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STERIC EFFECTS IN SUBSTITUTED HALOCARBONYLS OF MOLYBDENUM AND TUNGSTEN

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Abbreviations

dpe	1,2-bis(diphenylphosphino)ethane
dpm	bis(diphenylphosphino)methane
dam	bis(diphenylarsino)methane
diars	*o*-phenylenebis(dimethylarsine)

A. INTRODUCTION

The aim of this review is to evaluate the results obtained in the preparation of a range of phosphine and arsine substituted halocarbonyls of molybdenum(II) and tungsten(II). There will be no mention of chromium, for while its zero-valent carbonyl chemistry is often similar to that of molybdenum and tungsten, it is quite different in oxidation state (II) which is the subject of this review.

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When a variety of complexes can be isolated in a system it is often difficult to distinguish between the effects of the two competing influences of steric and electronic factors. However, in these substituted halocarbonyls it would appear that almost all the many variations observed on changing the halogen, the Group V donor atom, and perhaps even the Group VI transition metal itself, are explicable within a self-consistent steric argument.

If one assumes that the effective atomic number rule (inert gas formalism) applies in these systems, then the natural coordination number of molybdenum and tungsten(II) is seven, and indeed many of the complexes to be discussed are seven coordinate. On the other hand the metals frequently exhibit six coordination and it appears to be interaction between the ligands, rather than steric crowding of seven donor atoms about the metal, which is the dominating influence in the formation of six coordinate complexes. This supposition is shown to be reasonable by the fact that less sterically active phosphines and arsines often give seven coordinate complexes under similar conditions and in addition, of course, seven and eight coordinate complexes are well known for molybdenum and tungsten in higher oxidation states. Under these circumstances it is difficult to justify the appearance of six coordinate complexes for the larger divalent ions on the basis of simple steric crowding of seven donor atoms about the metal.

Thus the overall theme of this review will be to summarise, and where possible rationalise, the observed stereochemistry of the substituted halocarbonyls of molybdenum(II) and tungsten(II). It is convenient to examine first the complexes formed with potentially bidentate phosphine and arsine ligands. In these derivatives there is more scope for variation in steric effects and the use of additional experimental techniques, particularly NMR spectroscopy, allows the steric arguments to be placed on a firm foundation. Much of the behaviour observed in the derivatives of monodentate phosphines and arsines is consistent with the steric arguments, but in the opinion of the author the evidence available from these systems alone would not be sufficient to distinguish unambiguously between steric and electronic effects.

B. PREPARATIVE METHODS

There are two principal methods of preparing substituted halocarbonyls of molybdenum(II) and tungsten(II). The older method developed mainly by Lewis and his associates[1-4] can be represented by the general equation

$$M(CO)_6 + 2\,L \longrightarrow M(CO)_4L_2 \xrightarrow{X_2} M(CO)_3L_2X_2$$

although there are several variations of this basic reaction. For example, in the equation L is represented as a monodentate ligand, but the reaction works equally well if L is bidentate or even tridentate[2]. With bidentate ligands oxidation of zero-valent complexes of both the types $M(CO)_4L$ and $M(CO)_2L_2$ has been investigated. The major difficulty of this reaction lies in the oxidation procedure. In general it may be said that oxidation with iodine is satisfactory and the divalent metal carbonyl complexes are obtained in good yield. Difficulties are sometimes encountered in the preparation of bromo compounds due to further preferential oxidation of the required complex by free bromine; the method is impracticable for chloro derivatives as formation of higher oxidation state compounds with loss of all the carbonyl groups invariably occurs. Indeed, chlorine oxidation of zero-valent complexes is becoming a general method of preparation of higher-oxidation-state chloro compounds[5].

The second general method of preparation of the compounds under discussion involves preparation of the parent halocarbonyls themselves followed by reaction with the appropriate ligand

$$M(CO)_6 \xrightarrow{X_2} M(CO)_4X_2 \xrightarrow{2\,L} M(CO)_3L_2X_2$$

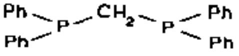
Prior to 1966 all attempts at the preparation of the halocarbonyls of molybdenum and tungsten had failed [3,6–8], but it was then discovered[9] that dichlorotetracarbonylmolybdenum(II) could be prepared quantitatively by the interaction of hexacarbonyl molybdenum and liquid chlorine at −78°C. The corresponding bromo complex and the tungsten analogues were quickly isolated[10–12], but considerable effort was required before the diiodotetracarbonyls were finally prepared[13].

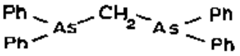
Difficulty is always experienced in isolating reasonable quantities of diiodotetracarbonylmolybdenum(II), so it is fortunate therefore that the original oxidative procedure proceeds so smoothly for iodo complexes. In our work it has become standard practice to use the halocarbonyls in all syntheses except in the iodo-molybdenum system and there the oxidative method is employed. Small-scale reactions with the diiodotetracarbonyl always confirmed that the same products were obtained by the two methods of synthesis which are therefore entirely complementary.

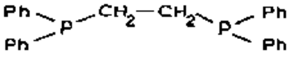
It will be noted later that it is often necessary to work in strict stoichiometric proportions in many of the reactions to be discussed and the advantages of using the air-stable solid halocarbonyls are obvious.

