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Applications of High-Performance Liquid Chromatography to Metal Carbonyl and Cluster Chemistry

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I. Introduction

Although the first organometallic compound, Zeise's salt, was described in 1830¹ and the first metal carbonyl, Ni(CO)₄, in 1890,² the development of the chemistry of metal carbonyls and in general of transition-metal organometallic compounds started much later, practically with the discovery of ferrocene (1951)³ and with the first rational synthesis of bis(benzene)chromium (1955).⁴

Organometallic chemistry is nowadays a largely interdisciplinary research field;⁵ inorganic, organic, analytical, and physical chemistry techniques are currently used for the study of organometallic compounds. These are, by definition, characterized by the presence of one or more metal–carbon (M–C) bonds, along with, possibly, other metal–element bonds, whereas coordination compounds contain "only" M–N, M–O, M–S, and other metal–donor bonds.

Although a clear-cut division between organometallic and coordination compounds is sometimes difficult (consider, e.g., the case of K₄Fe(CN)₆, a "classical" coordination compound, soluble in water, that contains six metal–carbon bonds), this classification is very useful for descriptive aims and actually gathers together compounds with similar chemical and physicochemical characteristics. Typical organometallic species such as mono- and polynuclear transition-metal carbonyls are low-polarity molecules, soluble in most common organic solvents, approaching the behavior of organic compounds.

Consequently, gravity column chromatography (CC) and thin-layer chromatography (TLC) have been and are extensively used for the separation of organometallics, whereas gas chromatography (GC), though currently used in organic chemistry, lacks usefulness in this field, requiring operating temperatures at which organometallic complexes often decompose. However, CC and TLC, when employable, suffer from difficulties such as long analysis times, insufficient separating efficiency, and lack of effective detection systems and quantitative capability.

On the other hand, high-performance liquid chromatography (HPLC), which has been applied extensively to the separation of numerous organic and biochemically active compounds, requires mild separation conditions, is characterized by high speed and efficiency, and can be coupled to sensitive, small-volume liquid-phase detectors.

Moreover, chromatographic analysis of organometallic mixtures carried out with CC or TLC is often complicated by the oxidative, hydrolytic, thermal, or photochemical instability of certain complexes, favored by long periods of contact with the adsorbent. Again HPLC can obviate these troubles since analyses are performed rapidly, using degassed solvents, stainless steel columns, and light exclusion.

For these reasons HPLC has successfully entered the field of organotransition-metal chemistry. Since the first separation reported by Veening and Willeford in 1969,⁶ several HPLC studies of organometallics have appeared in the literature, and three reviews^{7–9} have been devoted to the applications of HPLC to the analysis and separation of organometallic and coordination compounds.

In this paper we survey the recent progress achieved in HPLC separations of mono- and polynuclear metal carbonyls, including phosphine-, arene-, and cyclopentadiene-substituted derivatives. Also separations involving metallocenes, metallocene dichlorides, and cyanometalated anions are covered, in such a way that the field of organotransition-metal chemistry is almost completely encompassed.

Papers dealing with studies on the behavior of classes of compounds, in connection with the nature of the stationary and the mobile phases, are collected in sections III–V. Chiefly synthetic works, which take advantage of the use of HPLC in studying reaction



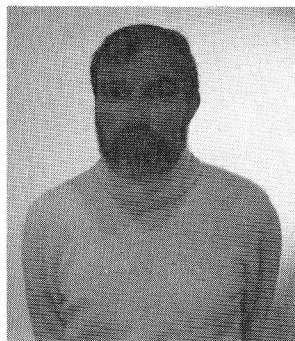
Antonella Casoli was born in 1956 and received her degree in chemistry from the University of Parma in 1980. She is now a Researcher in Analytical Chemistry at the Istituto di Chimica Generale ed Inorganica of the University of Parma. Her research interests are in the areas of applications of liquid chromatography in the metalloorganic field and in the selective extractions of cations with new ligands.



Alessandro Mangia received his degree in chemistry from the University of Parma in 1965. Since that year he has been on the Faculty of Chemistry of this University, and he is presently Professor of Analytical Chemistry. His research interests include applications of chromatography in the metalloorganic field, the synthesis of new ligands, and their use for selective extraction of cations.



Giovanni Predieri obtained his degree in chemistry from the University of Parma in 1972. He was Assistente Universitario at the same university and, after two postdoctoral fellowships at the Laboratoire de Chimie de Coordination of the University of Strasbourg (in 1981 and in 1984), he is now Professore Associato at the University of Parma. In 1988 he received the "Arturo Miolati" award for his research activity in Inorganic Chemistry. Organometallic chemistry is presently his major research field, including synthesis, characterization, and reactivity of new compounds as well as their chromatographic behavior.



Enrico Sappa obtained his degree in chemistry from the University of Turin in 1964. After a postdoctoral appointment, he started his academic career as Lecturer and Assistant Professor at the Istituto di Chimica Generale of the same University; he is now Associate Professor at the Department of Inorganic, Physical and Materials Chemistry of the University of Turin. His present research interests include metal carbonyl and cluster chemistry, reactivity of multi-site-bound small molecules on clusters, and homogeneous and heterogeneous catalysis.



Marco Volante was born in Turin in 1962. He received his degree in chemistry from the University of Turin in 1987. Presently, he has a fellowship from the Associazione Tecnica Automobile (ATA) at the Department of Inorganic, Physical and Materials Chemistry of the University of Turin for studying the properties of neoceramic compounds.

pathways and in separating products, are reviewed in section VI.

II. Experimental Techniques

A. Stationary Phases

The rapid development of HPLC during the past years has been made possible by fundamental advances both in the materials available to the chromatographer and in the techniques suitable for the separation of more and more classes of compounds.

The introduction of small-diameter silica particles with controlled porosity led to the first high-performance columns. Another major advance was the introduction of chemically bonded phases in which surfaces of porous silica are functionalized with organosilanes, especially bearing long-chain hydrocarbon fragments such as *n*-octyl and *n*-octadecyl. This is the case of reversed-phase (RP) chromatography, in which the mobile liquid phase is generally an organic-aqueous mixture. The development of paired-ion chromatography and ion-exchange chromatography allowed separation of ionic species, whereas improvements in gel permeation packing materials further extended the

range of applicability of the HPLC methods. The availability of these different modes of liquid chromatography makes HPLC a versatile separation technique for inorganic, organic, and biochemical samples.

In the field of organotransition-metal compounds normal-phase (adsorption and partition) and reversed-phase (partition) HPLC are the two most widely used methods. Among ion-exchange and ion-pair reversed-phase HPLC, the latter is rapidly gaining in popularity for the determination of anionic and cationic organometallic species paired with suitable counterions. Recently, it has been successfully applied in the separation and determination of stable cyanometalated anions in liquid samples coming from metallurgical processes^{10,11} (section IIIA).

When organometallics are unstable to the chromatographic process, i.e., adsorption on silica or interaction with water in RP conditions, size-exclusion chromatography (SEC) can overcome these difficulties. SEC uses a porous, inert stationary phase, which operates on the basis of molecular size, with larger molecules eluting first. The mechanism is very soft, involving only the differential diffusion of eluted species into the solvent-filled pores. A major application of this technique has been developed for low-valent complexes of nickel and iron¹² (section IIIA).

Furthermore, inclusion phenomena are possibly responsible for chiral recognition, via cyclodextrin-bonded phases, toward metallocene enantiomers. This technique has permitted the separation of 13 enantiomeric pairs of ferrocenes, ruthenocenes, and osmocenes¹³ (section IIIC).

Besides applications on the analytical scale, i.e., simple speciations and determinations of compounds in complex mixtures, HPLC can be used in separations of products in workable amounts. This has been made possible by the availability of large-size packed columns, which have started to be prepared by HPLC producers. Preparative-scale HPLC is a rapidly expanding technique among organometallic synthesizers, and hence the reports in this field will be discussed in an appropriate section (section VI).

