

Note

Behaviour of mono-, bi- and trinuclear Group VI, VII and VIII metal carbonyl complexes in high-performance liquid chromatography

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(First received October 18th, 1985; revised manuscript received November 24th, 1985)

The effectiveness of high-performance liquid chromatography (HPLC) as a separation and analysis tool for complex mixtures of mono- and bimetallic derivatives^{1–5} and of clusters^{6–8} is well established. We obtained satisfactory separations of substituted and unsubstituted tri- and tetrametallic clusters of iron, ruthenium, osmium and nickel using reversed-phase or adsorption chromatography^{9,10}. Tetrahedral nickel–osmium clusters, derived from $C_5H_5NiOs_3H_3(CO)_9$ through substitution of one carbonyl by a Group V donor ligand, have also been separated by HPLC¹¹.

The following parameters influence the separations of metal clusters.

Nuclearity of the cluster

Generally, an increase in the nuclearity of the metal cluster results in an increase in the retention time. For example, on RP-18, $Ph_3PAuRu_3(CO)_9C_2\text{-tert.}-C_4H_9$ is eluted after $HRu_3(CO)_9C_2\text{-tert.}-C_4H_9$ ⁹ and, on Si 60, $(C_5H_5)_2Ni_2Ru_3(CO)_8C_2R_2$ is eluted after $Ru_3(CO)_8C_4R_4$ ¹⁰.

The substituents on the cluster

A series of dinuclear alkyne–carbonyl iron derivatives of the general formula $Fe_2(CO)_6(RC_2R')_2$ was chromatographed on a RP-18 column. The elution order appeared to be related to Taft's σ_1 parameter for the substituents R and R' (ref. 5). In the series $C_5H_5NiOs_3H_3(CO)_8L$, the nature of the ligand L strongly influences the retention times, in spite of the size of the whole cluster¹¹.

The nature of the metals in the cluster

Clusters with the same nuclearity, shape and substituents but different metals are effectively separated by HPLC. In the series $M_3(CO)_{12}$ (M = Fe, Ru, Os), $HM_3(CO)_9C_2\text{-tert.}-C_4H_9$ (M = Ru, Os) on RP-18⁹ and $C_5H_5NiM_3H_3(CO)_9$ (M = Ru, Os) on Si 60 (ref. 10) the elution times increase with decreasing electronegativity of the metals under reversed-phase conditions, and increase with increasing electronegativity on a silica column.

The shape of the cluster

Unfortunately, examples of identical clusters with different shapes are not known. However, small changes in substituents cause drastic changes in otherwise very similar clusters. For instance, replacing two hydrides in tetrahedral $C_5H_5NiRu_3H_3(CO)_9$ by an acetylene ligand produces $C_5H_5NiRu_3H(C_2HR)(CO)_9$ which assumes a butterfly shape. The butterfly cluster is eluted after the tetrahedral cluster from an Si 60 column with hexane-tetrahydrofuran as the eluent¹⁰. This elution sequence is unexpected because the butterfly complex has the more lipophilic ligand and should be retained less strongly than the tetrahedral cluster. The observed retention sequence is probably caused by the shapes of the clusters.

As part of a study of separation techniques for organometallic complexes and of the parameters influencing the separation of these complexes, we have investigated mixtures of mono-, bi- and trimetallic complexes which could be formed in reactions used for their preparations. Mixtures of structurally analogous complexes were also investigated.

EXPERIMENTAL

The mono- and dinuclear complexes were purchased from Fluka or Strem Chemicals. $Fe_2(CO)_6(SCH_3)_2$ prepared as described¹² was obtained as a mixture of *syn*- and *anti*-isomers. The trinuclear Ni_2Fe complexes were obtained and purified according to established procedures^{13,14}.

The chemical inertness of the compounds in acetonitrile, methanol and tetrahydrofuran (THF) was tested by maintaining them in these solvents for several hours at room temperature and by monitoring the IR spectra (CO stretching region) in solution before and after the chromatographic experiments.

The chromatographic separations were performed using a Perkin-Elmer Series 3B chromatograph, equipped with a Rheodyne 7105 injection valve and a LC-75 variable-wavelength UV-visible detector. Stainless-steel columns (25 × 0.4 cm I.D.) filled with 10- μ m LiChrosorb Si 60 and RP-18 (E. Merck, Darmstadt, F.R.G.) were used. The flow-rate was 1 ml/min. The eluates were monitored at 265 nm. Acetonitrile or THF solutions (5 μ l) of the compounds were injected. Hexane-THF was the mobile phase for the Si 60 and water-methanol for the RP-18 column.

