Short Communication

High-performance liquid chromatographic separation of heterometallic 1,1'-bis(diphenylphosphino)ferrocene-substituted metal carbonyls

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ABSTRACT

The normal-phase, isocratic high-performance liquid chromatographic analysis of a series of 1,1'-bis (diphenylphosphino)ferrocene (dppf)-substituted metal carbonyl compounds, namely $(OC)_9Mn_2(dppf)M$ $(CO)_5$, where M = Cr, Mo, W; $(OC)_9Mn_2(dppf)Fe(CO)_4$ and $(OC)_9Mn_2(dppf)Mn_2(CO)_9$ is described. A column packed with silica bonded with polar secondary amino–cyano groups was used after preliminary experiments showed that conventional silica columns were unsatisfactory for separation. The mobile phase used was isooctane–chloroform (92:8, v/v). On the basis of the results obtained, the retention behaviour of the compounds studied is discussed.

INTRODUCTION

The first reported separation of organometallic compounds by high-performance liquid chromatography (HPLC) was in 1969 [1]. Since then its use has greatly increased. Although thin-layer chromatography (TLC) is still often used in organometallic chemistry, it suffers from several limitations, including long analysis times, low adequate efficiency of separation and poor detection capability. All of these problems can be circumvented by HPLC. Moreover, HPLC can be applied to compounds prone to instability, whether thermal, oxidative or photochemical, etc. Several reviews of the application of HPLC to the analysis of organometallic and coordination compounds, have been published in recent years [2–5]. In the analysis of organometallics, much attention has been focused on carbonyl complexes, which are important in many synthetic and catalytic processes [6–9]. A review was recently devoted to the HPLC separation of these species [5].

This paper describes the normal-phase, isocratic HPLC separation of five 1,1'-bis(diphenylphosphino)ferrocene (dppf)-substituted metal carbonyl compounds, namely $(OC)_9Mn_2(dppf)M(CO)_5$ (M = Cr, **1**; Mo, **2**; W, **3**); $(OC)_9Mn_2(dppf)Fe(CO)_4$
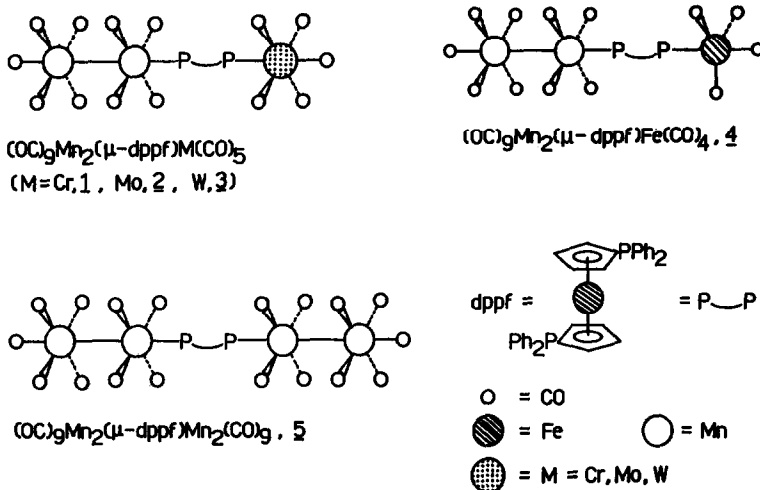
Fig. 1. Structures of the dppf-substituted metal carbonyls studied.

(4) and $(OC)_9Mn_2(dppf)Mn_2(CO)_9$ (5). Fig. 1 shows the structures of these cluster compounds. A study of these mixed-metal polynuclear complexes allows the examination of the effect of the metal, within a similar ligand environment, on their chromatographic retention behaviour. For comparison purposes, the parent compound, $Mn_2(CO)_{10}$ (6), was included in the study.

In addition to the aforementioned problems with TLC, the compounds under consideration here cannot be satisfactorily separated by this technique because of the similarities of their geometrical and chemical properties. An additional advantage of HPLC is that the separation takes only 8 min, as reported below.

EXPERIMENTAL

A Shimadzu LC-6A pump equipped with a Shimadzu Model SPD-6A variable-wavelength UV spectrophotometric detector was used. A Whatman Partisil 5 PAC (5 μm) column (100 mm × 4.6 mm I.D.) was used for separations. Chromatographic data were collected and analysed on a Shimadzu Chromatopac C-R3A data processor. The eluent flow-rate was typically 0.5 ml min^{-1}. The detection wavelength was 254 nm. The mobile phase compositions used in this work included 87:13, 90:10 and 92:8 (v/v) isooctane–chloroform.

All solvents were of HPLC grade from various suppliers, and were filtered through a Millipore membrane filter and degassed by ultrasonication before use. Mobile phases were prepared by measuring exact volumes of the individual components and then mixing them to give the desired compositions.

Sample solutions were filtered before being introduced into the column by means of a Rheodyne Model 7125 injection valve. Typically, 5–10-μl samples were injected. HPLC runs were carried out at least in triplicate. The reproducibility of retention times between runs was ±2% or better.

The metal carbonyl compounds investigated have been previously synthesized

and characterized; details have been reported elsewhere [10,11]. Fresh solutions of the compounds, shielded from sunlight, were used. The integrity of the compounds (in solutions of chloroform), based on their carbonyl absorptions, was checked by infrared spectroscopy.

RESULTS AND DISCUSSION

Owing to their inherently poor solubilities in the traditional solvents used in reversed-phase HPLC such as methanol and acetonitrile (neat or in combination with water), the decision was made to separate the dppf-substituted metal carbonyls by normal-phase HPLC. Conventionally, for normal-phase HPLC, columns packed with silica are used. However, in recent years, the use of columns packed with silica bonded with polar groups has become more popular.

