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Note

High-performance liquid chromatography of homo- and hetero-tetra-metallic iron, ruthenium, osmium and nickel clusters

A. CASOLI, A. MANGIA* and G. PREDIERI

Istituto di Chimica Generale ed Inorganica, Universita' di Parma, Via M. D'Azeglio 85, 43100 Parma (Italy)
and

E. SAPPA

Istituto di Chimica Generale ed Inorganica, Universita' di Torino, Corso M. D'Azeglio 48, 10125 Torino (Italy)

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As a part of research on the high-performance liquid chromatography (HPLC) of metal complexes¹, we studied the behaviour of bi- and trimetallic alkyne-carbonyl derivatives in a reversed-phase system. The separation of mixtures of bimetallic iron alkyne-carbonyl derivatives having different structures and numbers of substituents on the same $\text{Fe}_2(\text{CO})_6$ basic unit was achieved². The same results were obtained for homo-trimetallic carbonyl and alkyne-carbonyl clusters, all showing a triangular metal atom arrangement³.

Concerning the bimetallic derivatives, we observed that the dipole moment of the molecule, and also the electron donor power of the alkyne substituents (expressed as the Taft constant, σ_1) influenced the separation. For the trimetallic complexes, the presence of different substituents and the electronegativity of the metals were found to affect the chromatographic behaviour.

In each of the above-mentioned series of derivatives the same basic metal arrangement was present, whereas in this work we have considered homo- and hetero-tri- and tetrametallic clusters, characterized both by different substitution and by different metal cores (tetrahedral, "butterfly", planar).

The chosen complexes belong to different series of compounds. In the first there are the homometallic tetrahedral complexes $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ (complex 1)^{4,5} and $\text{H}_2\text{Ru}_4(\text{CO})_{13}$ (complex 2)⁶, the heterometallic tetrahedral $\text{CpNiM}_3(\text{CO})_9(\mu\text{-H})_3$ ($\text{M} = \text{Ru}$, complex 3a; $\text{M} = \text{Os}$, complex 3b)⁷ and the derivatives $\text{Fe}_3(\text{CO})_8(\text{HC}_2\text{Me})_4$ (complex 4)⁸ and $\text{H}_3\text{Ru}_3(\text{CO})_9\text{CCH}_2\text{Bu}^t$ (complex 5)⁹, all characterized by M_3C tetrahedral cores. In particular, complexes 3a and 5 were found to show isolobal relationships, according to Hoffmann¹⁰, in an earlier paper¹¹.

We also chose the butterfly structures $\text{Ru}_4(\text{CO})_{12}(\text{C}_2\text{Ph}_2)$ (complex 6)¹² and $\text{CpNiM}_3(\text{CO})_9(\mu\text{-H})(\text{C}=\text{CHR})$ ($\text{M} = \text{Ru}$, $\text{R} = \text{Pr}^t$, complex 7a¹³; $\text{M} = \text{Os}$, $\text{R} = \text{Bu}^t$, complex 7b¹⁴). Complexes 3a and b and 7a and b are chemically related¹⁴. The structures of the above complexes are shown in Fig. 1.

The second series is formed by the iron clusters $\text{Fe}_3(\text{CO})_8(\text{C}_2\text{Et}_2)(\text{HC}_2\text{Me})$ (8a), $\text{Fe}_3(\text{CO})_8(\text{HC}_2\text{Et})_2$ ("ic isomer", complex 8b) and $\text{Fe}_3(\text{CO})_8(\text{C}_2\text{Et}_2)$ (8c)^{15,16},

