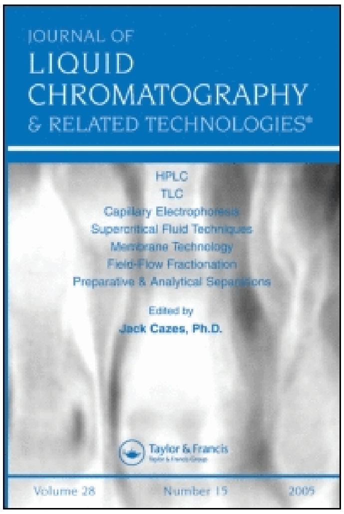

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Chunhang Li[a]; T. K. Lincoln Neo[a]; Hian Kee Lee[a]; T. S. Andy Hor[a]
[a] Department of Chemistry, National University of Singapore, Kent Ridge, Republic of Singapore

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HIGH PERFORMANCE LIQUID CHROMATOGRAPHY OF ALKYL-CHAINED DIPHOSPHINES AND GROUP 6 AND 7 BINARY CARBONYLS

Chunhang Li, T. K. Lincoln Neo,[†]
Hian Kee Lee,* T. S. Andy Hor

Department of Chemistry
National University of Singapore
Kent Ridge
Republic of Singapore 119260

ABSTRACT

This paper reports on the reversed phase high performance liquid chromatography (HPLC) of Group 6 carbonyl complexes [$M(CO)_6$ where M = Cr, Mo, W] and their Group 7 homonuclear [$M_2(CO)_{10}$ (M = Mn, Re)] and heteronuclear [$MnRe(CO)_{10}$] counterparts together with PPh_3 and its analogous alkyl-chained diphosphine ligands [$Ph_2P(CH_2)_nPPh_2$ where Ph = C_6H_5, n = 1 to 6]. Complete separations are achieved among the congeneric carbonyls and homologous phosphines on a reversed phase C_{18} column, using acetonitrile and water as the mobile phase. Separation between the Mn-Re bonded decacarbonyl from its parent, Mn_2 and Re_2 carbonyls, is also attained. The elution pattern is governed by the molecular size and mass and influenced by the nature of the central metal.

INTRODUCTION

The use of HPLC as a separatory and synthetic tool in organometallic chemistry has been reviewed.[1] Recent developments have shown its value in the study of carbenes[2] and di,[3] tri,[4] and polynuclear[5] carbonyl complexes. We have also extended this technique to the separation of structurally similar homo-[6] and heterometallic[7] phosphine bridged complexes and co-ordination isomers.[8]

Surprisingly, however, little is known of the use of HPLC in the separation of the parent carbonyls and the free diphosphine ligands. Although, separation of these compounds by GC has met with some success,[9] the use of the technique for organometallics has its limitations because of the thermal sensitivity of many of the M-C bonded complexes. The separation of Gp 6 carbonyls has been reported by reversed phase HPLC on a C_{18} column, but complete separation could not be achieved.[10] In our previous work on Gp 7 binary carbonyls, a phenyl-column gave incomplete separation[8] under normal phase conditions. We were, also, not completely successful in separating the carbonyls on a silica column by normal phase chromatography, although, Coville *et al.*[11] had reported satisfactory separation on a preparative silica-based column (under normal-phase conditions). Little information is available on separation of the free diphosphines. As these materials are common precursors to a host of organometallic complexes,[12] it is imperative that a reliable method be developed, such that, the separatory conditions of these substances can be identified. This would alleviate the common problems encountered in the purification of inorganic reaction mixtures. It would also give a pointer to the study of more complex mixtures containing phosphine-substituted carbonyl complexes. In this paper, we report the use of a reversed phase C_{18} column in the separation of Group 6 & 7 carbonyls and all the common alkyl-chained diphosphines.

