DAB)(=3). Column, 150 x 3 mm I.D.; stat. phase, CN-bonded; mob. phase, n-heptane; detection, 250 nm.

Table 2. Capacity factors of $M_2(CO)_6$(DAB) complexes on various phase systems

Stationary phase	silica		CN - bonded	Diol - bonded	ODS - bonded	
Mobile phase	a	b	a	a	c	d
	Capacity factors					
Compounds (see table 1)						
1	>>	≈1(br)	0.5	0.3	1.8	1.5
2	>>	2-4(v.br.)	0.4	0.3	2.2	1.8
3	1.6	0.1	0.9	0.5	1.8	1.3
4	1.5	0.1	0.6	0.5	2.7	2.7
5	4.7	0.3	2.6(t)	1.0	1.3	1.0
6	4.0	0.2	2.0(t)	0.7	1.5	1.1

a = Heptane

b = CH_2Cl_2/Heptane (1:3)

c = THF/water (7:3)

d = Methanol/water (19:1)

v.br. = very broad

br. = broad

t = tailing

>> = not eluted

action with silica gives rise to an extensive peak broadening. With 25% (v/v) CH_2Cl_2 in heptane for example, injection of $Ru_2(CO)_6$ (tert.-butyl DAB) results in a peak which is extended over retention times corresponding to a capacity factor region of 2 to 4. However, with the CN- and diol-bonded phase normal peakshapes are observed for $Ru_2(CO)_6$(DAB) (see fig. 1). The iron complexes show a normal behaviour on the three polar adsorbents, while the cobalt-manganese complexes give rise to tailing peaks on the CN-bonded phase, although to a much smaller extent when compared with the ruthenium complexes on bare silica.

$M_2(CO)_n$(IAE) complexes

The reaction of $M_2(CO)_6$(DAB) (M = Ru or Mo) with a second DAB molecule can result in the formation of $M_2(CO)_n$IAE (n = 4, 5 or 6) complexes (IAE = bis [alkylimino-alkylaminoethane]), in which a C-C bond is formed between the two DAB units$^{(30,31)}$. The structure of $Ru_2(CO)_5$(IAE) is shown in table 3. In $Ru_2(CO)_4$(IAE) the bridging carbonyl group is lost and a metal-metal bond is formed. $Mo_2(CO)_6$(IAE) is equivalent to $Ru_2(CO)_4$(IAE) with the exception that it contains one extra terminal carbonyl group on each molybdenum atom. The chromatographic results obtained for the compounds listed in table 3 are given in tables 4 and 5.

Table 3. $M_2(CO)_n$(IAE) complexes

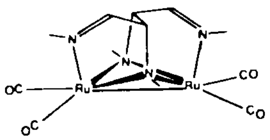
Compounds	Nr.	Structure of $Ru_2(CO)_5$(IAE)
$Ru_2(CO)_5$(tert.-butyl IAE)	1	
$Ru_2(CO)_5$(cyclo-hexyl IAE)	2	
$Ru_2(CO)_4$(cyclo-hexyl IAE)	3	
$Mo_2(CO)_6$(tert.-butyl IAE)	4	

Table 4. Capacity factors of $M_2(CO)_n$(IAE) complexes on various phase systems

Stationary phase	silica				CN-bonded				Diol-bonded			
Mobile phase	a	b	c	d	a	b	c	d	a	b	c	d
	Capacity factors											
Compounds (see table 3)												
1	>>	>>	>>	0	14	0.8	0.4	0	2.5	0.7	0.1	0
2	>>	>>	>>	0	15	0.9	0.4	0	2.3	0.7	0	0
3	>>	>>	>>	0	>>	>>	>>	0	>>	>>	>>	0
4	>>	1.0	0.3	0.2	4.0	0.1	0	0.1	2.5	0.7	0	0.1

a = CH_2Cl_2/Heptane (1:3) >> = not eluted

b = CH_2Cl_2/Heptane (1:1)

c = CH_2Cl_2

d = THF

Table 5. Capacity factors of $M_2(CO)_n$(IAE) complexes on various phase systems.

