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THE HIGH PRESSURE LIQUID CHROMATOGRAPHIC SEPARATION OF CIS AND TRANS DIENONE-IRON CARBONYL COMPLEXES AND OF Ψ-ENDO AND Ψ-EXO DIENOL-IRON CARBONYL COMPLEXES ON 10 m SILICA

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SUMMARY

High Pressure Liquid Chromatography (HPLC) has been used to separate cis and trans dienone-iron carbonyl complexes having different σ and π bonded moieties, and ψ-endo and ψ-exo dienol-iron carbonyl complexes. TLC predicts the appropriate solvent polarity needed and elution order on microparticulate silica columns. Data is reported for methylene chloride and methylene chloride-acetonitrile mobile phases on 10 μm silica.

INTRODUCTION

High Pressure Liquid Chromatography (HPLC) is now a major analytical separatory technique and shows much promise in the preparative mode also. Its development has been accelerated by the introduction of microparticulate (5 μm and 10 μm diameter) substrates for partition, adsorption, ion exchange and exclusion, which give very high column efficiencies. They have been widely used for organic separations but infrequently applied to organometallic problems. The routine use in the latter area of such methods as classical open column chromatography and thin layer chromatography (TLC) on silica

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and alumina, for preparation and purification suggest a natural progression to the related high efficiency method of HPLC and the preexisting information in the area may provide useful guidelines to the application of high resolution methods. It seems likely that HPLC methods will exceed gas chromatographic techniques in organometallic applications since vapor phase thermal stability is no longer a necessary criterion.[1]

Earlier studies utilized the then available larger mesh substrates (35-75 μm) which give relatively low efficiencies. Such studies included separations of arene tricarbonyl chromium complexes [2,3], organomercurials[4] and cyclopentadienyl cobalt carboranes.[5] Lillya and Graf[6] used reverse phase partition to separate cis and trans dienone-iron carbonyl complexes using the results to measure their reactivity to electrophiles. Recently Enos, Geoffroy and Risby have demonstrated the greater potential of microparticulate column substrates in the separation of rhodium and iridium triphenylphosphine complexes[7] including geometrical isomers and oxygen adducts. They also resolved metal cluster complexes in the reverse phase partition mode.[8] We have reported the effective separation of transition metal Schiff base compleces on both adsorption[9] and reverse phase columns.[10]

The present paper reports the behavior of isomeric iron carbonyl complexes on 10 μm silica adsorptive substrates, relating the separation to those noted by TLC.

EXPERIMENTAL

Synthesis and identification of the dienone-iron carbonyl complexes are reported elsewhere,[11] as are synthesis and assignment of relative configuration for the dienol complexes.[12] The triphenylphosphine derivatives and methyl ethers were prepared by D. G. Gresham.[13]

A Tracor-Chromatec Model 3100 Liquid Chromatograph was used. The pumping system consists of an electronically driven reciprocating piston giving a maximum pressure of 1000 psi. A U.V. detector with a single detection wavelength of 254 nm, a full scale sensitivity of 0.01 A.U. and a flow cell volume of 8 μl. was used. The column was a commercially available 10 μm silica column (Partisil - 10, Whatman 30 cm. x 4 mm. I.D.). Certified ACS grade solvents were used without prior purification.

Results and Discussion

Thin layer chromatography on silica was first carried out on the iron tricarbonyl compounds to assess their purity and the po-

TABLE

Liquid Chromatographic Retention Data for Iron Tricarbonyl Complexes. (TLC data obtained under same conditions in all cases; R_f values are mean values) Methylene chloride mobile phase for TLC and HPLC.

Complex	Isomers	R_f	HPLC Retention Volume (ml.)
Butadienone Iron Tricarbonyl	cis	0.58	40.0
	trans	0.75	12.0
Butadienol Iron Tricarbonyl	ψ- endo	0.54	14.5
	ψ- exo	0.39	25.0
4-Methyl Butadienol Iron Tricarbonyl	ψ- endo	0.54	16.0
	ψ- exo	0.34	34.1
Butadienol Iron Tricarbonyl Methyl Ether	ψ- endo	0.90	5.4
	ψ- exo	0.85	7.5
Butadienone Iron Dicarbonyl Triphenylphosphine	cis	0.30	11.8*
	trans	0.58	5.4

*Mobile Phase used was 10% acetonitrile in methylene chloride (see text).

tential separation of their isomer pairs by high pressure adsorption chromatography. Various solvent systems were assessed and methylene chloride found to be optimal for the range of compounds studied. R_f values are listed in the Table as are the retention volumes subsequently observed in HPLC on silica with methylene chloride as eluent also. In all cases the cis isomer of a particular complex was found to have a lower R_f value than the trans isomer and similarly the exo isomer of an exo - endo pair was always retained more than the endo isomer.

