Low-frequency Infrared Spectra of Some Phosphine-substituted Group VI Metal Carbonyls

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The far-infrared spectra (700—130 cm.$^{-1}$) of phosphine-substituted Group VI metal carbonyl derivatives of the type $M(CO)_{6-x}(PPh_3)_x$, and $M(CO)_{6-2y}$ (Diphos)$_y$, where M = Cr, Mo, and W; $x = 1$, 2, or 3; $y = 1$ or 2, and Diphos = 1,2-bisdiphenylphosphinoethane, are reported. By analogy with the spectra of the parent hexacarbonyls, infrared-active metal–carbon–oxygen bending and metal–carbon stretching modes of vibration are assigned and these occur in the ranges 700—500 and 500—300 cm.$^{-1}$, respectively. Absorptions observed in the region 200—130 cm.$^{-1}$ are tentatively assigned as metal–phosphorus stretching vibrations.

INFRARED spectra of metal carbonyls and their substituted derivatives in the carbonyl stretching region (2150—1700 cm.$^{-1}$) have been studied extensively, but until recently instrumental limitations have prevented detailed investigations of absorptions due to metal–carbon–oxygen bending [δ(MCO)], metal–carbon stretching [ν (MC)], and metal–ligand stretching [ν (ML)] modes of vibration. Whereas carbonyl stretching modes are observed in a unique region of the infrared spectrum, *ca.* 2000 cm.$^{-1}$, both δ(MCO) and ν(MC) vibrations occur within a similar frequency range and fall in a range which is rich in the absorptions due to the vibrations of other attached ligands. As coupling between various vibrations of the same symmetry can then be expected, the spectra will be complex. For our purpose, the term " M–C–O bending mode " is used merely as a convenient name to denote that band which is considered to contain the highest percentage of M–C–O bending character and is " essentially " a metal–carbon–oxygen deformation.

Force-constant calculations for the Group VI metal hexacarbonyls indicate that, at least for these cases, all the ν(MC) modes of vibration occur at lower frequencies than the δ(MCO) vibrations.[1,2] For $M(CO)_6$ the deformation modes occur at 668, 593, and 585 cm.$^{-1}$ and the stretching vibrations at 441, 368, and 374 cm.$^{-1}$, where M = Cr, Mo, and W, respectively. Subsequent work has indicated that this order is retained in octahedral substituted metal carbonyls [3] and for a large range of phosphine-substituted metal carbonyls Adams [4] has suggested that bands in the region 682—468 cm.$^{-1}$ may be assigned as δ(MCO) vibrations. In contrast, a recent study of the Raman and infrared spectra of $Ni(CO)_3(PPh_3)$ [5] has assigned one δ(MCO) vibration at a lower frequency than the ν(MC) mode. However, the differences in stereochemistry and co-ordination number between this compound and the octahedral metal carbonyls discussed above may be significant factors.

As part of our investigations into the infrared spectra of metal–phosphorus compounds, we report the far-infrared spectra (700—150 cm.$^{-1}$) of Group VI metal hexacarbonyls substituted with triphenylphosphine and 1,2-bisdiphenylphosphinoethane (Diphos). δ(MCO) modes of vibration have been reported previously for derivatives containing the chelating phosphine [4] and our band assignments are in agreement. However, no band below 468 cm.$^{-1}$ was reported and the compounds are reinvestigated here over the whole range (700—130 cm.$^{-1}$).

Table 1 summarises the number and types of infrared-active bands expected for each member of the substituted octahedral metal carbonyl series, calculated by use of simple group-theoretical techniques, and based on the assumption that the substituents behave as point sources as far as the symmetry of the whole molecule is concerned.