Stationary phase	Silica		CN-bonded		ODS-bonded		
Mobile phase	a	b	a	b	c	c'	d
	Capacity factors						
Compounds (see table 3)							
1	3.2	0.6	1.0	0.3	>>	0.5	>>
2	2.9	0.3	1.0	0.1	>>	0.8	>>
3	2.8	0.5	0.7	0.1	>>	0.8	>>
4	>>	*	*	0.5	0.5	-	0.8

a = THF/Heptane (1:3); b = THF/Heptane (1:1); c = THF/water (7:3); c' = THF/water (7:3) + TEA (5mM); d = Methanol/water (19:1). * = decomposition. >> = not recovered.

The ruthenium IAE complexes show a strong interaction with silica. These complexes cannot be eluted from silica with CH_2Cl_2/heptane mixtures (0-100% CH_2Cl_2). On the CN- and diol-bonded phases this interaction appears to be diminished for $Ru_2(CO)_5$(IAE), but not for $Ru_2(CO)_4$(IAE). However, with THF both are eluted unretained from silica as well as from the CN- and diol-bonded phases. Table 5 shows that with THF/heptane mixtures these complexes can be eluted from these adsorbents with intermediate retention. The capacity factors of $Ru_2(CO)_5$(IAE) on the CN-bonded phase with CH_2Cl_2/heptane (1:1) and with THF/heptane (1:3) are almost equal. $Ru_2(CO)_4$(IAE) is not recovered from this adsorbent in the first experiment, while in the latter it is eluted before the $Ru_2(CO)_5$(IAE) complexes. This shows that $Ru_2(CO)_4$(IAE) decompases on the CN-bonded phase with CH_2Cl_2/heptane mixtures as the mobile phase.

In reversed phase LC also a strong interaction of the ruthenium IAE complexes with the C_{18} bonded phase was observed. In this case elution with THF containing mobile phases did not diminish this interaction. Even with pure THF or CH_2Cl_2 these complexes were not eluted from the C_{18} bonded phase. In order to examine the possible influence of the length of the bonded alkyl chain, experiments with C_2 and C_8 bonded phases were performed with THF and CH_2Cl_2 as the mobile phase. The results were the same as with the C_{18} bonded phase.

It appeared that the use of dimethylsulfoxide/THF mixtures had a favourable influence on the elution of the ruthenium IAE complexes from the C_{18} bonded phase. Normal retention behaviour was observed. However, dimethylsulfoxide reacts rapidly with other ruthenium complexes ($Ru_2(CO)_6$(DAB) and $Ru_3(CO)_{12}$). This prevents the simultaneous analysis of these complexes in reaction mixtures. Addition of amines to a mobile phase consisting of THF/water also enables the elution of the ruthenium IAE complexes. The influence of several types of amines was investigated. Only minor differences were found between different types of amines (ammonia, n-propylamine, n-decylamine, tri-ethylamine, tri-n-octylamine). However, it appeared that the maximum recovery of $Ru_2(CO)_4$(cyclo-hexyl IAE) from the column was about 80%. Moreover the recovery was found to depend on the flow-rate and on the mobile phase composition. It must be concluded, and it has been confirmed by experimental results, that accurate quantitative results for these complexes cannot be obtained with such a chromatographic phase system.

Comparison with the results obtained for $Mo_2(CO)_6$(tert.-butyl IAE) shows that this complex can be eluted in most cases. This reveals that the presence of ruthenium,and not the IAE structure itself, is responsible for the strong interaction with bare and chemically modified silica. This is in accordance with the results obtained for $M_2(CO)_6$(DAB); a similar behaviour has also been reported for tris(2,2'-bipyridyl ruthenium) complexes(26).

