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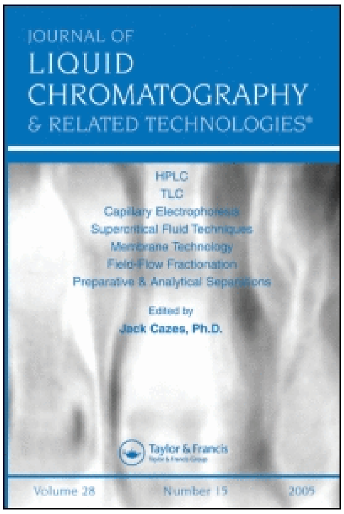

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High-Performance Liquid Chromatography of Group 6 Dimetal Decacarbonyl Complexes Singly-Bridged by Diphosphine Ligands

Kah-Ching Tan[a]; T. S. Andy Hor[a]; Hian Kee Lee[a]
[a] Department of Chemistry, National University of Singapore Kent Ridge, Republic of Singapore

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HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY OF GROUP 6 DIMETAL DECACARBONYL COMPLEXES SINGLY-BRIDGED BY DIPHOSPHINE LIGANDS

KAH-CHING TAN, T. S. ANDY HOR, AND HIAN KEE LEE*
Department of Chemistry
National University of Singapore
Kent Ridge
Republic of Singapore 0511

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ABSTRACT

The normal-phase high-performance liquid chromatography of a series of Group 6 dimetal decacarbonyl complexes, of the form $(OC)_5M(P(CH_2)_nP)M(CO)_5$, where M = Cr, Mo and W, and $P(CH_2)_nP$ = diphenylphosphinyl bridge with n = 2-6, is reported. Chromatography was carried out on a stainless steel column packed with silica to which polar amino-cyano groups have been bonded; hexane-chloroform was used as mobile phase. The retention behaviour of these homometallic complexes is discussed.

INTRODUCTION

The first reported use of high-performance liquid chromatography (HPLC) for the separation of organometallic compounds in 1969 (1) has subsequently engendered widespread interest in, and applicability of, the technique in inorganic chemistry. Several reviews have been published in recent years, reflecting the amount of work done in the area (2-5). Metal carbonyl complexes, in particular, have received considerable attention (5).

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*Author to whom correspondence should be addressed

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Normal-phase and reversed-phase HPLC (in both isocratic and gradient elution modes) have been used for separating metal carbonyl complexes. Previously, we reported the separation of a series of *1,1'-bis*(diphenylphosphino)ferrocene (dppf)-substituted metal carbonyl compounds (6,7) on columns packed with silica particles bonded with polar amino-cyano groups. The bonded-silica stationary phase afforded a measure of selectivity to the separation of the aforementioned compounds which could not otherwise be resolved with columns packed with conventional silica. This paper reports further investigations on the use of such a stationary phase under normal-phase conditions in the separation of Group 6 dimetal decacarbonyl complexes.

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The compounds considered in this work are of the form:

$$(OC)_5M(P(CH_2)_nP)M(CO)_5$$

where M = Cr, Mo and W, and $P(CH_2)_nP$ = *bis*(diphenylphosphinyl) bridge, *viz.* $[Ph_2P(CH_2)_nPPh_2]$ with n = 2 (dppe); 3 (dppp); 4 (dppb); 5 (dppp'), and 6 (dpph) (see Figure 1).

EXPERIMENTAL

Chromatographic separations were performed on a Shimadzu (Kyoto, Japan) Model LC-6A pump equipped with a Shimadzu Model SPD-6A variable wavelength UV spectrophotometric detector (with detection wavelength set at 254 nm), and a Whatman (Clifton, NJ, USA) Partisil 5 PAC (polar amino-cyano) column (5-µm particle size; 100 mm x 4.6 mm I.D.). Chromatographic data were collected and analysed on a Shimadzu Chromatopac C-R3A data processor. Eluent flow rate was 0.5 $mLmin^{-1}$. The binary mobile phase evaluated was hexane-chloroform, in the following compositions 93:7, 95:5 and 97:3 (%, v/v).