C. THE LIGANDS

The bulk of the work to be described in this review is concerned with the derivatives of three bidentate ligands and several simple monodentate groups. The bidentate ligands, with the abbreviations used for their formulae, are shown below.


bis(diphenylphosphino)methane
(dpm)

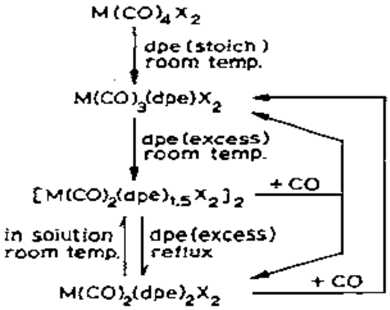

bis(diphenylarsino)methane
(dam)


1,2-bis(diphenylphosphino)ethane
(dpe)

The complexes with dpe will be considered first and certain variations which are observed as the halogen is changed will be noted. Detailed comparison with the dpm will then be made and the marked differences will be analysed in terms of steric effects. The effect of changing the Group V donor from phosphorus to arsenic is shown by the study of the dam compounds.

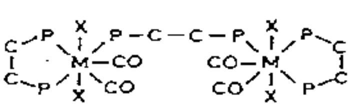
D. COMPLEXES WITH 1,2-BIS(DIPHENYLPHOSPHINO)ETHANE

The reaction scheme summarises the products obtained by reacting dpe with the halocarbonyls[14]. The reactions to the left of the diagram refer to all the halo derivatives, but those to the right are specific to the iodo complexes and will be discussed in more detail below.



Treatment of acetone or dichloromethane solutions of the halocarbonyls with the controlled amount of dpe at room temperature yields the monosubstituted tricarbonyls $M(CO)_3(dpe)X_2$ as crystalline solvates. It may be noted that the stabilities of the tricarbonyls towards further attack by dpe decreases in the order I > Br > Cl and W > Mo and in fact $Mo(CO)_3(dpe)Cl_2$ can only be isolated with difficulty. However, once separated from the reaction mixture the compounds are quite stable to air and moisture in solution and in the solid state.

When an excess of dpe is allowed to react at room temperature with the dihalotetracarbonyls in either acetone or dichloromethane solution, orange crystalline precipitates form after a period of several hours. The empirical formula of the products is $M(CO)_2(dpe)_{1.5}X_2$, requiring them to be formulated as dimers to give an integral number of dpe molecules. Unfortunately, the slight solubility of these compounds precluded a direct determination of their molecular weights, but it is believed that they have the structure shown (the phenyl groups and methylene protons have been omitted for clarity).



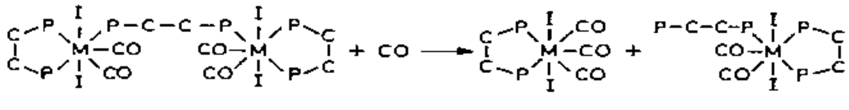
The proposed structure involves a chelating dpe ligand on each metal and the third dpe molecule bridges the two metal atoms. The environment about the metal is similar to that observed (see p. 275) in complexes of the type $M(CO)_2(dpm)_2X_2$ where it has been shown unequivocally by NMR that one of the dpm ligands is chelated and the other is acting as a monodentate ligand. Some chemical evidence for the bridged structure in the case of $[M(CO)_2(dpe)_{1.5}I_2]_2$ will be presented below.

A third class of compound, $M(CO)_2(dpe)_2X_2$, may be prepared by refluxing the parent halocarbonyls, or either of the previously described types of complex, with excess dpe. Although the empirical formulae of all of the complexes of this type are the same, the iodo compounds show a significant difference from the other halo derivatives in that they are ionic and should be formulated as *cis*-$[M(CO)_2(dpe)_2I]I$ (*cis* referring only to the relative stereochemistry of the carbonyl groups).

The neutral complexes $M(CO)_2(dpe)_2X_2$ (X = Cl, Br) are presumably seven coordinate and contain one chelated and one monodentate dpe molecule, exactly analogous to the previously mentioned dpm derivatives. Unfortunately NMR did not prove useful in this case since in solution the compounds rapidly lose dpe to reform the dimeric $[M(CO)_2(dpe)_{1.5}X_2]_2$ which then precipitates.

With the iodo complexes $[M(CO)_2(dpe)_2I]I$ there are two possibilities for the structure of the cation. The dpe molecules can remain non-equivalent, i.e., one chelated and one monodentate so as to give a six-coordinate cation, or alternatively both dpe molecules could be chelated to give a seven-coordinate complex. Although NMR again proved unsuccessful in this particular case, it did show in the corresponding dpm complexes (see p. 276) that the dpm ligands remained non-equivalent and that those cations are six-coordinate. Some chemical evidence that the situation is similar in the dpe–iodo complexes is provided by their reaction with carbon monoxide, as shown in the reaction scheme. Merely bubbling the gas through a solution of $[M(CO)_2(dpe)_2I]I$ leads to the gradual formation of $M(CO)_3(dpe)I_2$ with loss of one molecule of dpe. This reaction, which does not proceed with the non-ionic chloro and bromo analogues, is consistent with the presence of a less-strongly bound, monodentate dpe molecule. Furthermore, if the cation is only six-coordinate there is an easy site of attack, for small molecules such as carbon monoxide, which is not available in the case of the seven-coordinate chloro and bromo analogues.

Carbon monoxide also reacts quite rapidly at room temperature and pressure with the iodo–dpe bridged complexes, but not with the other halo–dpe bridged compounds. The products obtained initially are equimolar quantities of $M(CO)_3(dpe)I_2$ and $[M(CO)_2(dpe)_2I]I$ according to the equation



although the ionic product reacts further with carbon monoxide.

It is proposed that this cleavage reaction occurs with the iodo derivatives only because of interaction between the coordination spheres of the two metal atoms in the bridged complex, due to the large halogen, causes weakness at the M–P bond of the bridging ligand.

