High-performance liquid chromatography of the coordination isomers of triphenylphosphine-substituted homo- and hetero-bimetallic carbonyl complexes of manganese and rhenium

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Abstract

The isocratic normal-phase high-performance liquid chromatography of a series of triphenylphosphine (PPh_3)-substituted homo- and hetero-dinuclear metal carbonyl complexes $[MM'(CO)_{10-n}(PPh_3)_n$, where M, M' = Mn, Re; $n = 1, 2$] is reported. A column packed with silica bonded with phenyl groups was used after preliminary experiments showed that columns packed with conventional silica, and with silica bonded with amion-cyano groups were unsatisfactory for separation. The mobile phases used were hexane–toluene (98:2) and hexane–dichloromethane (90:10). The results suggest that besides the symmetry-imposed polarity of the complexes, the nature of the metal and substituent ligand also determine their retention characteristics.

Keywords: Complex formation; Carbonyl compounds; Manganese; Rhenium; Metals; Triphenylphosphine compounds

1. Introduction

The separation of organometallic complexes by high-performance liquid chromatography (HPLC) was first reported by Veening et al. in 1969 [1]. Since then its use in inorganic chemistry has gained much popularity. HPLC can be successfully applied to the study of transition metal clusters [2] especially in the area of reaction monitoring and product separation. Due to the importance of carbonyl complexes in many synthetic and catalytic processes, several HPLC studies on these species [3–5] have emerged in recent years.

In previous papers [6–8], we have reported the normal-phase HPLC separation of 1,1′-bis-

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(diphenylphosphino)ferrocene (dppf)-substituted metal carbonyl complexes. In this paper, we discuss the separation of triphenylphosphine-substituted metal complexes, namely $(Ph_3P)(OC)_4Re–Re(CO)_4(PPh_3)$, **4**; $(Ph_3P)(OC)_4Mn–Re(CO)_4(PPh_3)$, **5**; $(Ph_3P)(OC)_4Mn–Mn(CO)_4(PPh_3)$, **6**; $(Ph_3P)(OC)_4Mn–Re(CO)_5$, **7**; $(OC)_5Re–Re(CO)_4(PPh_3)$, **8**; $(OC)_5Mn–Mn(CO)_4(PPh_3)$, **9**; $(OC)_5Mn–Re(CO)_4(PPh_3)$, **10**. For comparison purposes, the parent complexes **1**, $Mn_2(CO)_{10}$, **2**, $Re_2(CO)_{10}$ and **3**, $MnRe(CO)_{10}$ are also included. The structures of these complexes are confirmed by spectroscopic data and shown in Fig. 1 [9–12]. These are homo- and hetero-bimetallic complexes of Mn and Re with the presence of metal–metal bonding. The PPh_3 group can bind to either metal centre or both. In either case, the effective atomic
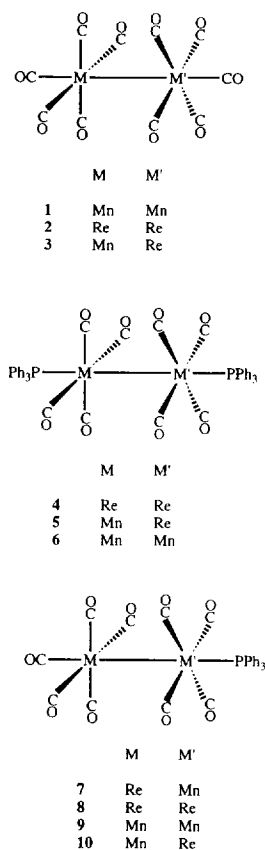
Fig. 1. Structures of the parent and substituted complexes.

number (EAN) rule requires the preservation of the metal–metal bond. Apart from some isolated studies, there has been no systematic chromatographic study of similar bimetallic systems in the literature. In this system, since the incoming ligand, viz. PPh_3, can enter either at the Mn or Re site, a series of coordination isomers can be envisaged. Our study of these isomers allows the examination of the effects of the metal, polarity of the metal–metal bond, and substitution behaviour of PPh_3 on the chromatographic retention behaviour of complexes with the same ligand environments.

