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HIGH-PERFORMANCE LIQUID CHROMATOGRAPHIC SEPARATION OF METAL CARBONYL COMPLEXES SUBSTITUTED WITH BRIDGING AND CHELATING 1,1'-BIS(DIPHENYLPHOSPHINO)FERROCENE

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ABSTRACT

The high-performance liquid chromatography of metal carbonyl complexes including those containing the 1,1'-bis(diphenylphosphino)ferrocene ligand is reported. Separations were performed on a column packed with silica bonded with polar amino-cyano groups. The results suggest that it is the polarity of the complexes that largely determines their retention characteristics under the conditions considered.

INTRODUCTION

The part played by high-performance liquid chromatography (HPLC) in the analysis of inorganic

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complexes has assumed considerable importance in the past twenty years, ever since the separation of organometallic complexes by this technique was first reported by Veening et al in 1969 (1). HPLC offers several advantages over thin-layer chromatography (TLC), which has been the traditional separatory and preparative technique in this field. These include greater resolution, higher detection sensitivity, shorter analysis times and a wider range of stationary phases available for the optimization of separations.

In a previous paper (2), we reported the HPLC separation of a series of 1,1'-bis(diphenylphosphino)ferrocene-substituted metal carbonyl complexes on a column packed with silica to which were bonded polar amino-cyano groups. The separation was carried out under normal-phase conditions. The present paper present results of similar HPLC analyses of related complexes. Specifically, the following complexes were investigated: $(OC)_5Mo(dppf)Mo(CO)_5$, $(OC)_5Cr(dppf)Cr(CO)_5$, $(OC)_5W(dppf)W(CO)_5$, $Mo(CO)_4(dppf)$, $Cr(CO)_4(dppf)$ and $W(CO)_4(dppf)$, where dppf = 1,1'-bis(diphenylphosphino)ferrocene. For comparison, the parent metal carbonyls, $M(CO)_6$ ($M = Cr, Mo$ and W), and two other related complexes containing manganese, $Mn_2(CO)_{10}$ and $(OC)_9Mn_2(dppf)Mn_2(CO)_9$ (both of which have no Cr, Mo and W equivalents), were also considered. These manganese complexes were subjects of a previous study on mixed-metal carbonyls (2). The structures of all these complexes are given in Figure 1.

EXPERIMENTAL

Chromatographic separations were performed on a Shimadzu (Japan) LC-6A pump equipped with a Shimadzu

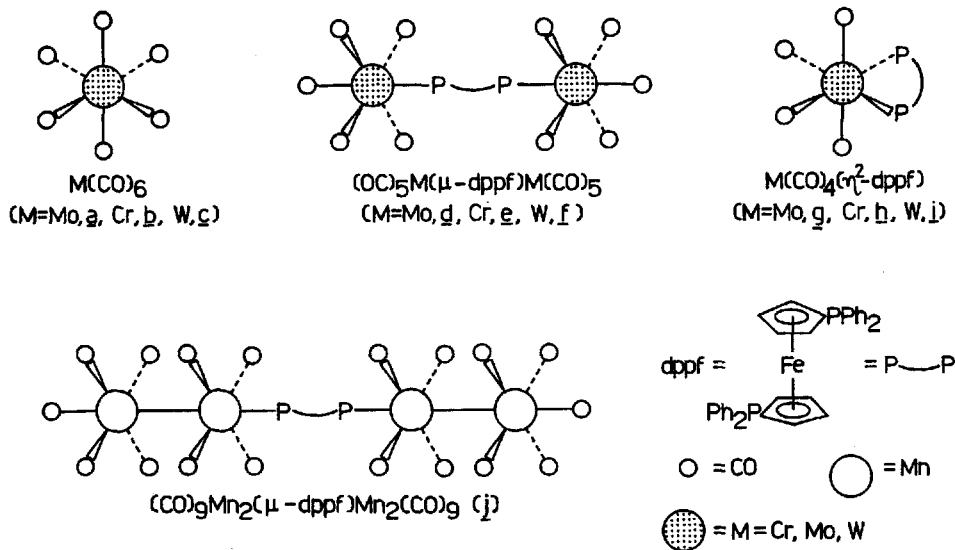


Figure 1. Structures of metal carbonyls studied in this work.