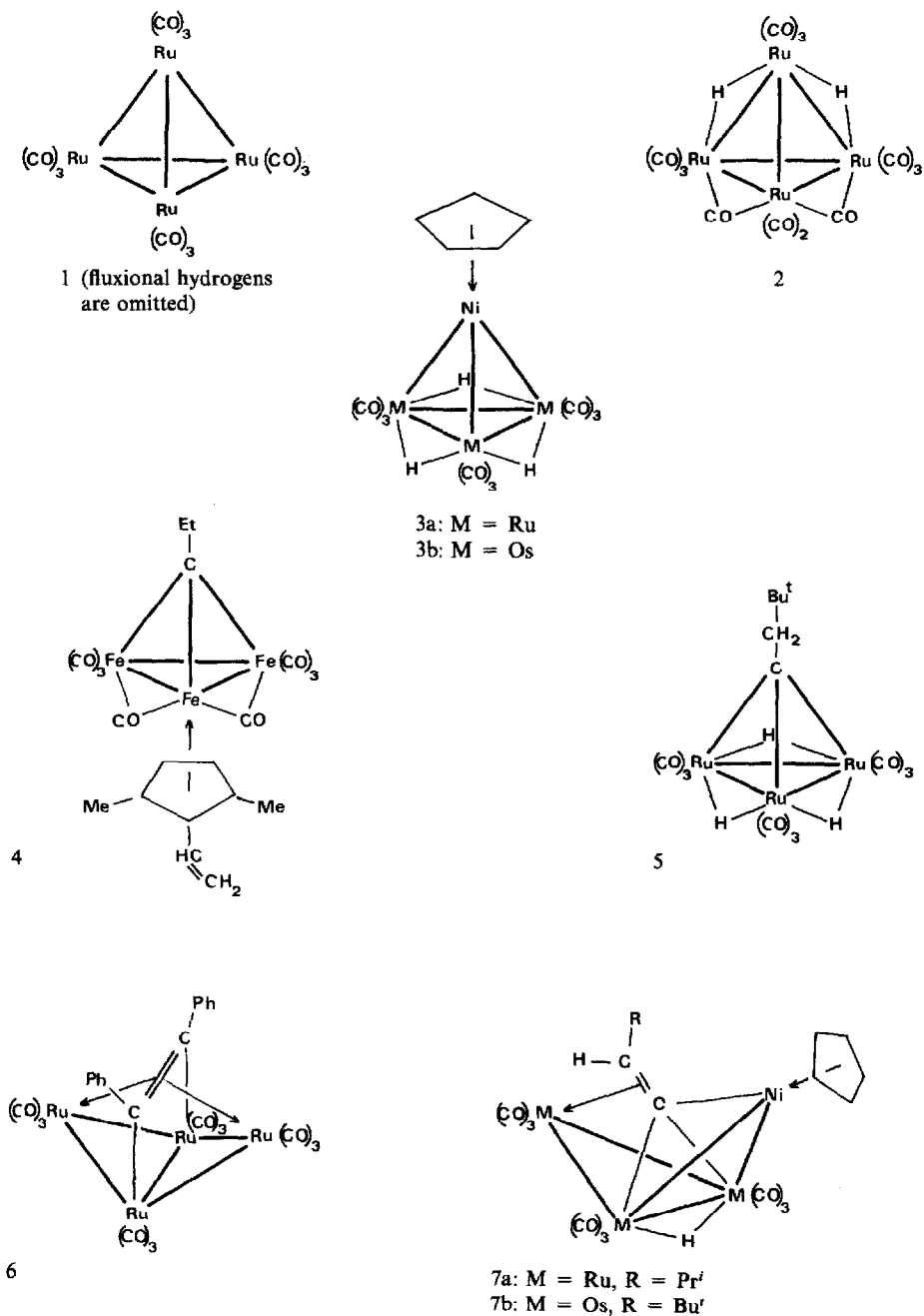
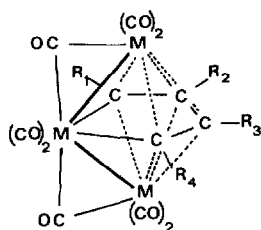


Fig. 1. Structures of the tri- and tetrametallic clusters of the first series.

by the ruthenium clusters $\text{Ru}_3(\text{CO})_8(\text{C}_{12}\text{H}_{18})$, ($\text{C}_{12}\text{H}_{18}$ = two dimerized and dehydrogenated 4-methylpent-2-yne molecules), two substitution isomers, complexes 9a and 9b)¹⁷ and by the ruthenium-nickel cluster $\text{Cp}_2\text{Ni}_2\text{Ru}_3(\text{CO})_8(\text{C}_2\text{Ph}_2)$ (complex 10)¹⁸.