B. Detectors and Special Devices

The instrumentation ancillary to these high-performance columns required development of specialized pumps to drive liquid flows with high precision and low pulsation through the small-particle columns and, above all, sensitive and selective detectors capable of monitoring a variety of physical properties. First UV and refractive index and then more selective detectors based on fluorescence and amperometry/coulometry were developed for HPLC.

For organometallic systems the variable-wavelength spectrophotometric detector is the most widely used, owing to the high-absorptivity electronic absorption maxima of most organotransition-metal compounds. Nevertheless, electron spin resonance (ESR),^{14,15} inductively coupled plasma (ICP),¹⁶⁻¹⁸ and Fourier transform infrared (FTIR)¹⁹ detectors have been recently investigated.

Combined HPLC-ESR permitted isolation of some stable organometallic "radical" complexes such as the carbonyl(quinone)rhenium radical for a full spectroscopic characterization.¹⁴ The technique is very sen-

sitive and specific; nevertheless, it suffers from severe limitations, being able to detect only unpaired-electron species, unfortunately rather rare in organometallic chemistry.

On the other hand, combination of ICP with HPLC is a promising technique, which, although there are high investment costs, presents in principle a wide range of applications, low detection limits for a large number of elements, and the possibility of simultaneous multielement monitoring. It has been applied to different organoiron compounds, without finding, in RP conditions, any serious restriction on the flow rate or on the mobile phase.¹⁶ The use of nonaqueous elution mixtures in the SEC mode has been made possible by means of a new spray chamber designed to facilitate analyses in relatively high-volatility organic solvents and to interface the liquid chromatograph and the ICP spectrometer.¹⁷ Again, organoiron compounds, i.e., substituted ferrocenes, have been detected in this way, along with some organometallic compounds of main-group elements and acetylacetato complexes.¹⁸

Finally, combination of FTIR with HPLC has been applied to detect some Cr(CO)₃ adducts with aromatic rings of amino acids in reversed-phase separations.¹⁹ The technique is rather sensitive and specific, but the position and the narrowness of the spectral windows available limit the number of possible applications considerably.

Low-temperature HPLC (LT-HPLC) represents another major advance in that it offers the potential for the separation of thermally labile species. An HPLC device for the separation of thermolabile organometallic compounds at temperatures down to -80 °C has been developed. By means of this device, the separation of the physically quasi-identical molecules (Cp)Mn(CO)₂(N₂) and (Cp)Mn(CO)₃ (Cp = cyclopentadienyl) has been achieved, in adsorption conditions, on a preparative scale.²⁰ Owing to the thermolability of the dinitrogen complex, the entire apparatus, from the injection valve to the fraction collector, has been maintained refrigerated.

Another useful device, shown in Figure 1, has been designed to continuously monitor the high-pressure reactions with HPLC without perturbing the reaction system.²¹ This system has allowed the study of reactions with molecular hydrogen of trinuclear ruthenium clusters containing nitric oxide ligands by periodically analyzing samples. The tubing between the reaction autoclave and HPLC is flushed with hexane and evacuated to prepare for each new injection. The total volume of each sample removed is 0.4 mL.

III. Mononuclear Species

A. CO and Other σ-Donors

HPLC separations involving mononuclear organometallic complexes containing only σ-donor ligands are collected in Table I. The first six items contain neutral molecular species chromatographed under different conditions, whereas items 7 and 8 refer to cyanometalated anions separated by means of ion-pair reversed-phase chromatography (IPRP).

In reversed-phase conditions Mo(CO)₆ is eluted after the Cr and W analogues in this order, according to the decreasing electronegativity.²⁴ On the other hand,

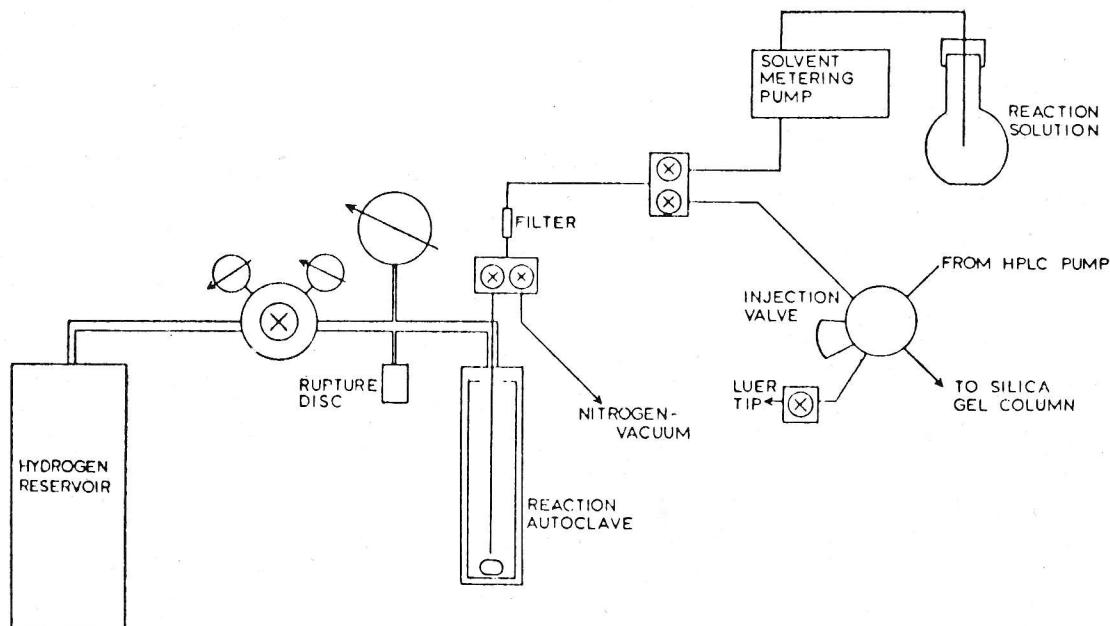


Figure 1. Scheme of the apparatus used to monitor, via HPLC, the reactions of ruthenium clusters with high-pressure H_2 . Reprinted from ref 21; copyright 1985 American Chemical Society.

TABLE I. σ -Donor Mononuclear Compounds

no.	class of compounds	stationary phase	eluent ^a	mode ^b	detector ^c	ref	note
1	$MCl(CO)(PPh_3)_2$ ($M = Rh, Ir$)	Lichrosorb (silica)	HX/T	NP	UV	22	reaction with O_2 was monitored
2	$Ni(P(OR)_3)_4$, $H_2Fe(dppe)_2$, and related complexes	μ -Styragel	T	SE	UV	12	SEC over a variety (24) of complexes and P-donor ligands
3	$Mo(CO)_6$, $Mo(CO)_4(LL)$ (LL = bidentate ligand)	Zorbax-C8	E/W	RP	UV, ICP	16	comparison between UV and ICP
4	$Fe(CO)_{5-n}P(OR)_3)_n$ ($n = 2, 3$)	Lichrosorb RP-18 Lichrosorb Si 60	M HX/T	RP	UV	23	separation of four pairs of iron(0) complexes
5	$M(CO)_6$ ($M = Cr, Mo, W$)	Lichrosorb RP-18	M/W	RP	UV	24	poor separation between W and Mo
6	$ReX(CO)_5(X = Cl, I)$ $MnBr(CO)_5$	Lichrosorb RP-18 Lichrosorb Si 60	M/W HX/T	RP NP	UV	24	separations related to electronegativity differences
7	$[M(CN)_m]^{n-}$ ($M = Cu^+, Ag^+, Au^+$, $Fe^{2+}, Fe^{3+}, Co^{3+}, Pd^{2+}, Pt^{2+}$)	Novapak C ₁₈	W/A	IPRP	UV	10	evaluation of detection limits and calibration graph for Au
8	$[M(CN)_m]^{n-}$ ($M = Cu^+, Ag^+, Au^+$, $Fe^{2+}, Fe^{3+}, Co^{3+}, Ni^{2+}$)	Novapak C ₁₈	Me ₄ NOH Bu ₄ NHSO ₄	IPRP	UV	11	detection limits

^a HX = *n*-hexane; T = tetrahydrofuran; E = ethanol; W = water; M = methanol; A = acetonitrile. ^b NP = normal phase; SE = size exclusion; RP = reversed phase; IPRP = ion-pair reversed phase. ^c UV = spectrophotometric detector; ICP = inductively coupled plasma detector.