DISCUSSION

The mixtures of metal carbonyls, chromatographed on the RP-18 reversed-phase column and on the Si 60 column, are listed in Table I. Chromatographic data concerning the separations illustrated in Fig. 2 and 3 are given in Table II.

The hexacarbonyls $M(CO)_6$ ($M = Cr, Mo, W$) could not be separated on the Si 60 column. The separation on the RP-18 column with methanol-water as eluent was incomplete (Fig. 1). The retention times increased with decreasing electronegativity of the metals (Cr 1.56, W 1.40, Mo 1.30) as observed earlier for $M_3(CO)_{12}$ ($M = Fe, Ru, Os$)⁹. All of the other mixtures of mononuclear complexes (Table I) were separated on both columns. The only recalcitrant compounds were the two isomers of $(CH_3S)_2Fe(CO)_6$, which had the same retention times under all conditions investigated. The retention times of the compounds $Re(CO)_5Cl$, $Re(CO)_5I$

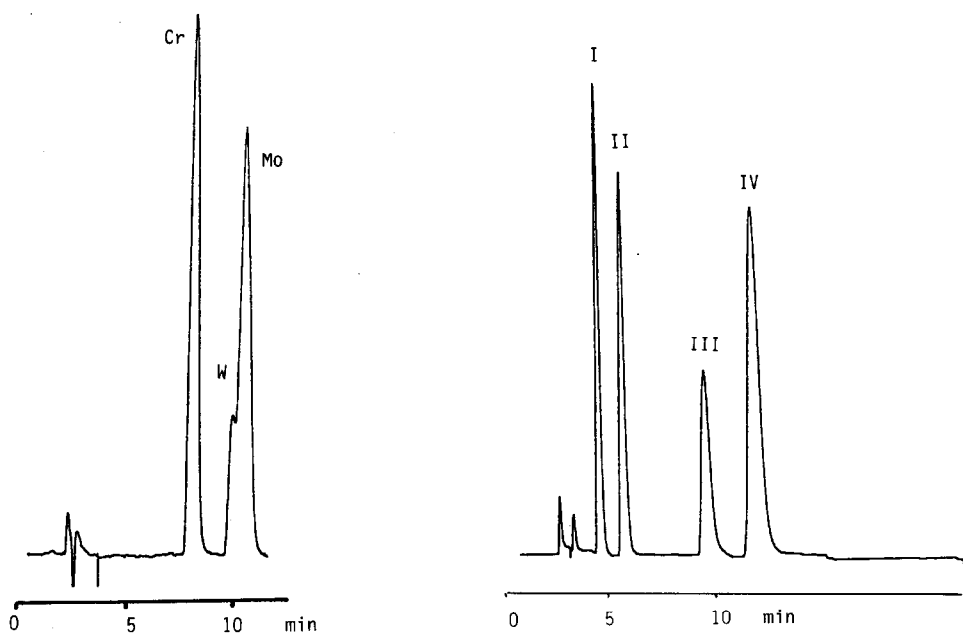


Fig. 1. Separation of $M(\text{CO})_6$ ($M = \text{Cr}, \text{Mo}, \text{W}$) on RP-18. Mobile phase: methanol-water (70:30); flow-rate, 1 ml/min. Detection: UV, 265 nm.

Fig. 2. Separation of $\text{C}_7\text{H}_9\text{Cr}(\text{CO})_3$ (I), $(\text{CH}_3)_3\text{C}_6\text{H}_3\text{Cr}(\text{CO})_3$ (II), $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$ (III) and $\text{CH}_3\text{O}_2\text{CC}_6\text{H}_5\text{Cr}(\text{CO})_3$ (IV) on Si 60. Mobile phase: hexane-THF (90:10); Flow-rate, 1 ml/min. Detection: UV, 265 nm.