Complexes 8 and 9 are characterized by an "open", bent $\text{M}_3(\mu\text{-CO})_2$ metal frame (which has been found to be very "rigid"), on which two alkyne molecules dimerize, giving rise to a metallacyclopentadienic ring; the latter may give rise to several isomers when differently substituted alkynes are present. The same metal core is also found in $(\text{Cp})\text{NiRu}_3(\text{CO})_6(\mu\text{-CO})_2(\text{C}_6\text{H}_9)$ (two isomers) and in complex 10, in which, however, one alkyne only is coordinated¹⁸. As CpNi is "isolobal" with $\equiv\text{CR}^{10}$, these complexes are related to 8 and 9. Indeed, one or two atoms of nickel replace the carbons in the metallacyclopentadienic ring without seriously affecting



8a: $\text{M} = \text{Fe}$; $\text{R}_1 = \text{R}_2 = \text{Et}$, $\text{R}_3 = \text{Me}$, $\text{R}_4 = \text{H}$

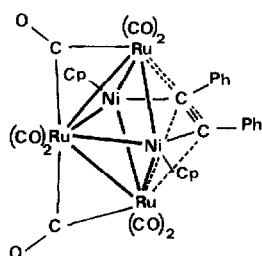
8b: $\text{M} = \text{Fe}$; $\text{R}_1 = \text{R}_3 = \text{H}$, $\text{R}_2 = \text{R}_4 = \text{Et}$

8c: $\text{M} = \text{Fe}$; $\text{R}_1 = \text{R}_2 = \text{R}_3 = \text{R}_4 = \text{Et}$

9a: $\text{M} = \text{Ru}$; $\text{R}_1 = \text{R}_3 = \text{Me}$, $\text{R}_2 = \text{CHMe}_2$, $\text{R}_4 = \text{C}(\text{CH}_2)\text{Me}$

9b: $\text{M} = \text{Ru}$; geometrical isomer of 9a

(complex 1b of ref. 17)



10 ($\text{Cp} = \text{cyclopentadienyl}$)



cluster frame common to 9 and 10

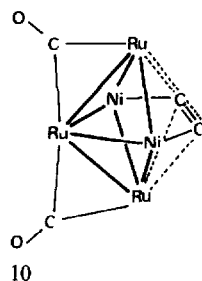
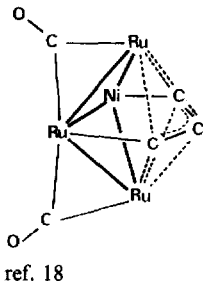
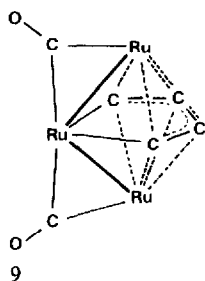


Fig.2. Structures of the clusters of the second series containing the $\text{M}_3(\mu\text{-CO})_2$ metal frame (8-10) and (below) illustration of substitution of $\equiv\text{CR}$ groups with the isolobal CpNi within the trimetallic Ru clusters.

the structural parameters of the $M_3(CO)_2$ frame¹⁸. Unfortunately, the "allylic" complexes $(Cp)NiRu_3(CO)_6(\mu-CO)_2(C_6H_9)$ were found to decompose readily under the separation conditions adopted, and were not considered in this work.

The structures of complexes 8–10 are shown (together with the basic metal core and the isolobal pattern) in Fig. 2.

