

1065. *Low-frequency Infrared Spectra of Metal Carbonyl Halides and their Derivatives.*

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The infrared spectra of neutral and anionic metal carbonyl halides of Groups VI, VII, and VIII have been studied in the 800—200 cm^{-1} region. Bands due to metal-carbon stretching vibrations and metal-carbon-oxygen bending vibrations are assigned, where possible, by analogy with the infrared spectra of the Group VI hexacarbonyls.

Bands due to metal-chlorine and metal-bromine stretching vibrations have also been located, and splitting of these bands in some of the chlorides has been ascribed to vibrations involving the chlorine-35 and chlorine-37 isotopes. The far-infrared spectra of some substitution products of the manganese carbonyl halides have been studied, and the effect of substitution on the metal-halogen stretching frequencies is discussed.

THE infrared spectra of metal carbonyl halides and their derivatives have been studied extensively in the CO stretching frequency region (*ca.* 2000 cm^{-1}), but the metal-carbon and metal-halogen stretching vibrations [$\nu(\text{MC})$ and $\nu(\text{MX})$] and the metal-carbon-oxygen bending vibrations [$\delta(\text{MCO})$] have received little attention owing to the lack of suitable spectrometers. The infrared spectra of a series of such compounds of the Group VI, VII, and VIII transition metals have now been studied in the 800—200 cm^{-1} region. Some of the results formed the subject of a preliminary communication.¹

The CO stretching frequencies and the force-constants of unsubstituted metal carbonyls decrease markedly with decreasing oxidation state of the metal ($\nu(\text{CO})$ drops *ca.* 100 cm^{-1} per unit drop in oxidation state), while the MC stretching frequencies increase correspondingly. This trend is clear from the data on an isoelectronic series of metal carbonyls, *e.g.* $\text{Fe}(\text{CO})_4^{2-}$, $\text{Co}(\text{CO})_4^-$, $\text{Ni}(\text{CO})_4$, and is assumed to be due to greater $d_\pi-p_\pi$ bonding in the M-CO bond in the lower oxidation states.² For a given series of metal carbonyl halides, $\nu(\text{CO})$ generally increases with the electronegativity of the halogen.³ It is therefore of interest to correlate $\nu(\text{MX})$, $\nu(\text{MC})$ and $\nu(\text{CO})$ vibrations for a closely related series of metal carbonyl halides and to investigate their dependence on the oxidation state of the metal and the electronegativity of the halogen.

The octahedral complexes of general formula $\text{M}(\text{CO})_5\text{X}$ ($\text{M} = \text{Mn}(\text{I}), \text{Re}(\text{I}), \text{Cr}(\text{0}), \text{Mo}(\text{0}),$ or $\text{W}(\text{0})$; $\text{X} = \text{Cl}, \text{Br}$ or I) and $\text{M}(\text{CO})_4\text{X}_2$ ($\text{M} = \text{Fe}(\text{II})$ or $\text{Os}(\text{II})$; $\text{X} = \text{Cl}, \text{Br}$ or I) all contain a metal atom with a d_ϵ^6 electron configuration, and are therefore ideal for this purpose.

Metal-Carbon Stretching Vibrations and Metal-Carbon-Oxygen Bending Vibrations.—Until recently, few unambiguous assignments of $\nu(\text{MC})$ and $\delta(\text{MCO})$ vibrations in metal carbonyls have been made, principally because both types of vibration occur with similar frequencies. There must also be some mixing between bends and stretches of the same symmetry, so that, for example, a $\nu(\text{MC})$ vibration may be only "essentially" a stretching vibration.

However, recent force-constant calculations by Murata and Kawai⁴ and by Jones⁵ on the Group VI hexacarbonyls have clearly demonstrated that, at least in these cases, all the $\nu(\text{MC})$ vibrations lie below the $\delta(\text{MCO})$ vibrations. The relevant figures are reproduced in Table I, together with the CO and MC force constants. These latter clearly indicate that there is a reciprocal relationship between the degree of CO and MC π -bonding. Recent work on tertiary phosphine substitution products of molybdenum hexacarbonyl suggests that

¹ M. A. Bennett and R. J. H. Clark, *Chem. and Ind.*, 1963, 861.