Thus in the dpe system there are three effects which can be observed as the halogen is varied:

(*i*) reactivity of $M(CO)_3(dpe)X_2$ towards further attack by dpe;
(*ii*) instability of the iodo–dpe bridged dimers;
(*iii*) ionic character and reactivity of $[M(CO)_2(dpe)_2I]I$.

In isolation, these results for the dpe system would be of little value, but when compared with the results obtained with dpm there can be little doubt that they are due to steric effects.

E. COMPLEXES WITH BIS(DIPHENYLPHOSPHINO)METHANE

The products of the reaction of dpm with the halocarbonyls of molybdenum and tungsten are considerably more diverse than those obtained with dpe, and they clearly emphasize the effect of varying the halogen.

Dichlorotetracarbonylmolybdenum(II) and tungsten(II) and also dibromotetracarbonyltungsten(II) react with dpm to give $M(CO)_2(dpm)_2X_2$ as the first identifiable product[15]. There is no evidence in these systems for the existence of isolable quantities of the intermediate tricarbonyl complex $M(CO)_3(dpm)X_2$ corresponding to the dpe derivatives. It has recently been shown that these neutral complexes may be isomerised to the ionic *cis* dicarbonyl complexes merely by refluxing, thus the overall reaction sequence is

$$M(CO)_4X_2 \xrightarrow{\text{dpm, room temp.}} M(CO)_2(dpm)_2X_2 \xrightarrow{\text{reflux}} cis\text{-}[M(CO)_2(dpm)_2X]X$$

PMR spectroscopy has proved to be very useful in determining the type of coordination exhibited by the dpm ligands.

The region of the NMR spectrum due to the methylene protons of dpm in the complexes $M(CO)_2(dpm)_2X_2$ is shown in Fig. 1. Spectrum A is that of the free ligand, the methylene absorption is actually a 1:2:1 triplet ($J_{P\text{-}H} = 1.4$ Hz) due to the two equivalent ^{31}P atoms. All of the tungsten complexes show a clear triplet ($J_{P\text{-}H} = 11$ Hz) at about $\tau = 4.8$–5.0 which is assigned to a chelated dpm molecule. Each of these compounds also shows another resonance of equal intensity at about $\tau = 5.8$–6.0 which is assigned to a monodentate dpm ligand. In a first-order analysis a quartet of lines of equal intensity might be expected for a monodentate dpm due to spin-coupling of the methylene protons with two non-equivalent phosphorus nuclei. In this case the quartet is not resolved, but a similar quartet has been clearly resolved [16] for the compound $Mo(CO)_5(dpm)$. The intensities of the two methylene resonances are in the ratio 2:2:40 with the complex phenyl resonance which occurs near $\tau = 2.8$, exactly as required by the structure containing one chelated and one monodentate dpm. In contrast the molybdenum compounds exhibit little structure in the methylene proton spectrum, although they do show two clearly defined resonances. This effect was originally ascribed to the magnitude of the nuclear spin of molybdenum[15], but there is now little doubt that it is in fact due to exchange between the chelated and monodentate dpm ligands. Variable-temperature studies on the corresponding dam complexes clearly demonstrate this phenomenon, and the exis-