$Mo(CO)_6$ can be separated from certain substitution compounds with N-donor bidentate ligands.¹⁶ In the latter case the ICP detector has been conveniently used, giving a response for the parent hexacarbonyl species superior to that of the spectrophotometric detector.

The carbonyl halogenide complexes of items 1 and 6 of Table I have been effectively separated under normal-phase and reversed-phase conditions, respectively. Separation occurs by virtue of the different nature of the metals in *trans*- $[MCl(CO)(PPh_3)_2]$ ²² and of the electronegativity differences between the metal and the halogen in the rhenium and manganese halides.²⁴

Separations on silica of some carbonyl-phosphite-iron(0) complexes of item 4 are reported in Figure 2 along with their structural schemes. The methyl derivatives Ia and IIa can be separated only on silica, whereas for the other pairs, an effective separation has been achieved also under RP conditions. In all cases the bis(phosphite) derivatives show lower retention volumes. Separation of the four complexes I (not possible on the C-18 column) has been obtained on silica even though a two-step gradient was necessary. The

elution order follows the decreasing number of carbon atoms in the alkyl chains.²³

Modern size-exclusion chromatography (SEC) for separation of organometallic compounds has been applied to a variety of low-valent Ni and Fe complexes containing P-donor ligands¹² (item 2 of Table I). The inherently gentle mechanism, the use of deoxygenated solvents, and the use of a packing with no reactive oxygens allow chromatography of fairly reactive and sensitive compounds. The retention volume is a function of molecular weight as shown in Figure 3, which reports the molecular weight (M_w) vs retention volume (V_R) calibration obtained with a series of ligands and nickel(0) complexes.

Finally, items 7 and 8 of Table I report two independent works concerning the separation and determination by ion-pair reversed-phase chromatography of cyanometalated anions in metallurgical plant solutions.^{10,11} This method eliminates the problems of precise pH and temperature control, reproducibility, and short column life that are associated with ion exchange. The simplicity and accuracy of the procedure make it indispensable for rapid determination of these

TABLE II. (Arene)chromium Compounds (Benchrotrenes): (Arene) $\text{Cr}(\text{CO})_3$

no.	arene	stationary phase ^a	eluent ^b	mode ^c	detector ^d	ref	note
1	substituted benzenes	Carbowax 400/Porasil C	TP	NP	UV	6	the first separation over a four-component mixture
2	dimethylnaphthalene	as in 1	TP	NP	UV	25	two isomers; thermostated columns
3	benzanthracenes	as in 1 or Corasil I	TP	NP	UV	26	two isomers; small preparative scale
4	substituted benzenes (mainly)	Carbowax 400 on Corasil	OT/D	NP	UV	27	23 derivatives
5	Ph_3E ($\text{E} = \text{Sb}, \text{Bi}$)	Silasorb-600	HP/DX	NP	UV	28	6 derivatives
6	aromatic amino acids	μ -Bondapack C ₁₈	M/W (buffer)	RP	UV, FTIR	19	FTIR detection
7	substituted benzenes	Rosil-NH ₂ ODS β -CD	P/HP M/W M/W	NP RP RP	UV	29	study on the retention mechanisms
8	substituted benzenes and cycloheptatriene	Lichrosorb RP-18 Lichrosorb Si 60	M/W HX/T	RP NP	UV	24	comparison with cymantrenes

^a Rosil-NH₂ = amino-bonded Rosil; ODS = octadecyl silica; β -CD = β -cyclodextrin. ^b TP = 2,2,4-trimethylpentane; OT = isoctane; D = dichloromethane; HP = *n*-heptane; DX = dioxane; M = methanol; W = water; P = propanol; T = tetrahydrofuran. ^c NP = normal phase; RP = reversed phase. ^d UV = spectrophotometric detector; FTIR = Fourier transform infrared detector.

TABLE III. π -Donor Mononuclear Compounds (Other Than Benchrotrenes)

no.	class of compounds ^a	stationary phase ^b	eluent ^c	mode ^d	detector ^e	ref	note
1	(diene) $\text{Fe}(\text{CO})_3$ (dienone) $\text{Fe}(\text{CO})_3$	ODS Permaphase	M/W	RP	UV	30	capacity factors for eight pairs of isomers
2	(butadienone) $\text{Fe}(\text{CO})_3$ (butadienol) $\text{Fe}(\text{CO})_3$	Partisil-10	D	NP	UV	31	separation of isomers
3	(PhC_7H_7) $\text{Fe}(\text{CO})_3$	Hypersil	HX	NP	UV	32	separation of four isomers
4	(Cp^{I}) $\text{Mn}(\text{CO})_3$ (cymantrenes)	Carbowax 400 on Corasil	D/OT	NP	UV	27	six substituted derivatives
5	(Cp^{I}) $\text{Mn}(\text{CO})_3$	Lichroprep Si 60	HX	NP	UV	20	low-temperature separation
6	(Cp^{I}) $\text{Mn}(\text{CO})_3$	Silochrom C-80, Silasorb 600	HX/ET	NP	UV	33	comparison with BiPh_3 and ferrocene analogues
7	(Cp^{I}) $\text{Mn}(\text{CO})_3$	Lichrosorb Si 60	HX/T	NP	UV	24	comparison with benchrotrenes
8	(Cp^{I}) $\text{Co}(\text{cyclobutadienes})$	Lichrosorb RP-18 Ultraspheres ODS	M/W A/W M/W	RP	UV	34	separation of a variety of isomers

^a PhC_7H_7 = phenylcycloheptatriene; Cp = cyclopentadienyl; Cp^{I} = monosubstituted cyclopentadienyl (RC_5H_4); Cp^{II} = methylcyclopentadienyl (MeC_5H_4). ^b ODS = octadecyl silica. ^c M = methanol; W = water; D = dichloromethane; HX = *n*-hexane; OT = isoctane; ET = ether; T = tetrahydrofuran; A = acetonitrile. ^d RP = reversed phase; NP = normal phase. ^e UV = spectrophotometric detector.

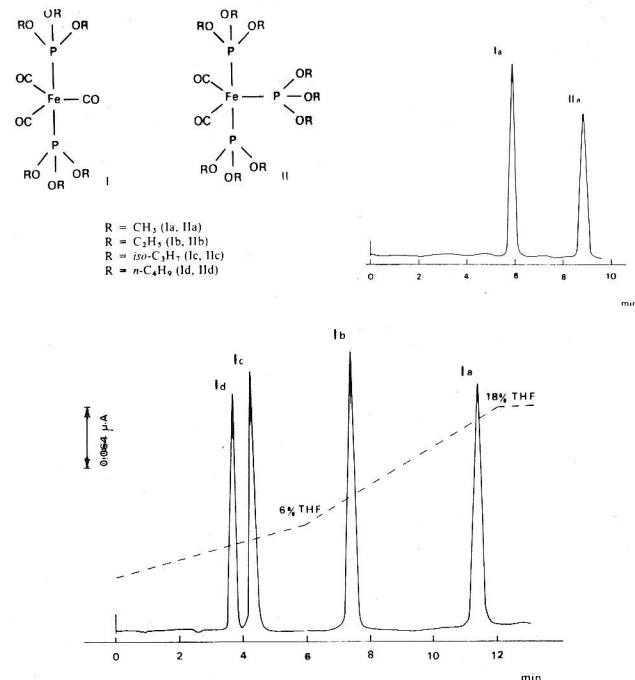


Figure 2. Structural schemes and separations on silica of phosphite-substituted carbonyl-iron complexes. For the lower separation a two-step linear gradient was necessary. Item 4 of Table I. Reprinted from ref 23; copyright 1983 Elsevier Science Publishers.

species in the fields of extractive metallurgy and environmental protection.