The third series belongs to a different structural arrangement, and is based on hetero-trimetallic clusters, characterized by M_2Ni ($M = Fe, Ru$) or MNi_2 ($M = Fe, Ru$) triangular cores. These are substituted with acetylides, alkynes and sulphur. Analogies in the electron donor ability and coordination to metal centres within sulphur and alkynes (or alkyne derived ligands) have already been emphasized¹⁹. To this third series belong the following derivatives: $CpNiFe_2(CO)_6C_2Bu^t$ (complex 11)²⁰, $CpNi_2M(CO)_3(C_2Ph_2)$ ($M = Fe$, 12a; $M = Ru$, 12b)²¹ and $Cp_2Ni_2Fe(CO)_3S$ (complex 13)²². The structures of 11–13 are shown in Fig. 3.

EXPERIMENTAL

The complexes 1–7 were obtained by the procedure already described^{4–14} and were crystallized from hydrocarbons or chloroform–hydrocarbons, when possible; their nature and purity were checked by IR and ¹H NMR spectroscopy (comparison with known samples) and, in part, by mass spectrometry.

Complexes 8a and 8b were obtained as described earlier¹⁵; in particular, 8 was obtained by using a mixture of two different alkynes. The complexes were identified by means of elemental analyses, IR and ¹H NMR spectroscopy and mass spectrometry.

Complexes 8c¹⁶ and 9–13^{17,18,20–22} were obtained as previously reported.

The HPLC separations were performed using a Perkin-Elmer Series 3B liquid chromatograph, equipped with Rheodyne 7105 injection valve and an LC-75 variable-wavelength UV–visible detector. Stainless-steel columns (25 × 0.4 cm I.D.) con-

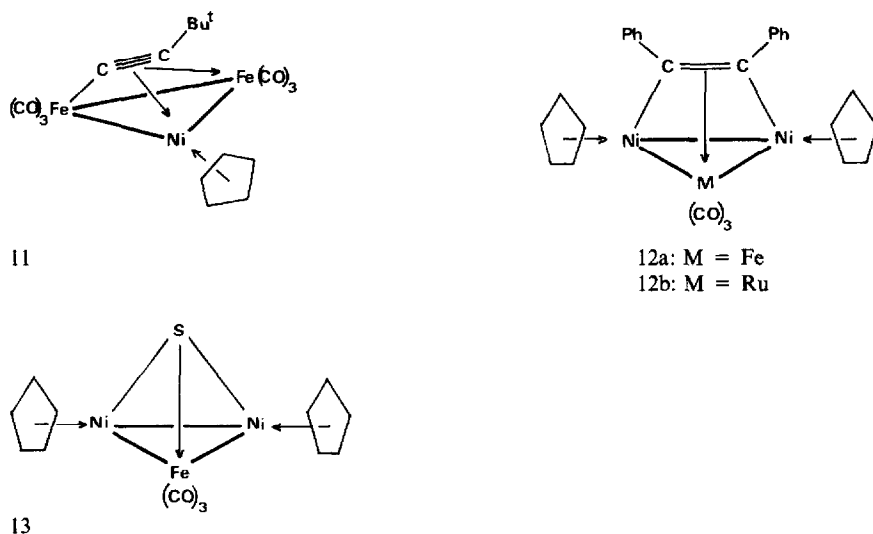


Fig. 3. Structures of the hetero-trimetallic clusters of the third series.

taining LiChrosorb Si-60 and LiChrosorb RP-18, mean particle size $10\ \mu\text{m}$ (E. Merck, Darmstadt, F.R.G.), were used. Solvents were of HPLC grade (Carlo Erba, Milan, Italy). Isocratic separations were performed at a flow-rate of $1\ \text{cm}^3\ \text{min}^{-1}$. Acetonitrile solutions of the complexes with concentrations of about 20 ppm were used; $5\text{-}\mu\text{l}$ volumes were injected. Column eluates were monitored at 265 nm. A Perkin-Elmer 238B infrared spectrophotometer was used to check the column eluates.

RESULTS AND DISCUSSION

For the chromatographic separations two different sets of columns and operating conditions were necessary. It is worth noting that whereas the homo-trimetallic clusters already reported³ are easily separated in the reversed-phase mode, with methanol-acetonitrile on an RP-18 column complexes 1-7 frequently decompose, and often they are not separated under these conditions. Instead, a silica column operated with *n*-hexane-tetrahydrofuran (THF) mixtures was found to be more effective.