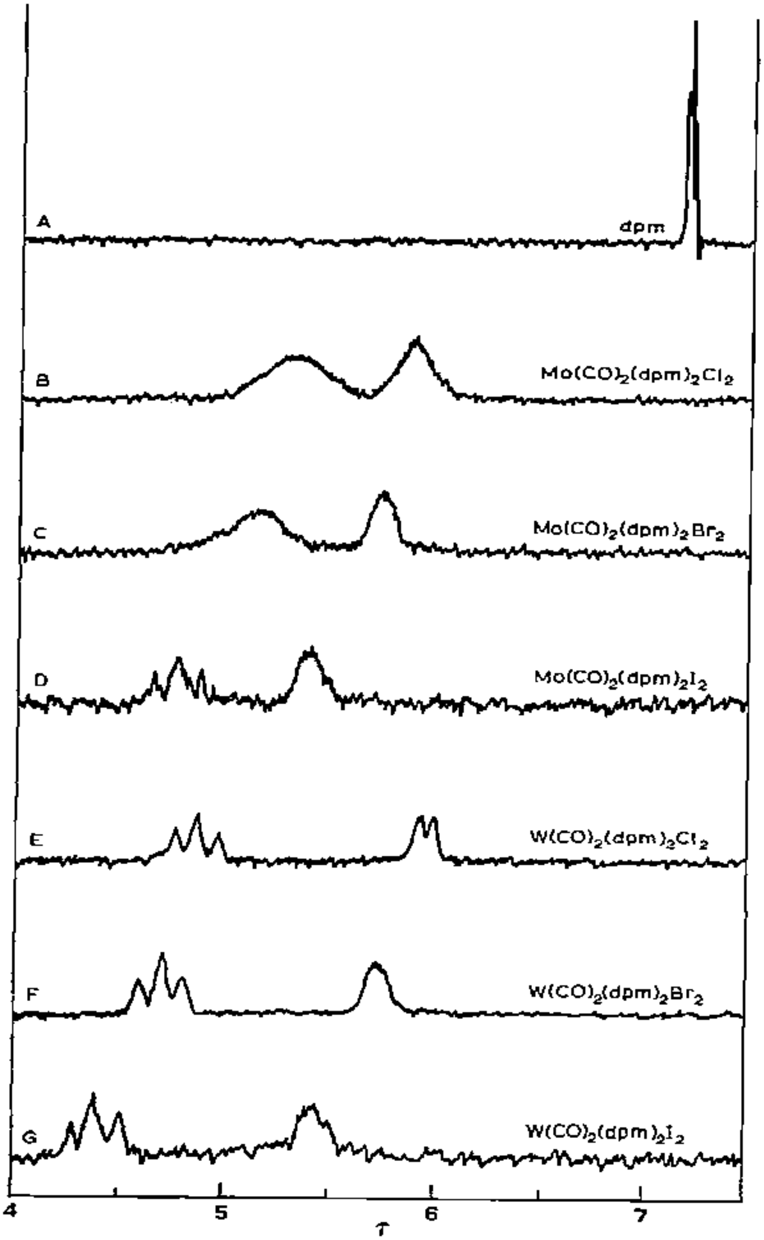


Fig. 1. NMR spectra of $M(CO)_2(dpm)_2X_2$ (methylene proton region); A, dpm; B, $Mo(CO)_2(dpm)_2Cl_2$; C, $Mo(CO)_2(dpm)_2Br_2$; D, $Mo(CO)_2(dpm)_2I_2$; E, $W(CO)_2(dpm)_2Cl_2$; F, $W(CO)_2(dpm)_2Br_2$; G, $W(CO)_2(dpm)_2I_2$.

tence of fine structure in the spectrum of $Mo(CO)_2(dpm)_2I_2$ confirms that the lack of resolution in its chloro and bromo analogues is not a function of the nuclear properties of molybdenum[17].

A most useful result which emerges from these and all the other recorded spectra is that bidentate and monodentate dpm (and dam) ligands can be readily distinguished by the chemical shift of the methylene protons.

In the ionic complexes *cis*-$[M(CO)_2(dpm)_2X]X$ the question arises, exactly as with *cis*-$[M(CO)_2(dpe)_2I]I$, whether the ligand molecules remain non-equivalent as in the neutral non-ionic isomer, or whether on elimination of the halide ion the second dpm chelates. It will be recalled that in the dpe case chemical evidence suggested that the cation was six-coordinate with the dpe molecules remaining non-equivalent. NMR studies have shown that this is certainly the case in the corresponding dpm complexes. For example, the spectrum of *cis*-$[Mo(CO)_2(dpm)_2Cl]Cl$ shows resonances of the correct intensities at $\tau = 5.32$ and 6.00 assigned to the bidentate and monodentate ligand molecules respectively[19].

Dibromotetracarbonylmolybdenum(II) reacts with dpm to give $Mo(CO)_2(dpm)_2Br_2$ which like the previous compounds can be converted to the ionic form by refluxing, but in addition the intermediate tricarbonyl complex $Mo(CO)_3(dpm)Br_2$ can be isolated as shown in the equation.

$$\begin{tikzcd} Mo(CO)_4Br_2 \arrow[r, "dpm"] & Mo(CO)_3(dpm)Br_2 \arrow[r, "dpm"] & Mo(CO)_2(dpm)_2Br_2 \arrow[d, "reflux"] \\ & & {[Mo(CO)_2(dpm)_2Br]Br} \end{tikzcd}$$

Since both molybdenum and tungsten complexes of the type $M(CO)_3(dpm)I_2$ can be prepared (see below), the isolation of $Mo(CO)_3(dpm)Br_2$ fits nicely into the order of reactivities of complexes of the type $M(CO)_3(L{-}L)X_2$ [$L{-}L$ = dpe or dpm]. It was noted that the stabilities of $M(CO)_3(dpe)X_2$ towards further attack by dpe decreased in the order $I > Br > Cl$ and $W > Mo$. In the dpm case the same general trend is followed except that perhaps $W(CO)_3(dpm)Br_2$ should have been isolated.

The reactions of dpm with the diiodotetracarbonyls are shown in the next reaction scheme[18,20]. The room-temperature reaction between dpm and the iodocarbonyls in either acetone or dichloromethane solution leads to the formation of a mixture of yellow

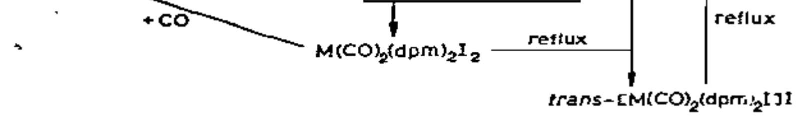


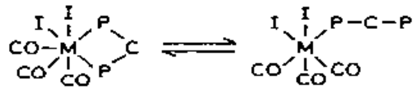
TABLE 1

Carbonyl stretching frequences

Compound	Carbonyl modes in solid state (cm^{-1})				
$Mo(CO)_3(dpe)Br_2$	2060		1977		1917
$[Mo(CO)_2(dpe)_{1.5}Br_2]_2$		1935		1855	
$Mo(CO)_2(dpe)_2Br_2$		1938		1854	
$Mo(CO)_3(dpm)Br_2$	2050		1975		1925
α-$Mo(CO)_3(dpm)I_2$	2050		1990		1935
β-$Mo(CO)_3(dpm)I_2$	2045		1960		1930 (sh)
$[Mo(CO)_2(dpm)_{1.5}Br_2]_2$		1935		1860	
$Mo(CO)_2(dpm)_2Br_2$		1940		1865	
cis-$[Mo(CO)_2(dpm)_2Br]Br$		1940		1865	
$Mo(CO)_2(dpm)_2I_2$		1940		1865	
cis-$[Mo(CO)_2(dpm)_2I]I$		1940		1865	
trans-$[Mo(CO)_2(dpm)_2I]I$			1890		
$Mo(CO)_3(dam)_2Cl_2$	2040		1970		1920
$Mo(CO)_3(dam)I_2$	2040		1975		1920
$Mo(CO)_3(dam)_2I$	2020		1950		1920
$Mo(CO)_2(dam)_2I_2$		1940		1865	
$Mo(CO)_3(PPh_3)_2Cl_2$	2045		1952		1903
$W(CO)_3(PPh_3)_2Cl_2$	2020		1940		1895
$W(CO)_2(PPh_3)_2Cl_2$		1960		1875	
$Mo(CO)_3(AsPh_3)_2Cl_2$	2038		1965		1925
$Mo(CO)_3(SbPh_3)_2Cl_2$	2035		1965		1920