Metal–Carbon–Oxygen Deformation and Metal–Carbon

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Stretching Vibrations.—Comparison of the observed spectra with those of the free ligands and phosphine-substituted complexes not containing carbonyl groups enabled assignments of infrared-active metal–carbon–oxygen deformation and metal–carbon stretching modes of vibration to be made. The pure hexacarbonyls all exhibit a single peak *ca.* 600 cm.$^{-1}$ owing to δ(MCO) vibrations and the substituted complexes all show a series of one to four peaks in this region. Since the phosphine ligands do not absorb strongly here these peaks are especially clear and it appears likely that they are essentially δ(MCO) vibrations. A further series of bands is observed in the range 500—350 cm.$^{-1}$ although the spectra are more complex owing to the presence of bands associated with the phosphine ligands. Additional bands in this region are tentatively assigned as ν(MC) vibrations. Tables 2 and 3 record the maxima which are assigned as δ(MCO) and ν(MC) vibrations for the triphenylphosphine- and diphosphine-substituted complexes, respectively.

TABLE 1

Infrared-active vibrations of substituted octahedral metal carbonyls

Molecular type	Symmetry group	Species of ν(MC) or ν(CO)	Species of δ(MCO)	Species of (ML)	No. of infrared active modes		
					ν(MC) or ν(CO)	δ(MCO)	(ML)
$M(CO)_6$	O_h	$A_{1g} + E_g + T_{1u}$*	$T_{1g} + T_{2g} + T_{1u}* + T_{2u}$	—	1	1	—
$M(CO)_5L$	C_{4v}	$2A_1* + B_1 + E$	$A_1* + A_2 + B_1 + B_2 + 3E*$	A_1*	3	4	1
trans-$M(CO)_4L_2$	D_{4h}	$A_{1g} + B_{1g} + E_u$*	$A_{2g} + B_{2g} + E_g + A_{2u}* + B_{2u} + E_u$	$A_{1g} + A_{2u}$*	1	2	1
cis-$M(CO)_4L_2$ ...	C_{2v}	$2A_1* + B_1* + B_2$*	$2A_1 + 2A_2 + 2B_1* + 2B_2$*	$A_1* + B_2$*	4	6	2
trans-$M(CO)_3L_3$	C_{2v}	$2A_1* + B_2$*	$A_1* + A_2 + 2B_1* + 2B_2$*	$2A_1* + B_2$*	3	5	3
cis-$M(CO)_3L_3$ ...	C_{3v}	$A_1* + E$*	$A_1* + A_2 + 2E$*	$A_1* + E$*	2	3	2
trans-$M(CO)_2L_4$	D_{4h}	$A_{1g} + A_{2u}$*	$E_g + E_u$*	$A_{1g} + B_{1g} + E_u$*	1	1	1
cis-$M(CO)_2L_4$ ...	C_{2v}	$A_1* + B_2$*	$A_1* + A_2 + B_1* + B_2$*	$2A_1* + B_1* + B_2$*	2	3	4
$M(CO)L_5$	C_{4v}	A_1*	E	$2A_1* + B_1 + E$*	1	1	3

Vibrational modes active in the infrared are marked with an asterisk.

TABLE 2

δ (MCO) and ν (MC) absorption frequencies (cm.$^{-1}$) of triphenylphosphine-substituted complexes

Complex	δ(MCO)			ν(MC)		
	Cr	Mo	W	Cr	Mo	W
$M(CO)_5(PPh_3)$	673s 654s 548m	609s 584vs	—	462s,br 414m	402m,sh 387m,sh 374s,br	—
trans-$M(CO)_4(PPh_3)_2$	671s 640s	629s 580s	621s 575s	477m	394s,br	396s,br
cis-$M(CO)_4(PPh_3)_2$	—	611s 582vs 548m	—	—	452m 444m 412s 376s	—
cis-$M(CO)_3(PPh_3)_3$	—	637s 599s	619s 597m	—	440m 408s	444m 409s

m = Medium, s = strong, sh = shoulder, br = broad, v = very.