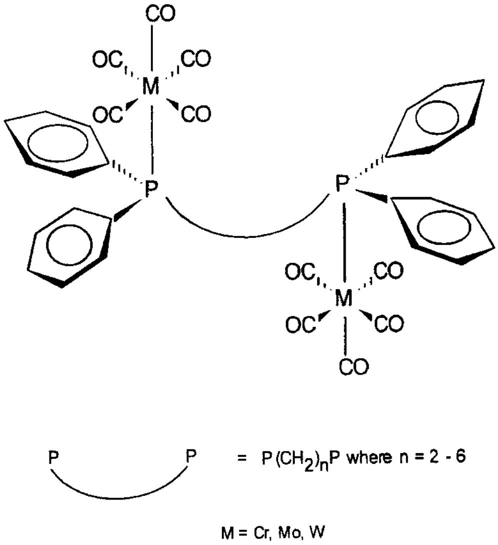

Figure 1 Structures of metal carbonyl complexes studied in this work.

All solvents (HPLC-grade, from various suppliers) were filtered through Millipore (Milford, MA, USA) membrane filters (0.45-μm pore size), 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 using a Rheodyne (Cotati, CA, USA) Model 7125 injection valve. 5-10 μL of samples were injected. HPLC runs were carried out at least in triplicate. Reproducibility of retention times between runs was ±2% or better.

Typical procedures for the preparation of some of the compounds considered in this work follow the published method (8), and are briefly described below:

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(a) $(OC)_5Mo_2(\mu\text{-dppf})$

Trimethylamine *N*-oxide (TMNO) (0.212 gm) was added to a suspension of $Mo(CO)_6$ (0.504 gm) in acetonitrile (20 mL) at 0°C. With vigorous stirring, a yellow colour steadily developed over 20 min. To this solution was added dppe (0.384 gm) and the resulting light-brown solution was kept at -15°C for 15 hr. The mixture was reduced in volume to about 10 mL and filtration yielded colourless crystals. The product was recrystallized from dichloromethane-methanol.

(b) $(OC)_5Cr(\mu\text{-dppb})Cr(CO)_5$

A mixture of $Cr(CO)_6$ (0.301 gm), dppb (0.263 gm) and TMNO (0.170 gm) in tetrahydrofuran (100 mL) was stirred for 2 hr. to give a green suspension. Evaporation to dryness gave a green residue which was redissolved in dichloromethane and applied onto a silica-coated TLC plate. Elution with dichloromethane-hexane (30:70) yielded the yellow product which was recrystallized from dichloromethane-methanol.

(c) $W(OC)_5W(\mu\text{-dpph})W(CO)_5$

$W(CO)_6$ (0.300 gm) and dpph (0.175 gm) were dissolved in tetrahydrofuran (100 mL). TMNO (0.099 gm) was then added. Completion of the reaction was indicated by the disappearance of the phosphine ligand when checked by TLC. The resulting yellow solution was evaporated to dryness under vacuum. The product was reconstituted in dichloromethane and precipitated by addition of excess methanol. The solid was purified by recrystallization from dichloromethane-methanol.

All the other complexes were synthesized under conditions slightly modified from those described.

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Fresh solutions of the compounds (individual and in mixtures), shielded from light, were used for the HPLC. The integrity of the compounds (in solutions of chloroform), based on their carbonyl absorptions, was periodically checked by infrared spectroscopy.

For chromatographic analysis, solutions of all the complexes were prepared in hexane-chloroform (50:50). All the compounds considered exhibited acceptable and useful solubilities in only certain solvents or combinations of these solvents. Their insolubilities in solvents normally used for reversed-phase HPLC precluded their analysis by this mode.

RESULTS AND DISCUSSION

Three hexane-chloroform compositions (93:7, 95:5 and 97:3) were initially evaluated to optimize the separation of the complexes considered in this work. The 93:7 and 95:5 eluent mixtures did not provide satisfactory resolution of some of the components. Better separation was achieved by using the 97:3 mobile phase which was adopted for all subsequent separations. The capacity factors (*k'*) of all the carbonyl complexes studied are listed in Table 1.