and orange crystals each of which has been individually identified as $M(CO)_3(dpm)I_2$. The IR spectra of the two isomers in the carbonyl stretching region are quite different (Table 1), but the solution spectra of either isomer, or a mixture of isomers, are identical and indicate that an equilibrium between the isomers is rapidly attained in solution. In agreement with this the isomers cannot be separated by chromatography and slow crystallisation gives only the yellow (α) isomer. Rapid precipitation gives a mixture of isomers and the only method of obtaining the orange (β) isomer is by hand picking of crystals from these mixtures.

α-$M(CO)_3(dpm)I_2$ has an IR spectrum in the solid state which is very similar to those of known seven-coordinate complexes such as $M(CO)_3(PPh_3)_2X_2$ and $M(CO)_3(dam)I_2$. For the dam complexes there is NMR evidence that the ligand is chelated (see p. 282), so it is concluded that $M(CO)_3(dpm)I_2$ is also seven-coordinate in the α-isomer. For the β-isomer, which is a non-electrolyte, there are two possibilities. If the dpm is chelated then the β-isomer must be a different geometrical isomer and a minor rearrangement of the relative conformation of the ligands about the metal would be sufficient to cause the isomerism. Alternatively, a more plausible explanation involves an equilibrium of the type



The IR spectra of the β-isomers are unusual for seven-coordinate deriviatives and may be an indication of some unusual structural feature, such as six coordination. The emergence of an equilibrium between seven and six coordination would be most likely to occur with the combination of the largest halogen and the most sterically active ligand, namely dpm. Thus, although there is at present no definitive evidence to distinguish between the two possibilities, it would appear likely that the β-isomer is six-coordinate with a monodentate dpm ligand.

Since the equilibrium between the isomers of $M(CO)_3(dpm)I_2$ is rapidly established in solution it is of no consequence whether individual isomers or a mixture are used for subsequent reactions. $M(CO)_3(dpm)I_2$ readily reacts with further dpm to give substances of empirical formula $M(CO)_2(dpm)_2I_2$, but there are, in fact, three isomers of this complex obtainable from this reaction.

The reaction at room temperature gives a mixture of neutral $M(CO)_2(dpm)_2I_2$ and *cis*-$[M(CO)_2(dpm)_2I]I$ and these may be readily separated by chromatography. The neutral complex is seven-coordinate and is entirely equivalent to its chloro and bromo analogues. As noted above, its NMR spectrum shows P—H coupling with a triplet centered at $\tau = 4.67$ and an unresolved band of equal intensity at $\tau = 5.39$. The only difference between the iodo compounds and their other halo analogues is that the iodo complexes react with carbon monoxide to reform $M(CO)_3(dpm)I_2$. This reaction indicates that the monodentate dpm is less firmly bound to the metal than in the other halo compounds, presumably because of steric crowding around the metal.

Cis-$[M(CO)_2(dpm)_2I]I$ is also analogous to the corresponding chloro and bromo compounds and like them it does not react with carbon monoxide (compare with *cis*-$[M(CO)_2(dpe)_2I]I$) but these comparisons with the dpe system will be discussed in more detail below.

If neutral $M(CO)_2(dpm)_2I_2$ is refluxed in an inert solvent it forms the two ionic isomers *cis*- and *trans*-$[M(CO)_2(dpm)_2I]I$ with the *cis* isomer predominating (*cis* and *trans* referring only to the relative stereochemistry of the carbonyl groups). On prolonged refluxing the *trans* isomer is converted to *cis*. These ionic isomers can be readily separated[20] and have been characterised individually. The IR spectra of these isomers and a representative number of the other complexes discussed so far are given in Table 1.

The distribution of isomers of the complexes with formula $M(CO)_2(L—L)_2X_2$ (L—L = dpe or dpm) is as shown below.

	dpm	dpe
Cl	molecular + *cis*-ionic	molecular
Br	molecular + *cis*-ionic	molecular
I	molecular + *cis*- + *trans*-ionic	*cis*-ionic

In the neutral molecular complexes maximum crowding around the metal occurs in the dpm—iodo complexes and least steric interaction is found in the dpe—chloro complexes. The neutral complexes have all been shown to be seven-coordinate and they decrease in stability as the steric interactions become stronger. In the dpe system the *cis*-ionic complex appears only with the iodo derivatives. In the more sterically crowded dpm complexes room-temperature reaction gives the neutral isomers for the chloro and bromo systems. but these are readily converted to the *cis*-ionic form on refluxing. With the larger iodine, the room-temperature reaction gives both the neutral and *cis*-ionic forms of $M(CO)_2(dpm)_2I_2$ and refluxing produces the *trans*-ionic isomer. The emergence of the *trans* isomer is a strong indication of steric forces. The *cis* isomer would be expected to be the most stable six-coordinate structure on electronic considerations and the *trans* form would be favoured on steric grounds. It is in just this situation that the *trans* isomer appears.