Model SPD-6A variable wavelength UV spectrophotometric detector. A Whatman Partisil 5 PAC (polar amino-cyano) column (100 mm x 4.6 mm I.D.; 5 μ m particle size) was used for separations. Chromatographic data were collected and analysed on a Shimadzu Chromatopac C-R3A data processor. Detection was at 254 nm. The mobile phase was hexane-chloroform (92:8, % v/v), at a flow rate of 0.5 mL min⁻¹.

HPLC-grade solvents (from various suppliers) were used; they were degassed prior to use by ultrasonication. Mobile phases were prepared by measuring exact volumes of the individual components and then mixing them to give the desired compositions (A + B addition method) (3).

Sample solutions were prepared in the mobile phase, and their integrity was evaluated by infrared spectroscopy. They were filtered before being introduced into the column via a Rheodyne Model 7125 injection valve. Typically, 5 to 10 μL of samples were injected. HPLC runs were carried out at least in triplicate. Reproducibility of retention times between runs were $\pm 2\%$ or better.

The synthesis and characterisation of all the complexes studied in this work have been previously reported (4).

RESULTS AND DISCUSSION

Figure 2 shows a chromatogram of the metal carbonyl complexes considered in the present work. The mobile phase composition of hexane-chloroform (92:8, % v/v) was found to be the optimum for the separation of most of the components although in some cases, resolution was poor and could not be improved with other eluent systems. Previously, it was found that the stationary phase used here (silica bonded with polar amino-cyano groups) provided a selectivity not possible with conventional silica for the separation of related complexes (2). No attempt was therefore made to use conventional silica-packed columns for this work. Neither was reversed-phase HPLC mode considered because of the poor solubilities of all the complexes in the traditional reversed-phase solvents.

The octahedral, unsubstituted $\text{M}(\text{CO})_6$ ($\text{M} = \text{Cr}, \text{Mo}$ and W) complexes could not be resolved and exhibited the fastest elution as Figure 1 shows, an observation

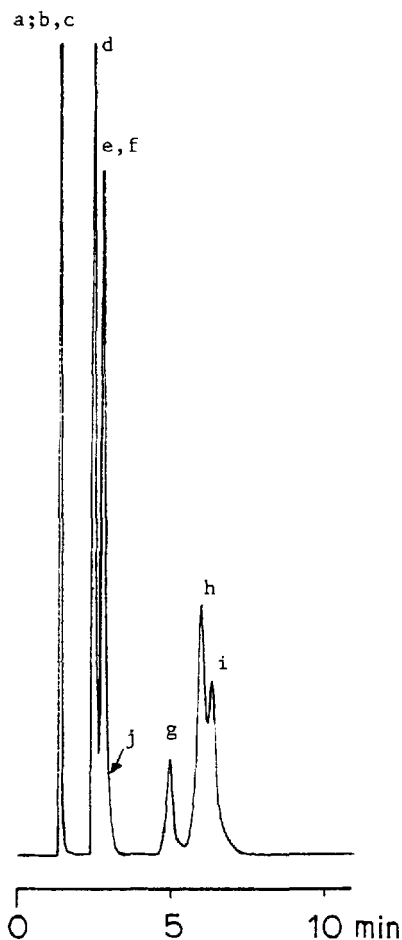


Figure 2. Normal-phase liquid chromatogram of metal carbonyl complexes on a Whatman Partisil 5 PAC column (100 mm x 4.6 mm I.D.; 5 μ m particle size). Mobile phase: Hexane-chloroform (92:8). Flow rate: 0.5 mL min^{-1} . Peak identities: (a) $\text{Mo}(\text{CO})_6$ ($k' = 0.025$); (b) $\text{Cr}(\text{CO})_6$ ($k' = 0.025$); (c) $\text{W}(\text{CO})_6$ ($k' = 0.025$); (d) $(\text{OC})_5\text{Mo}(\text{dppf})\text{Mo}(\text{CO})_5$ ($k' = 0.81$); (e) $(\text{OC})_5\text{Cr}(\text{dppf})\text{Cr}(\text{CO})_5$ ($k' = 1.02$); (f) $(\text{OC})_5\text{W}(\text{dppf})\text{W}(\text{CO})_5$ ($k' = 1.03$); (g) $\text{Mo}(\text{CO})_4(\text{dppf})$ ($k' = 2.60$); (h) $\text{Cr}(\text{CO})_4(\text{dppf})$ ($k' = 3.30$); (i) $\text{W}(\text{CO})_4(\text{dppf})$ ($k' = 3.60$); (j) $(\text{OC})_9\text{Mn}_2(\text{dppf})\text{Mn}_2(\text{CO})_9$ ($k' = 1.18$).