² R. S. Nyholm, Tilden Lecture *Proc. Chem. Soc.*, 1961, 273; E. W. Abel, *Quart. Rev.*, 1963, **17**, 137, 143; and references quoted therein.

³ R. J. Irving and E. A. Magnusson, *J.*, 1956, 1860.

⁴ H. Murata and K. Kawai, *J. Chem. Phys.*, 1957, **27**, 605; *Bull. Chem. Soc. Japan*, 1960, **33**, 1008.

⁵ L. H. Jones, *J. Chem. Phys.*, 1962, **36**, 2375; *Spectrochim. Acta*, 1963, **19**, 329.

TABLE 1.

 $\delta(\text{MCO})$ and $\nu(\text{MC})$ vibrational modes* in Group VI hexacarbonyls in the vapour phase.

	$\delta(\text{MCO})$				$\nu(\text{MC})$			f_{Co}	f_{Mo}
	$\nu_7(t_{1u})$	$\nu_{10}(t_{2g})$	$\nu_{12}(t_{2u})$	$\nu_5(t_{1g})$	$\nu_2(a_{1g})$	$\nu_8(t_{1u})$	$\nu_4(e_g)$		
Cr(CO) ₆	668	562	512	534	390	441	363	17.87	2.03
Mo(CO) ₆	593	506	512	481	392	368	344	18.12	1.81
W(CO) ₆	585	509	520	484	420	374	363	17.70	2.15

* Frequencies in cm^{-1} , force constants in millidynes/Å.

this order of frequencies is retained in substituted octahedral metal carbonyls. For example, the compound *trans*-Mo(CO)₄(P Et₃)₂, which has approximately D_{4h} symmetry, has two infrared-active bands in the 600 cm^{-1} region, but only one in the 400 cm^{-1} region.⁶ This is consistent only with the assignment of the former bands as $\delta(\text{MCO})$ vibrations ($a_{2u} + e_u$) and the latter as a $\nu(\text{MC})$ vibration (e_u) (Table 2). Suggestive evidence that bands in the range 468—682 cm^{-1} in some substituted metal carbonyls are due to $\delta(\text{MCO})$ vibrations has also been advanced recently.⁷

TABLE 2.

Infrared-active vibrations of octahedral metal carbonyls and metal carbonyl halides.

Molecular type	Point group	Species of $\nu(\text{MX})$	Species of $\nu(\text{MC})$ or $\nu(\text{CO})$	Species of $\delta(\text{MCO})$	No. of i.r.-active $\nu(\text{MX})$	No. of i.r.-active $\nu(\text{MC})$ or $\nu(\text{CO})$	No. of i.r.-active $\delta(\text{MCO})$
M(CO) ₆	O_h	—	$a_{1g} + e_g + t_{1u}$	$t_{1g} + t_{2g} + t_{1u} + t_{2u}$	—	1	1
M(CO) ₅ X	C_{4v}	a_1	$2a_1 + b_1 + e$	$a_1 + a_2 + b_1 + b_2 + 3e$	1	3	4
M(CO) ₄ X ₂ (<i>trans</i>)	D_{4h}	$a_{1g} + a_{2u}$	$a_{1g} + b_{1g} + e_u$	$a_{2g} + b_{2g} + e_g + a_{2u} + b_{2u} + e_u$	1	1	2
M(CO) ₄ X ₂ (<i>cis</i>)	C_{2v}	$a_1 + b_2$	$2a_1 + b_1 + b_2$	$2a_1 + 2a_2 + 2b_1 + 2b_2$	2	4	6

Neutral and anionic species of the type M(CO)₅X belong to the point group C_{4v} , and should show three infrared-active $\nu(\text{MC})$ and four infrared-active $\delta(\text{MCO})$ vibrations (Table 2). In fact, five to eight bands and shoulders are seen in the 340—650 cm^{-1} region (Table 3).

TABLE 3.

Absorption bands of the M(CO)₅X and M₂(CO)₁₀ species in the 200—700 cm^{-1} region.