An interesting omission from the isolated isomers is the neutral form of $M(CO)_2(dpe)_2I_2$. It will be recalled however that the formation of this bis(dpe) complex from the bridged $[M(CO)_2(dpe)_{1.5}I_2]_2$ required refluxing, and this in turn is the means by which the molecular $M(CO)_2(dpm)_2X_2$ complexes are converted to the *cis*-ionic form. To isolate neutral $M(CO)_2(dpe)_2I_2$ a room temperature method of preparation would be required. It is interesting to note that iodine oxidation of $Mo(CO)_2(dpe)_2$ produces an anomalous result[1] and oxidation proceeds only to the monovalent state to give $[Mo(CO)_2(dpe)_2]^+$ so that at present a room-temperature preparation of $M(CO)_2(dpe)_2I_2$ is not available.

When it is realised that dpm exerts greater steric effects than dpe, the different behaviour of the $M(CO)_2(L{-}L)_2X_2$ complexes with carbon monoxide can be rationalised. The complexes $M(CO)_2(dpm)_2I_2$ are the only neutral isomers to react with carbon monoxide to reform $M(CO)_3(dpm)I_2$. As noted above, this implies that the monodentate dpm ligand is very weakly bound to the metal and this in turn may be responsible for the decreased exchange between the chelated and monodentate dpm ligands as evidenced by the NMR spectrum. On the other hand the ionic dpm complexes *cis*-$[M(CO)_2(dpm)_2X]X$ do not absorb carbon monoxide even though the cations are only six-coordinate. This could be interpreted to mean that because of the relaxing of the steric interaction as the halide ion is eliminated, the non-chelated dpm is now more firmly bonded to the metal. The distortion of the positions of the phenyl rings about the phosphorus atoms as a result of the formation of the four-membered ring must be sufficient to block effectively the entry of a carbon monoxide molecule to form a cation of the type $[M(CO)_3(dpm)_2X]^+$. However, the steric effect of dpe is not so great, presumably due to the more flexible nature of the ligand, and in addition the non-bonded phosphorus atom is more remote from the metal in $[M(CO)_2(dpe)_2I]I$, so this complex does in fact slowly absorb carbon monoxide with subsequent loss of the non-chelated dpe molecule. Thus it is the iodo complexes $M(CO)_2(dpm)_2I_2$ and *cis*-$[M(CO)_2(dpm)_2I]I$ which are anomalous in their behaviour towards carbon monoxide.

It will have been noted that so far there has been no mention of dpm bridged complexes analogous to $[M(CO)_2(dpe)_{1.5}X_2]_2$. In fact the dpm dimers have never been observed in the interaction of dpm with the halocarbonyls, nor do the neutral compounds $M(CO)_2(dpm)_2X_2$ decompose in solution to give the dimers (compare with dpe). However, the chloro– and bromo–dpm bridged dimers have been prepared by other methods.

The trichlorotetracarbonylmolybdate(II) ion, $[Mo(CO)_4Cl_3]^-$, reacts with dpm at room temperature to give a mixture of yellow neutral $Mo(CO)_2(dpm)_2Cl_2$, identical to the product obtained by reaction with the parent halocarbonyl, and orange crystalline $[Mo(CO)_2(dpm)_{1.5}Cl_2]_2$. The dpm dimer is similar to its dpe analogue except that it readily reacts with further dpm at room temperature to give $Mo(CO)_2(dpm)_2Cl_2$. It will be recalled that refluxing was required for this type of reaction to proceed for the dpe complexes.

Tribromotetracarbonylmolybdate(II), $[Mo(CO)_4Br_3]^-$, reacts[19] with dpm to give only neutral $Mo(CO)_2(dpm)_2Br_2$. Since it is obvious from the behaviour of the chloro–dpm bridged complex that the dpm dimers are very susceptible to attack by further dpm, interaction between $Mo(CO)_2(dpm)_2Br_2$ and the parent halocarbonyl $Mo(CO)_4Br_2$ was attempted to try to avoid the use of free dpm. After mixing the reactants at room temperature in dichloromethane, orange crystals of $[Mo(CO)_2(dpm)_{1.5}Br_2]_2$ slowly deposited over 24 h.

$[Mo(CO)_4I_3]^-$ reacted with dpm at room temperature to give only *cis*-$[Mo(CO)_2(dpm)_2I]I$ and all attempts to prepare the iodo–dpm bridged complex failed.

It is of interest to compare the stability of the dpe and dpm bridged dimers towards cleavage by excess ligand and by carbon monoxide. The two principal variables are the size of the halogen atoms and the length of the carbon chain between the phosphorus atoms in the bridging ligand. Both of these will have an effect on the interaction between the coordination spheres of the two metal atoms, and this in turn will effect the strength of the metal–phosphorus bond to the bridging ligand.

The stability of the dimers is actually reflected in the varying degree of difficulty in their preparation. Thus all the dpe dimers may be prepared directly from the halocarbonyls or from the $M(CO)_3(dpe)X_2$ complexes. This must mean that the dimers are more resistant to attack by free dpe than the tricarbonyl complexes since excess dpm is present in the system. The dpm bridged complexes are much more difficult to prepare and in the bromo case free dpm must be avoided in the system altogether. Naturally, once isolated, the reactivity of the bridged complexes parallels the difficulties of preparation. All of the dpe complexes require refluxing with excess ligand to form $M(CO)_2(dpe)_2X_2$, but the dpm complexes react rapidly at room temperature.

Finally reaction with carbon monoxide is instructive. Only $[M(CO)_2(dpe)_{1.5}I_2]_2$ in the dpe series is cleaved by carbon monoxide to give $M(CO)_3(dpe)I_2$ and $[M(CO)_2(dpe)_2I]I$. In the dpm series $[Mo(CO)_2(dpm)_{1.5}Br_2]_2$ reacts with carbon monoxide to give $Mo(CO)_3(dpm)Br_2$ and $Mo(CO)_2(dpm)_2Br_2$ but $[Mo(CO)_2(dpm)_{1.5}Cl_2]_2$ is unaffected by the gas at room temperature and pressure. Thus it may be seen that the effect of reducing the length of the carbon chain in the bridging ligand from dpe to dpm is similar to the effect of increasing the size of the halogen from bromine to iodine in the dpe series. All of these observations are consistent with the steric argument based on interaction between the two halves of the dimer molecule.