Pentacarbonyl Complexes.—Based on the C_{4v} symmetry assumed for $M(CO)_5L$ type complexes, as indicated in Table 1 four δ(MCO) and three ν(MC) infrared-active modes of vibration occur. In the 700—500 cm.$^{-1}$ region three bands are observed for M = Cr and two for M = Mo. Possibly the unobserved peaks are hidden beneath the very intense absorption due to triphenylphosphine at *ca.* 520—500 cm.$^{-1}$ or underneath the broad 584 cm.$^{-1}$ peak in the case of the molybdenum derivative. It is noteworthy that whereas only two δ(MCO) modes are reported for $Mo(CO)_5(PEt_3)$ at 610 and 580 cm.$^{-1,3}$ three bands at 607, 585, and 570 cm.$^{-1}$ are observed for the 1,2,5-triphenylphospholemolybdenum pentacarbonyl complex.[6] This may indicate that the 584 and 580 cm.$^{-1}$ maxima for the triphenylphosphine and triethylphosphine derivatives, respectively, are composed of two components. In the range 470—370 cm.$^{-1}$ two bands attributable to ν(MC) modes of vibration are observed. Again it is likely that the third expected band is hidden by absorptions due to triphenylphosphine. The peaks at 462 and 374 cm.$^{-1}$ for the chromium and molybdenum complexes, respectively, are broad and intense and it appears probable that these are the degenerate *E* vibrations.

Tetracarbonyl Complexes.—The group-theoretical treatment predicts two δ(MCO) and one ν(MC) bands for the *trans*-tetracarbonyl derivatives (D_{4v} symmetry), whereas for *cis* complexes (C_{2v} symmetry) the numbers are six and four, respectively. In the series *trans*-$M(CO)_4(PPh_3)_2$ two bands are observed in the region 700—550 cm.$^{-1}$ and these are assigned as δ(MCO) modes by analogy with the

TABLE 3

δ (MCO) and ν (MC) absorption frequencies (cm.$^{-1}$) of 1,2-bisdiphenylphosphinoethane-substituted complexes

Complex	δ(MCO)			ν(MC)		
	Cr	Mo	W	Cr	Mo	W
$M(CO)_4(Diphos)$	676s 660s,sh 636m	605s 591s 576s	594s 585s 567s	465m,sh 412m 372m	425s 403m 387s 365m	429s 410m 390s 372m
$M(CO)_2(Diphos)_2$	655s 639s 616s 577s	612s 588s 532s,sh	600m 583s 523s,sh	506s 463m,sh 420s	488s 415s	485s,sh 421s

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[6] R. C. Cookson, G. W. A. Fowles, and D. K. Jenkins, *J. Chem. Soc.*, 1965, 6406.

work of Poilblanc and Bigorgne for *trans*-$Mo(CO)_4PEt_3)_2$.[3] Similarly a single broad peak at *ca.* 400 cm.$^{-1}$ is attributed to the ν(MC) vibration. In the spectrum of *trans*-$Mo(CO)_4(PEt_3)_2$ deformation modes are assigned at 631 and 573 cm.$^{-1}$ and the stretching modes at 405 cm.$^{-1}$.

In contrast with the *trans* tetracarbonyls, spectra of the *cis* complexes are considerably more complex and seven or eight bands and shoulders are observed between 650 and 350 cm.$^{-1}$. For the diphosphine complexes Adams [4] has assigned three bands as δ(MCO) modes and suggests that the unobserved peaks lie either beneath the three bands already assigned or occur below 470 cm.$^{-1}$, the lower limit of his observations. It is also possible that additional bands might be overlaid by the intense absorptions due to the phosphine ligands at *ca.* 500 cm.$^{-1}$. For the molybdenum and tungsten complexes four bands were observed in the range 430—365 cm.$^{-1}$ and these are tentatively assigned as ν(MC) modes. They occur at higher frequencies in the chromium complexes.

Tricarbonyl Complexes.—For *cis* tricarbonyl compounds three δ(MCO) and two ν(MC) bands are predicted whereas for *trans* isomers five and three, respectively, are expected. From the two intense carbonyl stretching frequencies observed in the molybdenum complex $Mo(CO)_3(PPh_3)_3$ [7] it was suggested that a *cis* or symmetrical arrangement of carbonyl groups is present; measurements in the far-infrared region for molybdenum and tungsten complexes are consistent with this. Two strong bands occurring at *ca.* 600 cm.$^{-1}$ are assigned as δ(MCO) modes and the third band predicted for *cis* complexes may be hidden underneath the broad phosphine absorption at 510 cm.$^{-1}$. Two maxima at *ca* 400 cm.$^{-1}$ are probably the ν(MC) modes of vibration. The four observed bands are to be compared with the predicted total of five for *cis* isomers and eight for *trans* derivatives. Thus a formulation of the complexes as *cis* isomers is favoured.

