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HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY OF BIS(η^5-1,2,3,4,5-PENTAMETHYLCYCLOPENTADIENYL)-TITANIUM, ZIRCONIUM AND HAFNIUM DICHLORIDES

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SUMMARY

    The high-performance liquid chromatographic separation of bis(η^5-1,2,3,4,5-pentamethylcyclopentadienyl)-titanium, zirconium and hafnium dichlorides was demonstrated on cyano-bonded silica under normal-phase gradient elution conditions. Data reported include capacity factors, separation efficiencies, and compound resolutions. The linearity of detection is shown and detection limits are reported.

INTRODUCTION

    Organometallic compounds are of interest owing to their catalytic properties and biological activity but many of these are relatively labile and decompose in the presence of water and air. Thus they are not easily separated and analyzed by conventional chemical techniques[1,3,4]. Gas chromatography (GC) is not useful if the compounds are involatile or thermally unstable[1,3]. Thin-layer chromatography (TLC) and conventional column chromatography (LC), when employable, generally offer insufficient separating efficiency and tend to be slow[1]. High-performance liquid chromatography (HPLC) in contrast, is a versatile, efficient, relatively quick separation method for large, non-volatile, thermally labile compounds that are sensitive to air and water and, as such, is an ideal technique for the separation and study of many organometallics.

    HPLC separation of organometallics was first reported in 1969 by Veening and Willeford[5,6]. The primary use of HPLC in the separation and study of cyclopentadienyl-substituted organometallics, an area which has been frequently studied, was first reported in 1973 by Eberhardt *et al.*[7]. Since these initial reports, various HPLC studies of organometallics have appeared in the literature. Normal-phase and reversed-phase HPLC have been used in the separation of isomeric arene-tricarbonyl-chromium compounds[8], tricarbonyl(dienone)-iron compounds[9], ferrocene and ferrocene analogues[10], psi-*endo* and psi-*exo* dienol-iron-carbonyl isomers[11], *cis/trans*

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isomers of cyclopentadienyl-cobalt-cyclobutadiene[1,10], organomercurials[12], organotins[13], boron, cobalt, sulfur and iron metallocarborane-pi-complexes[2], nonacarbonyl-iron-di-*tert.*-butylsulfurdiimine reaction products and by-products[3], organophosphorus compounds[14], organoleads[15], nickel-based organometallics[16], and cyclopentadienyl-molybdenum-cyclobutadienes[4]. With specific reference to the HPLC separation of titanium, zirconium and hafnium compounds, however, no successful work appears to have been performed.

The problem of separating titanium, zirconium and hafnium compounds (Zr and Hf especially) has long existed and is considered a classical separation problem since these elements exhibit closely similar chemical properties. Paper chromatographic separations of group IVB compounds have been reported[22–25] but no separation of analogues of all three elements has appeared. Similarly, TLC for organometallic compounds has been demonstrated[26–34] but only a few studies[32,34–37] have dealt with group IVB organometallics. Ion-exchange chromatography[38–47] and GC[48,49] have also been considered but these techniques suffer from low efficiencies and long analysis times in the first case and the dependence on compound volatility and thermal stability in the latter. Finally, some column LC for zirconium/hafnium separations has been reported[50,51] but the extension of this work to trace analysis using HPLC has yet to be presented.

In this paper, the separation and quantitation of bis(η^5-1,2,3,4,5-pentamethylcyclopentadienyl)-titanium, zirconium and hafnium dichlorides, $(PMCP)_2TiCl_2$, $(PMCP)_2ZrCl_2$, and $(PMCP)_2HfCl_2$), on a cyano-bonded silica column is reported. Separation efficiencies, resolutions and capacity factors are given, as are detection limits for the various compounds.