in agreement with a previous study (2). Their capacity factors (k') of ca. 0.025 indicated that these complexes were subjected to minimal, if any, retention. Because all three complexes are symmetrical, they are non-polar; moreover, they are the smallest species being considered in this study. Thus, their minimal retention on the column is not surprising.

The chelates, $M(\text{CO})_4(\text{dppf})$ ($M = \text{Cr}, \text{Mo}$ and W), generally showed a much greater retention than the binary $M(\text{CO})_6$ (metal carbonyls containing only CO as ligands). The molecules have a net dipole due to this cis-substitution of the carbonyl by a bidentate dppf ligand, and thus are of comparatively higher polarity. The latter property is responsible for the stronger retention and appears to be more important than molecular size in determining retention behaviour in this situation. That this is so is shown by the lower retention exhibited by the (larger) dimeric analogues (see below). Amongst the chelates themselves, partial resolution was achieved for the Cr and W analogues; both were well separated from their Mo counterpart, as Figure 2 shows.

The respective $(\text{OC})_5M(\text{dppf})M(\text{CO})_5$ ($M = \text{Cr}, \text{Mo}$ and W) complexes exhibited lower retention than the chelates. Their respective overall dipole moments are low because of their symmetrically open structures in which dppf functions as a bridging unit (5). Thus, the retention behaviour of these species in comparison with the chelates reflects their lower polarities. The Cr and W complexes could not be completely resolved from each other, an observation similar to that made for the corresponding chelates.

Generally, the W complexes exhibited greater retention than those of Cr and Mo (Figure 2), an observation previously made for mixed-metal dppf complexes of the form $(OC)_9Mn_2(dppf)M(CO)_5$ ($M = Cr, Mo, W$) (2). This observation (2) led us to caution against the exclusive use of electronegativity (Cr - 1.56, W - 1.40, Mo - 1.30 on the Allred-Rochow scale (6)) to explain the retention characteristics of these types of complexes (7,8). Based on the relative electronegativities alone, the order of increasing retention would be expected to be Mo-complex < W-complex < Cr-complex. Since our results showed otherwise, it is therefore clear that within an analogous series of complexes, molecular size predominates over the electronegativity parameter in influencing retention.

The largest molecular species covered in the present work was $(OC)_9Mn_2(dppf)Mn_2(CO)_9$. This compound is expected to be non-polar because of the high degree of symmetry due to the diphosphine bridge. Its retention (between that of the $M(CO)_4(dppf)$ and $(OC)_5M(dppf)M(CO)_5$ species, but more akin to the latter) may be attributed to its higher overall polarity (and dipole moment), in comparison to the chelates, despite its larger size. Again, it appears that molecular size does not play a major role in determining its retention behaviour when compared to the $M(CO)_4(dppf)$ and $(OC)_5M(dppf)M(CO)_5$ series under these conditions.

As a matter of interest, the dimer $Mn_2(CO)_{10}$, of which the Cr, Mo and W have no counterparts (their existence is unknown), was also considered in this work. Our results show that this complex shared similar

retention properties with the $M(CO)_6$ series of complexes, i.e. it possesses minimal or no retention on the column. (Note: The chromatogram in Figure 2 does not include $Mn_2(CO)_{10}$.) The most likely explanation for this observation is its lack of polarity on the basis of molecular symmetry.

Our results indicate that the polarities of the metal carbonyl complexes, induced by the substitution of dppf, are generally more important determinants of their retention behaviour in normal-phase HPLC than the respective electronegativities of the metal centres. Molecular size does not appear to play as influential a role as polarity except within a particular analogous series of complexes.

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