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Short Communication

High-performance liquid chromatography of trinuclear ruthenium acetylido-carbonyl compounds

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ABSTRACT

The chromatographic behaviour of two groups of organometallic compounds derived from the basic framework $HRu_3(C{\equiv}CR)(CO)_9$ by substitution of the carbonyls with group-15 donor Iigands or by varying the R acetylenic substituent was studied. Separations were accomplished under both reversed- and normal-phase conditions in order to study the effect of the nature of the ligands or of the substituents on the elution order of these compounds.

INTRODUCTION

In the last decade there has been a rapid increase in the applications of high-performance liquid chromatography (HPLC) to metal carbony1 and cluster chemistry, owing to its superior efficiency compared with traditional column and thin-layer chromatography. Moreover column chromatography and thin-layer chromatography often cause oxidative, thermal or photochemical degradation of various organometallic compounds promoted by long contact times with the adsorbent, whereas HPLC is characterized by high-speed analysis and light exclusion; in particular, under reversed-phase conditions the possibility of decomposition is reduced owing to the deactivation of the silica surface. All these reasons make HPLC suitable for studying the behaviour of organometallic compounds.

Three previous reviews [1–3] have described the early progress in the HPLC separations of organometallic and coordination compounds. A more recent one [4] surveyed the progress achieved in the analysis of mono- and polynuclear metal carbonyls, including phosphine-, arene- and cyclopentadiene-substituted derivatives.

Recent papers in this field have described the chromatographic separations of neutral and

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cationic cluster compounds, with the double purpose of separating useful products and studying the behaviour of classes of compounds, in connection with the nature of the stationary and mobile phases [5–10]. More recently, facile separations of several enantiomeric "chiral-at-metal" cyclopentadienyl organometallic complexes were obtained with a commercially available HPLC column [11].

Studying the reactivity of alkynes towards metal carbonyls, we prepared two sets of hydrido-carbonyl ruthenium clusters, formally derived from the basic triangular metal framework $HRu_3(C{\equiv}CR)(CO)_9$ depicted in Fig. 1. The first set was obtained by substitution of the carbonyl ligands with EPh_3 (E = P, As, Sb) on the derivative with R = *tert.*-butyl, whereas the second was obtained maintaining the basic framework and varying the R function [R = Pr', Bu', $C(Me)_2OH$, $C(Me)_2NHCOC_6H_9$].

This paper deals with the HPLC behaviour of these two groups of compounds in reversed-phase and adsorption liquid chromatography. The complete list of the ruthenium hydrido-acetylide derivatives examined is reported in Table I. Interest in these compounds derives mainly from the fluxional behaviour of the acetylido ligands, which has been intensively investigated [12], as such information may be relevant to the mobility of small organic molecules on metal surfaces [13]. During the synthesis of these derivatives, complex mixtures are often produced, so that fast and reliable separation techniques are needed. HPLC coupled with specific and sensitive detectors can fulfil these requirements.

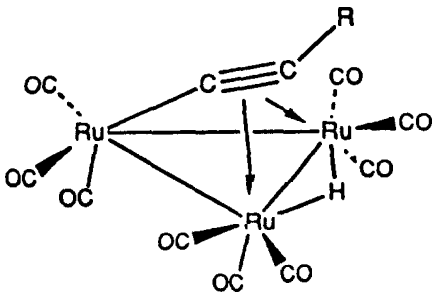

Fig. 1. Structural framework of the $HRu_3(C{\equiv}CR)(CO)_9$ derivatives.

TABLE I

FORMULAE AND ELECTRONIC ABSORPTION MAXIMA OF THE CLUSTERS

No.	Compound	λ_{max} (nm)
I	$HRu_3(C{\equiv}CBu^t)(CO)_9$	215,370
IIa	$HRu_3(C{\equiv}CBu^t)(PPh_3)(CO)_8$	300,370
IIb	$HRu_3(C{\equiv}CBu^t)(AsPh_3)(CO)_8$	300,390
IIc	$HRu_3(C{\equiv}CBu^t)(SbPh_3)(CO)_8$	290,390
III	$HRu_3(C{\equiv}CBu^t)(PPh_3)_2(CO)_7$	320,385
IV	$HRu_3(C{\equiv}CBu^t)(PPh_3)_3(CO)_6$	325,385
V	$HRu_3(C{\equiv}CBu^t)(PPh_2H)(CO)_8$	300,400
VI	$HRu_3(C{\equiv}CPr^i)(CO)_9$	280,360
VII	$HRu_3[C{\equiv}CC(Me)_2OH](CO)_9$	270,360
VIII	$HRu_3[C{\equiv}CC(Me)_2NHCOC_6H_9](CO)_9$	275.385

[a] Solvent, acetonitrile.