EXPERIMENTAL

An IBM Instruments (Danbury, CT, U.S.A.) microprocessor-controlled Model LC/9533 ternary gradient liquid chromatograph equipped with an IBM Instruments Model LC/9522 ultraviolet detector was used. The pumping system consists of an electronically driven three-headed reciprocating piston pump with pistons set 120° apart producing a flow that exhibits only slight variations. The LC/9522 UV detector is a single-wavelength unit set at 254 nm with a 10-μl flow-cell volume and a 10-mm pathlength. Prepacked silica and cyano-bonded silica (5.0 μm particle size) stainless-steel columns (250 mm × 4.5 mm I.D.) were also obtained from IBM Instruments. A Houston Instruments (Austin, TX, U.S.A.) Omniscribe linear chart recorder was used to record all chromatograms. All solvents were HPLC grade and were dried over molecular sieves and helium degassed. Qualitative and quantitative solutions of the compounds were prepared in methylene chloride. Stock solutions of *ca.* 120 μg/ml were prepared and serially diluted to produce the desired sample concentration.

The synthesis of $(PMCP)_2TiCl_2$ was as described by Bercaw *et al.*[17]. Lithium pentamethylcyclopentadienide and titanium trichloride were mixed in a dimethoxyethane solution and refluxed for 1 day. The resulting solution was extracted with chloroform, dried over anhydrous sodium sulfate and brought to a residue under reduced pressure. This residue was placed in the thimble of a Soxhlet extractor and reaction by-products were removed by extraction with HCl-saturated Skelly F. At

that point, the collection flask was replaced with HCl-saturated carbon tetrachloride and the remaining residue extracted for 16 h. Product was recovered from a rotary evaporator after removal of the carbon tetrachloride.

The preparation of $(PMCP)_2ZrCl_2$ has been described by Manriquez *et al.*[18]. A solution of lithium pentamethylcyclopentadienide and zirconium tetrachloride was prepared in dimethoxyethane and refluxed for 3 days. After solvent removal under high vacuum the resulting solid was dissolved in chloroform and mixed with a hydrochloric acid solution. The layers were separated and the organic portion was further washed with distilled water, dried over anhydrous sodium sulfate and evaporated in a rotary evaporator until crystals deposited. The product was collected on a Buchner funnel and washed with pentane.

$(PMCP)_2HfCl_2$ was prepared from a reaction between lithium pentamethylcyclopentadienide and hafnium tetrachloride in dimethoxyethane solution using a method analogous to that employed for the zirconium compound[19].

The retention volume (V_R) of each compound was obtained by multiplying the compound retention time (t_R) by the flow-rate. Column void volume (V_0) was determined as the retention volume of a non-retained solute, benzene. The capacity factor (k') for the three compounds was calculated from $k' = (V_R - V_0)/V_0$ where V_R was the apparent compound retention volume. Column efficiency (N) was computed from $N = 5.55(t_R/t_w)^2$, where t_w was the peak width at half peak height. Resolution (R) of adjacent peaks was obtained by dividing the distance between peak centers by the average peak width; $R = 2(t_2 - t_1)/(t_{w1} + t_{w2})$. Finally, detection limits for the compounds were determined as that amount which produced a response on the detector's most sensitive setting of twice the baseline noise.

RESULTS AND DISCUSSION

The chromatographic behavior of $(PMCP)_2TiCl_2$, $(PMCP)_2ZrCl_2$ and $(PMCP)_2HfCl_2$ was investigated to define conditions suitable for routine analytical and preparative HPLC of these compounds. These three group IVB compounds are
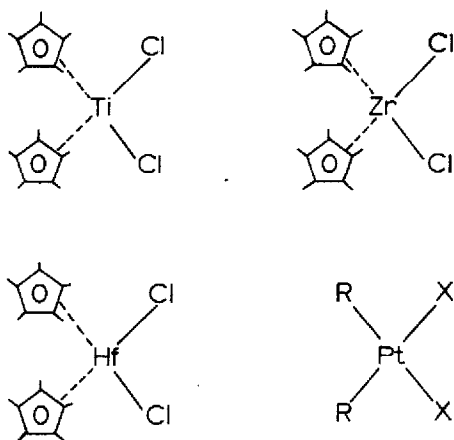

Fig. 1. Bis(η^5-1,2,3,4,5-pentamethylcyclopentadienyl) group IVB dichlorides and "*cis*-platinum" structural analogue.

of particular interest in that first they represent the classical chromatographic chal-
lenge of separating compounds with very similar properties and unknown chroma-
tographic behaviour and second because analytical determinations of these com-
pounds may prove significant if their structural relationship to "cis-platinum" com-
pounds provides noteworthy bioactivity (Fig. 1).