2. Experimental

Chromatographic separations were performed on a Perkin-Elmer (Norwalk, CT, USA) binary LC Model 250 pump equipped with a Perkin-Elmer Model LC

290 variable-wavelength UV spectrophotometric detector. A Whatman (Clifton, NJ, USA) Partisil 5 PAC (polar amino-cyano) column (100×4.6 mm I.D., 5 μm particle size), Phenomenex (Torrance, CA, USA) Ultremex silica column (150×2.0 mm I.D., 5 μm particle size) and Hichrom (Berkshire, UK) phenyl column (200×4.0 mm I.D., 5 μm particle size) were used for separations. Chromatographic data were collected and analysed on a Shimadzu (Tokyo, Japan) Chromatopac C-R6A data processor. The detection wavelength was 350 nm. The mobile phase compositions used in this work included pure hexane, hexane–toluene (98:2, v/v), and hexane–dichloromethane (90:10, v/v). The eluent flow-rate was 0.5 ml min^{-1}.

All solvents were of HPLC grade from various suppliers. Sample solutions were prepared in hexane–toluene (75:25, v/v) and hexane–dichloromethane (75:25, v/v), and were filtered before being introduced into the column by means of a Rheodyne Model 7125 injection valve. The concentrations of sample solutions used were in range 5–10 μg ml^{-1}. Typically, 20-μl samples were injected. HPLC runs were carried out at least in triplicate, and the reproducibility of retention times between runs was $\pm 1\%$ or better.

Binary carbonyls $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ were used as purchased without further purification. $MnRe(CO)_{10}$ [9] and substituted carbonyl complexes $(Ph_3P)(OC)_4Mn–Re(CO)_5$ [10], $(Ph_3P)(OC)_4Re–Re(CO)_5$ [11], $(OC)_5Mn–Re(CO)_4(PPh_3)$ [11], $(Ph_3P)(OC)_4Mn–Mn(CO)_5$ [12], $(Ph_3P)(OC)_4Re–Re(CO)_4(PPh_3)$ [12] and $(Ph_3P)(OC)_4Mn–Mn(CO)_4(PPh_3)$ [12] were prepared according to methods reported in the literature. The synthesis of $(Ph_3P)(OC)_4Mn–Re(CO)_4(PPh_3)$ has been reported [12]. However, for convenience, we have modified the preparation as follows: to a THF (20 ml) solution of $MnRe(CO)_{10}$ (0.080 g; 0.15 mmol) was added at 0°C, trimethylamine N-oxide dihydrate (TMNO), (0.050 g; 0.45 mmol), and the mixture was stirred at room temperature for 0.5 h. PPh_3 (0.205 g; 0.78 mmol) was then added and stirring was continued for another 10 h, after which the solvent was removed in a vacuum. The residue was dissolved in dichloromethane (5 ml) and chromatographed on a silica column (eluent: dichloromethane–hexane, 20:80, v/v; silica gel 60, 230–400 mesh ASTM, Merck).

Collection of the eluent and removal of solvent at reduced pressure afforded the required orange product. The compound was characterised by IR and NMR spectroscopy and elemental microanalysis.

3. Results and discussion

In our previous work [6–8], we found that the complexes considered therein had poor solubility in solvents such as methanol, acetonitrile and water; this precluded the use of reversed-phase HPLC for their separation. The present set of PPh_3-substituted bimetallic carbonyls behaves similarly, so normal-phase HPLC was used in this work.

In most cases, for normal-phase HPLC, columns packed with silica are used. In our work, we evaluated columns packed with unmodified silica, silica bonded with amino-cyano groups and silica bonded with phenyl groups. Preliminary experiments with the conventional silica column showed that no separation between 9, $Mn_2(CO)_9(PPh_3)$, and 8, $Re_2(CO)_9(PPh_3)$ was achieved. Use of the PAC column did not show improvement. The column packed with phenyl-bonded silica gave the best separation (Fig. 2) between compounds 8 and 9, and between two other isomers, 7 and 10. This is the first time that coordination isomers of the mixed-metal $MnRe(CO)_9L$ complexes have been separated by HPLC. With the phenyl column, the mobile phase composition of hexane–toluene (98:2) was found to be the most satisfactory for the separation of $M_2(CO)_9(PPh_3)$ and $MM'(CO)_9(PPh_3)$ species whereas hexane–dichloromethane (90:10) is best for the separation of $M_2(CO)_8(PPh_3)_2$ and $MM'(CO)_8(PPh_3)_2$ (Fig. 2, Fig. 3).