	$\nu(\text{MX})\dagger$	$\nu(\text{MC})$ and $\delta(\text{MCO})$								
Mn(CO) ₅ Cl	295m		403m		456sh	467m	546w	642vs	650sh	
Mn(CO) ₅ Br	218m	405sh	415m	419sh		466w	544w	635vs	650sh	
Mn(CO) ₅ I	< 200	402m	419s			461w	540w-m	630vs	650sh	
Re(CO) ₅ Cl	294m		346s	431w		484w	497sh	556m	592vs	634w
Re(CO) ₅ Br	202m		351s	431w		493w		553m	587vs	
Re(CO) ₅ I	< 200		360s	434w	471w	496w		547w-m	587vs	
Cr(CO) ₅ Cl	257m	411m	437s		472w	499w	553sh	563m	653vs	670w-m
Cr(CO) ₅ Br	< 200*	410m	435s		468vw	502vw		559m	652vs	673s
Cr(CO) ₅ I	< 200	414w	439s		465vw	500vw		557m	653vs	673s
Mo(CO) ₅ Cl	248m		346s	391w	454w	472w		543s	602vs	608sh
Mo(CO) ₅ Br	< 200*		356s	390w		468w		542s	598vs	614s
Mo(CO) ₅ I	< 200		363s	392w		466w		541s	595vs	613s
W(CO) ₅ Cl	258m		355s	410w-m	426w	444w	528w	554s	594vs	
W(CO) ₅ Br	< 200*		365s	408w-m	429w	468w		554s	590vs	603s
W(CO) ₅ I	< 200		368s	410w-m	429w	465w		553s	586vs	600s
Mn ₂ (CO) ₁₀	—		398m		430vw	469s		558w	646vs	
Re ₂ (CO) ₁₀	—		393s		431w	472w	506vw	535w	587vs	

* A preliminary investigation below 200 cm^{-1} indicates that $\nu(\text{M}-\text{Br})$ in these compounds lies in the 160—180 cm^{-1} region.† The frequency quoted refers to the $\nu(\text{M}-^{35}\text{Cl})$ vibration.

Abbreviations; vs = very strong, s = strong, m = medium, w = weak, sh = shoulder.

⁶ R. Poilblanc and M. Bigorgne, *Bull. Soc. chim. France*, 1962, 1301.⁷ D. M. Adams, *J.*, 1964, 1771.

Figs. 1 and 2. On the evidence already presented, the higher frequency bands should be due to $\delta(\text{MCO})$ vibrations, whilst the lower ones should arise from $\nu(\text{MC})$ vibrations. Although the distinction between these band-assignments is not clear-cut, there is a very slight tendency, with a given metal, for $\delta(\text{MCO})$ to decrease, and for $\nu(\text{MC})$ to increase in passing

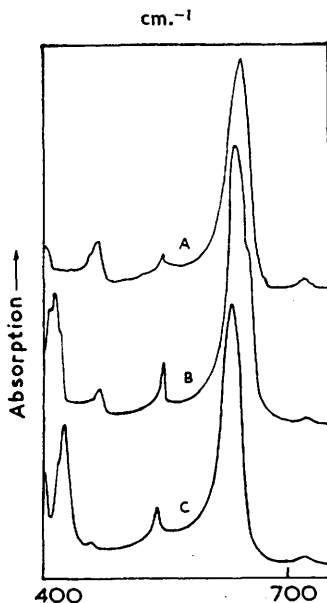


FIG. 1. Infrared spectra of A, $\text{Mn}(\text{CO})_5\text{Cl}$; B, $\text{Mn}(\text{CO})_5\text{Br}$ and C, $\text{Mn}(\text{CO})_5\text{I}$ in the 400—750 cm^{-1} region.

from chloride to bromide to iodide. The $\nu(\text{CO})$ vibrations of $\text{M}(\text{CO})_5\text{X}$ complexes have recently been analysed in detail;⁸ for example, the assignments for $\text{Mn}(\text{CO})_5\text{Cl}$ are; 2138w (a_1^{1b}); 2054s (e); 1999 m (a_1^{1a}), where a_1^{1a} refers to the vibration of the axial carbonyl group, and a_1^{1b} refers to the symmetric vibration of the four carbonyl groups in the plane (frequencies