In a previous HPLC study (9) of related complexes, differences in electronegativity of the metal centres was used to rationalize the retention behaviour of the compounds. Basing this argument on the Allred-Rochow electronegativity scale (Cr = 1.56, W = 1.40, Mo = 1.30) (10), the order of increasing retention should be Mo-complex < W-complex < Cr-complex. This observation (9) was originally made with respect to $M_3(CO)_{12}$ (M = Fe, Ru and Os) and $M(CO)_6$ (M = Cr, Mo and W) complexes. On the basis of this aforementioned work, we attempted (6,7) to confirm a possible

TABLE 1
Capacity Factors (k') of Homometallic Diphosphine Complexes Obtained from Chromatography of Individual Components and Mixtures. Mobile Phase Composition: Hexane-Chloroform (97:3). Other Conditions as Given in Experimental Section. See Text for Explanation of Abbreviations.

	$(OC)_5M(dppx)M(CO)_5$		
	M = Cr	Mo	W
dppe	5.30	3.87	5.71
dppp	8.91	6.96	11.27
dppb	5.64	4.33	6.64
dppp'	7.03	5.58	8.77
dpph	6.40	4.98	7.87

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electronegativity-retention correlation with related metal-carbonyl complexes possessing two or more metal centres and *1,1'-bis*(diphenylphosphino)ferrocene (dppf) as the ligand (the only structural variation being the type of metal centre involved), as in $(OC)_9Mn_2(dppf)M(CO)_5$ or $(OC)_5M(dppf)M(CO)_5$ (M = Cr, Mo, W). Our finding was that there was no unequivocal relationship; specifically, the W-dppf complexes exhibited greater retention than those of Cr and Mo. Similar observations were made in the present work for the $(OC)_5M(P(CH_2)_nP)M(CO)_5$ series (n = 2-6) as data in Table 1 show, *i.e.* in general, (reading along the rows), the W complexes exhibited the greatest retention followed by the Cr complexes, and finally the Mo analogues. The present observations thus argue against the exclusive use of metal electronegativities to account for the retention behaviour of these types of complexes.

Within a particular set of the five homometallic complexes, with each differing only in the number of CH_2 units, another possible parameter that could conceivably play a role in determining retention behaviour for the series of complexes considered in this work is molecular size. We have in the past speculated (7) on the influence this property might have in explaining retention characteristics of several metal-carbonyl complexes with dppf as the ligand; however, we found the correlation tenuous. Similarly, when considering each of the three respective sets of homometallic species (*i.e.* where M is common) in the present work, absolute size may be ruled out as the sole contributor to retention behaviour as the capacity factors listed in Table 1 (reading down the table) show no obvious trend. Size, however, may play a secondary role, as explained below.

We next turned our attention to the consideration of relative polarities, as determined by overall dipole moments, of the complexes in the present study. Differences in polarity can best be illustrated by referring to Figure 2. In the complex with dppe as ligand, for example, the dipole moments along the (two sets of) methylene carbon and phosphorus bonds are equal and opposite to each other (*i.e.* the molecule has a centre of symmetry, *i*), producing a zero net dipole. When this is applied to the other diphosphine complexes, one can generalize that all the even-numbered CH_2 homologues show an *i* symmetry that nullifies the localised dipoles on the carbonyl and phosphine moeities. This results in these species possessing a zero dipole moment. On the other hand, the odd-numbered CH_2 homologues lack an *i* symmetry (although an approximate σ (mirror) plane exists in the less stable *syn* conformation), and thus have their dipole moments aligned in such a way that an overall dipole prevails for the molecule. The result of this is possession of polar character by the molecule. In effect, therefore, it is the relative polarity (based on *i* or lack of it thereof) of the complexes that appears to play the predominant role in determining retention behaviour. Accordingly, complexes with odd-numbered CH_2 homologues (*i.e.* where dppp, dppp' are the ligands) would be expected to be more retained under normal-phase HPLC conditions, than those with ligands containing even-numbered CH_2 units (*i.e.* dppe, dppb and dpph) which are fundamentally non-