In this work, a column packed with silica bonded with polar secondary amino–cyano groups was used (hence the proprietary description of PAC for the column). The carrier solvent was isooctane, with chloroform making up the binary mixture. Preliminary experiments with conventional (unmodified) silica columns showed that no separation amongst the compounds considered could be achieved. It was surmised that, with the PAC column, the presence of bonded secondary amino–cyano groups on the silica would impart a measure of selectivity to the stationary phase, a selectivity that should be greater than if a column packed with unmodified silica was used. The better selectivity would therefore translate into satisfactory separation of the compounds. This turned out to be the case for some of the compounds considered, as

Fig. 2. Normal-phase liquid chromatogram of dppf-substituted metal carbonyls on a Whatman Partisil 5 PAC (5 μm) column (100 mm $\times$ 4.6 mm I.D.). Mobile phase, isooctane–chloroform (92:8, v/v); flow-rate, 0.5 ml min^{-1}; detection wavelength, 254 nm. Compounds: 1 = (OC)$_9$Mn$_2$(dppf)Cr(CO)$_5$ (k' = 1.49); 2 = (OC)$_9$Mn$_2$(dppf)Mo(CO)$_5$ (k' = 1.49); 3 = (OC)$_9$Mn$_2$(dppf)W(CO)$_5$ (k' = 1.71); 4 = (OC)$_9$Mn$_2$(dppf)Fe(CO)$_4$ (k' = 1.99); 5 = (OC)$_9$Mn$_2$(dppf)Mn$_2$(CO)$_9$ (k' = 1.70).

shown by the chromatogram in Fig. 2, which was obtained using isooctane–chloroform (92:8, v/v) as the eluent. Compounds 2, 3 and 4 were resolved from one another. However, 1 could not be separated from 2 or 3 from 5. Apart from isooctane–chloroform, mobile phases such as isooctane–dichloromethane and hexane–dichloromethane were also used in order to separate the recalcitrant pairs, but without success.

    In an attempt to arrive at a compromise between resolution and reasonable analysis times, several other isooctane–chloroform compositions were investigated, including 90:10 and 87:13. With the exception of the 90:10 composition, which provided a slightly inferior resolution (but with shorter retention times) of the same three compounds than that afforded by the 92:8 system, the other eluent provided unsatisfactory separation. As expected for normal-phase HPLC, as the proportion of the non-polar component (isooctane) in the mobile phase is raised, an increased retention of the analytes is observed.

Order of elution
    Using isooctane–chloroform (92:8) as the eluent, 6 had the shortest elution time; in fact, its capacity factor (k') of 0.03 suggests that it underwent minimal retention, if any, on the column (the use of isooctane–dichloromethane and hexane–dichloromethane as eluents did not improve the retention characteristics of 6). As shown by the capacity factors in Fig. 2, 2 eluted after 6, followed by 3 and finally 4. As described previously, separation of the Cr and Mo complexes (1 and 2), and W and Mn_4 complexes (3 and 5) could not be achieved under the present conditions.

    Several workers have attempted to correlate the chromatographic elution order of similar complexes with cluster size, geometry and electronic environment [12–15]. It is clear, however, that much of the issue remains speculative and more evidence is needed before a general correlation between retention behaviour and such parameters may be arrived at. Nevertheless, it appears that minor changes in the metal and ligand environment are sufficient to alter the retention characteristics of these compounds. Our results show that all the dppf-substituted complexes possess greater retention than the parent binary carbonyl, 6, an observation in agreement with what has been previously determined for PPh_3 complexes [16]. Earlier work on $M(CO)_6$ (M = Cr, Mo, W) on a Si 60 column failed to resolve these binary carbonyls [17] (that is, carbonyls containing only CO as ligands), although a partial separation in the reversed-phase mode using a C_{18} column was reported. Our finding that the W complex 3, can be resolved from the other Group 6 congeners is noteworthy, although it is unclear why the W complex should have a greater retention than the Cr (and the co-eluting Mo) complexes {the electronegativity of W being 1.40 (Allred–Rochow scale), which is intermediate between the values for Cr (1.56) and Mo (1.30) [18]}. This observation suggests that caution should be exercised in the use of electronegativity to rationalize the retention behaviour of analogous complexes [17,19]. On the other hand, the greater retention of the W complex may be due to the higher steric requirement of the $W(CO)_5$ moiety. The greater retention of 5 (which co-elutes with 3) in comparison to 1 and 2 may be understood in terms of the higher nuclearity of the cluster. It should be pointed out that although 5 is the largest cluster studied, its size may not be the sole factor in determining its retention characteristics. The latter may also be attributed to the lower polarity and dipole moment of 5 compared with 1 or 2, an inherent consequence of the symmetrical diphosphine

bridge in the molecule. This influence of dipole moment is also possibly reflected by the most strongly retained component (4) of the series of compounds studied, in which the $Fe(CO)_4$ moeity possesses lower local symmetry than the other $M(CO)_5$ moieties. This therefore results in a higher overall dipole moment for the molecule than that for 5.

Our choice of the open-form dppf-substituted carbonyl clusters allowed us to examine the effect of the metal on the HPLC characteristics of heterometallic systems. However, more examples of such compounds need to be available before a more meaningful interpretation of their retention behaviour may be made. Nevertheless, at this stage, it is conclusive that HPLC with UV detection offers a sufficiently high sensitivity for the analysis of these compounds, possessing only a slight variation in the metal centre. The obvious benefit that may be gained from the amenability of the compounds to HPLC separation is in the area of preparative liquid chromatography.

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