$Ru_2(CO)_4(DAB)_2$ and $Ru_3(CO)_{12}$

$Ru_2(CO)_4(DAB)_2$ can be obtained from the $Ru_2(CO)_4$(IAE) complexes after prolonged heating. In these complexes the C-C bond in the IAE ligand, holding the two DAB units together, is broken(31). These complexes have a structure which is similar to $Ru_2(CO)_6$(DAB) (table 1), with two carbonyl groups replaced by a second DAB molecule. Two complexes of this type, $Ru_2(CO)_4$(iso-propyl $DAB)_2$ and $Ru_2(CO)_4$(cyclo-hexyl $DAB)_2$, together with $Ru_3(CO)_{12}$, which is the starting material of the ruthenium DAB complexes studied(30), were investigated with the following mobile phase compositions: heptane, 25% (v/v) CH_2Cl_2 in heptane, 50% (v/v) CH_2Cl_2 in heptane, CH_2Cl_2 and THF for normal phase experiments and 70% (v/v) THF in water and 95% methanol in water for reversed phase experiments. The

Table 6. Capacity factors of $Ru_2(CO)_4(DAB)_2$ and $Ru_3(CO)_{12}$ on various phase systems.

Stationary phase	Silica		CN - bonded	Diol - bonded	ODS - bonded	
Mobile phase	a	b	a	a	c	d
	Capacity factors					
Compounds						
$Ru_2(CO)_4$(iso-propyl $DAB)_2$	1.8	0.2	0.5	0.4	2.7	3.1
$Ru_2(CO)_4$(cyclo-hexyl $DAB)_2$	1.0	0.1	0.2	0.2	5.4	3.5
$Ru_3(CO)_{12}$	0	0	0	0	3.4	1.6

a = Heptane; b = CH_2Cl_2/Heptane (1:3); c = THF/water (7:3); d = Methanol/water (19:1).

results for those phase systems in which the $Ru_2(CO)_4(DAB)_2$ complexes were retained, are shown in table 6. These complexes have no strong interaction with the adsorbents that were examined, in spite of the similarity in structure between $Ru_2(CO)_4(DAB)_2$ and the complexes $Ru_2(CO)_6(DAB)$ and $Ru_2(CO)_n(IAE)$ (n=4 or 5). The retention of $Ru_2(CO)_4(DAB)_2$ in normal phase LC

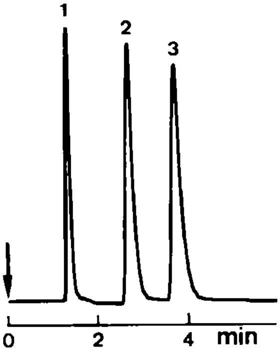


Figure 2.: Separation of a test mixture of $Ru_3(CO)_{12}$(=1), $Ru_2(CO)_4$(cyclohexyl $DAB)_2$(=2) and $Ru_2(CO)_4$(iso-propyl $DAB)_2$(=3). Column, 150x3 mm I.D.; stat. phase, silica; mob. phase, n-heptane; detection, 250 nm.

systems appears to be small, while $Ru_3(CO)_{12}$ is unretained in all these phase systems. An example of the separation of these three compounds on silica is shown in fig. 2. In the reversed phase experiments large changes in selectivity were observed.

$Ni(R_2N_4)_2$ complexes

The ligand in the bis(tetra-aza-diene)nickel complexes is related to the DAB ligand mentioned above in the sense that the iso-structural tetra-aza-diene group acts as a σ,σ-N,N-chelating ligand as is observed for DAB$^{(34)}$. The complexes studied and the chromatographic results obtained are listed in table 7 and 8.

The solubility in pure heptane was too low to detect these complexes. Therefore no capacity factors with n-heptane were obtained. The diol-bonded phase was not investigated as the retention of these complexes was expected to be smaller, but otherwise comparable with the retention on silica. As the $(R_2N_4)_2$ complexes decompose in dichloromethane, the solvent strength in normal phase LC was varied with THF/heptane mixtures of different composition (25%(v/v) and 50%(v/v) THF in heptane). With pure THF all complexes were unretained. The presence of a methoxy group on the aromatic substituents attached to the tetra-aza-diene ligand results in a signi-

Table 7. $Ni(R_2N_4)_2$ complexes

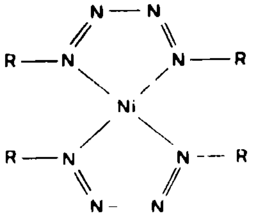
Compounds	Nr.	Structure
$Ni[(4\text{-}MeOC_6H_4)_2R_4]_2$	1	
$Ni[(4\text{-}MeC_6H_4)_2R_2]_2$	2	
$Ni[(3,5\text{-}Me_2C_6H_3)_2R_4]_2$	3	
$Ni[(4\text{-}ClC_6H_4)_2R_4]_2$	4	

Table 8. Capacity factors of $Ni(R_2N_4)_2$ complexes on various phase systems.