Before HPLC methods could be developed it was necessary to perform limited
solubility–stability studies to ascertain suitable chromatographic conditions. All of
the compounds showed sensitivity to oxygen and water as evidenced by their rapid
degradation when exposed to either. This reactivity precludes their direct preparation
as organometallic derivatives from aqueous solutions of these elements. Testing of
several solvents showed that both methylene chloride and chloroform provided suit-
able solvent characteristics with the former being the solvent of choice. Solutions in
dry degassed methylene chloride were stable for longer than 3 days at ambient tem-
peratures. However, 2-day periods of stability were more common with chloroform
solutions except in the case of $(PMCP)_2ZrCl_2$ where a significantly shorter period
(*ca.* 2 h) was noted. Unmodified silica was the first choice for an adsorbent since it
is frequently used for the isolation of organometallic complexes. Unfortunately, ex-
periments with a silica stationary phase and several different mobile phases proved
that insufficient column selectivity was available to achieve the desired separation.
Both $(PMCP)_2ZrCl_2$ and $(PMCP)_2HfCl_2$ exhibited no retention ($k' = 0$) even with
a hexane mobile phase. (Fig. 2 shows a typical chromatogram obtained on the silica
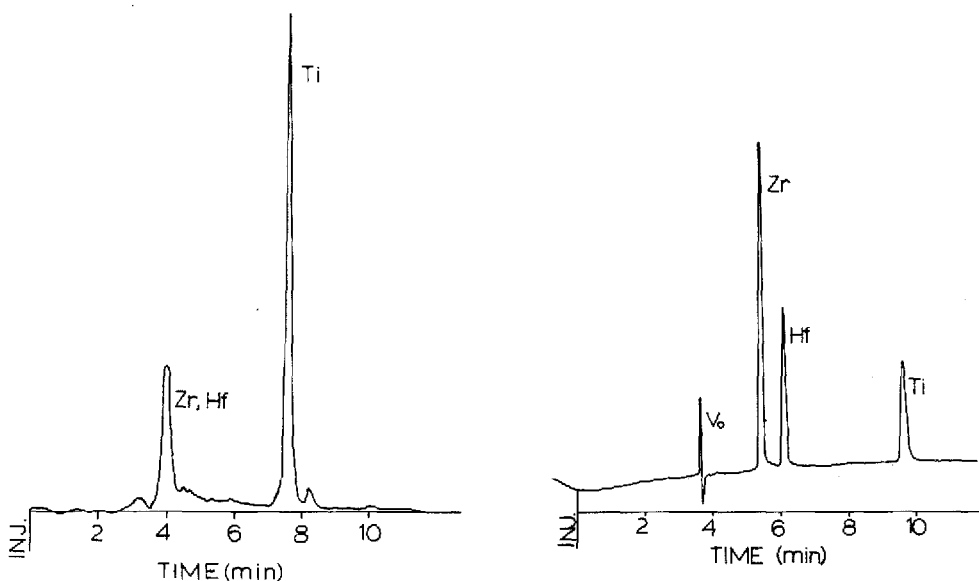adsorbent). In addition to lack of selectivity the silica stationary phase showed signs

Fig. 2. HPLC chromatogram of $(PMCP)_2TiCl_2$, $(PMCP)_2ZrCl_2$ and $(PMCP)_2HfCl_2$, on 5.0-μm silica.
Mobile phase flow-rate, 1.5 ml/min; detection, UV at 254 nm with attenuation 0.10 a.u.f.s. Amount of
each compound injected, *ca.* 200 ng.