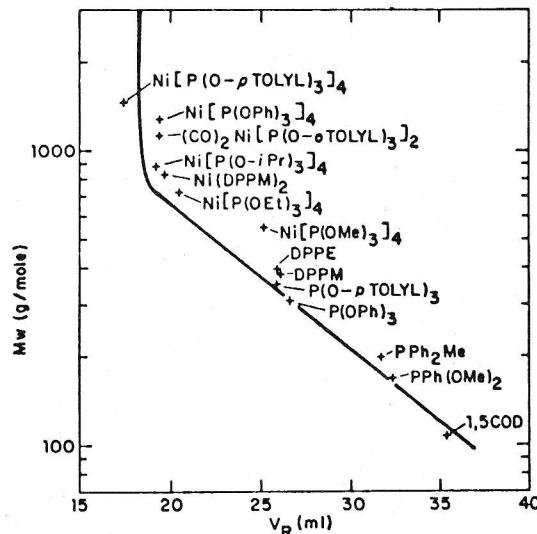


Figure 3. Molecular weight (M_w) versus retention volume (V_R) calibration for nickel complexes and free ligands under size-exclusion conditions. Item 2 of Table I. The solid line is a polystyrene calibration. Reprinted from ref 12; copyright 1978 Elsevier Sequoia SA.

B. CO and π -Donors

Applications in this field have been separated into two sets: Table II collects (arene)chromium compounds (benchrotrenes), whereas Table III contains all other metal complexes bearing π -donor ligands, namely, iron, manganese, and cobalt.

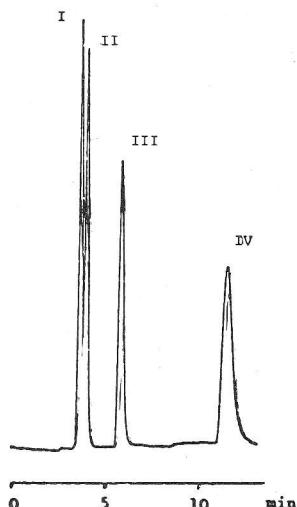


Figure 4. Separation on silica of $(\text{MeC}_5\text{H}_4)\text{Mn}(\text{CO})_3$ (I), $(\text{C}_5\text{H}_5)\text{Mn}(\text{CO})_3$ (II), $(\text{Me}_3\text{C}_6\text{H}_3)\text{Cr}(\text{CO})_3$ (III), and $(\text{C}_6\text{H}_6)\text{Cr}(\text{CO})_3$ (IV), emphasizing the different retention behavior of cymantrenes and benchrotrenes. Item 8 of Table II. Reprinted from ref 24; copyright 1986 Elsevier Science Publishers.

After the first HPLC separation of organometallic compounds, carried out on a mixture of four (arene)-chromium complexes,⁶ a variety of benchrotrenes were examined in both normal- and reversed-phase conditions (items 1–8 of Table II).

Isomers deriving from the reaction of hexacarbonylchromium with 2,3-dimethylnaphthalene²⁵ and with a dimethoxy-substituted benzanthracene²⁶ have been separated and quantitatively determined under normal-phase conditions. In the second case the separation of two isomeric complexes has been achieved on a preparative scale.

The study reported in item 4 represents the most extensive work in this field, 56 organometallic compounds of chromium, iron, and manganese having been considered.

On the other hand, the investigations of items 5 and 6 have been focused on two specific classes of compounds, i.e., the products of binding of the $\text{Cr}(\text{CO})_3$ fragment to the phenyl rings of either EPh_3 ($\text{E} = \text{Sb}$, Bi)²⁸ or certain amino acids.¹⁹ In this latter case the feasibility of using a Fourier transform infrared detector has been tested (section IIB).

Figure 4 shows a comparison between the chromatographic behavior on silica of two representative cyclopentadienylmanganese tricarbonyls and two (benzene)chromium tricarbonyls (item 8 of Table II), which are eluted in this order.²⁴ As the order of elution reverses under reversed-phase conditions, a substantial difference in the polarity characteristics between the two classes of molecules should exist, the cymantrenes appearing more hydrophobic.

Finally, item 7 of Table II reports the essential data of perhaps the first systematic study on the retention mechanisms of a class of organometallic compounds, namely, the (arene)chromium carbonyls.²⁹ Effects of solvent composition and ligand variation on the retention of these compounds have been studied, using an amino, an octadecyl silica (ODS), and a β -cyclodextrin (β -CD) bonded phase column in either a normal-phase or a reversed-phase mode. The retention behavior of the benchrotrenes with the amino column can be rationalized by the displacement model, while the reten-

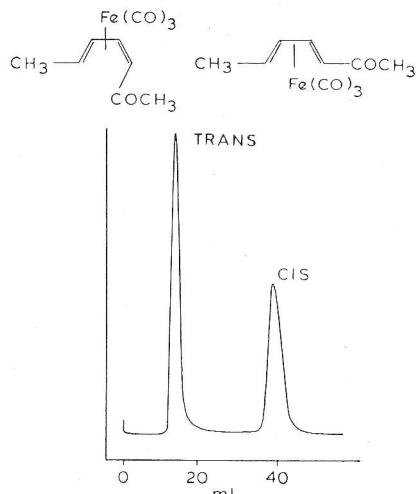


Figure 5. Separation of (*cis*-butadienone)- and (*trans*-butadienone)iron tricarbonyl complexes. Item 2 of Table III. Reprinted from ref 31; copyright 1977 Elsevier Sequoia SA.

tion on the ODS column depends on the expected solubilities of the examined compounds. On the other hand, mixed retention mechanisms, i.e., both an inclusion process and solvophobic interactions, are possibly operative for the β -CD column.

The first two items of Table III refer to separations of tricarbonyliron complexes of diene and dienones in both normal- and reversed-phase conditions.^{30,31} Separations of various isomers have been achieved, and Figure 5 illustrates the excellent resolution obtained in the separation of (*cis*-butadienone)- and (*trans*-butadienone)iron tricarbonyl.³¹

Under slightly different conditions, a mixture of four isomers of (phenylcycloheptatriene)iron tricarbonyl has been resolved, and the method has been used to study the thermal rearrangements of these molecules.

Cyclopentadienylmanganese tricarbonyl derivatives (cymantrenes) can be chromatographed both on normal- and on reversed-phase columns as reported in items 4–7 of Table III. Besides normal aromatic-ring substitution derivatives,^{24,27} some unusual products have been examined such as the dinitrogen complex (Cp)- $\text{Mn}(\text{CO})_2(\text{N}_2)$,²⁰ at low temperature, and the bis- and tris(cymantrenyl) derivatives of bismuth.³³

Finally, reversed-phase HPLC has been successfully applied to the separation, also on a preparative scale, of cyclopentadienyl(cyclobutadiene)cobalt complexes deriving from the reaction of $(\text{Cp})\text{Co}(\text{CO})_2$ with different alkynes bearing trimethylsilyl groups.³⁴ Although some of the compounds in the mixtures are moderately to strongly air sensitive and highly silylated products are exceedingly nonpolar and ordinarily inseparable, nevertheless quantitative isolation is possible by using octadecyl-modified (ODS) silica as a stationary phase and argon-saturated polar mobile phases.