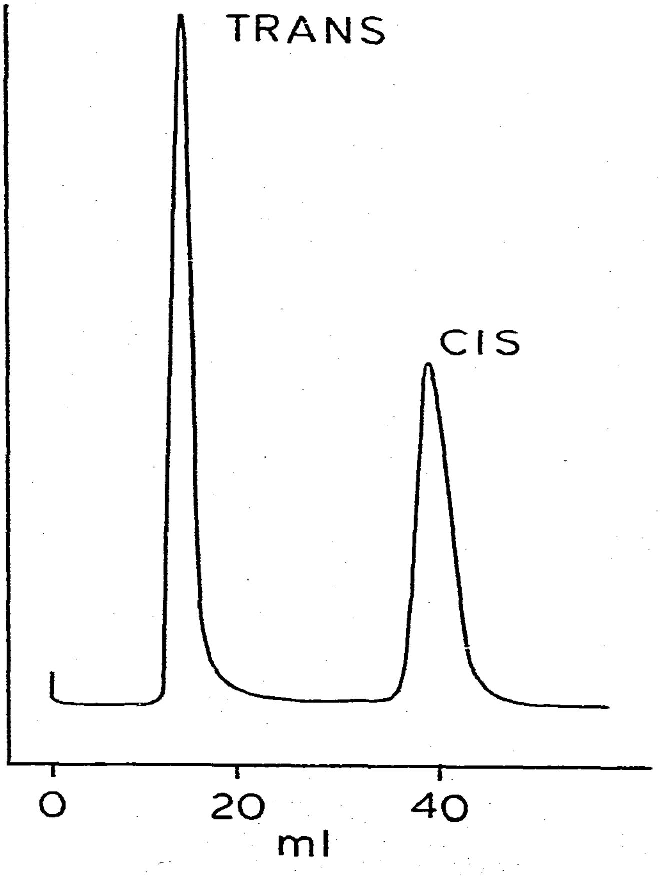
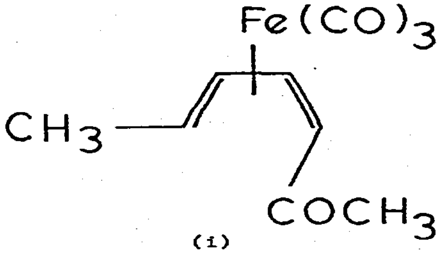


Figure 1. Separation of cis and trans Butadienone Iron Tricarbonyl Complexes. Column; 30 cm. x 4 mm I.D. Partisil SI-10 (Whatman Inc.), Mobile Phase - Methylene chloride. Retention Volumes; trans (I) - 12 ml., cis (II) - 40 ml.

Lillya and Graf[6] had previously utilized reverse phase liquid chromatography with large particle (37-75 μm) octadecyl bonded substrate whereon the cis isomer of the dienone iron tricarbonyl compound eluted prior to the trans isomer.

Figure 1 shows the excellent resolution obtained for these same complexes on a 10 μm silica column, the trans isomer showing a retention volume less than 1/3 that of the cis form. The elution order is now that predicted from the TLC R_f values although the resolution obtained is surprisingly good. The cis compound (i) clearly shows much stronger adsorptive characteristics and preparative scale HPLC would certainly be feasible in this case.



(i)
cis - isomer

(ii)
trans - isomer

The rationale for the observed separation of the ψ - exo and ψ- endo dienol iron tricarbonyl complexes provides an interesting observation on adsorption chromatographic mechanisms. As is clear from Figure 2, the ψ- endo compound is very well resolved from the ψ- exo form, eluting much before it. The most stable configuration of the ψ - exo alcohols places the hydroxyl group in a sterically accessible position away from the bulky $Fe(ligand)_3$ moiety.[12] These hydroxyl groups should interact with acidic and basic sites on the adsorptive stationary phase readily. By contrast, the hydroxyl groups of the ψ- endo alcohols prefer a sterically crowded position nearer to the iron atom. Thus, ψ - endo hydroxyl groups should interact with the stationary phase less readily than the ψ- exo groups.