Fig. 3. Separation of $(PMCP)_2TiCl_2$, $(PMCP)_2ZrCl_2$ and $(PMCP)_2HfCl_2$ on 5.9 μm cyano-bonded silica.
Mobile phase, gradient from 0 to 10% methylene chloride in hexane in 10 min; flow-rate, 1.0 ml/min;
detection, UV at 254 nm with attenuation 0.05 a.u.f.s. Amount of each compound injected, *ca.* 100 ng.

TABLE I

CHROMATOGRAPHIC PARAMETERS FOR HPLC SEPARATION

Conditions as in Fig. 3; V_0 = 3.65 ml.

	$(PMCP)_2TiCl_2$		$(PMCP)_2ZrCl_2$		$(PMCP)_2HfCl_2$
V_R (ml)	9.64		5.45		6.12
k'	1.64		0.49		0.68
N	22,768		16,455		20,750
R		11.9		2.23	
			10.2		

of reacting with the injected compounds, as indicated by the appearance of multiple peaks for a single pure analyte. Column regeneration was necessary after several chromatograms of this sort in order to restore the original selectivity and efficiency; this was accomplished by flushing with five column volumes each of hexane, tetrahydrofuran, and hexane. The lack of retention and selectivity on silica did however indicate that a somewhat less polar phase might provide the necessary conditions for the separation. A cyano-bonded silica adsorbent was thus investigated and after a series of mobile phase modifications yielded a set of conditions which allowed the separation of the group IVB organometallic analogues in reasonable time. Fig. 3 shows the separation of $(PMCP)_2TiCl_2$, $(PMCP)_2ZrCl_2$ and $(PMCP)_2HfCl_2$ on 5.0 μm cyano-bonded silica with gradient elution from 0 to 10% methylene chloride in hexane in 10 min. Table I is a summary of the chromatographic parameters for the three compounds under these conditions.

Extension of this separation to trace determinations employing similar conditions required that linearity of the detector response and suitably low detection limits be shown. Calibration curves were thus constructed for each of the compounds
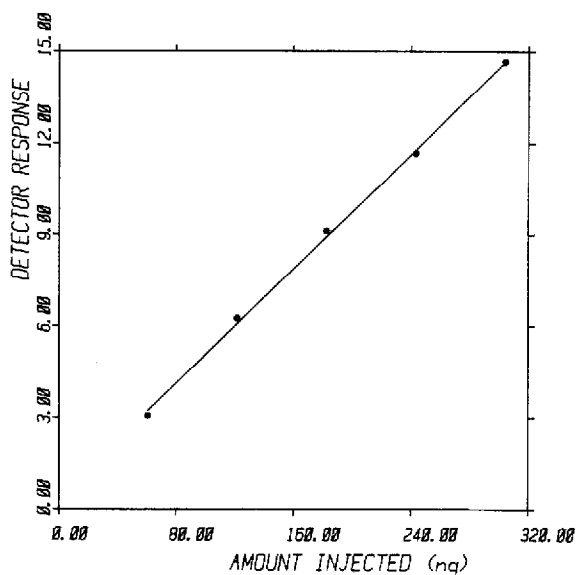

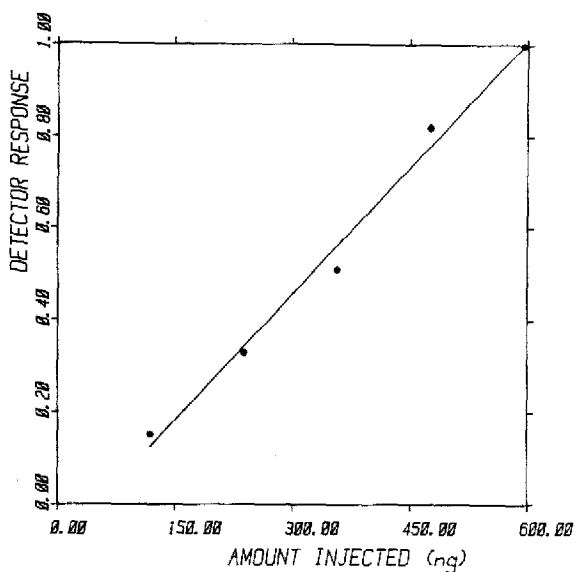Fig. 4. Calibration curve for $(PMCP)_2TiCl_2$. $y = 0.04705x + 0.3550$. $r = 0.9993$.