C. Metallocenes

Several ferrocenes have been effectively separated by means of HPLC under different experimental conditions, as reported in Table IV, items 1–8. The HPLC behavior of a variety (26 compounds) of ring-substituted ferrocene derivatives, including two pairs of diastereoisomers,²⁷ has been studied under normal-phase conditions. The geometrical isomers *cis*- and *trans*-4-

TABLE IV. Metallocenes and Metallocene Dihalides

no.	class of compounds ^a	stationary phase ^b	eluent ^c	mode ^d	detector ^e	ref	note
1	ferrocenes	Carbowax 400/Corasil	OT	NP	UV	27	26 compounds
2	ferrocenes	Corasil I/DC	OT/DC	NP	UV	35	14 compounds; preparative separation
3	ferrocenes	Carbowax 400 on Corasil	OT/B	NP	UV	36	determination of diastereomeric mixtures
4	ferrocene, acetylferrocene, and diacetylferrocene	silica gel Si 60	TL	NP	UV, ICP	16	comparison between UV and ICP
5	as in 4	μ -Bondapak C ₁₈	M/W	RP	UV	37	undergraduate experiment
6	as in 4	Styragel	TL or PY	SE	ICP	18	influence of the eluent
7	ferrocene and Fc ₃ E (E = Sb, Bi)	Silochrom C-80	HX/ET	NP	UV	33	comparison with cymantrene analogues
8	ferrocenes, ruthenocenes, osmocenes	β -cyclodextrin (bonded)	M/W	RP	UV	13	separation of 13 enantiomeric pairs
9	(Cp*) ₂ MCl ₂ (M = Ti, Zr, Hf)	cyano-bonded silica	HX/D	NP	UV	38	capacity factor calibration graphs and detection limits
10	(Cp') ₂ TiCl ₂	CN-10	HX/D	NP	UV	39	56 mono- and bisubstituted derivatives

^aFc = ferrocenyl; Cp* = pentamethylcyclopentadienyl; Cp' = substituted cyclopentadienyl (RR'C₅H₃). ^bDC = 2,2'-dicyanodiethyl ether. ^cOT = isoctane; D = dichloromethane; B = 1-butanol; TL = toluene; M = methanol; W = water; PY = pyridine; HX = n-hexane; ET = ether. ^dNP = normal phase; RP = reversed phase; SE = size exclusion. ^eUV = spectrophotometric detector; ICP = inductively coupled plasma detector.

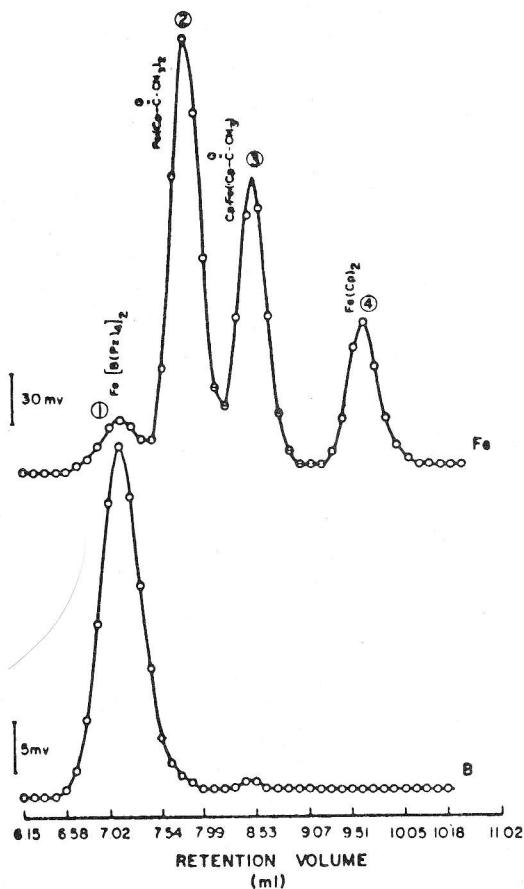


Figure 6. Separation of bis(tetrapyrazolyl borate)iron(II), 1,1'-diacetylferrocene, acetylferrocene, and ferrocene with ICP Fe and B detection. Item 6 of Table IV. Reprinted from ref 18; copyright 1981 American Chemical Society.

ferrocenylcyclohexene carboxylic acid methyl ester have been separated both analytically and preparatively.³⁵ The quantitative determination of diastereomeric mixtures of ferrocene carboxamides has also been reported.³⁶

Mixtures of ferrocene, acetylferrocene, and diacetylferrocene have been separated under normal-phase,¹⁶ reversed-phase,³⁷ or size-exclusion¹⁸ conditions. The inductively coupled plasma (ICP) detector has been successfully used with these compounds,^{16,18} and

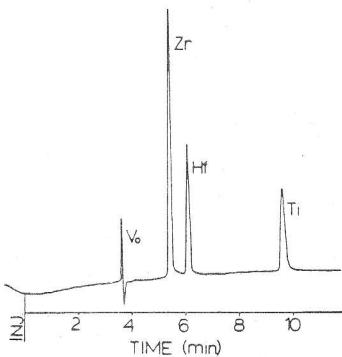


Figure 7. Separation of (Cp*)₂MCl₂ (Cp* = pentamethylcyclopentadienyl; M = Ti, Zr, Hf). Item 9 of Table IV. Reprinted from ref 38; copyright 1983 Elsevier Science Publishers.

Figure 6 illustrates their separation in the presence of bis(tetrapyrazolyl borate)iron(II), using both the iron and the boron emission lines.

As shown in item 7 of Table IV, normal-phase HPLC has been applied to the separation of unusual ferrocenyl and cymantrenyl derivatives of antimony and bismuth. The retention times of both decrease on going from Sb to Bi, the cymantrenyl ones being more retained.

Recently developed β -cyclodextrin-bonded columns have been shown to be particularly well suited to the separation of a variety of enantiomeric pairs of ferrocene, ruthenocene, and osmocene.¹³ Apparently, these compounds meet the requirements for chiral recognition in cyclodextrins, which seems to be due to a combination of their geometry (allowing inclusion complex formation) and the chirality of the two glucose carbons at the mouth of the cavity.

The last two items of Table IV concisely show two applications of HPLC to metallocene dihalides of group 4 elements. The utilization of a cyano-bonded silica stationary phase and gradient elution has allowed for the complete resolution of analogous complexes of Ti, Zr, and Hf³⁸ (Figure 7). Moreover, the HPLC parameters (namely, retention volumes, capacity factors, and separation efficiencies) of 56 mono- and disubstituted titanocene dichlorides have been evaluated, and the relationship between the chromatographic behavior and the structure of Ti complexes has been discussed accordingly.³⁹

TABLE V. Dinuclear Species

no.	class of compounds ^a	stationary phase	eluent ^b	mode ^c	detector ^d	ref	note
1	Fe ₂ (CO) ₆ (dab)	Zorbax-C8	E/W	RP	UV, ICP	16	comparison between UV and ICP
2	MM'(CO) ₆ (dab) (M = M' = Fe or Ru; M = Co, M' = Mn)	silica CN-bonded silica diol-bonded silica ODS-bonded silica	HP/D or HP/T	NP NP NP	UV	42	investigation on the retention behavior of selected organometallic complexes
3	M ₂ (CO) _n (iae) (M = Ru, n = 5; M = Mo, n = 6)	as in 2	M/W	RP	UV	42	as in 2
4	Ru ₂ (CO) ₄ (dab) ₂	as in 2	as in 2	as in 2	UV	42	as in 2
5	(Cp*)(CO) ₃ Mo—Mo(CO) ₃ (Cp*)	Ultrasphere ODS	A/W	RP	UV	34	three pairs of compounds
6	(Cp*)(CO) ₃ Mo≡Mo(CO) ₃ (Cp*)						
7	Fe ₂ (CO) ₆ (C ₂ R ₂) ₂ and related species	Lichrosorb RP-18	A/M	RP	UV	43	seven compounds
	Fe ₂ (CO) ₉ , Mn ₂ (CO) ₁₀ , (Cp) ₂ M ₂ (CO) _{2n} (M = Mo, n = 3; M = Fe, n = 2; M = Ni, n = 1)	Lichrosorb Si 60	HX/T	NP	UV	24	(Cp) ₂ Ni ₂ (CO) ₂ is retained

^adab = substituted diazabutadienes; iae = bis[(alkylimino)(alkylamino)ethane]; Cp* = monosubstituted cyclopentadienyl; Cp = cyclopentadienyl. ^bE = ethanol; W = water; HP = heptane; D = dichloromethane; T = tetrahydrofuran; M = methanol; HX = n-hexane. ^cRP = reversed phase; NP = normal phase. ^dUV = spectrophotometric detector; ICP = inductively coupled plasma.