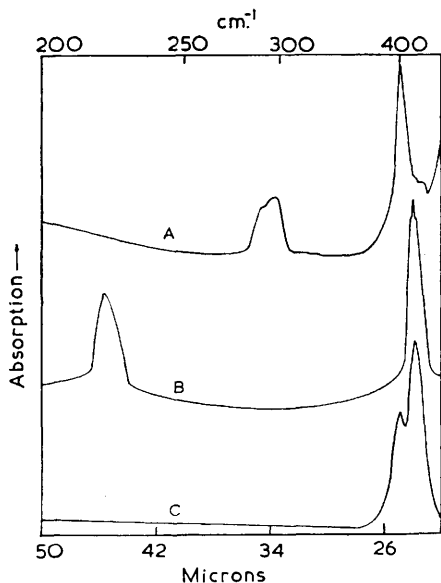


FIG. 2. Infrared spectra of A, $\text{Mn}(\text{CO})_5\text{Cl}$; B, $\text{Mn}(\text{CO})_5\text{Br}$ and C, $\text{Mn}(\text{CO})_5\text{I}$ in the 200—450 cm^{-1} region.

⁸ (a) L. E. Orgel, *Inorg. Chem.*, 1962, **1**, 25. (b) M. A. El-Sayed and H. D. Kaesz, *J. Mol. Spectroscopy*, 1962, **9**, 310.

in cm.^{-1}). (In Table 2 of reference 8a, the labels A_1^{1a} and A_1^{1b} have been interchanged inadvertently). We find that each compound of the type $M(\text{CO})_5X$ has a strong band at *ca.* 400 cm.^{-1} , which can be assigned as the $\nu(\text{MC})$ vibration of e symmetry on the basis of its intensity. This vibration has the same form as the $\nu(\text{MC})$ vibration of t_{1u} symmetry in $M(\text{CO})_6$, and in fact the $\nu(\text{MC})$ vibrations of e symmetry in $\text{Cr}(\text{CO})_5X^-$, $\text{Mo}(\text{CO})_5X^-$ and $\text{W}(\text{CO})_5X^-$ ($X = \text{Cl, Br or I}$) give rise to frequencies close to the $\nu(\text{MC})$ vibrations of t_{1u} symmetry in the corresponding hexacarbonyls ($441, 368$ and 374 cm.^{-1} for $\text{Cr}(\text{CO})_6$, $\text{Mo}(\text{CO})_6$ and $\text{W}(\text{CO})_6$ respectively.) Each carbonyl halide also shows a very strong band in the 600 cm.^{-1} region, which presumably arises from a $\delta(\text{MCO})$ vibration similar in form to the infrared-active $t_{1u}\delta(\text{MCO})$ vibration of the Group VI hexacarbonyls ($668, 593$ and 585 cm.^{-1} for $\text{Cr}(\text{CO})_6$, $\text{Mo}(\text{CO})_6$ and $\text{W}(\text{CO})_6$ respectively).

Further comment is not justified at this stage, particularly with regard to certain of the weak bands and shoulders, which could arise from combination bands or solid-state splittings. However, the close similarity in this region between the spectra of different halides of a given metal is illustrated in Fig. 1 for the manganese derivatives.

It is perhaps significant that the $e \nu(\text{MC})$ vibration of the anionic species $[M(\text{CO})_5X]^-$ lies $7\text{--}34 \text{ cm.}^{-1}$ above that of the corresponding neutral species $[M(\text{CO})_5X]^0$ of the same transition series; the drop in the corresponding $\nu(\text{CO})$ vibration of e symmetry is⁹ about 150 cm.^{-1} . These observations are consistent with current ideas on the degree of π -bonding between the metal and carbonyl groups.² The greater the negative charge on the metal atom, the greater is the degree of $M\text{--CO } d_\pi\text{--}p_\pi$ bonding, and the lower the degree of $\text{CO } \pi$ -bonding; this results in higher $\nu(\text{MC})$ and lower $\nu(\text{CO})$ frequencies.

Complexes of the type $M(\text{CO})_4X_2$ can theoretically occur as *cis*- and *trans*-isomers. Iron carbonyl iodide has been assigned a *cis*-configuration on the basis of its high dipole moment (3.6D) in solution,¹⁰ and an *X*-ray study¹¹ has shown that the ruthenium analogue is also *cis* (the corresponding chloride and bromide are not known at present). The appearance of four carbonyl bands in the infrared spectra of the iron carbonyl halides strongly suggests that all these compounds are *cis*,¹² though the iodo-derivative may partly isomerise on irradiation in solution.^{12b} Osmium carbonyl iodide has been reported to occur in two forms, which may be the expected isomers.¹³ Molecules of the type *cis*- $M(\text{CO})_4X_2$ are expected to show four infrared-active $\nu(\text{MC})$ vibrations and six infrared-active $\delta(\text{MCO})$ vibrations (Table 2), and in fact nine or ten bands are seen in the $650\text{--}360 \text{ cm.}^{-1}$ region of the infrared spectra of the iron carbonyl halides (Table 4). This evidence strongly supports the *cis* configuration

TABLE 4.