The parent complexes $M_2(CO)_{10}$ and $MM'(CO)_{10}$ in our work have the shortest retention time (with hexane as eluent). This observation is in agreement with what has been previously determined [6,7]. In fact, capacity factors (k') of 0.103, 0.141, 0.206 for complexes 1, 2, 3, respectively, suggest that these species undergo minimal, if any, retention.

The mono-substituted complexes of both homometallic $M_2(CO)_9(PPh_3)$ and heterometallic $MM'(CO)_9(PPh_3)$ and the disubstituted complexes $M_2(CO)_8(PPh_3)_2$ and $MM'(CO)_8(PPh_3)_2$ (M, M' = Mn or Re) show much greater retention than their
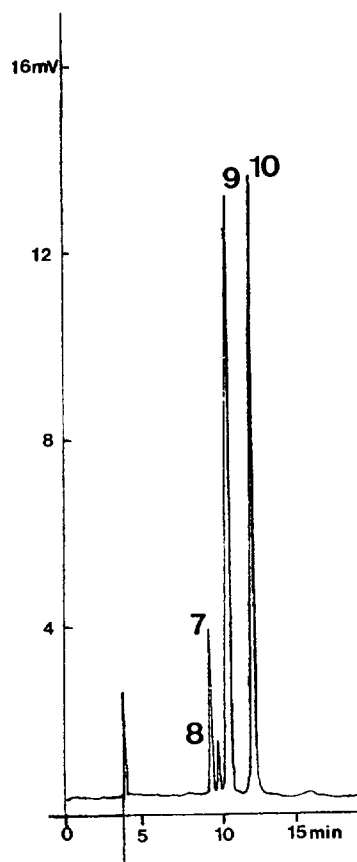

Fig. 2. Normal-phase HPLC chromatogram of monosubstituted complexes on a Hichrom phenyl column (200×4.0 mm I.D., 5 μm particle size). Mobile phase, hexane–toluene (98:2, v/v); flow-rate, 0.5 ml min^{-1}; detection wavelength, 350 nm. Compounds: 7=$(Ph_3P)(OC)_4MnRe(CO)_5$, $(k'=1.61)$; 8= $Re_2(CO)_9(PPh_3)$, $(k'=1.75)$; 9=$Mn_2(CO)_9(PPh_3)$, $(k'=1.89)$; 10=$(OC)_5MnRe(CO)_4(PPh_3)$, $(k'=2.32)$.

parent complexes. It appears that minor changes in metal and ligand environment are sufficient to alter the retention characteristics of these complexes. The introduction of triphenylphosphine increases the retention. This is in agreement with that found in tri- and tetranuclear iron and nickel complexes [13].

The bis(triphenylphosphine)-substituted complexes possess greater retention than the mono-substituted analogues (Fig. 4), even though the latter are more polar, based on symmetry grounds (with the introduction of a hetero-ligand to one of the metal atoms). The number of phosphine ligands is hence an important factor in determining the elution charac-
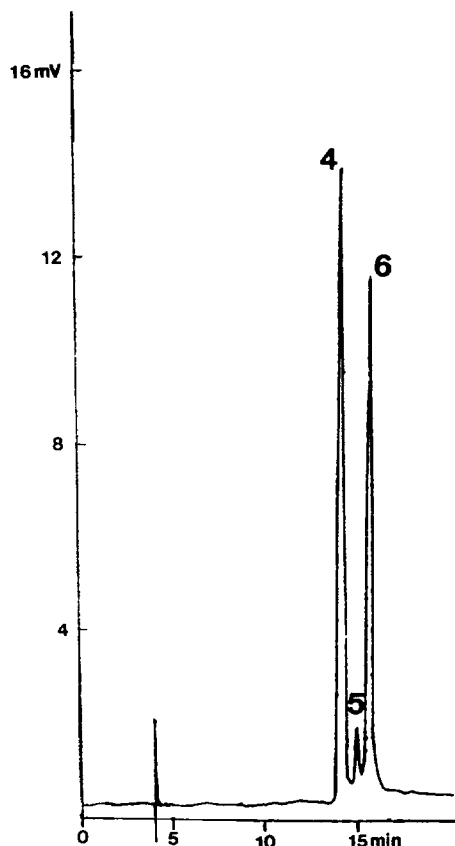
Fig. 3. Normal-phase HPLC chromatogram of disubstituted complexes on a Hichrom phenyl column (200×4.0 mm I.D., 5 μm particle size). Mobile phase, hexane–dichloromethane (90:10, v/v); flow-rate, 0.5 ml min^{-1}; detection wavelength, 350 nm. Compounds: **4**=Re$_2$(CO)$_8$(PPh$_3$)$_2$, (k'=2.50); **5**= MnRe(CO)$_8$(PPh$_3$)$_2$, (k'=2.76); **6**=Mn$_2$(CO)$_8$(PPh$_3$)$_2$, (k'= 2.96).

