

Note

High-performance liquid chromatography of triangular ruthenium clusters containing bidentate group-15 donor ligands

ANTONELLA CASOLI, ALESSANDRO MANGIA and GIOVANNI PREDIERI*

Istituto di Chimica Generale ed Inorganica, Università di Parma, Viale delle Scienze, I-43100 Parma (Italy)

and

ENRICO SAPPA

Dipartimento di Chimica Inorganica, Chimica Fisica e Chimica dei Materiali, Università di Torino, Corso M. d'Azeglio 48, I-10125 Torino (Italy)

(Received July 3rd, 1989)

High-performance liquid chromatography (HPLC) has successfully entered the field of organotransition metal chemistry, owing to its superior efficiency compared with traditional column and thin-layer chromatography. Moreover, HPLC analyses are performed rapidly, using degassed solvents, with stainless-steel columns and with the exclusion of light, so preventing possible decomposition processes, and make use of sensitive, small-volume, liquid-phase detectors.

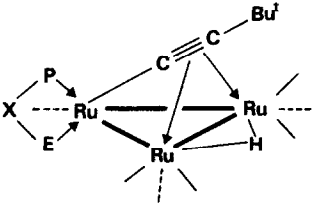
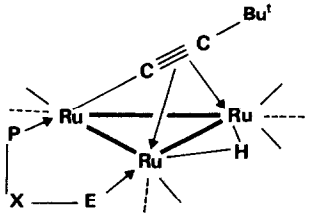
Since the first separation of a mixture of arenechromium carbonyls, reported in 1969 by Veening *et al.*¹, several HPLC studies of organometallics have been reported and have been the subject of three reviews²⁻⁴ devoted to separations of organometallic and coordination compounds; very recently, another review⁵ surveyed the applications of the HPLC to metal carbonyl and cluster chemistry.

The chromatographic behaviour of several tri- and tetranuclear neutral metal-carbonyl clusters had been examined previously⁶⁻¹¹, and we found that the nuclearity of the cluster, the nature of the metals and the type of substituents influence the separations of these species.

Continuing these investigations, we report here a study of the influence of different group-15 bidentate ligands on the HPLC behaviour of the substituted triangular ruthenium cluster $\text{HRu}_3(\text{C}\equiv\text{CBu}^t)(\text{CO})_9$ (**1**) ($\text{Bu}^t = \textit{tert.}$ -butyl). Indeed, by reaction of **1** with dppm (dppm = $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ where Ph = phenyl), we have recently synthesized¹² the chiral cluster $\text{HRu}_3(\text{C}\equiv\text{CBu}^t)(\text{CO})_7(\mu\text{-dppm})$, which crystallizes as an ordered racemic array of the two enantiomers. It is the only product of the above reaction and the dppm ligand bridges a Ru-Ru hydride-free edge (1,2-derivative; see Table I).

On the other hand, by reacting the parent cluster **1** with the bidentate ligands $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{EPh}_2$ (E = P, dppe; E = As, dppeae) in the presence of $(\text{CH}_3)_3\text{NO}$, we obtained¹³ in both instances two isomers of the complexes $\text{HRu}_3(\text{C}\equiv\text{CBu}^t)(\text{CO})_7(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{EPh}_2)$. In the first isomer, the ligands chelate the ruthenium atom opposite to the bridging hydride (1,1-derivative), whereas in the second one, they bridge a hydride-free edge (1,2-derivative), as shown in Table I. In contrast, the rigid diphosphine *cis*- $\text{Ph}_2\text{PCH}=\text{CHPPh}_2$ (c-dppet) gives only the 1,1-derivative.

TABLE I
STRUCTURES AND ELECTRONIC ABSORPTION MAXIMA OF THE CLUSTER
 $\text{HRu}_3(\text{C}\equiv\text{CBu}^t)(\text{CO})_7(\text{Ph}_2\text{PXEPH}_2)$

Structure ^a	Substituents	No.	$\lambda_{\text{max}}(\text{nm})^b$
	X = CH ₂ CH ₂ , E = PPh ₂	2a	240, 286, 363
	X = CH ₂ CH ₂ , E = AsPh ₂	2b	<240, 285, 361
	X = CH=CH, E = PPh ₂	2c	242, 283, 366
	X = CH ₂ CH ₂ , E = PPh ₂	3a	<240, 295sh, 370sh
	X = CH ₂ CH ₂ , E = AsPh ₂	3b	243, 305sh, 371sh
	X = CH ₂ , E = PPh ₂	3d	241, 300sh, 376sh

^a Carbonyls in equatorial (solid bonds) and axial (dashed bonds) positions are omitted for clarity; P = PPh₂.

^b Solvent, dichloromethane; sh = shoulder.