Before discussing the chromatographic behaviour of the complexes, it is worth making some comments about their general behaviour in the reversed-phase mode and on silica. The ease of decomposition on the RP-18 column and in the presence of acetonitrile is probably due to the reactivity of the M-M' bonds in the hetero-metallic clusters; in fact, the reactivity of hetero-metallic clusters (considering the metal-metal bond) is higher than that of comparable homo-metallic structures, because of the "polarity" of the M-M' bond^{2,3}. This is a limiting factor in the use of HPLC in the separation of this kind of cluster.

On the other hand, under the separation conditions (and temperatures) adopted, very limited decomposition has been observed on silica, although it is well known that carbonyl complexes may interact with silica, being chemisorbed and then modified with relative ease. Hence the use of silica columns, in addition to the separation and identification of homo- and hetero-metallic clusters, may provide some information about the silica-cluster interactions and the possibility of the latter migrating on a silica surface without being affected.

With reference to the problem of the reaction of these compounds with the metallic parts of the column and of the instrument, a preliminary indication of their inertness was obtained; acetonitrile solutions of these compounds were allowed to remain in contact with stainless steel for long period and the CO stretching bands of the compounds, which were then used for the chromatographic analysis, did not show any variation even after 24 h.

The eluates from the silica column were checked; fractions corresponding to the peaks were collected and their IR spectra were run in the CO stretching region. Because of the high intensity of these absorption bands, spectra of suitable intensity and resolution were obtained using a conventional dispersive spectrophotometer, collecting fractions from successive injections. The fractions were dried and the residues dissolved in *n*-hexane to run IR spectra. All the compounds examined show the characteristic absorption pattern in the CO stretching region, the positions and the relative intensities of the bands being maintained, as shown, for examples, for compounds 3b, 6 and 8a in Fig. 4.

When considering the chromatographic behaviour of series of compounds, it

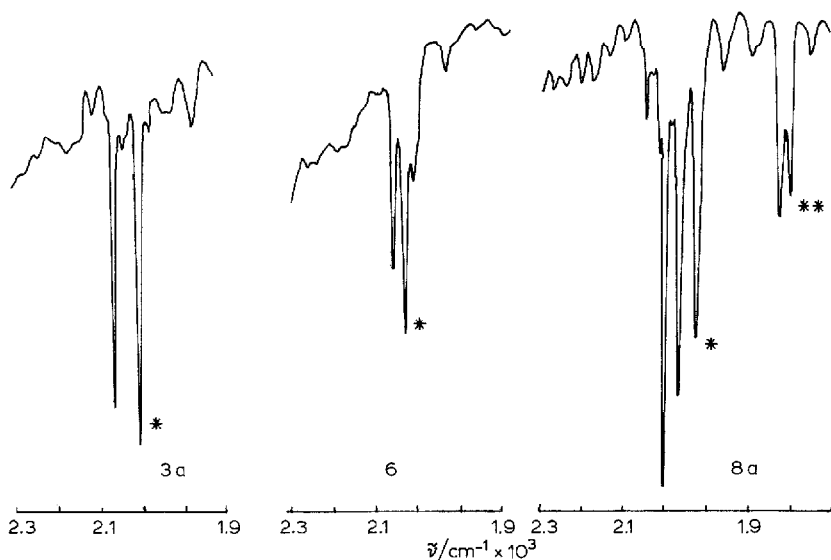


Fig. 4. IR spectra of some compounds in the column eluates: (a) $\text{CpNiRu}_3(\text{CO})_9(\mu\text{-H}_3)$; (b) $\text{Ru}_4(\text{CO})_{12}(\text{C}_2\text{Ph}_2)$; (c) $\text{Fe}_3(\text{CO})_8(\text{C}_2\text{Et}_2)(\text{HC}_2\text{Me})$. * ν (CO) terminal; ** ν (CO) bridging.