Fig. 5. Calibration curve for (PMCP)$_2$ZrCl$_2$. $y = 0.001832x + 0.0928$. $r = 0.9941$.

using the conditions previously described. Figs. 4–6 show the results of a linear regression of the data acquired for each complex. For each the correlation coefficient of the regression is large enough to justify the assumption of a linear response over the range studied ($R > 0.99$). Finally, detection limits for the complexes were determined as the amount of compound injected which produced a signal of twice baseline noise on the detector's most sensitive setting (0.001 a.u.f.s.). Each of the compounds exhibited nearly the same detection limit of *ca.* 0.6 ng. This was not surprising since
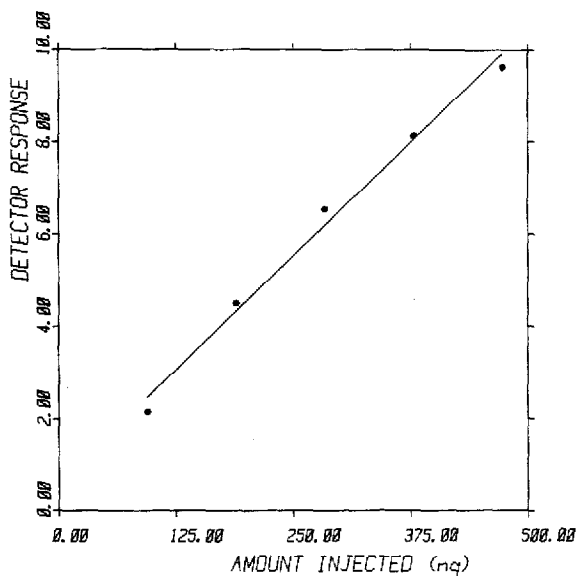

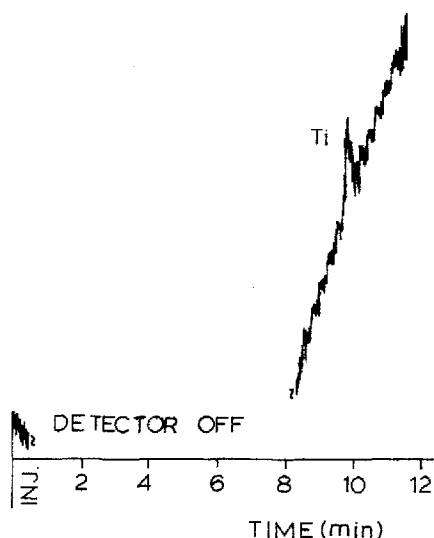Fig. 6. Calibration curve for (PMCP)$_2$HfCl$_2$. $y = 0.01971x + 0.605$. $r = 0.9952$.

Fig. 7. Detection limit chromatogram for $(PMCP)_2TiCl_2$. Attenuation, 0.001 a.u.f.s.; 610 pg of compound injected. All other conditions as in Fig. 3.

the molecules share common chromophores. Fig. 7 shows the detection limit chromatogram for the $(PMCP)_2TiCl_2$ complex.

CONCLUSION

HPLC was shown to be a useful technique in the determination of Group IVB organometallic analogues. The utilization of a cyano-bonded silica stationary phase and normal-phase gradient elution allowed for the complete resolution of analogous complexes of titanium, zirconium and hafnium. The selectivity offered by the reported HPLC conditions coupled with the linearity of the UV response and sub-nanogram detection limits demonstrates the possibility of trace analysis of transition metal organometallics by HPLC. Although these particular compounds are not sufficiently stable in aqueous media for derivatization from ionic solutions of metal hydrolysis products, the fact that they are separable suggests fruitful investigation of other compound classes which may be directly applied for analytical metal determinations. HPLC can be a useful analytical technique in the determination of organometallic compounds sensitive to air and water as it provides for rapid separation and accurate analysis of species exhibiting very similar chemical properties.

ACKNOWLEDGEMENTS

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