Absorption bands of the $M(\text{CO})_4X_2$ species in the $200\text{--}700 \text{ cm.}^{-1}$ region.

	$\nu(\text{MX})$		$\nu(\text{MC})$ and $\delta(\text{MCO})$									
$\text{Fe}(\text{CO})_4\text{Cl}_2$	294m	318m	368w	391w	419m	427m	437sh	502w	570s	583vs	593vs	622w
$\text{Fe}(\text{CO})_4\text{Br}_2$	217m	237m	375w	392vw	422w	430m	440sh	503w	575s	585m	593vs	
$\text{Fe}(\text{CO})_4\text{I}_2$	<200	<200	382w	391w	415w	445m		504w	575s	587m	592vs	631vw
$\text{Os}(\text{CO})_4\text{Cl}_2$	298m	328m	452m	*								
$\text{Os}(\text{CO})_4\text{Br}_2$	$\sim 200\text{m}$	223m	445m	*								

* Insufficient sample available for measurements above 455 cm.^{-1} .

for these compounds, because a total of only three bands would be expected for the *trans* configuration (Table 2). Again, there is no simple way to distinguish between the $\nu(\text{MC})$ and $\delta(\text{MCO})$ vibrations. However, the lowest frequency band under discussion (368 cm.^{-1} in iron

⁹ E. W. Abel, I. S. Butler, and J. G. Reid, *J.*, 1963, 2068.¹⁰ E. Weiss, *Z. anorg. Chem.*, 1956, **287**, 223.¹¹ L. F. Dahl and D. L. Wampler, *Acta Cryst.*, 1962, **15**, 946.¹² (a) C. G. Barraclough, J. Lewis, and R. S. Nyholm, *J.*, 1961, 2582. (b) K. Noack, *Helv. Chim. Acta*, 1962, **45**, 1847.¹³ W. Hieber and H. Stallmann, *Chem. Ber.*, 1942, **75**, 1472.

carbonyl chloride) probably arises from a $\nu(\text{MC})$ vibration, because it occurs 7 cm.^{-1} higher in the bromide and 14 cm.^{-1} higher in the iodide. This trend parallels the corresponding decrease in the four $\nu(\text{CO})$ frequencies observed in the series $\text{Fe}(\text{CO})_4\text{X}_2$, the average values of which are^{12b} chloride, 2120, bromide 2108, iodide 2082 cm.^{-1} . This may be ascribed to the more electronegative halogen withdrawing more charge from the metal, thus reducing the degree of $\text{M-CO } d_{\pi}-p_{\pi}$ bonding. This would cause $\nu(\text{CO})$ to be greatest, and $\nu(\text{MC})$ to be smallest, in the chloride. It must, however, be noted that the trends observed in the other possible $\nu(\text{MC})$ vibrations both for compounds of the type $\text{Fe}(\text{CO})_4\text{X}_2$ and $\text{M}(\text{CO})_5\text{X}$ are a little erratic, and indeed the slight change in the $\nu(\text{CO}) a_1^{1a}$ frequency of $\text{M}(\text{CO})_5\text{X}$ complexes with changing X is the reverse of the expected order.⁸ Insufficient samples of the analogous osmium compounds were available for complete investigation, but only one $\nu(\text{MC})$ vibration appears below 455 cm.^{-1} .