Fig. 4. Normal-phase HPLC chromatogram of **4**= Re$_2$(CO)$_8$(PPh$_3$)$_2$; **5**=MnRe(CO)$_8$(PPh$_3$)$_2$; **6**= Mn$_2$(CO)$_8$(PPh$_3$)$_2$; **8**=Re$_2$(CO)$_9$(PPh$_3$); **9**=Mn$_2$(CO)$_9$(PPh$_3$) and **10**=(OC)$_5$MnRe(CO)$_4$(PPh$_3$) on a Hichrom phenyl column (200×4.0 mm I.D., 5 μm particle size). Mobile phase, hexane–dichloromethane (90:10, v/v); flow-rate, 0.5 ml min^{-1}; detection wavelength, 350 nm.

teristic. The effect of phosphine and phenyl groups in delaying elution has been discussed elsewhere [13,14]. These phenyl groups interact more strongly with the stationary phase (silica bonded with phenyl groups), thus enabling disubstituted complexes to have greater retention than monosubstituted complexes. Besides, the higher solubility of M$_2$(CO)$_9$(PPh$_3$) and MM'(CO)$_9$(PPh$_3$) compared to the disubstituted analogues in the mobile phases would also enable the former to elute faster than their disubstituted counterparts.

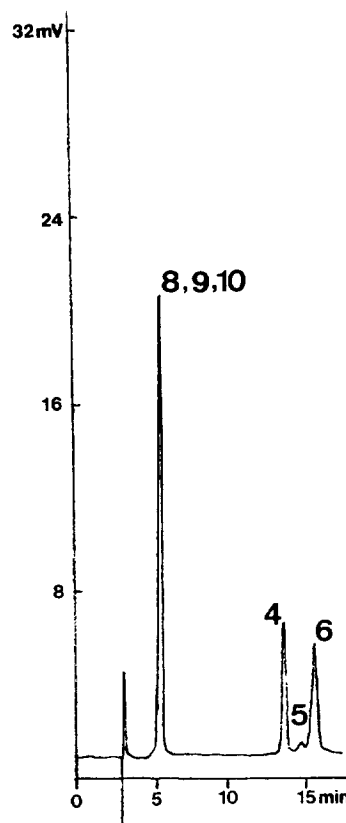### 3.1. Retention behaviour of M$_2$(CO)$_8$(PPh$_3$)$_2$ and MM'(CO)$_8$(PPh$_3$)$_2$ (M, M'=Re, Mn)

The chromatogram for this series of complexes (**4–6**) is shown in Fig. 3; the mobile phase is hexane–dichloromethane (90:10). Based on size and mass considerations, the Re$_2$ complex should be more retained than the Mn$_2$ complex. And, on polarity grounds, the Mn–Re complex (possessing a dipole) should be eluted last. However, this trend was not observed. Instead, the Re$_2$ complex was eluted first, followed by the Mn–Re complex and

finally the Mn_2 complex. This result may be explained as follows: for a small molecule like the parent binary $M_2(CO)_{10}$ (M=Mn, Re), the small difference between Mn and Re in terms of mass and size (Re>Mn) may be significant. Thus, the elution order is determined by these parameters. When a ligand such as PPh_3 is introduced, other considerations assume greater importance, including the size of the ligand (PPh_3 is much larger than both Re and Mn, so that the size difference between the metals becomes insignificant), and degree of symmetry of the molecule. With two PPh_3 units, one on each end of the metal–metal bond, these complexes are essentially symmetrical, as confirmed by IR spectroscopy, and the electronic effects of metals, in terms of their electronegativities (Mn=1.60, Re=1.43 on the Allred scale [15]) are responsible for the observed retention trend. Complexes with metals of higher electronegativities are known to be retained strongly [16,17].