$M_2(CO)_6(DAB)$ 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	

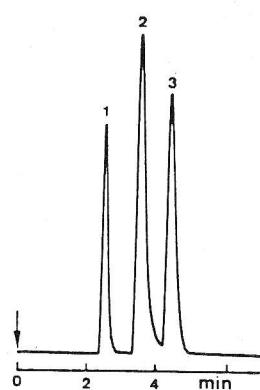


Figure 8. Structural scheme and separation of some substituted diazabutadiene (dab) complexes: $Ru_3(CO)_{12}$ (1), $Ru_2(CO)_6$ (Bu^t-dab) (2), and $Fe_2(CO)_6$ (Bu^t-dab) (3). Item 2 of Table V. Reprinted from ref 42; copyright 1981 Marcel Dekker.

Finally, the utilization (not included in Table IV) of some ferrocene reagents for the derivatization of amines⁴⁰ and alcohols⁴¹ in HPLC with electrochemical detection has been investigated. Ferrocenyl azide and 3-ferrocenylpropionyl azide condense readily with, e.g., hydroxy steroids, forming urethanes, which can be detected electrochemically with high sensitivity and without interference from the common electroactive compounds.⁴¹

IV. Dinuclear Species

HPLC separations involving dinuclear carbonyl compounds are summarized in Table V.

The behavior of several complexes of iron, ruthenium, cobalt, manganese, and molybdenum with diazabutadiene (dab) and related ligands has been examined on a nonpolar (C-18) and three polar (silica, CN bonded, and diol bonded) stationary phases.⁴² Figure 8 shows the structure of the dab complexes and the separation

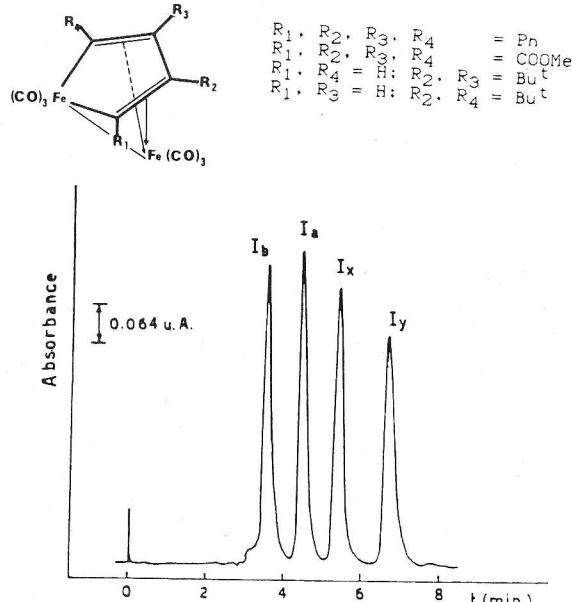


Figure 9. Structural scheme and separation of dinuclear iron compounds. Item 6 of Table V. Reprinted from ref 43; copyright 1983 Elsevier Science Publishers.

of a test mixture containing $Ru_2(CO)_6$ (Bu^t-dab), the iron homologue, and $Ru_3(CO)_{12}$. Under both normal- and reversed-phase conditions the retention behavior of the dinuclear complexes studied appears to depend on the type of metal as well as on the nature of the substituents in the ligands.

The iron-dab complexes have also been detected by an ICP device, and their response factors have been evaluated and compared with those of other iron compounds, including ferrocenes.¹⁶

Moreover, three dinuclear molybdenum (Mo—Mo) complexes and the corresponding less carbonylated (Mo≡Mo) species (item 5 of Table V), which are unstable to either basic alumina or silica gel and often inseparable on Fluorisil, have been cleanly separated on a RP column;³⁴ the triply bound compounds, eluting before the singly bound ones, appear relatively more polar.

In Figure 9 the complete separation of the dinuclear iron compounds depicted in the accompanying structure is illustrated. The elution order appears to be related to Taft's polar substituent constant σ , the retention volume increasing as σ decreases⁴³ in RP conditions.

TABLE VI. Cluster Compounds

no.	class of compounds ^a	stationary phase	eluent ^b	mode ^c	detector ^d	ref	note	
1	$H_4Ru_4(CO)_{12}$, $H_2FeRu_3(CO)_{12}$, and $HFeCo_3(CO)_{10}(PPh_3)_2$	Corasil II-C ₁₈	M/W	RP	UV	44	separation of products resulting from photolysis of the $FeCo_3$ derivatives	
2	$HRu_{3-n}Os_nCo(CO)_{13}$ ($n = 0-3$)	μ -Porasil	HX	NP	UV	45	effective separation	
3	$M_3(CO)_{12}$ ($M = Fe, Ru, Os$)	Lichrosorb RP-18	A/M	RP	UV	46	Ru and Os not well separated	
4	$HM_3(CO)_9(C_2Bu^t)$ ($M = Ru, Os$) and related compounds	Lichrosorb RP-18	A	RP	UV	46	6 compounds	
5	tetrahedral and butterfly Ru_4 and $CpNiM_3$ ($M = Ru, Os$) derivatives	Lichrosorb Si 60	HX/T	NP	UV	47	9 compounds; separation of the homologues	
6	$M_3(CO)_8(C_2R_2)_2$ ($M = Fe, Ru$)	Lichrosorb Si 60	HX/T	NP	UV	47	5 compounds	
7	$(Cp)_2Ni_2M(CO)_3(C_2Ph_2)$ ($M = Fe, Ru$)	Lichrosorb RP-18	M/A	RP	UV	47	effective separation	
8	$(Cp)_2NiOs_3H_3(CO)_8L$ ($L = \text{monodentate ligand}$)	Lichrosorb RP-18	M/A	RP	UV	48	10 substitution derivatives	
9	$(Cp)_2NiFe_2(CO)_5(L)(tba)$ ($L = CO, PPh_3$)	Lichrosorb Si 60	HX/T	NP	UV	49	PPh_3 causes longer retention time	
10	$(Cp)_2Ni_2Fe_2(CO)_6(C_2R_2)$	Lichrosorb RP-8	M/A	RP	UV	49	$(Cp)_2Ni_2Fe_2(CO)_6(PPh_2)(C_2R_2)$	
11	gold clusters	Chromspher C18	E/W	RP	UV	50	5 cationic clusters	
12	M-Au clusters ($M = Os, Ru, Re, Pt$)	Dynamax C18	NH_4NO_3	E/W/A	RP	UV	50	12 cationic clusters
							NH_4PF_6	

^a Cp = cyclopentadienyl. ^b M = methanol; W = water; HX = n-hexane; A = acetonitrile; T = tetrahydrofuran; C = chloroform; E = ethanol. ^c RP = reversed phase; NP = normal phase. ^d UV = spectrophotometric detector.