F. COMPLEXES WITH BIS(DIPHENYLARSINO)METHANE

Two important differences exist between the dpm and dam systems. It is found that the four-membered ring formed by chelating a dam molecule to the metal is invariably weak and is readily cleaved by carbon monoxide or excess ligand. In addition the effect of substituting the larger arsenic atom for phosphorus results in a marked decrease in the steric pressures caused by the phenyl rings of the ligand since the aromatic systems are naturally moved further away from the neighbouring ligands. Both of these effects contribute to the marked differences observed between the dpm and dam derivatives.

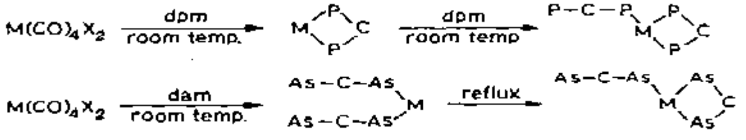
Dichloro- and dibromo-tetracarbonyl molybdenum and tungsten(II) react[21] with dam at room temperature to give complexes of the type $M(CO)_3(dam)_2X_2$, which, on warming in solution, are converted to $M(CO)_2(dam)_2X_2$. These latter complexes react readily with carbon monoxide to reform the tricarbonyl compounds $M(CO)_3(dam)_2X_2$ so that a reversible carbon monoxide carrying system is established according to the equation

$$M(CO)_4X_2 \xrightarrow{\text{dam, room temp.}} M(CO)_3(dam)_2X_2 \underset{CO}{\overset{\text{reflux}}{\rightleftharpoons}} M(CO)_2(dam)_2X_2$$

The structures of the complexes $M(CO)_2(dam)_2X_2$ are exactly analogous to the corresponding dpm derivatives, their NMR spectra show that they contain one chelated and one monodentate dam ligand, but this is the only major point of similarity with the dpm system.

The intermediate tricarbonyl complexes $M(CO)_3(dam)_2X_2$ are different in stoichiometry to those observed with dpm. They are non-electrolytes and since they cannot be eight-coordinate they must contain two monodentate dam ligands. The NMR spectra of the iodo complexes of this type confirm this structure.

The differences between the dpm and the dam systems are thought to be due to the different stabilities of the chelate rings. The reactions may be represented diagrammatically as follows:



With dpm the first ligand molecule to coordinate also chelates strongly and the slow step is the introduction of the second (monodentate) ligand. With dam the first observed product contains two monodentate ligands and the comparatively slow step is chelation of one of them. However, in view of the fact that $M(CO)_3(dam)I_2$ is isolated as an intermediate in the formation of $M(CO)_3(dam)_2I_2$ (see below) it is quite possible that $M(CO)_3(dam)X_2$ is also an intermediate in the chloro and bromo systems, but if it is, it reacts so rapidly with further dam that it is not observed. Further evidence of the weak chelating character of dam is provided by the action of carbon monoxide on $M(CO)_2(dam)_2X_2$ to yield $M(CO)_3(dam)_2X_2$. This type of reaction does not proceed with any of the dpm complexes.

We believe that the easy cleavage of the dam chelate ring is due to the fact that the arsenic atoms are so much larger than phosphorus that one carbon atom is no longer sufficient to bridge between them in the chelated complex. The result of the steric strain is to weaken the metal arsenic bond resulting in easy cleavage of this bond. This idea is supported by the fact that chelate rings formed by 1,2-bis(diphenylarsino)ethane, the arsenic analogue of dpe, appear to be far more stable towards cleavage by carbon monoxide[21].

Another interesting difference from the dpm system is that in no case, not even in the iodo complexes, do the neutral derivatives of the type $M(CO)_2(dam)_2X_2$ ionise to give $[M(CO)_2(dam)_2X]X$. It will be recalled that this is a prominent feature of the dpm system and with the iodo complex even the less sterically active dpe gave $[M(CO)_2(dpe)_2I]I$. This lack of ionisation can be understood if it is assumed that it is interaction of the phenyl groups with the coordinated ligand which causes the halogen to ionise. This view is consistent with the facts in the chemistry of the phosphorus ligands and the steric forces would naturally be less in the dam case merely due to the larger size of the arsenic atoms.

As with the other ligands, the reactions of dam with the diiodotetracarbonyls are rather more complex than those with the other halocarbonyls and they provide striking evidence of the ease of cleavage of the chelated dam system[22]. There are three types of iodo–dam complex and they are all in mutual equilibrium as shown by the general equation

$$M(CO)_3(dam)I_2 + dam \rightleftharpoons M(CO)_3(dam)_2I_2 \rightleftharpoons M(CO)_2(dam)_2I_2 + CO$$

These reactions are all true equilibria and they are all rapidly attained in solution at room temperature except for the change $W(CO)_3(dam)_2I_2 \rightarrow W(CO)_2(dam)_2I_2$ which requires reflux temperature in chloroform for it to proceed.

All of the complexes have been isolated and the equilibria have been followed both by IR and NMR spectroscopic techniques. In addition, the latter clearly shows that in $M(CO)_3(dam)_2I_2$ both dam molecules are acting as monodentate ligands, in $M(CO)_3(dam)I_2$ the ligand is chelated and in $M(CO)_2(dam)_2I_2$ one is monodentate and one bidentate. Thus the rapid interchange between these complexes confirms the facile cleavage of the chelated dam ring system by either excess ligand or carbon monoxide.