EXPERIMENTAL

Synthesis and spectrometry

The reactions were performed under a nitrogen atmosphere in conventional three-necked flasks equipped with a gas inlet and water condenser. Solvents were dried by standard procedures. The reaction mixtures were evaporated to small volume under reduced pressure and the products were separated by means of preparative TLC. IR spectra of liquid samples were recorded in NaCl cells on a Perkin-Elmer 580B or Nicolet 5PC instrument. ^1H and ^{31}P NMR spectra were registered on a Bruker CXP 200 spectrometer at room temperature.

The trinuclear hydrido-clusters $HRu_3(C{\equiv}CR)(CO)_9$ were prepared by reaction of $Ru_3(CO)_{12}$ with a suitable alkyne according to the standard method accomplished for R = Bu' [14]. The alkynes used were commercial products, except that used for the preparation of compound VIII, the synthesis of which has already been described [15]. The monosubstituted derivatives $HRu_3(C{\equiv}CBu^t)(EPh_3)(CO)_8$ were obtained by applying the established procedure for E = P [14]: addition of Me_3NO drastically shortened the reaction times. Compound V was obtained by the same method utilized in the case of PPh_3 as substituent [14]. The di- and trisubstituted derivatives with PPh_3 were obtained by reaction of $HRu_3(C{\equiv}$

$CBu^t)(AsPh_3)(CO)_8$ with an excess of PPh_3 in the presence of Me_3NO (refluxing heptane, nitrogen atmosphere, 6 min). IR and ^1H NMR data for the disubstituted compound have been given previously [14]; its ^{31}P NMR spectrum, in C^2HCl_3, showed two resonances at 37.7 and 53.0 ppm. The synthesis of the trisubstituted cluster $HRu_3(C \equiv CBu^t)(PPh_3)_3(CO)_6$ (IV) has not been previously reported; its analytical and spectral data are as follows: P, found 6.7, calculated for $C_{66}H_{55}O_6P_3Ru_3$ 6.93%; IR (heptane), 2013 m, 1997 vs, 1978 s, 1953 m, 1941 mw cm-'; ^1H NMR (C^2HCl_3, tetramethylsilane) δ -19.5 ppm [triplet of doublets, ^1H, μ-H, $^2J(H,P)$ 9.0 Hz, $^3J(H,P)$ 2.5 Hz]; ^{31}P NMR (C^2HCl_3, 85% H_3PO_4, external reference), δ 46.9 s , 42.3 s, 34.6 s ppm.

The UV-visible spectra of all compounds in acetonitrile were recorded on a Kontron Uvikon 860 spectrophotometer; all compounds exhibit absorption maxima in the range 270-400 nm (Table I).

Chromatography

Preparative TLC plates (Kieselgel 60 PF_{254}, Merck) were utilized; separations were accomplished by using light petroleum-diethyl ether (90: 10) as the mobile phase.

The chromatographic separations were performed using a Perkin-Elmer Series 3B chromatograph with a Rheodyne Model 7161 injection valve and an LC-75 variable-wavelength UV-visible detector. Stainless-steel columns (25 cm x 4.6 mm I.D.) filled with 5-μm LiChrosorb Si 60 or RP-13 (Merck) were used; the flow-rate was 1.0 ml/min. Dichloromethane solutions (5 μl) of the compounds were injected; mobile phases for the Si 60 and RP-18 columns are given in Table II together with the chromatographic parameters for the compounds examined. The elution without decomposition of the compounds was checked using FT-IR spectrometry. Fractions containing the separated compounds were concentrated under nitrogen and their IR spectra were measured using the mobile phase as reference to subtract the IR spectrum of the eluent.