Metal-Halogen Stretching Frequencies.—Table 3 shows clearly that manganese carbonyl chloride has a band at 295 cm.^{-1} , which is completely absent from the spectrum of the corresponding iodide, and from the parent carbonyl. This band is also absent from the spectrum of manganese carbonyl bromide, but a new band appears at 218 cm.^{-1} . Accordingly, these new bands are considered to arise from essentially $\nu(\text{MnCl})$ and $\nu(\text{MnBr})$ vibrations respectively, and this conclusion is substantiated by the observation that the fraction $\nu(\text{MnBr})/\nu(\text{MnCl}) = 0.74$, a value close to that found for the asymmetric stretching vibration (t_2) of a long series of tetrahedral anions of the type¹⁴ MX_4^{n-} (M = first row transition metal; $\text{X} = \text{Cl, Br}$). The $\nu(\text{MX})$ vibration has the same symmetry (a_1) as two of the $\nu(\text{MC})$ vibrations, so that some degree of coupling between them might have been expected (especially to the a_1^{1a} vibration). However there is no evidence to suggest that this is large.

It is somewhat surprising that $\nu(\text{ReCl})$ in rhenium carbonyl chloride (294 cm.^{-1}) occurs at essentially the same frequency as $\nu(\text{MnCl})$ in the analogous manganese derivative. This implies a higher force-constant for the Re-Cl bond than for the Mn-Cl bond, but the reason for any bond-strengthening is not yet clear. The $\nu(\text{ReBr})$ vibration in rhenium carbonyl bromide occurs at 202 cm.^{-1} ; this indicates a lower value of $\nu(\text{MBr})/\nu(\text{MCl}) = 0.69$ for a third-row transition metal. The above result is suggested by simple calculations based on the crude assumption that the M-X portion of the molecule approximates to a diatomic system, and that only the reduced mass alters in passing from chloride to bromide. On the assumption of a mass $M = 55$ (*i.e.* for Mn), then $\nu(\text{MBr})/\nu(\text{MCl}) = 0.81$, whereas if $M = 186$ (*i.e.* for Re), $\nu(\text{MBr})/\nu(\text{MCl}) = 0.73$.

The anionic derivatives $[\text{M}(\text{CO})_5\text{Cl}]^-$ ($\text{M} = \text{Cr, Mo, or W}$), measured as their tetraethylammonium salts, have $\nu(\text{MC})$ vibrations higher than those of the neutral species $\text{M}(\text{CO})_5\text{Cl}$ ($\text{M} = \text{Mn or Re}$) as discussed above, but the $\nu(\text{MX})$ vibrations occur *ca.* 40 cm.^{-1} to lower frequencies, while $\nu(\text{CO})$ vibrations occur $80-150 \text{ cm.}^{-1}$ to lower frequencies.⁹ The dihalogenotetracarbonyl manganate ions $[\text{Mn}(\text{CO})_4\text{X}_2]^-$ ($\text{X} = \text{Cl, Br or I}$), recently isolated as their tetraethylammonium salts,¹⁵ also have their $\nu(\text{CO})$ vibrations at *ca.* 100 cm.^{-1} to lower frequencies than the analogous neutral species¹² $\text{Fe}(\text{CO})_4\text{X}_2$, but $\nu(\text{MnX})$ is in the same position as in $\text{Mn}(\text{CO})_5\text{X}$. These results suggest that $\nu(\text{MX})$, like $\nu(\text{CO})$, is strongly dependent on the oxidation state of the metal in the complex, but that it is relatively unaffected by the overall charge on the octahedral unit. The dependence of $\nu(\text{MX})$ on oxidation state is general, and is well illustrated¹⁴ by the change of the infrared-active t_2 vibration of the anions FeX_4^{n-} ($\text{X} = \text{Cl or Br}$) with n , *e.g.* in the tetraethylammonium salts of FeCl_4^- and FeCl_4^{2-} , the t_2 vibration occurs at 378 and 282 cm.^{-1} respectively, while in FeBr_4^- and FeBr_4^{2-} , the corresponding frequencies are at 290 and 216 cm.^{-1} respectively.

The carbonyl halides of iron, $\text{Fe}(\text{CO})_4\text{X}_2$ ($\text{X} = \text{Cl or Br}$), show two well defined $\nu(\text{MX})$ bands separated by *ca.* 25 cm.^{-1} , each showing a $\nu(\text{MBr})/\nu(\text{MCl})$ ratio of 0.74 (Fig. 3). This observation confirms the *cis*-arrangement for the two halogen atoms, leading to a molecular

¹⁴ R. J. H. Clark and T. M. Dunn, *J.*, 1963, 1198.