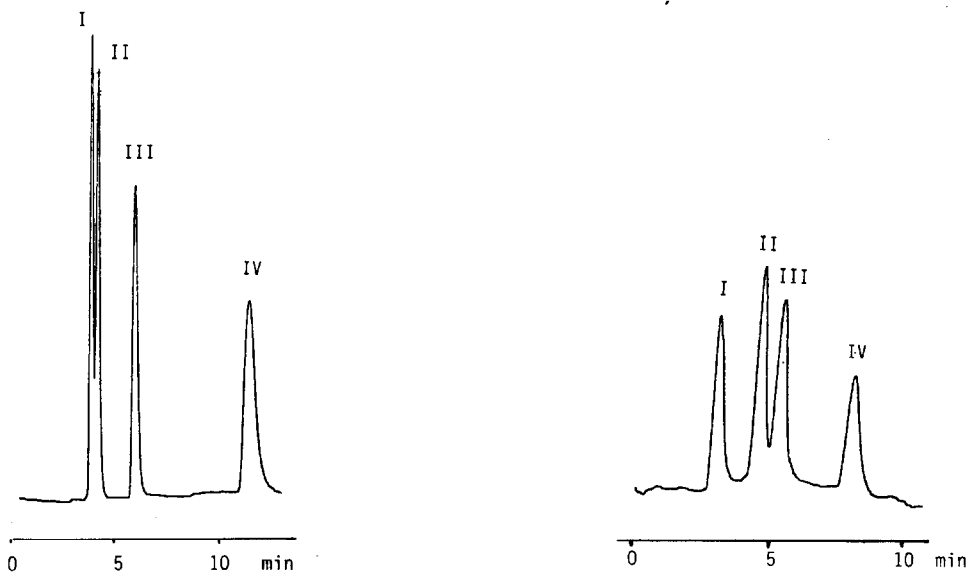


Fig. 3. Separation of $\text{CH}_3\text{C}_5\text{H}_4\text{Mn}(\text{CO})_3$ (I), $\text{C}_5\text{H}_5\text{Mn}(\text{CO})_3$ (II), $\text{Me}_3\text{C}_6\text{Cr}(\text{CO})_3$ (III) and $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$ (IV) on Si 60. Mobile phase: hexane-THF (99:1); flow-rate 1 ml/min. Detection: UV, 265 nm.

Fig. 4. Separation of $\text{Fe}_2(\text{CO})_9$ (I), $(\text{C}_5\text{H}_5)_2\text{Ni}_2\text{Fe}(\text{CO})_5$ (II), $(\text{C}_5\text{H}_5)_2\text{Ni}_2\text{Fe}(\text{CO})_3\text{C}_2\text{Ph}_2$ (III) and $(\text{C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_4$ (IV) on Si 60. Other details as in Fig. 2.

TABLE I
RETENTION TIMES, ELUENT AND COLUMN MATERIALS FOR THE SEPARATION OF METAL COMPLEXES

Mixture separated and retention times (min)	Column	Eluent	Flow-rate (ml/min)
Cr(CO) ₆ 8.6, W(CO) ₆ 10.7, Mo(CO) ₆ 11.2	RP-18	Methanol-water (70:30)	1.0
Re(CO) ₅ Cl 3.1, Re(CO) ₅ I 6.2	RP-18	Methanol-water (65:35)	1.0
Re(CO) ₅ Cl 5.0, Re(CO) ₅ I 4.3	Si 60	Hexane-THF (85:15)	1.0
Re(CO) ₅ I 5.5, Mn(CO) ₅ Br 6.7	Si 60	Hexane-THF (99:1)	1.0
C ₅ H ₅ Mn(CO) ₃ 5.5, CH ₃ C ₅ H ₄ Mn(CO) ₃ 7.1	RP-18	Methanol-water (72:28)	1.0
C ₃ H ₃ Mn(CO) ₃ 4.2, CH ₃ C ₃ H ₄ Mn(CO) ₃ 3.9	Si 60	Hexane-THF (99:1)	1.0
C ₆ H ₆ Cr(CO) ₃ 4.3, CH ₃ O ₂ CC ₆ H ₅ 4.7, C ₇ H ₈ * 7.4, (CH ₃) ₃ C ₆ H ₃ 9.0	RP-18	Methanol-water (68:32)	1.0
C ₆ H ₆ Cr(CO) ₃ 9.7, CH ₃ O ₂ CC ₆ H ₅ 12.3, C ₇ H ₈ * 4.1, (CH ₃) ₃ C ₆ H ₃ 5.4	Si 60	Hexane-THF (90:10)	1.0
C ₆ H ₆ Cr(CO) ₃ 3.9, C ₃ H ₃ Mn 5.3, CH ₃ C ₃ H ₄ Mn 7.0	RP-18	Methanol-water (70:30)	1.0
CH ₃ C ₃ H ₄ Mn(CO) ₃ 3.9, C ₃ H ₃ Min 4.2, (CH ₃) ₃ C ₆ H ₃ Cr 6.1, C ₆ H ₆ Cr 12.1	Si 60	Hexane-THF (99:1)	1.0
Fe ₂ (CO) ₉ 2.9, (C ₃ H ₅) ₂ Ni ₂ Fe(CO) ₅ 4.6, (C ₃ H ₅) ₂ Ni ₂ Fe(CO) ₃ C ₂ (C ₆ H ₅) ₂ 5.4, (C ₃ H ₅) ₂ Fe ₂ (CO) ₄ 8.3, (C ₃ H ₅) ₂ Ni ₂ (CO) ₂ (completely retained)	Si 60	Hexane-THF (90:10)	1.0
Fe ₂ (CO) ₉ 2.1, Mn ₂ (CO) ₁₀ 2.4, Fe ₂ (CO) ₆ (SCH ₃) ₂ 2.6	Si 60	Hexane-THF (99.7:0.3)	1.5
(C ₃ H ₅) ₂ Mo ₂ (CO) ₆ 5.4, (C ₃ H ₅) ₂ Fe ₂ (CO) ₄ 8.3	Si 60	Hexane-THF (90:10)	1.0
(C ₃ H ₅) ₂ Fe ₂ (CO) ₄ 3.7, (C ₃ H ₅) ₂ Fe(CO) ₂ I 4.7	Si 60	Hexane-THF (60:40)	1.0