RESULTS AND DISCUSSION

The primary aim of this work was to investigate the chromatographic behaviour of a number of substituted derivatives of cluster $HRu_3(C \equiv CBu^t)(CO)_9$ containing group-15 donor ligands. The substitution with a group-15 donor ligand is regiospecific [14], as the first entering ligand EPh_3 is fixed on the Ru atom a-bonded to the acetylide moiety. The second and third substituting ligands coordinate respectively the other two Ru atoms bridged by the hydrido ligand. Coordination should occur in positions *cis* to H, as suggested by the low $^2J(H,P)$ value [16].

The parent compound and the mono- and disubstitution PPh_3 derivatives have already been well characterized [14,17]; the $AsPh_3$ and the $SbPh_3$ monosubstituted derivatives exhibit

TABLE II

RETENTION TIMES, MOBILE PHASES AND COLUMN MATERIALS

Mixture of compounds[a] and retention times (min)	Column	Mobile phase	Note
I (4.91), IIa (6.64), III (7.37), IV(8.57)	RP-18	Acetonitrile-methanoI(80: 20)	Fig. 1
I (3.13), IIa (4.34), III (8.73), IV(19.65)	Si-60	Hexane-dichloromethane (90: 10)	Fig. 2
I (5.06), V (5.49), IIa (7.37)	RP-18	Acetonitrile	Fig. 3
IIc (5.30) IIb (5.48), IIa (5.73)	Si-60	Dichloromethane	–
VII (3.96), VIII (4.37), VI (4.77), I (5.10)	RP-18	Acetonitrile	Fig. 4
I (2.81), VI (3.24), VII (9.25), VIII (17.71)	Si-60	Hexane-dichloromethane (gradient from 80 : 20 to 60 : 40 in 4 min, hold for 2 min)	–

[a] Compound numbers as in Table I.

the same spectroscopic patterns of the PPh_3 derivative, in particular the expected single resonance at -21 ppm in the ^1H NMR spectrum due to the bridging hydride. The analytical and multinuclear NMR data for the trisubstituted derivative with PPh_3, reported under Experimental, agree with the proposed formula.

The separation of the ruthenium derivatives **I, IIa, III** and **IV** was performed under reversed-phase conditions by using acetonitrile-methanol (80:20) as the mobile phase. In this series, the elution times increase with increase in the number of bulky substituents (PPh_3) on the metal clusters (Fig. 2). The peak at 3.90 min corresponds to the free phosphine, used in the substitution reaction. The high efficiency obtained in this separation is noteworthy; the number of theoretical plates is 4500 for **IV.** The shape of the peaks and their symmetry indicate the elution without decomposition not only for the parent compound but even for the coordination derivatives, having phosphine as ligand, as confirmed by the FT-IR spectra of the corresponding eluates.

The substitution of CO groups with PPh_3 causes longer retention times also in adsorption chromatography, as already observed [7,18]. This behaviour suggests that rather than polarity, the increase in the molecular surface area and the steric hindrance are determining factors. The separation of the parent cluster **(I)** from mono-, di- and trisubstituted products with phosphine was obtained as shown in Fig. 3; under these conditions the derivative containing three phosphine ligands shows a different chromatographic behaviour to the clusters **I, IIa** and **III:** the bulkiness of the polysubstituted compounds appears to play a relevant role in the chromatographic behaviour. However, for these compounds the efficiency of the silica column is not as good as that observed under reversed-phase mode.

The influence exerted by the nature of the substituents on the chromatographic behaviour of the parent compounds **I** is also evidenced by the separation shown in Fig. 4: under reversed-phase conditions (RP-18 column, acetonitrile mobile phase) the bulkiness and the polarity of the phosphine substituents (PPh_2H, PPh_3) appear to be effective in determining the elution