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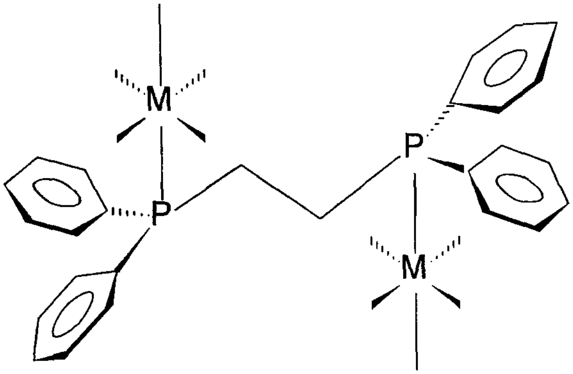

Figure 2 Dimetal decacarbonyl with *1,1'-bis*(diphenylphosphino)ethylene ligand.

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polar. The data given in Table 1 support this explanation. While size (with respect to the length of the ligand methylene chain) contributes to retention behaviour (note the increase in retention corresponding with the increasing length of the even-numbered ligand chain), it is polarity, when it exists, that predominates. Note that the same order of retention is observed for different metal centres with the odd-numbered-CH_2 complexes exhibiting a sudden and sharper increase in retention compared to those containing ligands with even-numbered CH_2 units. Figure 3, which is a plot of $(OC)_5MPh_2P(CH_2)_nPPh_2M(CO)_5$ (n = 2-6) *vs.* capacity ratio with data from Table 1, makes clear this observation. We had previously observed (7), as pointed out above, that polarity played a more significant role than electronegativity, than hitherto surmised, in influencing retention behaviour for complexes of this nature. The results of the present study have provided a stronger case for this view.

It is evident from Figure 3 that the capacity factors of the dppp complexes show sharper increases than those of dppp'. With data from only two sets of odd-numbered CH_2 complexes, it is difficult to establish with certainty why this is so. However, it may

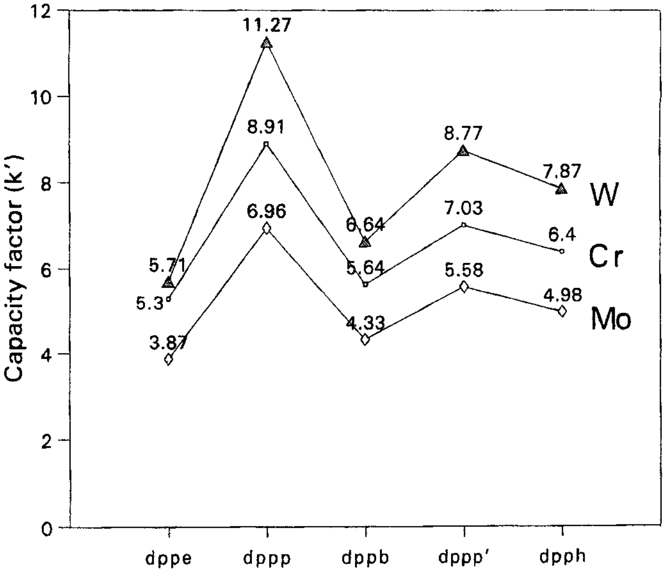

Figure 3 Plot of capacity factor (*k*') *vs.* $(OC)_5MPh_2P(CH_2)_nPPh_2M(CO)_5$ (M = Cr, Mo, W; n = 2-6)

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be speculated that the dppp complex, with only three CH_2 units, has limited rotational motion, in contrast to the dppp' complex which has five CH_2 units. The bigger molecule could conceivably partake of a higher degree of twisting along the methylene linkage, providing individual dipoles within the molecule with the means of cancelling out. On the other hand, the smaller dppp complex, being more rigid, possesses a more definite and specific molecular dipole, elevating its relative polarity *vis-à-vis* the dppp' complex.

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