EXPERIMENTAL

HPLC was 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 fully-endcapped Metaphase Crestpak (JASCO, Tokyo, Japan) $C_{18}S$ column (150 mm x 4.6 mm I.D.; 5 μm particle size; claimed 50,000 theoretical plates per metre) was used for separations. Chromatographic data were collected and analyzed on a Shimadzu (Tokyo, Japan) Chromatopac C-R6A data processor. UV detection was at 254 nm. The mobile phase used was acetonitrile-water (70:30, v/v; 80:20, v/v; 90:10, v/v) at flow rates of 0.8 mL min^{-1} and 0.6 mL min^{-1}.

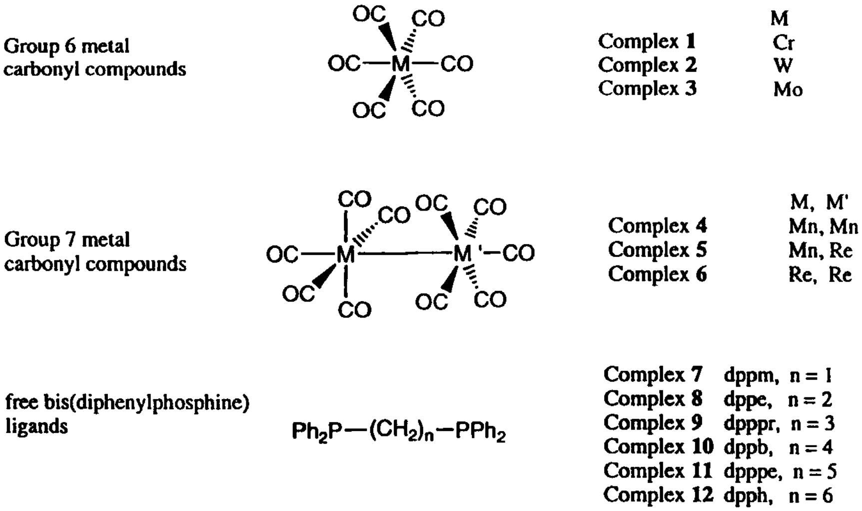

Figure 1. Structures of carbonyl complexes **1** - **6** and free diphosphine ligands **7** - **12**.

All solvents were of HPLC-grade from various suppliers. Sample solutions (conc. ~ 50 ppm) were prepared in pure acetonitrile, and were filtered through a 0.45 μm PTFE membrane filter before being introduced into the column by a Rheodyne Model 7125 injection valve. Typically, 5-10 μl aliquots were injected. HPLC runs were carried out, at least, in triplicate. The reproducibility of retention times between runs was ±2% or better.

With the exception of $MnRe(CO)_{10}$, all the compounds studied in this work were used as purchased. $MnRe(CO)_{10}$ was prepared according to literature methods.[9a]

RESULTS AND DISCUSSION

The structures of Gp 6 carbonyls, *viz.* $Cr(CO)_6$, **1**, $W(CO)_6$, **2** and $Mo(CO)_6$, **3**; Gp 7 carbonyls, *viz.* $Mn_2(CO)_{10}$, **4**, $MnRe(CO)_{10}$, **5** and $Re_2(CO)_6$, **6**, and the diphosphine ligands, *viz.* bis(diphenylphosphino)methane (dppm), **7**, 1,2-bis(diphenylphosphino)ethane (dppe), **8**, 1,3-bis(diphenylphosphino) propane (dpppr), **9**, 1,4-bis(diphenylphosphino)butane (dppb), 10, 1,5-bis(diphenylphosphino)pentane (dpppe), **11**, and 1,6-(diphenylphosphino) hexane (dpph), **12**, are shown in Fig. 1.