Artificial mixtures of these compounds have been subjected to HPLC analyses in order to gain more information about the influence exerted by the substituent ligand on the chromatographic behaviour of molecular clusters.

EXPERIMENTAL

All the triruthenium clusters described were obtained according to the method used for dppm and reported elsewhere¹². The chemical inertness of the products in acetonitrile, tetrahydrofuran and hexane was tested by maintaining them in these solvents for several hours at room temperature and by monitoring the IR spectra (CO stretching region) of the solutions before and after the chromatographic experiments.

The chromatographic separations were performed using a Perkin-Elmer Series 3B chromatograph with a Rheodyne 7105 injection valve and an LC-75 variable wavelength UV-visible detector. Stainless-steel columns (25 × 0.4 cm I.D.) filled with 10- μm LiChrosorb Si 60 or RP-8 (Merck) were used; the stability of the complexes towards stainless steel was tested as reported previously for other heterometallic clusters¹¹. The flow-rate was 1.0 or 1.5 ml/min and the eluates were monitored at 260 nm. The UV-visible spectra of all the compounds were recorded on a Jasco 505 spectrophotometer (Table I); two of them (compounds **2b** and **3b**) are shown in Fig. 1.

Dichloromethane solutions (5 μl) of the compounds were injected; mobile phases for the Si 60 and RP-8 columns are listed in Table II. Solvents were of HPLC grade (Carlo Erba).

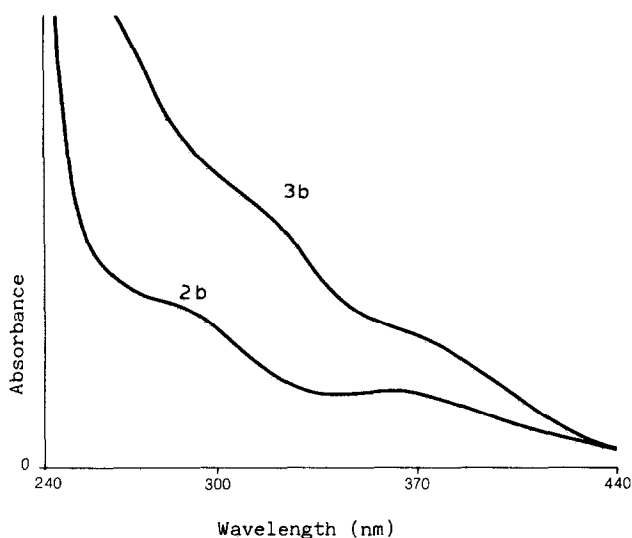


Fig. 1. Electronic spectra of **2b** and **3b** in dichloromethane.

DISCUSSION

The mixtures of clusters chromatographed on the RP-8 and Si 60 columns are listed in Table II. Figs. 2 and 3 show two of the separations reported in Table II.

As indicated in Table I and Fig. 1, all the compounds examined exhibit an intense electronic absorption maximum at about 240 nm and two shoulders at higher wavelengths, which are more pronounced for compounds **2** (1,1-derivatives).

Under reversed-phase condition (RP-8, acetonitrile) the separations are generally unsatisfactory, all the clusters giving close retention times (Table II). Neither

TABLE II
RETENTION TIMES, ELUENTS AND COLUMN MATERIALS

Mixtures of compounds ^a with retention times (min) in parentheses	Column	Eluent ^b	Flow-rate (ml/min)	Note
1 (3.7), 3a (3.8), 2a (4.1)	RP-8	A	1	—
3a (3.5), 2a (3.7)	RP-8	A-M(50:50)	1	—
3b (3.5), 2b (3.6)	RP-8	A-M(50:50)	1	—
3d (3.8), 3b (4.0)	RP-8	A	1	—
1 (3.8), 3a (3.9), 3d (4.0)	RP-8	A-W(75:25)	1	—
1 (1.7), 2a (4.3), 3a (7.0)	Si 60	H-T(75:25)	1.5	Fig. 2
1 (1.8), 2a (1.9), 3a (2.0)	Si 60	H-C(75:25)	1.5	—
2b (3.8), 3b (5.0)	Si 60	H-T(75:25)	1.5	Fig. 3
3b (5.0), 3d (6.8)	Si 60	H-T(75:25)	1.5	—
2a (4.3), 2c (4.6)	Si 60	H-T(75:25)	1.5	—

^a Compound numbers as in Table I.

^b A = acetonitrile; M = methanol; W = water; T = tetrahydrofuran; C = chloroform; H = hexane.