* C₇H₈ = Cycloheptatriene.

TABLE II

CHROMATOGRAPHIC DATA FOR THE SEPARATIONS IN FIGS. 2 AND 3

Column: LiChrosorb Si 60, void volume 2.7 ml.

Compound	Capacity factor, k'	Resolution, R_s	Plate number, N
<i>Fig. 2</i>			
$C_7H_8Cr(CO)_3$	0.5	2.8	1697
$(CH_3)_3C_6H_3Cr(CO)_3$	1.0	6.7	1844
$C_6H_6Cr(CO)_3$	2.6	2.6	2353
$CH_3O_2CC_6H_5Cr(CO)_3$	3.6		1670
<i>Fig. 3</i>			
$CH_3C_5H_4Mn(CO)_3$	0.45	0.7	1488
$C_4H_4Mn(CO)_3$	0.55	3.9	1122
$(CH_3)_3C_6H_3Cr(CO)_3$	1.3	8.0	2150
$C_6H_6Cr(CO)_3$	3.5		2347

and $Mn(CO)_5Br$ are determined by the electronegativity differences, Δ , between the metal and the halogen (ΔReI 0.75, $\Delta MnBr$ 1.14, $\Delta ReCl$ 1.37)^{15,16}. On the Si 60 column the retention times increase with increasing Δ , whereas on RP-18 the retention times increase with decreasing Δ .

In the series $RC_5H_4Mn(CO)_3$ and $RC_6H_5Cr(CO)_3$ (Figs. 2 and 3) the polarity of the substituent R (Taft's σ_1 , ref. 17) seems to determine the retention times. Retention times on the Si 60 column increase with increasing σ (CH_3 , 0; H, 0.49; CH_3O_2C , 2.00). On the RP-18 column the trends are mixed. The large separation of $C_6H_6Cr(CO)_3$ from $C_5H_5Mn(CO)_3$, obtained either on the RP-18 or on the silica column, is probably caused by the difference in electron-withdrawing power between the fragments C_5H_5Mn and C_6H_6Cr .

The polynuclear compounds could not be separated on the RP-18 column, because they reacted with the required polar mobile phases. Separation of these complexes was achieved on the Si 60 column. Although the number of compounds investigated is too small to deduce general statements about the factors that determine retention times, the separation shown in Fig. 4 illustrates the effect of the nuclearity and of the substituents in the case of the first three compounds. Surprisingly, $(C_5H_5)_2Fe_2(CO)_4$ exhibits a greater retention time than those of the trinuclear compounds, which could be related to the presence of bridging carbonyl ligands, also present in $(C_5H_5)_2Ni(CO)_2$, which is completely retained.

ACKNOWLEDGEMENTS

This work was financially supported by CNR, Italy.

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