¹⁵ E. W. Abel and I. S. Butler, *J.*, 1964, 434.

symmetry of C_{2v} , in agreement with the evidence quoted in the previous section. The $\nu(\text{Fe I})$ vibrational frequencies must lie below 200 cm.^{-1} . Osmium carbonyl chloride also shows two well defined $\nu(\text{MX})$ bands at 298 and 328 cm.^{-1} (*i.e.* frequencies similar to, but slightly higher than, those of the corresponding iron compound), and hence this complex also has the *cis*-configuration. The analogous bromide has one $\nu(\text{MX})$ vibration at 223 cm.^{-1} and a second near 200 cm.^{-1} , the limit of the present instrument. This gives a $\nu(\text{MBr})/\nu(\text{MCl})$ ratio for the osmium compounds of 0.68 , very close to that found for the rhenium compounds.

The $\nu(\text{MCl})$ frequencies reported all refer to the $\nu(\text{M-}^{35}\text{Cl})$ vibration, but with the compounds $\text{Mn}(\text{CO})_5\text{Cl}$, $\text{Re}(\text{CO})_5\text{Cl}$ and $[\text{Et}_4\text{N}][\text{W}(\text{CO})_5\text{Cl}]^-$ a shoulder is apparent at *ca.* 6 cm.^{-1} to lower frequencies, and this is believed to arise from the $\nu(\text{M-}^{37}\text{Cl})$ vibration (the relative abundances of $^{35}\text{Cl}:^{37}\text{Cl}$ are $0.755:0.245$).¹⁶ Conditions are favourable for observing the isotopic splitting of a non-degenerate vibration with manganese, for it has only one stable isotope (mass number 55), but they are not favourable for chromium (with stable mass numbers $50, 52, 53, 54$) or iron (stable mass numbers $54, 56, 57, 58$), where band-broadening

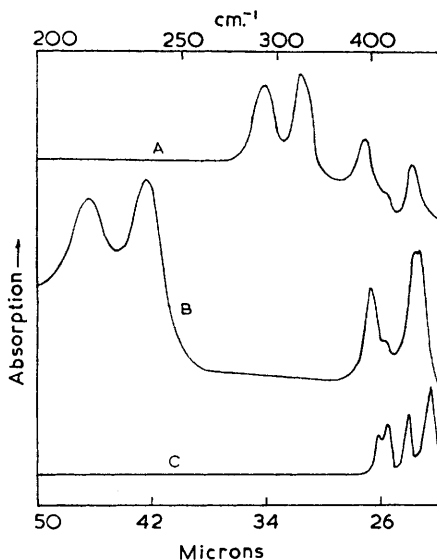


FIG. 3. Infrared spectra of A, $\text{Fe}(\text{CO})_4\text{Cl}_2$; B, $\text{Fe}(\text{CO})_4\text{Br}_2$ and C, $\text{Fe}(\text{CO})_4\text{I}_2$ in the $200\text{--}450 \text{ cm.}^{-1}$ region.

due to the presence of several metallic isotopes would blur the isotopic splittings arising from the chlorine isotopes. Rhenium has two (185 and 187) and tungsten has five ($180, 182, 183, 184, 186$) stable isotopes, but the chlorine isotopic splitting is apparent despite this, because of the lessened influence of a metal of high atomic weight on the reduced mass of the system. Degenerate vibrations would, of course, be ambiguous in this respect, for such vibrations could split as a result of solid-state interactions, but $\nu(\text{MX})$ in the compounds $\text{M}(\text{CO})_5\text{X}$ is non-degenerate (a_1), and thus we feel confident that the splitting observed is indeed isotopic in origin; this conclusion is substantiated by calculations¹ that assume that the system approximates to a diatomic one, with the metal vibrating against ^{35}Cl and ^{37}Cl . As the mass of the metal varies from 50 to ∞ , the isotopic splitting is thereby calculated to vary from 5 to 8 cm.^{-1} (found 6 cm.^{-1}). An isotopic splitting of the $\nu(\text{MX})$ vibration has also been observed¹⁷ in the compound PMe_3AuCl .

Solution Spectra.—It is clearly desirable to obtain the spectra of the carbonyl halides in solution in order to be certain that none of the bands or band splittings arises from solid-state

¹⁶ J. H. Beynon, "Mass Spectrometry and its Applications to Organic Chemistry," Elsevier Publ. Co., Amsterdam, 1960.