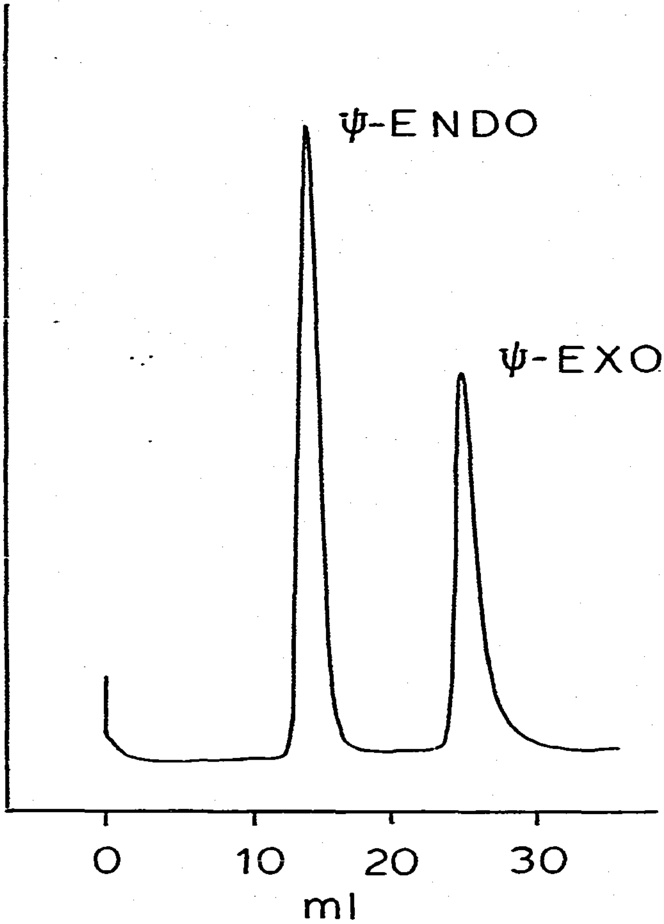


Figure 2. Separation of ψ - endo and ψ- exo Butadienol Iron Tricarbonyl Complexes. Column as in Figure 1, Mobile Phase - Methylene chloride. Retention Volumes; ψ - endo (I) - 14.5 ml., ψ - exo (II) - 25.1 ml.

Methyl substitution in the 4 position of the butadienol moiety produced less polar species which showed a compound pair each of which gave somewhat higher retention volumes than their non-substituted analogues (16 and 34.5 ml. vs. 14.5 and 25.1 ml.).

The previously discussed cis and trans butadienone isomers were the precursors of the ψ - endo and ψ- exo alcohols respectively. It may be noted that the adsorption HPLC elution orders are reversed in this case with respect to precursor and derived species and there would be ample resolution available to quantitate the cis-dienol/ψ- endo and the trans-dienol/ψ- exo pairs.

The effect of change in substituent group polarity on HPLC characteristics was investigated for the methyl ethers corresponding to the exo and endo alcohols. The separation is shown in Figure 3 where it is seen that the increase in R_f values for the endo and