3.2. Retention behavior of $M_2(CO)_9(PPh_3)$ and $MM'(CO)_9(PPh_3)$ (M, M'=Re, Mn)

Under the conditions whereby the disubstituted PPh_3 complexes could be separated (mobile phase of hexane–dichloromethane, 90:10; phenyl column), the monosubstituted complexes were eluted very fast and could not be resolved·(Fig. 4), unless a less polar mobile phase (hexane–toluene, 98:2) was used (Fig. 2). The complete separation of the congeners 8 and 9, together with the two coordination isomers of the heterometallic complexes 7 and 10, is noteworthy. The presence of a single unit of PPh_3 affords a measure of asymmetry (cf. two PPh_3 units on either terminal of the metal–metal centres) to the complexes. This asymmetry induces a net dipole to the M–M (or M–M') bond and accentuates the size differences between the two halves of the molecule, which govern the retention characteristics of these complexes. The relative retention characteristics of the heterometallic complexes 7 and 10 demonstrate the importance of induced polarity of the Mn–Re bond due to PPh_3 substitution on either metal. Without phosphine, as in the parent carbonyls, a small dipole exists due to the electronegativity difference between the metals, viz. $Mn^{\delta-}-Re^{\delta+}$. Upon PPh_3 coordina-

tion, an induced dipole, i.e., bond polarization, arises due to the donation of σ-electrons from the ligand (i.e., phosphine) to the metal. This σ-donor ability of PPh_3, supplemented by its π-accepting character, has been well established [18]. Thus, a ligand with good σ-donating property would increase the charge on the atom and hence reduce its electronegativity. Based on this reasoning, one would expect the electronegativity gap between Mn and Re to reduce when PPh_3 is attached to Mn but increase when it is attached to Re. A second factor which could contribute to this behaviour is the change of electron distribution on the Mn–Re bond, which results in a change of the polarity. Since it is well known that carbonyl is a better π-acceptor than most common phosphines [18], replacement of a carbonyl group by phosphine would lead to less back-bonding and an excess of π-electron density on the metal. The alleviation of this unfavourable build-up of electron density leads to the metal releasing this extra electron load to the remaining carbonyls, and very importantly here, to the neighbouring metal (which is more capable of accepting the charge because of the greater number of carbonyls present). Effectively, a phosphine substitution on one metal would lead to an increased charge on the other metal viz. $M^{\delta-}-M'^{\delta+}-PPh_3$. As a result, substitution at Re would reinforce the original bond dipole but substitution at Mn would diminish it. The third reason is the size disparity between the two halves of the dimetal complexes. Since $Mn(CO)_n$ is smaller in terms of mass and size compared to $Re(CO)_n$, substitution at Re would increase this size difference while substitution at Mn would reduce it. This size disparity increases the interaction between the complex and the stationary phase, and hence increases the retention.

With the homometallic species 8 and 9, a similar explanation applies. The higher electronegativity of Mn enables the π-electron to be more favourably withdrawn from PPh_3. This gives rise to a stronger dipole in 9 in comparison to 8, which causes a greater retention of the former. Notice also that the size asymmetry in Mn complex 9 is greater than that in the Re complex 8. The extent to which PPh_3 exerts its influence on the M–M' bond (where M, M'=Re, Mn) thus depends on the nature of M and

M', i.e., whether M=M', and if PPh₃ is bonded to Mn or Re. The effects are intermediate where they concern the homometallic species which elute between the two heterometallic complexes.

Several workers have attempted to correlate retention behaviour of complexes similar to those considered here with cluster size, geometry, electronic environment, etc. [19–22]. However, there is hitherto no clear evidence that a single factor or parameter can fully account for the chromatographic behaviour observed. What seems to be clear is that the metal or molecule size alone does not determine the elution behaviour, especially when ligands such as phosphine are introduced to the molecular core. The resulting bond polarization thus appears to have a strong influence on the retention characteristics. This bond polarity, as far as metal–metal bonded species are concerned, cannot be predicted simply by citing electronegativity difference of the metals alone. In this regard, we have shown that heterometallic congeners are not necessarily retained more than their homometallic counterparts. The interplay of several parameters, whose relative contributions change according to the nature of the complexes, must be evaluated carefully in the understanding of the retention behaviour of such compounds.

Acknowledgments

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