Dicarbonyl Complexes.—The δ(MCO) modes have been assigned previously for the molybdenum and tungsten bis-diphosphine dicarbonyl complexes [4] and our spectra agree with this interpretation. A formulation of these complexes as *cis* isomers has been suggested on the basis of two bands in the carbonyl stretching region. The far-infrared spectra are also consistent with the *cis* isomer, three δ(MCO) and two ν(MC) modes of vibraion being observed. The spectrum of the chromium. complex has not previously been reported and indicates the presence of a mixture of *cis* and *trans* isomers. From a total of seven bands in the range 700—350 cm.$^{-1}$, four peaks are attributable to δ(MCO) and three to γ(MC) modes of vibration. In addition, the spectrum of this complex in the carbonyl stretching region shows three maxima, two arising from the *cis* and one from the *trans* isomer.

A comparison of the observed frequencies for different metal atoms indicates that both δ(MCO) and ν(MC) follow the same trend in frequency change as do the pure hexacarbonyls. Thus the increased mass of the central metal atom, caused by the replacement of chromium with molybdenum, is reflected in the considerable decrease in the value of δ(MCO) and ν(MC) frequencies. Similarly, a comparison of the spectra of molybdenum and tungsten derivatives shows that, although the decrease is much less marked, the same tendency is observed for δ(MCO) modes of vibration. In considering stretching vibrations, however, ν(MC) values are very slightly higher in the case of tungsten, an effect noted also with other hexacarbonyls.

Current theories for bonding in metal carbonyl complexes suggest that increasing substitution with relatively poor $d\pi$ acceptors such as phosphines (as compared with carbon monoxide) will lead to an enhancement of the metal–carbon π-bonding in the remaining carbonyl groups with a consequent increase in the metal–carbon bond order and hence ν(MC) and δ(MCO). It can be seen that this trend is generally followed in the triphenylphosphine complexes but that exceptions occur with *cis*-$Mo(CO)_4PPh_3)_2$ and the diphosphine series of derivatives. However, it must be emphasised that, particularly in these cases, not all the predicted peaks are assigned and thus it is extremely difficult to make comparisons.

Similar general frequency trends are noted in the spectra of the halogen oxidation products of these complexes,[8] a lowering of both δ(MCO) and ν(MC) frequencies reflecting an increase in oxidation state. In some cases the lowering of δ(MCO) is sufficient to cause some of the maxima to overlap with the phosphine absorptions at *ca.* 500 cm.$^{-1}$, resulting in spectra of a rather complex nature. These will be reported later in full.

Different stereochemical arrangements do give rise to slightly different absorption patterns of δ(MCO) and ν(MC) frequencies and these measurements provide a useful means of confirming assignments which have previously been suggested on the basis of carbonyl stretching modes of vibration. On the present evidence it appears that δ(MCO) modes are more sensitive to changes in oxidation state, stereochemistry, and degree of substitution than ν(MC) vibrations.

Metal–Phosphorus Stretching Vibrations.—Few assignments of metal–phosphorus stretching frequencies have been made until recently. The first and most conclusive of these is the evidence of Woodward and Hall,[9] based on the Raman spectrum of tetrakistrifluorophosphinenickel(0), $Ni(PF_3)_4$. In this investigation three (A_1) fundamentals are observed at 954, 534, and 195 cm.$^{-1}$ and these are assigned as a P–F stretching mode, a PF_3 " umbrella " vibration, and a Ni–P stretching vibration, respectively. In the investigation of complexes of the type R_3P–AuX and R_3P–AuX_3, where R = alkyl or aryl and X = halogen, bands observed in the range

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400—350 cm.$^{-1}$ are assigned as metal–phosphorus stretching frequencies.[10] More recently a band observed at 192 cm.$^{-1}$ in the Raman spectrum of $Ni(CO)_3PPh_3$ has has been tentatively assigned as a metal–phosphorus stretching vibration.[5] Spectra of various triethylphosphine-substituted platinum complexes have been interpreted to indicate that ν(MP) occurs in the range 442—410 cm.$^{-1}$.[11,12] Finally, the spectra of complexes of the type $MX_2(PPh_3)_2$, where M = Zn^{II}, Cd^{II}, and Hg^{II} (X = Cl, Br, and I) give rise to ν(MP) in the region 170—100 cm.$^{-1}$.[13]