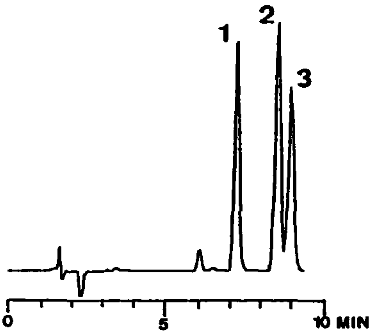

Figure 2. Reversed phase liquid chromatogram of Gp 6 metal carbonyl compounds on a Metaphase Crestpak C_{18} column (150 mm x 4.6 mm I.D.; 5 μm particle size). Mobile phase: acetonitrile-water (70:30). Flow rate: 0.8 mL min^{-1}. Detection wavelength: 254 nm. Peak identity: **1** = $Cr(CO)_6$ (k' = 2.55); **2** = $W(CO)_6$ (k' = 3.19); **3** = $Mo(CO)_6$ (k' = 3.39).

To arrive at a compromise between resolution and reasonable analysis times, different compositions of the mobile phase (acetonitrile-water) and flow rates were tested. The most satisfactory results for different groups of compounds were obtained under different conditions, as listed below:

a) Gp 6 metal carbonyl compounds: acetonitrile-water (70:30); 0.8 mL min^{-1}

b) Gp 7 metal carbonyl compounds: acetonitrile-water (80:20); 0.8 mL min^{-1}

c) Free diphosphine ligands: acetonitrile-water (90:10); 0.6 mL min^{-1}

The Gp 6 carbonyls can be completely separated by using the above conditions. $Cr(CO)_6$ was the most rapidly eluted, followed in turn, by $W(CO)_6$ and $Mo(CO)_6$. (Fig. 2). A similar trend was observed by Casoli *et al.*[10] on a reversed phase C_{18} column, although, the separation of the heavier congeners was incomplete. Our earlier use of a polar amino-cyano (PAC) column under normal phase conditions had failed to achieve any separations amongst this family.[6b,7] The superior performance of the Metaphase Crestpak C_{18} column (fully-endcapped spherical silica particles, with 18% carbon loading), in this case, is hence notable.

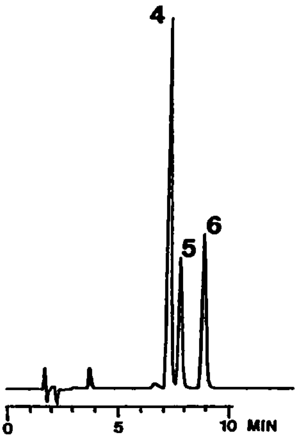

Figure 3. Reversed phase liquid chromatogram of Gp 7 metal carbonyl compounds on a Metaphase Crestpak C_{18} column (150 mm x 4.6 mm I.D.; 5 μm particle size). Mobile phase: acetonitrile-water (80:20). Flow rate: 0.8 mL min^{-1}. Detection wavelength: 254 nm. Peak identity: **4** = $Mn_2(CO)_{10}$ (*k*' = 2.58); **5** = $MnRe(CO)_{10}$ (*k*' = 2.84); **6** = $Re_2(CO)_{10}$ (*k*' = 3.39).

The elution behaviour has been rationalized based on the electronegativities of the central metal atoms (χ_{Cr} 1.56, χ_W 1.40, χ_{Mo} 1.30; Allred-Rochow scale), *viz.* elution time increases with decreasing electronegativities. Based on this principle, $Re_2(CO)_{10}$ (χ_{Re} 1.43) was expected to elute later than $Mn_2(CO)_{10}$ (χ_{Mn} 1.60). This is indeed observed with the heterobimetallic $MnRe(CO)_{10}$ sandwiching between the two homometallic dimers, all of which are segregated (Fig. 3). Although the $Re^{\delta+}$ - $Mn^{\delta-}$ bond is polarized, this does not appear to have any significant effect on the elution behaviour. The electronegativity factor is also manifested by the size effect. Large molecules are known to elute on HPLC after their smaller counterparts for solutes of similar molecular configurations and polarities. In fact, the proximity of the $Mo(CO)_6$ and $W(CO)_6$ peaks and their significantly larger capacity factors (*k*') compared to that of $Cr(CO)_6$ demonstrate the importance of the size influence.