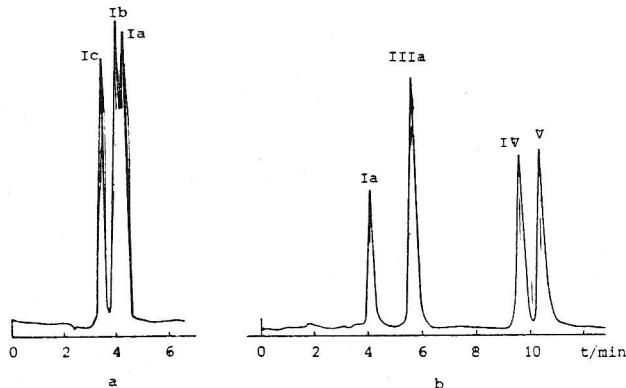


Figure 10. (a) Separation of $M_3(CO)_{12}$ ($M = Fe$ (Ic), Os (Ib), and Ru (Ia)) on a C-18 column. Item 3 of Table VI. (b) Separation of $Ru_3(CO)_{12}$ (Ia), $HRu_3(C\equiv CBu^t)(CO)_9$ (IIIa), $Ph_3PAuRu_3(C\equiv CBu^t)(CO)_9$ (IV), and $HRu_3(C\equiv CBu^t)(CO)_8(PPh_3)$ (V). Item 4 of Table VI. Reprinted from ref 46; copyright 1984 Elsevier Science Publishers.

In the $(Cp)_2M_2(CO)_n$ series of item 7, the retention increases as n decreases, the nickel derivative being completely retained.

V. Clusters

Table VI reports the essential data regarding HPLC separations of transition-metal clusters. The first ten items contain tri-, tetra-, and pentanuclear species of the iron triad, sometimes bearing also nickel or cobalt atoms, whereas the last two items describe the separations of cationic gold clusters. Two works, not included in the table, concerning metallacarboranes, are reported at the end of the section.

The chromatographic behavior of the transition-metal clusters is substantially in accordance with the trends commonly found in liquid chromatography for less complex molecules. Two major parameters influence the separations of neutral metal clusters: (i) the nature of the metals and (ii) the type of substituents.

In fact, in the three series $M_3(CO)_{12}$ ($M = Fe, Ru, Os$) (Figure 10a), $HM_3(C\equiv CBu^t)(CO)_9$ ($M = Ru, Os$), and

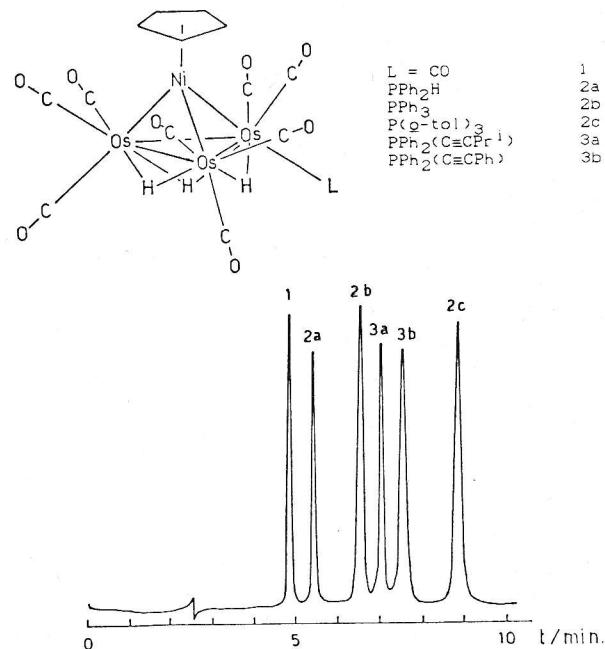


Figure 11. Structural scheme and separation of the tetrahedral cluster $(Cp)_2NiOs_3H_3(CO)_9$ (1) and its phosphine monosubstituted derivatives. Item 8 of Table VI. Reprinted from ref 48; copyright 1985 Elsevier Science Publishers.

$(Cp)_2NiM_3H_3(CO)_9$ ($M = Ru, Os$), the retention times increase with decreasing electronegativity of the metals under reversed-phase conditions and increase with increasing electronegativity in the NP mode.

An example of the substituent effect is given by the series $(Cp)_2NiOs_3H_3(CO)_8L$, where the nature of the ligand L strongly influences the retention behavior in spite of the size of the whole cluster.⁴⁸ On a C-18 column the parent cluster (L = CO) and five phosphine monosubstituted derivatives have been well separated (Figure 11).

Also the nuclearity and the shape of the clusters have been invoked in an attempt to rationalize all experimental results,²⁴ but the effectiveness of these effects is far from being well demonstrated.

TABLE VII. Reactions Monitored by Means of HPLC

no.	reaction ^a	stationary phase ^b	eluent ^c	mode ^d	detector ^e	ref	note
1	acylation of (diene)Fe(CO) ₃	ODS Permaphase	M/W	RP	UV	30	recognition of isomeric products
2	thermal rearrangements of cobaltacarboranes	Porasil A	HX/D	NP	UV	53, 54	also preparative-scale, kinetic study
3	reaction of IrCl(CO)(PPh ₃) ₂ with O ₂	Lichrosorb	HX/T	NP	UV	22	production of IrCl(O ₂)(CO)(PPh ₃) ₂
4	photolysis of IrH ₃ (PPh ₃) ₃	Zorbax-SIL	HX/T	NP	UV	22	mer and fac isomers
5	photolysis of HFeCo ₃ (CO) ₁₀ (PPh ₃) ₂	Corasil II-C ₁₈	M/W	RP	UV	44, 55	recognition of products
6	thermal rearrangements of (phenylcycloheptatriene)Fe(CO) ₃	Hypersil	HX	NP	UV	32	also preparative scale
7	reaction of Fe ₂ (CO) ₉ with RN=S=NR	Zorbax-C8	M/W	RP	UV	56	also preparative scale
8	reaction of tetrานuclear clusters with CO	μ -Porasil	HX	NP	UV	57	cluster fragmentation
9	reaction of Ru ₃ (CO) ₁₂ and Ru ₂ (CO) ₆ (dab) with dab	Zorbax-ODS	T/W	RP	UV	58	kinetic analysis
10	photoinduced reactions of tetranuclear clusters with PPh ₃ and H ₂	μ -porasil	HX	NP	UV	59	quantum yield
11	reaction of H ₂ FeRu ₃ (CO) ₁₃ with PPh ₃	μ -Porasil	HX	NP	UV	60	kinetic study
12	reaction of Fe ₂ (CO) ₉ with benzotriphosphole	μ -Porasil	HX/EA	NP	UV	61	also preparative scale for major components
13	reaction of HRu ₃ (CO) ₁₀ NO with H ₂	silica gel	HX	NP	UV	22	kinetic analysis; see section II.B
14	reaction of Fe ₂ (CO) ₈ [C ₆ H ₄ (PPh ₃) ₂] with RLi	μ -Porasil	HX/EA	NP	UV	62	quantitation of the products

^adab = 1,4-diazabutadiene. ^bODS = octadecyl silica. ^cM = methanol; W = water; HX = n-hexane; D = dichloromethane; T = tetrahydrofuran; EA = ethyl acetate. ^dRP = reversed phase; NP = normal phase. ^eUV = spectrophotometric detector.

The separation under RP conditions (Figure 10b) emphasizes the retardation of compounds IV and V, both bearing a PPh₃ ligand, compared to the parent cluster IIIa. This effect appears to be general, when considering also the separations of item 9 (Table VI), where the substitution of a CO with PPh₃ causes longer retention times in either the RP or the NP mode.⁴⁹

The separations of the cationic gold clusters, reported in the last two items of Table VI, are dominated by the effect of the charge.⁵⁰ More highly charged gold clusters are retained less than lower charged clusters; there is also an increase in retention time with increasing number of surrounding phosphines. The charged nature of these clusters requires the use of aqueous solvent mixtures containing a dissolved salt such as NH₄NO₃ or NH₄PF₆. On silica gel or alumina this effect can most satisfactorily be explained in terms of an ion-exchange process. Nevertheless, on a C-18 reversed-phase column, where also the nonprotic NaBF₄ can be used, an ion-pairing mechanism cannot be ruled out completely.