In considering these apparently conflicting assignments it should be emphasised that owing to the differing stereochemistries, electronic configurations, and oxidation states in these complexes it is extremely difficult to make meaningful comparisons. In the investigation of metal–halogen stretching frequencies,[14] the position of the absorption is very dependent upon the oxidation state of the metal. An increase in oxidation state causes a marked increase in frequency. Thus, whereas for $Ni(PF_3)_4$ and $Ni(CO)_3PPh_3$ the nickel atom is present in an oxidation state of zero, the gold complexes above display oxidation states of 1 and 3. Also the nature of the phosphine and degree of phosphine substitution in the complex may have a significant effect on the position of ν(MP). Thus it is quite conceivable that the metal–phosphorus stretching frequencies so far reported are correctly assigned.

TABLE 4

Infrared absorption bands in the 130—230 cm.$^{-1}$ region

Complex	Obs. band centres (cm.$^{-1}$)				
$Cr(CO)_5(PPh_3)$		206w	~230m,br		
$Mo(CO)_4(PPh_3)$		204m	~220m,br		
trans-$Mo(CO)_4(PPh_3)_2$		194m	~220m,br		
cis-$Mo(CO)_4(PPh_3)_2$	160m	173m	191m	200m	~220m,br
trans-$W(CO)_4(PPh_3)_2$		194m	~230m,br		
$Mo(CO)_3(PPh_3)_3$		200w	~230m,br		
$W(CO)_3(PPh_3)_3$		204w	~230m,br		
$Mo(CO)_4(Diphos)$		172m	191s		
$W(CO)_4(Diphos)$		182m	186s		
cis-$Mo(CO)_2(Diphos)_2$		186s	207m		
cis-$W(CO)_2(Diphos)_2$		174m	210m		

For the complexes studied here the metal atoms are all in zero oxidation state and might be expected to display similar values of ν(MP) to that observed for $Ni(CO)_3PPh_3$, although it must be conceded that the stereochemistries are different. The spectra of representative compounds were investigated in the range 230—130 cm.$^{-1}$ with a Michelson interferometer and the observed bands are recorded in Table 4. The triphenylphosphine complexes all show a broad featureless absorption at the upper end of the range 220—230 cm.$^{-1}$ which can be assigned to the δ(CPC) expected from the Raman spectrum of the ligand.[15] The remaining bands are tentatively assigned as metal–phosphorus stretches.

EXPERIMENTAL

Preparation of Complexes.—The complexes $Cr(CO)_5PPh_3$ and $Mo(CO)_5PPh_3$ were prepared by the method of Matthews *et al.*,[16,17] by reaction of the hexacarbonyl and triphenylphosphine in refluxing diglyme.

Direct reaction of triphenylphosphine and the hexacarbonyl at 140—160° afforded the series *trans*-$M(CO)_4(PPh_3)_2$, for M = Cr, Mo, and W,[18] and *cis*-$Mo(CO)_4(PPh_3)_2$ was prepared as described previously.[19] The trisubstituted derivatives were obtained by the reaction of triphenylphosphine with the cycloheptatriene-metal tricarbonyl.[7]

The diphosphine complexes $M(CO)_4(Diphos)$ and $M(CO)_2(Diphos)_2$ were prepared by the method of Chatt and Watson.[20]

Spectral Measurements.—In the range 700—450 cm.$^{-1}$ spectra were measured on a Perkin-Elmer model 221 double-beam spectrometer with a cæsium bromide prism, and for the region 450—200 cm.$^{-1}$ a Grubb–Parsons double-beam grating spectrophotometer, type DM4, Mark II, was employed. Spectra of the complexes were recorded as Nujol mulls supported between polyethylene discs.

A Michelson-type interferometer was used for measurements below 200 cm.$^{-1}$, the samples being prepared as polyethylene pellets.

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