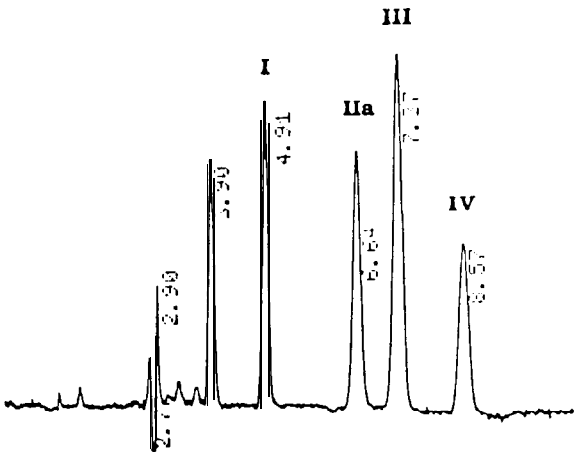

Fig. 2. Separation of $HRu_3(C{\equiv}CBu^t)(CO)_9$ (I), $HRu_3(C{\equiv}CBu^t)(PPh_3)(CO)_8$ (IIa), $HRu_3(C{\equiv}CBu^t)(PPh_3)_2(CO)_7$ (III) and $HRu_3(C{\equiv}CBu^t)(PPh_3)_3(CO)_6$ (IV) on RP-18. Mobile phase, acetonitrile-methanol (80:20); flow-rate, 1 cm^3/min; detection, UV at 265 nm. Values at peaks indicate retention times in min (also in Figs. 3-5).

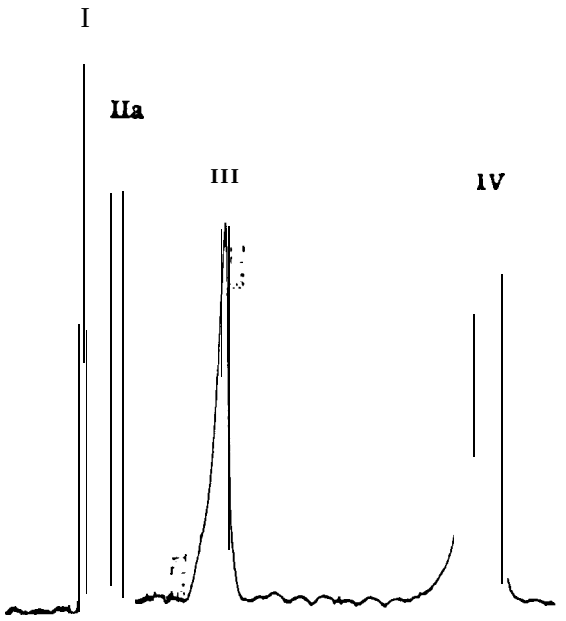

Fig. 3. Separation of $HRu_3(C{\equiv}CBu^t)(CO)_9$ (I), $HRu_3(C{\equiv}CBu^t)(PPh_3)(CO)_8$ (IIa), $HRu_3(C{\equiv}CBu^t)(PPh_3)_2(CO)_7$ (III) and $HRu_3(C{\equiv}CBu^t)(PPh_3)_3(CO)_6$ (IV) on Si-60. Mobile phase, hexane-dichloromethane (90: 10); flow-rate, 1 cm^3/min; detection, UV at 350 nm.

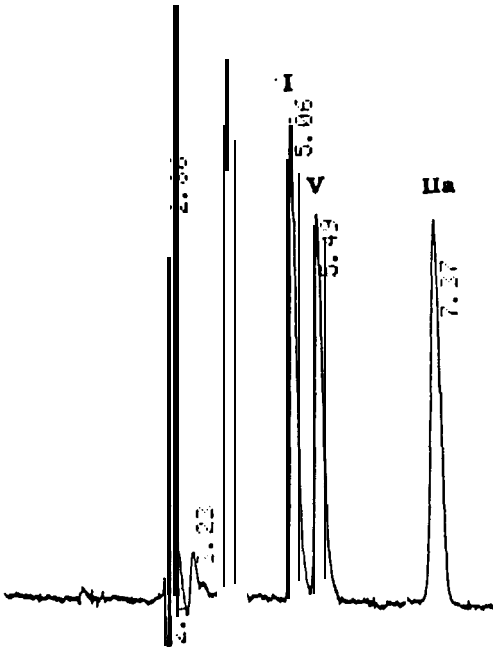

Fig. 4. Separation of $HRu_3(C\equiv CBu^t)(CO)_9$ (I), $HRu_3(C\equiv CBu^t)(PPh_2H)(CO)_8$ (V) and $HRu_3(C\equiv CBu^t)(PPh_3)(CO)_8$ (IIa) on RP-18. Mobile phase, acetonitrile; flow-rate, 1 cm³/min; detection, UV at 265 nm.