Stationary phase	Silica		CN - bonded		ODS - bonded	
Mobile phase	a	b	a	b	c	d
	Capacity factors					
Compounds (see table 7)						
1	3.3	0.7	1.0	0.2	0.7	2.3
2	0.3	0.1	0.2	0	1.5	5.1
3	0.1	0	0.1	0	2.5	10.2
4	0.1	0	0.1	0	3.1	-*

a = THF/Heptane (1:3)
b = THF/Heptane (1:1)
c = THF/water (7:3)
d = Methanol/water (19:1)

* insoluble in methanol

ficantly larger retention compared with the complexes having methyl- and chloro-groups. The retention of these complexes in all phase systems studied is very small. In reversed phase LC the elution order is exactly reversed as can be seen from table 8 and fig. 3a and 3b.

Variation of solvent strength in reversed phase LC

In reversed phase chromatography the solvent strength of the mobile phase can be varied by means of the concentration of the organic solvent in the mobile phase. An increase in the concentration of the organic solvent results in a decrease of the retention. It has been frequently shown that there is a linear relationship between the organic solvent concentration of the mobile phase and the logarithm of the capacity ratio(39). This was investigated with different amounts of THF in the mobile phase for some of the complexes used in this study. The results are shown in fig. 4, together with

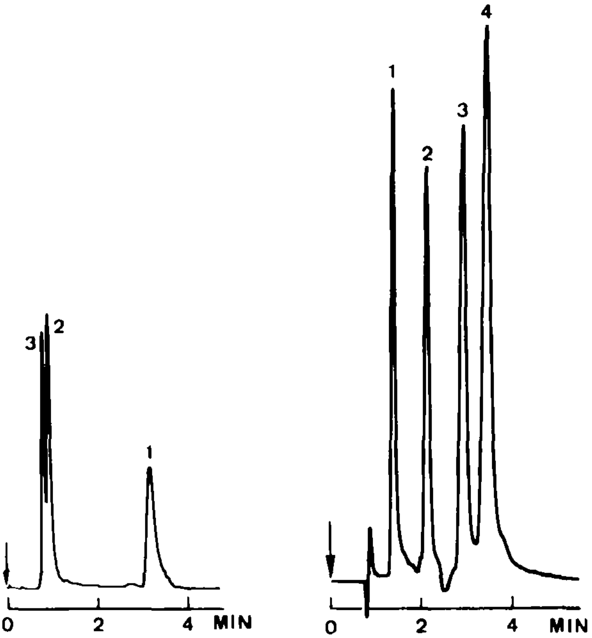


Figure 3.: Separation of test mixture of tetra-aza-diene nickel complexes using reversed phase (a) and normal phase chromatography (b). Peak numbers correspond to table 7.
a) Column, 150 x 4.6 mm. I.D.; stat. phase, C_{18}-bonded; mob. phase, 70% (v/v) THF in water; detection, 250 nm.
b) Column, 150 x 3 mm I.D.; stat. phase, silica; mob. phase, 25% (v/v) THF in n-heptane; detection, 250 nm.

the results obtained for toluene, a compound which was found to obey this relationship(40).

The chromatographic behaviour of the ruthenium and iron carbonyl complexes is fairly similar. $Ru_3(CO)_{12}$ and $Ru_2(CO)_4$ (iso-propyl DAB)$_2$ do not obey the linear relationship between log K and the THF concentration in the mobile phase. A distinct difference in the slope obtained for the nickel-bis (tetra-aza-diene) complex compared to the ruthenium and iron carbonyl complexes can be observed. In the case of toluene the influence of the THF concentration on the capacity factor is clearly different. These results show that for similar com-