is worth noting the separation, on the silica column, of tetrahedral complexes characterized by the tetrahedral Ru_3X arrangement ($\text{X} = \text{Ru}, \text{Ni}, \text{C}$). Fig. 5a shows the separation of the complexes 5, 1 and 3a, obtained using *n*-hexane with a low content of THF (*ca.* 0.1%) as the mobile phase. Under the same conditions, the tetrahedral complexes 2 and 4, which have CO groups in a bridging position, are retained and require a more polar solvent mixture (50:50 *n*-hexane-THF) for elution. Under these conditions the separation factor is $R_s = (V'_R)_4/(V'_R)_2 = 1.75$.

With a mobile phase of low polarity (99:1 *n*-hexane-THF) the tetrahedral complex 1 and the butterfly complex 6 are eluted with a separation factor $R_s = 6.4$; the elution of the butterfly derivative appears to be adversely affected by its bulks and for steric reasons.

Using an almost apolar mobile phase (*n*-hexane-0.1% THF) the separation of the two homologous cyclopentadienyl derivatives of Ru and Os (3a and 3b), which have a tetrahedral skeleton, was obtained (Fig. 5b). Even in this instance, in spite of the bulkiness of the complexes, the different natures of the metal atoms in the cluster core make an effective separation possible, as already observed for $\text{Ru}_3, \text{Os}_3(\text{CO})_{12}$ ³.

The substitution of two hydrogen atoms in compounds 3a and 3b with a $\text{C}=\text{CHR}$ group in a bridging position between Ni and Ru or Os atoms causes the change in the structure from tetrahedral to butterfly (7a and 7b). The separation of the ruthenium derivatives 3a and 7a ($R_s = 1.7$), using the mobile phase *n*-hexane-THF (50:50) shows a higher retention volume for the compound with the butterfly structure compared with the tetrahedral structure. The same behaviour was observed for the osmium derivatives 3b and 7b, of which the butterfly derivative is more retained ($R_s = 1.8$), as also occurs for the tetrahedral and butterfly complexes 1 and 6.

Concerning metal clusters of series II, which have the "open" $\text{M}_3(\mu\text{-CO})_2$

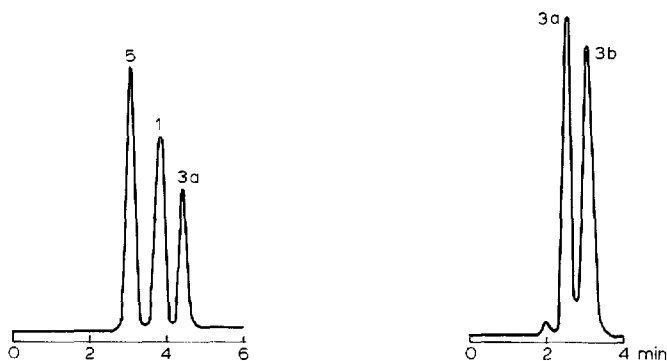


Fig. 5. (a) Separation of the tetrahedral ruthenium complexes $\text{H}_3\text{Ru}_4(\text{CO})_{12}$ (1), $\text{CpNiRu}_3(\text{CO})_9(\mu\text{-H})_3$ (3a) and $\text{H}_3\text{Ru}_3(\text{CO})_9\text{CCH}_2\text{Bu}'$ (5). Column, LiChrosorb Si-60; mobile phase, *n*-hexane-0.1% THF; flow-rate, $1 \text{ cm}^3 \text{ min}^{-1}$; detector, UV, 265 nm. (b) Separation of the ruthenium and osmium homologues $\text{CpNiRu}_3(\text{CO})_9(\mu\text{-H})_3$ (3a) and $\text{CpNiOs}_3(\text{CO})_9(\mu\text{-H})_3$ (3b). Column, LiChrosorb Si-60; mobile phase, *n*-hexane-0.1% THF. Other conditions as in (a).

metal frame (Fig. 2), the iron clusters 8a, 8b and 8c were separated on a silica column using *n*-hexane-THF (98:2) as the mobile phase. In spite of the bulkiness of the structure, an effective separation in the order 8c, 8a, 8b (Fig. 6a) was obtained, on the basis of the nature of the substituents on the metallacyclopentadienic ring as already observed². Using the RP-18 column with acetonitrile-methanol (99:1) as the mobile phase, the elution order of these compounds becomes 8b, 8a, 8c.