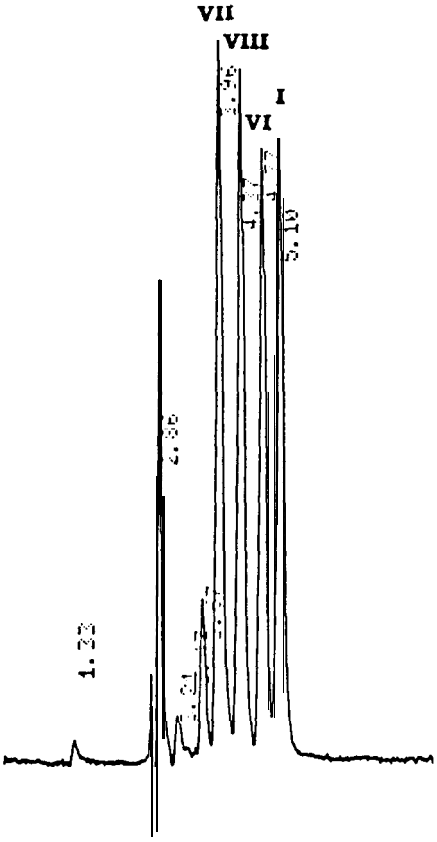

Fig. 5. Separation of $HRu_3[C\equiv CC(Me)_2OH](CO)_9$ (VII), $HRu_3[C\equiv CC(Me)_2NHCOC_6H_9](CO)_9$ (VIII), $HRu_3(C\equiv CPr^i)(CO)_9$ (VI) and $HRu_3(C\equiv CBu^t)(CO)_9$ (I). Conditions as in Fig. 4.

order of these structurally related species. As in the chromatogram in Fig. 2, the signal at 3.87 min corresponds to the free triphenylphosphine.

For the substitution products of $HRu_3(C\equiv CBu^t)(CO)_9$ with PPh_3, $AsPh_3$ and $SbPh_3$, under normal-phase conditions (silica column, dichloromethane mobile phase) the elution order is clearly correlated with the electronegativity of the donor atoms, in spite of the complexity of the whole cluster, as was found in a previous work [19]. In fact, the retention times increase with increasing electronegativity in the normal-phase mode (Table II). In contrast, under reversed-phase conditions all the compounds examined exhibit very close retention times so that the chromatographic behaviour of the monosubstitution products with EPh_3 could not be rationalized.

Concerning the second group of compounds, Fig. 5 shows the chromatographic separation of the different hydrido-acetylido ruthenium enneacarbonyl derivatives under reversed-phase conditions. On the C_{18} column, the presence of *iso*-propyl and *tert*.-butyl substituents on the coordinated alkyne causes higher retention times for I and VI with respect to those of more polar derivatives (VII and VIII), even though the differences in the retention volumes are not particularly high.

A more relevant difference in the retention volumes of these compounds is observed on the silica column, as the normal-phase conditions enhance the polarity characteristics owing to the presence of functional groups such as hydroxyl or amide. Liquid-solid chromatography is the preferred technique for the separation of compounds possessing multifunctionality, as the most polar group generally dominates the adsorption mechanism, although all constituent groups contribute to retention. To obtain the separation of

these compounds, a two-step gradient with hexane-dichloromethane was necessary, as basic compounds are retained very strongly because of the slightly acidic characteristics of the surface of silica gel. The retention order of I, VI, VII and VIII follows the polarity order of the substituents on the alkyne chain. In particular, the derivative VII is retained by silica, owing to the presence of the polar hydroxyl moiety, which can interact strongly with the surface silanol groups. On the other hand, the derivative containing the amide group in the alkyne chain (VIII) is much more retained by the silica than VII because of the polar interaction via hydrogen bonding and of the more basic properties of the amide moiety.

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