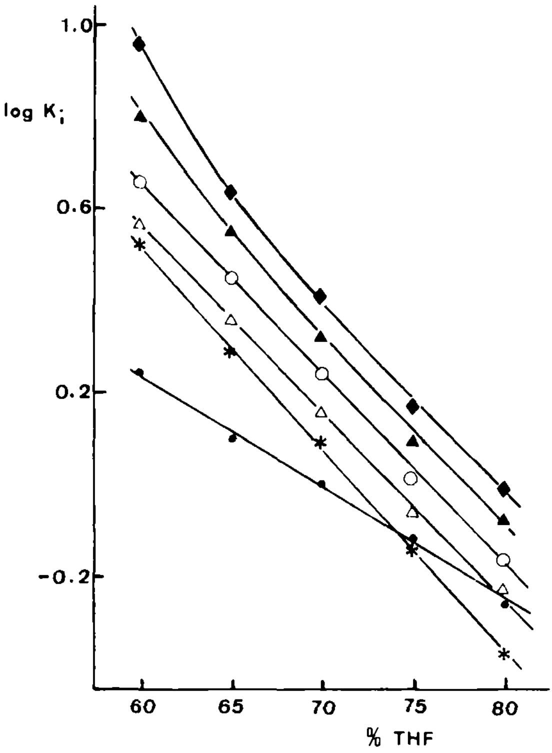


Figure 4. Effect of the THF concentration on the capacity ratio of various complexes and of toluene. Column, 150 x 4.6 mm I.D.; stat. phase, C_{18}-bonded; mob. phase, THF in Water; = $Ru_3(CO)_{12}$,
= $Ru_2(CO)_4$ (iso-propyl DAB)$_2$, = $Ru_2(CO)_6$ (t.-butyl DAB),
= $Fe_2(CO)_6$ (t.-butyl DAB), = $Ni[(4\text{-}MeC_6H_4)_2N_4]_2$,
= toluene

plexes (e.g. the ruthenium and iron carbonyl complexes) a parallel dependence of the capacity factor on the organic modifier content is found. This indicates that from the retention data of similar complexes the retention of other, corresponding, complexes can be predicted.

CONCLUSION

In normal phase LC the retention behaviour of the organometallic complexes studied, appears to depend strongly on the type of metal atom present and also on the type of polar substituents in the ligands. Differences in the alkylgroups on the ligands have less influence on the retention. Some ruthenium carbonyl complexes show a strong interaction with silica. The use of CN- and diol-bonded stationary phases appears to be advantageous to elute these complexes, which are not recovered from unmodified silica. Unfortunately the retention on these bonded phases is small for the considered complexes and this limits the application. In this respect very nonpolar solvents, like perfluoroalkanes, might be used to obtain a larger retention. Remarkable selectivity differences for the CN-bonded phase compared to silica and the diol-bonded phase have not been observed for the complexes used in this study.

In reversed phase LC the retention of the organometallic complexes is markedly influenced by polar and non-polar groups on the ligand as well as by the type of metal atom present. Corresponding ruthenium and iron carbonyl complexes showed a similar dependence of the capacity factor on the organic modifier content. However, the changes in selectivity, resulting from the use of THF or methanol as the organic modifier in the mobile phase, cannot be summarized in general rules.

The results, obtained for the organometallic complexes used in this study, are in accordance with the trends commonly found in liquid chromatography for less complex molecules.