The observation of $M(CO)_3(dam)I_2$ in the iodo system, analogous to the dpe and dpm derivatives, is interesting and as noted above this type of complex could be a reactive intermediate in the other halo–dam systems. The larger iodine atom may be sufficient to slow down the rate of attack of dam on the $M(CO)_3(dam)$ moiety to allow its isolation. If this is the case then the order of reactivities of $M(CO)_3(dam)X_2$ towards excess ligand apparently follows the same trends as noted earlier for the dpe and dpm systems, but the different nature of the product of the reaction in the dpm series is noteworthy.

G. REACTIONS WITH MONODENTATE LIGANDS

The halocarbonyls $M(CO)_4X_2$ react[9–11,13] with the ligands RPh_3 (R = P, As, Sb) to give seven coordinate complexes of the type $M(CO)_3(RPh_3)_2X_2$. In all cases the triphenylphosphine complexes *only* are readily decomposed by refluxing in inert solvents such as dichloromethane to give rather insoluble blue compounds of the general formula $M(CO)_2(PPh_3)_2X_2$. These dicarbonyl derivatives rapidly react with carbon monoxide to reform the original tricarbonyls[23] so that the system is a very efficient carbon monoxide carrier.

$$M(CO)_3(PPh_3)_2X_2 \rightleftharpoons M(CO)_2(PPh_3)_2X_2 + CO$$

The corresponding triphenylarsine- and triphenylstibine-tricarbonyl derivatives could not be decomposed to the corresponding dicarbonyl complexes under any of the experimental conditions investigated.

It could be argued that it is steric interaction from the three phenyl groups of each phosphine that interferes with one of the carbonyl groups causing it to be labile. This would then be consistent with the fact that the arsine- and stibine-tricarbonyl derivatives are stable, exactly as in the comparison of dam with the other phosphorus ligands. Unfortunately, the trend in ease of decomposition of the phosphine tricarbonyl derivatives with varying halogen is not easily reconciled with a steric argument since it is observed that it is the chloro complexes which are most readily decomposed and $W(CO)_3(PPh_3)_2I_2$ which is the most stable.

The structure of the blue dicarbonyl complex $Mo(CO)_2(PPh_3)_2Br_2$ has recently been determined by single-crystal X-ray crystallographic techniques[24]. The complex is monomeric but the ligands are arranged about the metal in a non-octahedral configuration. The molybdenum atom is approximately coplanar with the carbonyl groups and the bromine atoms but the phosphorus atoms, one on either side of the plane containing the other groups, are neither *cis* nor *trans* to each other. The P—Mo—P angle is 127.8°. Unfortunately the structure of the corresponding tricarbonyl complex could not be solved but it is clear from the structure of the dicarbonyl that there will be considerable interaction between the incoming carbonyl group and the phenyl rings of one of the phosphines.

Moss and Shaw[5] observed interesting effects by replacing triphenylphosphine with other phosphines. Triethylphosphine provided a reversible carbon monoxide carrying system very similar to that described above for triphenylphosphine, but the less sterically active dimethylphenylphosphine gave very different results. Complexes of the type $Mo(CO)_3(PMe_2Ph)_2X_2$ readily lost a molecule of carbon monoxide but the products obtained were dimeric $[Mo(CO)_2(PMe_2Ph)_2X_2]_2$ which were formulated as seven-coordinate halogen-bridged species. It could reasonably argued that the formation of such a dimeric complex with triphenylphosphine or triethylphosphine was prevented by steric effects due to interaction of the phenyl rings on the phosphines and this is supported by the fact that with dimethylphenylphosphine it was possible to isolate $Mo(CO)_2(PMe_2Ph)_3X_2$ but all attempts to coordinate a third triphenylphosphine molecule failed[25].

Moss and Shaw[5] also noted that the ease of decomposition of the tricarbonyl complexes $Mo(CO)_3(PMe_2Ph)_2X_2$ decreased in the order $Cl > Br > I$, exactly as in the triphenylphosphine series.

The change in nature of the decomposition product obtained from $M(CO)_3(PPh_3)_2X_2$ and $Mo(CO)_3(PMe_2Ph)_2X_2$ is understandable in terms of steric effects, as is the stability of the corresponding triphenylarsine derivatives in both series. However, the order of stabilities of the phosphine tricarbonyl species with varying halogen, and also the observation[5] that the tungsten complexes $W(CO)_3(PMe_2Ph)_2X_2$ did not decompose at all, do not appear to have a simple explanation in terms of a steric argument. More work is required in the monodentate ligand systems, but on the evidence at present available it does appear that there is a much more delicate balance between steric and electronic effects in monodentate ligand derivatives than in those of the chelating ligands.

H. COMPLEXES WITH OTHER LIGANDS

Nyholm et al.[26–29] have prepared a large number of carbonyl complexes of molybdenum(II) and tungsten(II) containing bidentate and tridentate arsenic ligands. Although there are a number of similarities between their results and those described above it is difficult to make a comparison of the results on steric grounds. There are two reasons for this difficulty; first the ligands used, e.g. diars [*o*-phenylenebis(dimethylarsine)] are rather inflexible and cannot act as only monodentate ligands easily – thus their versatility is less than that of dam in this regard. Secondly the well-known ability of diars to stabilise unusual oxidation states of transition metals results in the formation of a number of complexes of oxidation states III and IV by simple halogen oxidation of the zero valent derivatives. Thus for these reasons it is almost impossible to compare these results with those for dpe, dpm and dam.

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