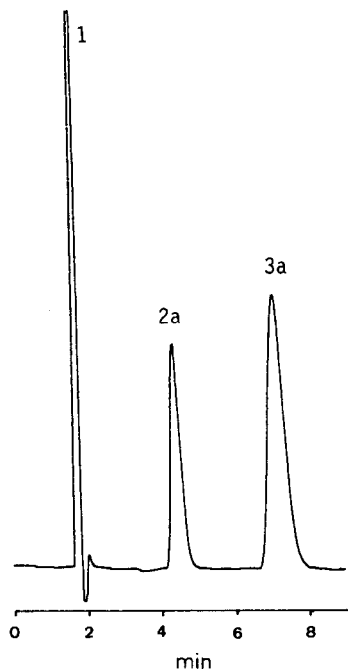


Fig. 2. Separation of **1**, **2a** and **3a** on silica; chromatographic conditions are reported in Table II. Resolution (R_s), 6.6 and 3.2; plate numbers (N), 1156, 838 and 652.

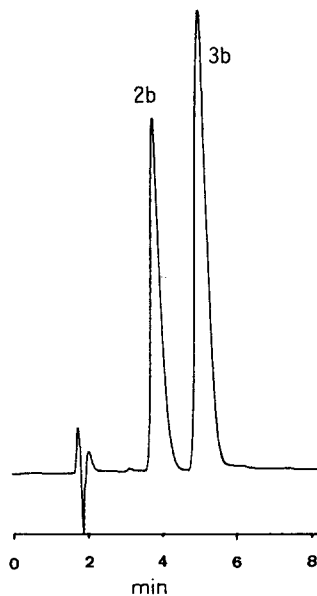


Fig. 3. Separation of **2b** and **3b** on silica; chromatographic conditions are reported in Table II. Resolution (R_s), 1.5; plate numbers (N), 358 and 560.

addition of methanol to the mobile phase, nor addition of water, which however causes slight retardation, produce any significant improvement.

In contrast, under normal-phase conditions, good separations have been achieved on silica, although chloroform should not be used in the mobile phase because, owing to its great affinity for these compounds, it produces a drastic unselective lowering of the retention times. Nevertheless, with hexane-tetrahydrofuran (75:25) as the mobile phase, even if the parent compound **1** is almost unretained, the pairs of isomers **2a**–**3a** and **2b**–**3b** are well separated in this order (Figs. 2 and 3, respectively). As this order of elution reverses under reversed-phase conditions, a substantial difference in the polarity characteristics between the 1,1- and the 1,2-isomers should exist, the latter appearing more polar.

Under the same conditions, compound **2c**, containing an unsaturated $\text{CH}=\text{CH}$ chain in the ligand, is slightly more retained than **2a**, whereas **3d**, containing a methylene bridge, exhibits a shorter retention time than **3a**.

Finally, it is interesting that on the silica column, for the same isomers, the retention times are clearly related to the electronegativity of the different donor atoms of the ligands, as was found in a previous study⁹. In fact, **2a** and **3a**, which contain two phosphorus atoms, are eluted after **2b** and **3b**, which contain one phosphorus atom and one less electronegative arsenic atom.

ACKNOWLEDGEMENT

This work was financially supported by CNR, Italy.

REFERENCES

- 1 H. Veening, J. M. Greenwood, W. H. Shanks and B. R. Willeford, *Chem. Commun.*, (1969) 1305.
- 2 H. Veening and B. R. Willeford, *Rev. Inorg. Chem.*, 1 (1979) 281.
- 3 B. R. Willeford and H. Veening, *J. Chromatogr.*, 251 (1982) 61.
- 4 H. Veening and B. R. Willeford, *Adv. Chromatogr.*, 22 (1983) 117.
- 5 A. Casoli, A. Mangia, G. Predieri, E. Sappa and M. Volante, *Chem. Rev.*, 89 (1989) 407.
- 6 A. Mangia, G. Predieri and E. Sappa, *Anal. Chim. Acta*, 149 (1983) 349.
- 7 A. Mangia, G. Predieri and E. Sappa, *Anal. Chim. Acta*, 152 (1984) 289.
- 8 A. Casoli, A. Mangia, G. Predieri and E. Sappa, *J. Chromatogr.*, 303 (1984) 404.
- 9 A. Casoli, A. Mangia, G. Predieri and E. Sappa, *Anal. Chim. Acta*, 176 (1985) 259.
- 10 A. Casoli, A. Mangia, G. Predieri and E. Sappa, *J. Chromatogr.*, 355 (1986) 285.
- 11 A. Casoli, A. Mangia, G. Predieri and E. Sappa, *J. Chromatogr.*, 447 (1988) 187.
- 12 G. Predieri, A. Tiripicchio, C. Vignali and E. Sappa, *J. Organomet. Chem.*, 342 (1988) C33.
- 13 E. Sappa, G. Predieri, A. Tiripicchio and C. Vignali, *J. Organomet. Chem.*, (1989) in press.