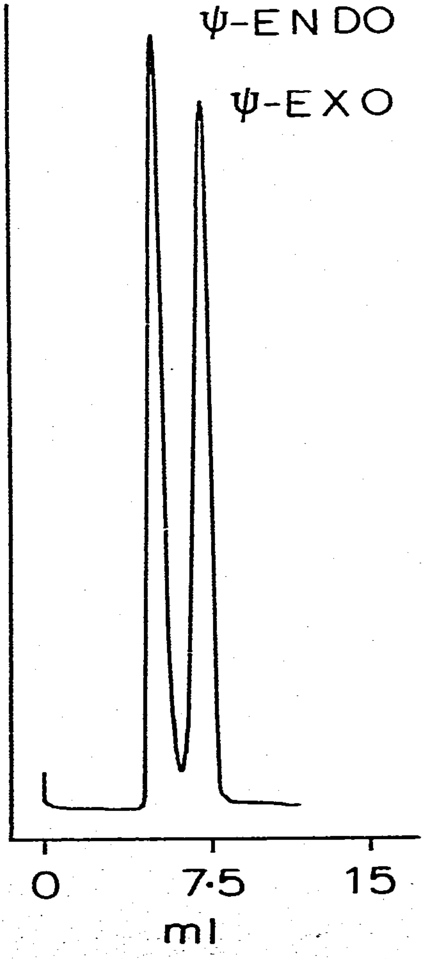


Figure 3. Separation of ψ - endo and ψ- exo Butadienol Iron Tricarbonyl Methyl Ether Complexes. Column as in Figure 1, Mobile Phase - Methylene chloride. Retention Volumes; ψ- endo (I) - 5.4 ml., ψ - exo (II) - 7.5 ml.

exo pair over those for the alcohols is reflected in the reduced retention volumes noted. Ethers are generally considered less polar than the corresponding alcohols and are certainly less acidic. The predicted lesser interaction with adsorptive substrates is clearly proven. In this case the resolution between the isomers is less than for the other examples; greater resolution could certainly be obtained however if a somewhat less polar eluent were used, such as a mixture of methylene chloride and hexane.

To investigate the effect on HPLC behavior of alteration of substituent groups on the iron atom, the isomeric pair of dienone iron dicarbonyl triphenylphosphine complexes (cis and trans), similar to those shown in Figure 1 (one ϕ_3P group having replaced one CO substituent) was first investigated by TLC. In the Table it is seen that the R_f value for the cis isomer is reduced to 0.30 while that of the trans isomer is identical to that for the cis dienone iron tricarbonyl isomer (0.58), this reflecting the increase in polarity imparted by the substitution of the triphenylphosphine moiety.

An adequate HPLC baseline separation was obtained in this case using a mobile phase of 10% acetonitrile in methylene chloride (trans 5.4 ml, cis 11.8 ml.). The use instead of pure methylene chloride in this case would ensure a good separation of the two analogous cis complexes (one having the σ - CO and the other the σ - ϕ_3P group).

The chromatographic examples cited above serve to illustrate the power of TLC on silica for the prediction of the elution characteristics of these organometallics in adsorption HPLC. Although precise correlation of R_f values with elution volumes is not possible, the order of elution and probable separatory efficiency of high pressure adsorption chromatography is well established.

The compounds investigated illustrate the chromatographic effects resulting from various types of functionality changes and serve to confirm predicted changes in polarity and adsorptive interaction which make the separations possible. The power of all modes of HPLC certainly should be more exploited in organometallic chemistry than has been the case up to the present time.

Acknowledgements.

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References

1. G. Guiochon and C. Pommier, Gas Chromatography in Inorganics and Organometallics Ann Arbor Science Publishers (Ann Arbor, Michigan) 1973.
2. H. Veening, J.M. Greenwood, W,H. Shanks, and B.R. Willeford, Chem. Commun. 1305 (1969).
3. H. Veening, B.R. Willeford, R.J. Seyler, and S.A. Gardner, J. Organometal. Chem., 60, 271 (1973).
4. W. Funsaka, T. Hanai, and K. Fujimura, J. Chrom. Sci., 12, 517 (1974).
5. W.J. Evans and M.F. Hawthorne, J. Chromatog., 88, 187 (1974).
6. R.E. Graf and C.P. Lillya, J. Organometal. Chem. 47, 413 (1973).
7. C.T. Enos, G.L. Goeffroy, and T.H. Risby, Anal Chem. 48, 990 (1976).
8. C.T. Enos, G.L. Goeffroy, and T.H. Risby, J. Chrom. Sci., 15, 83 (1977).
9. P.C. Uden and F.H. Walters, Anal. Chem. Acta, 79, 174 (1975).
10. P.C. Uden, D.M. Parees and F.H. Walters, Anal Letters 8, 795 (1975).
11. R.E. Graf and C.P. Lillya, J. Organometal. Chem., 122, 377 (1976).
12. N.A. Clinton and C.P. Lillya, J. Amer. Chem. Soc., 92, 3058 (1970) and D.E. Kuhn and C.P. Lillya, ibid., 94, 1682 (1972).
13. D.G. Gresham, C.D.J. Kowalski, and C.P. Lillya, paper in preparation.