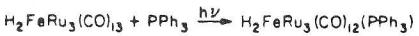
Finally, the HPLC behavior (not reported in Table VI) of two series of neutral metallacarboranes has been studied under normal-phase liquid-solid conditions,⁵¹ whereas a variety of heteroborane anions, including six metallacarboranes, have been chromatographed under ion-pair reversed-phase conditions.⁵²

VI. Applications to Synthesis

A. Monitoring the Reactions

The efficacy of HPLC in following the course of reactions by monitoring the increase in peak areas for the products as the reactants' peak areas decrease is now universally recognized. The early expectations of the first pioneering separations have all been fulfilled, and HPLC is becoming a routine, rapid, and powerful tool for studying organometallic reaction pathways.

Representative examples in the field of reaction monitoring for mono-, di-, and polynuclear complexes are given in Table VII. A rapid survey of the data



2/1 hexane/CH₂Cl₂

0.5 ml/min

μ -PORASIL COLUMN

λ 254 nm DETECTOR

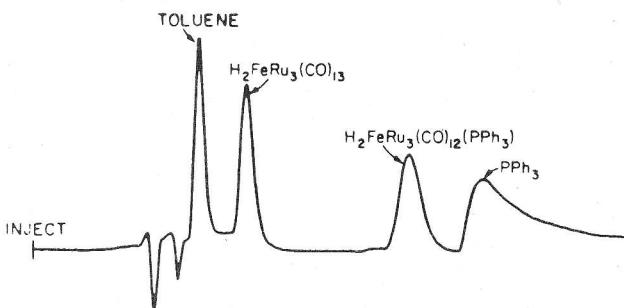


Figure 12. Chromatogram obtained at an intermediate stage of a photoinduced substitution reaction. Item 10 of Table VII. Reprinted from ref 59; copyright 1981 American Chemical Society.

shows that most applications deal with iron-triad compounds, and all separations are performed by using variable-wavelength spectrophotometric detectors, under either normal- or reversed-phase conditions.

Figure 12 emphasizes the usefulness of the method, showing a liquid chromatogram obtained at an intermediate stage of photolysis during the photosubstitution of PPh₃ for CO in an iron-ruthenium cluster.⁵⁹

B. Preparative Scale

Parallel to the analytical separations in a qualitative or quantitative way, several works have demonstrated the efficacy of preparative HPLC in separating products in workable amounts by using large-size packed columns.

Perhaps the first preparative HPLC separations of organotransition-metal compounds were those involving the geometric isomers of ferrocenyl esters²⁵ and of (benzanthracene)chromium complexes,²⁶ already reported in sections IIIC and IIIB, respectively.

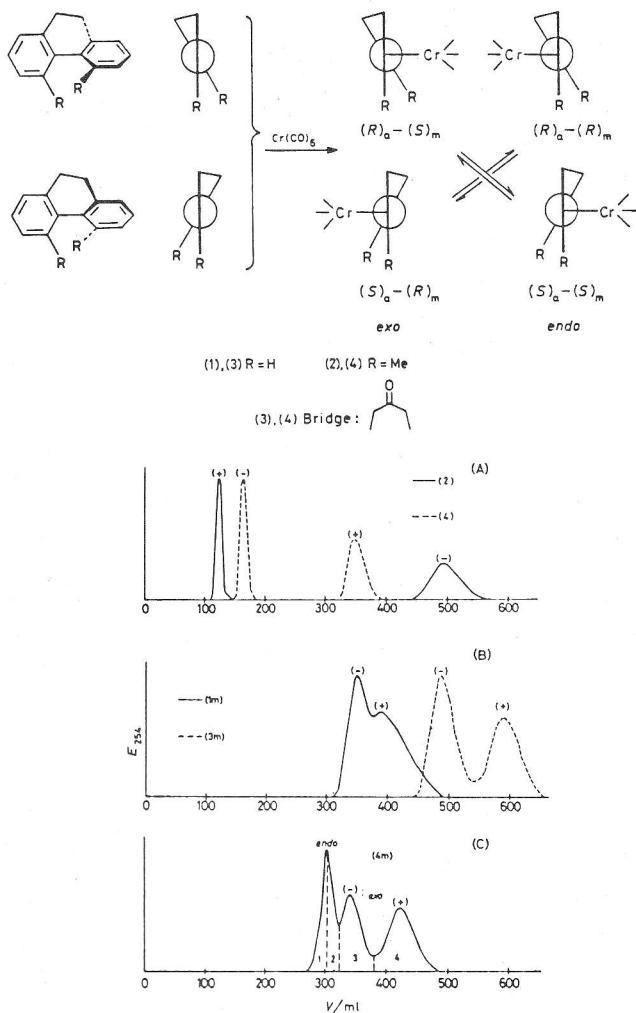


Figure 13. Structural schemes and some chromatographic resolutions on triacetylcellulose of the bridged biphenyls 1, 2, 3, and 4 and their stereoisomeric $\text{Cr}(\text{CO})_3$ complexes 1m, 2m, 3m, and 4m. (A) Separation of the enantiomeric pairs of the dimethylated biphenyls 2 and 4. (B) Complexation of 1 and 3 yields only the exo complexes 1m and 3m. (C) From the racemic mixture of 4m all four stereoisomers have been obtained. Reprinted from ref 66; copyright 1983 The Chemical Society.

Several applications of preparative HPLC to synthetic works appear also in Table VII, along with the reaction monitoring, particularly at items 2, 6, 7, and 12.

As reported in section II B, the utilization of an integral HPLC-ESR apparatus has permitted the separation of the rhenium carbonyl-*o*-quinone radical complex in amounts suitable for characterization purposes,¹⁴ while a low-temperature HPLC device has allowed the separation on a preparative scale of a thermolabile manganese-dinitrogen complex²⁰ (see also section II B).

A variety of cobalt organometallics deriving from the reaction of diynes⁶³ and diynenes⁶⁴ with $(\text{Cp})\text{Co}(\text{CO})_2$ have been preparatively separated with standard equipment under reversed-phase conditions.

Preparative separations into enantiomers of ferrocene and (arene)tricarbonylchromium derivatives have been achieved by using medium-pressure chromatography on microcrystalline triacetylcellulose (TAC) at ambient temperature.⁶⁵ The procedure generally gives both enantiomers in semipreparative amounts, sufficient for the determination of chiroptical properties and further transformation.

Chiral biphenyls and their tricarbonylchromium complexes, depicted by the schemes of Figure 13, can be conveniently resolved in this way.⁶⁶ As shown in Figure 13, the mono- $\text{Cr}(\text{CO})_3$ exo complexes of 9,10-dihydrophenanthrene (1) and of the corresponding *o*,*o'*-bridged ketone 3 (1m and 3m, respectively) have been separated into enantiomers, whereas the mixtures of the dimethylated biphenyls 2 and 4 (2m and 4m, respectively) have been separated in one run into all four stereoisomers, i.e., the enantiomers of the exo and endo forms.

In the field of clusters, the separations of cationic gold clusters by means of reversed-phase HPLC, reported also in section V, were performed also on a preparative scale.⁵⁰

A key passage in the synthesis of $\text{H}_2\text{FeRu}_3(\text{CO})_{13}$ is the chromatographic separation that has been achieved by using a preparative-scale high-pressure liquid chromatograph on a silica column.⁶⁷

Finally, the two diastereoisomers obtained by the substitution of a carbonyl by an asymmetric monophosphine over the chiral cluster ($\mu_3\text{-CH}_3\text{C}$) $\text{Co}_3(\text{CO})_7\text{-}(\text{Ph}_2\text{PCH}_2\text{PMe}_2)$ have been preparatively separated under reversed-phase conditions (C-18), eluting with a methanol/water mixture.⁶⁸

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