The ability of the $C_{18}S$ column to facilitate the separation of $MnRe(CO)_{10}$ from its homonuclear parents is remarkable. Not only does it exhibit its effectiveness in dealing with congeneric mixtures, but also illustrates its value as a tool of purification in organometallic synthesis.

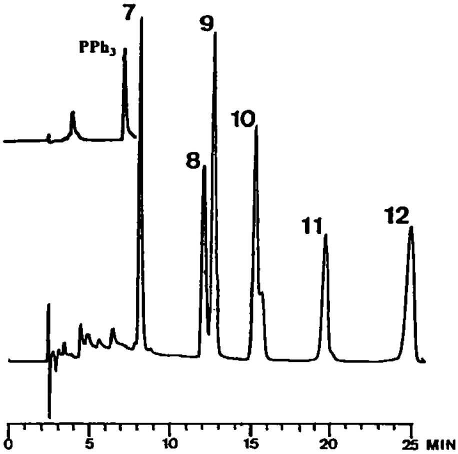

Figure 4. Reversed phase liquid chromatogram of triphenylphosphine (insert, on the same scale) and free diphosphine ligands on a Metaphase Crestpak C_{18} column (150 mm x 4.6 mm I.D.; 5 μm particle size). Mobile phase: acetonitrile-water (90:10). Flow rate: 0.6 mL min^{-1}. Detection wavelength: 254 nm. Peak identity: **7** = dppm (k' = 2.20); **8** = dppe (k' = 3.72); **9** = dpppr (k' = 3.95); **10** = dppb (k' = 4.97); **11** = dpppe (k' = 6.69); **12** = dpph (k' = 8.74) and **PPh_3** (k' = 1.75).

The syntheses of $MnRe(CO)_{10}$ from $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ under photo- or thermolytic conditions or nucleophilic displacement of $ReBr(CO)_5$ by $Na[Mn(CO)_5]$ have been plagued with problems arising from the contamination of the homonuclear carbonyl parents[9a,13] The use of HPLC offers an effective purification means.

Our earlier success in the use of a PAC column in the separation of a series of Gp 6 phosphine-bridged dimers prompted us to use similar conditions for the free phosphine ligands. However the ligands appear to be strongly retained on the column based on a strong polar interaction between the amino-cyano bonded phase and the free phosphine sites in the ligands.[14] Under the present reverse phase conditions, PPh_3 and all the diphosphines tested are eluted according to the following order of increasing retention times: PPh_3 < dppm < dppe < dpppr < dppb < dpppe < dpph (Fig. 4). The full separation of this list of similar phosphines demonstrates the effectiveness of the $C_{18}S$ column in the use towards organometallic ligands. As expected, the difunctional phosphines are eluted after the monofunctional phosphine, PPh_3. The stepwise increase in the alkyl chain-length by adding a methylene ($-CH_2-$) unit is sufficient to influence and govern the elution behaviour of the diphosphines, in terms of size and mass effects. This is in contrast to our finding earlier on the separation by normal phase HPLC on a PAC column, of a series of diphosphine-bridged complexes $M_2(CO)_{10}(\mu\text{-P-P})$ (M = Gp 6 metal; P-P = diphosphine) whereby the polarity of complex overshadows the mass effect induced by the ligand.[6] This difference is however not surprising considering the much larger size of the complexes than the ligands and the added influence of the metal centers with the associated metal-ligand bonds on the complex. It also shows that minor changes in metal and ligand environment are sufficient to alter the retention characteristics of these complexes.

The success experienced in this study of isostructural, congeneric and homologous compounds has encouraged us to examine other complex isomers which could not be separated by conventional chemical or chromatographic means. Current work is in progress in this direction on the same multimetallic clusters and aggregates.

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[†]Present address: Raffles Junior College, 53 Mount Sinai Road, Singapore 276880.

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