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REFERENCES

1. Huber, J.F.K., Kraak, J.C., and Veening, H., Anal. Chem., 44 (1972) 1554.
2. Jones IV, D.R., and Manahan, S.E., Anal. Chem., 48 (1976) 502.
3. Gaetani, E., Laureri, C.F., Mangia, A., and Parolari, G., Anal. Chem., 48 (1976) 1725.
4. Heizmann P., and Ballschmitter, K., J. Chromatogr., 137 (1977) 153.
5. Tollincke, C.A., and Risby, T.H., J. Chromatogr. Sci., 16 (1978) 448.
6. Liska, O., Lehotay, J., Brandsteterová, E., and Guiochon, G., J. Chromatogr., 172 (1979) 384.
7. Uden, P.C., Bigley, I.E., and Walters, F.H., Anal. Chim. Acta, 100 (1978) 555.
8. Schwedt, G., Chromatographia, 12 (1979) 289.
9. Greenwood, J.M., Veening. H., and Willeford, B.R., J. Organometal. Chem., 38 (1972) 345.
10. Gardner, S.A., Seyler, R.J., Veening, H., and Willeford, B.R., J. Organometal. Chem., 60 (1973) 271.
11. Graf, R.E., and Lillya, C.P., J. Organometal. Chem., 47 (1973) 413.
12. Gresham, D.G., Lillya, C.P., Uden, P.C., and Walters, F.H., J. Organometal. Chem., 142 (1977) 123.
13. Haworth D.T., and Liu, T., J. Chromatogr. Sci., 14 (1976) 519.
14. Enos, C.T., Geoffroy, G.L., and Risby, T.H., Anal. Chem., 48 (1976) 990.
15. Pryde, A., J. Chromatogr., 152 (1978) 123.
16. Gasparrini, F., Misiti, D., Natile, G., and Galli, B., J. Chromatogr., 161 (1978) 356.

17. Evans, W.J. and Hawthorne, M.F., J. Chromatogr., 88 (1974) 187.

18. Plzák, Z., Plesek, J., and Stíbr, B., J. Chromatogr., 168 (1979) 280.

19. Funasaka, W., Hanai, T., and Fujimura, K., J. Chromatogr. Sci., 12 (1974) 517.

20. Bochkarev, M.N., Bortnikov, G.N., Makarenko, N.P., Maiorova, L.P., Kiselev, A.V., and Yashin, Ya.I., J. Chromatogr., 170 (1979) 53.

21. Enos, C.T., Geoffroy, G.L., and Risby, T.H., J. Chromatogr. Sci., 15 (1977) 83.

22. Gast, C.H., Nooitgedacht, F., and Kraak, J.C., J. Organomet. Chem., 184 (1980) 221.

23. Brinckman, F.E., Blair, W.R., Jewett, K.L., and Iverson, W.P., J. Chromatogr. Sci, 15 (1977) 493.

24. Gast, C.H., and Kraak, J.C., Int. J. Environm. Anal. Chem., 6 (1979) 297.

25. Botre, C., Cacace, F., and Cozzani, R., Anal. Lett., 9 (1976) 825.

26. Valenty, S.J. and Behnken, P.E., Anal. Chem., 50 (1978) 834.

27. Gast, C.H., Kraak, J.C., Staal, L.H., and Vrieze, K. in preparation.

28. Wehrli, A., and Huber, J.F.K., (Editor), Instrumentation for high performance liquid chromatography, Elsevier, Amsterdam, 1978, Chapter 6.

29. de Jong, A.W.J., Poppe, H. and Kraak, J.C., J. Chromatogr. 148 (1978) 127.

30. Staal, L.H., Polm, L.H., van Koten, G., and Vrieze, K., Inorg. Chim. Acta, 37 (1979) L 485.

31. Staal, L.H., Polm, L.H., Balk, R.W., van Koten, G., Vrieze, K. and Brouwers, A.M.F., Inorg. Chem., in press.

32. Staal, L.H., Oskam, A., Vrieze, K., Roosendaal, E., and Schenk, H., Inorg. Chem., 18 (1979) 1634.

33. Staal, L.H., Keysper, J., Polm, L.H., and Vrieze, K., to be published.

34. Overbosch, P., van Koten, G., and Overbeek, O., J. Am. Chem. Soc., 102 (1980) 2091.

35. Terwey-Groen, C.P., Vahlkamp, T., and Kraak, J.C., J. Chromatogr., Biomed. Appl., 145 (1978) 115.

36. Bakalyar, S.R., McIlwrick, R., and Roggendorf, E., J. Chromatogr., 142 (1977) 353.

37. Tanaka, N., Goodell, H., and Karger, B.L., J. Chromatogr., 158 (1978) 233.

38. Knox, J.K. (Editor), High performance liquid chromatography, Edinburgh University Press, Edinburgh, 1979.

39. Karch, K., Sebastian, I. and Halász, I, J. Chromatogr., 122 (1976) 3.

40. Tjaden, U.R., Thesis, University of Amsterdam, 1976.