On the silica column the positional isomers 9a and 9b and the "isolobal" derivative 10 were separated in that order using *n*-hexane-THF (95:5) as the mobile phase. The elution order is that expected from the increasing polarity and nuclearity.

The heterometallic complexes based on triangular cores (series III, Fig. 3) were tested on both silica and RP-18 columns.

On the silica column a poor separation was obtained, only complex 11 being

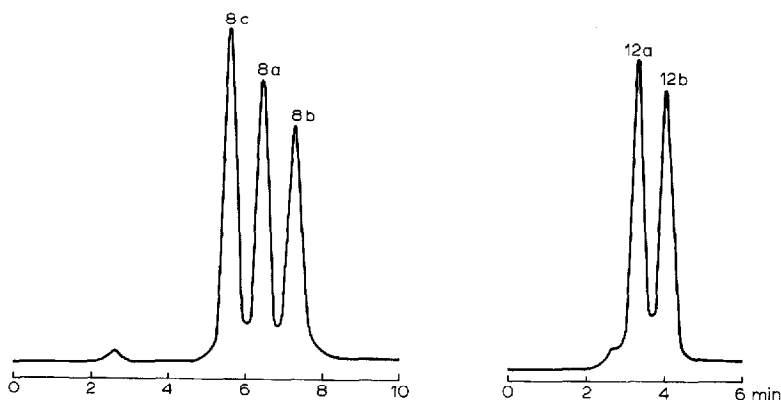


Fig. 6. (a) Separation of the "open" frame clusters $\text{Fe}_3(\text{CO})_8(\text{C}_2\text{Et}_2)(\text{HC}_2\text{Me})$ (8a), $\text{Fe}_3(\text{CO})_8(\text{HC}_2\text{Et})_2$ (8b) and $\text{Fe}_3(\text{CO})_8(\text{C}_2\text{Et}_2)$ (8c). Column, LiChrosorb Si-60; mobile phase, *n*-hexane-THF (98:2); flow-rate, $1 \text{ cm}^3 \text{ min}^{-1}$; detector UV, 265 nm. (b) Separation of the Fe and Ru homologues $\text{Cp}_2\text{Ni}_2\text{Fe}(\text{CO})_9(\text{C}_2\text{Ph}_2)$ (12a) and $\text{Cp}_2\text{Ni}_2\text{Ru}(\text{CO})_9(\text{C}_2\text{Ph}_2)$ (12b). Column, LiChrosorb RP-18; mobile phase, methanol-acetonitrile (30:70). Other conditions as in (a).

eluted before the mixture of complexes 12a and b and 13. This fact appears to be in contrast with the expected polarity in the acetylide, the two carbon atoms of which generally show different nucleophilic reactivities. On the RP-18 column using methanol-acetonitrile (30:70) as the mobile phase, the separation of the Fe and Ru homologues 12a and 12b was achieved (Fig. 6b), in spite of the bulky environment of the metals. Also in this instance, as already observed³, the iron derivative shows a lower retention time. The iron clusters of this series (11, 12a and 13) were separated using methanol-acetonitrile (40:60) as the mobile phase. Their corrected retention volumes are 2.4, 1.3 and 0.5, respectively.

From the above results, it is concluded that it is possible to separate complexes that are apparently very different either because of nuclearity or because of the nature of the substituents. However, under the same analytical conditions, complexes correlated by isolobal analogies are separated and the factors influencing the separations are close to those already discussed. The same happens when electronically related substituents with different natures are found on closely comparable metal frames. This illustrates further the considerable usefulness of HPLC in the separation of unusual mixtures of complexes.

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