¹⁷ G. E. Coates and C. Parkin, *J.*, 1963, 421.

effects. The most soluble of the carbonyl halides, the manganese derivatives, are unfortunately decomposed in electron-donor solvents. Their solubility in solvents in which they are stable is, moreover, not high, and appears to increase in the order $\text{CCl}_4 < \text{benzene} < \text{CHCl}_3 \sim \text{CH}_2\text{Br}_2 < \text{CH}_2\text{Cl}_2$. The infrared spectra in solution indicate essentially no change in the vibrational frequencies from their values in the solid state (Table 5). There is a slight

TABLE 5.

Comparison of solid and solution infrared data for $\text{Mn}(\text{CO})_5\text{Cl}$.*

Solid	CH_2Br_2	CH_2Cl_2	CHCl_3
403	410	407	406
	400sh	400sh	398
295	299	295	301

} $\nu(\text{MC})$ } $\nu(\text{MX})$ * Frequencies in cm^{-1} .

shift to higher frequencies of the lowest $\nu(\text{MnC})$ vibration in solution and a shoulder appears at slightly lower frequencies. The $\nu(\text{MnCl})$ vibration, which is only just observable, appears in the same position in methylene dichloride, but is raised very slightly in the other solvents. The band is insufficiently strong in solution in any solvent to detect the $\nu(\text{Mn-}^{37}\text{Cl})$ vibration. Hence, these considerations give a reasonable justification for the recording of mull spectra, in cases where solubility is insufficient for solution spectra to be obtained.

A further restriction on solution spectra is the requirement that the solvent should not absorb in the spectral region under study. The solvent methylene dibromide is clear in the spectral region of the low frequency instrument ($455\text{--}200\text{ cm}^{-1}$), methylene dichloride has bands at 286 and 455 cm^{-1} , chloroform has a band at 366 cm^{-1} , whilst benzene shows its lowest fundamental (e_{2u}) at 400 cm^{-1} ¹⁸, and a difference band at 300 cm^{-1} (this renders it quite unsuitable for the study of manganese carbonyl chloride in solution).

Manganese carbonyl bromide is less soluble than the chloride in all solvents tried. The $\nu(\text{MnC})$ vibration found at 415 cm^{-1} in the solid (with indications of shoulders both to higher and to lower frequencies) is raised marginally (and probably not significantly) to 416 cm^{-1} in chloroform and benzene, and to 417 cm^{-1} in methylene dichloride without change in band shape. The solubility is, however, insufficient and the instrument insufficiently sensitive near 200 cm^{-1} for any positive identification of $\nu(\text{MnBr})$ to be made in solution.

Substitution Products of Metal Carbonyl Halides.—Partial substitution of CO in metal carbonyls by less strongly π -bonding ligands causes the mean $\nu(\text{CO})$ of the remaining CO groups to decrease.² It is therefore of interest to determine the effect on $\nu(\text{MnX})$ of replacing one or more CO groups in the manganese carbonyl halides by a variety of neutral ligands. This part of the investigation is complicated by the fact that many ligands have fundamental absorptions in the $300\text{--}700\text{ cm}^{-1}$ region, which make the identification of $\nu(\text{MX})$, $\nu(\text{MC})$ and $\delta(\text{MCO})$ vibrations difficult or impossible. For this reason, a detailed analysis of the spectra could not be carried out. Also, the possibilities for coupling between vibrations of the same symmetry are increased by substitution, and metal-ligand stretching vibrations may occur in the $200\text{--}400\text{ cm}^{-1}$ region, *e.g.* see the recent study of $\nu(\text{MN})$ vibrations in metal-pyridine complexes.¹⁹

The results are shown in Table 6. The infrared spectra of these substituted derivatives show several additional bands in the 400 cm^{-1} and 600 cm^{-1} regions, which can be assigned to $\nu(\text{MC})$ and $\delta(\text{MCO})$ vibrations respectively, since they are absent from the spectra of the free ligands. The frequency of the $\nu(\text{MX})$ vibration in the substituted complexes is slightly lower than in the parent carbonyl chloride, the decrease depending on the degree of substitution (as shown by the mono- and bis-triphenylphosphine derivatives). Nitrogen-donor ligands have a greater effect on $\nu(\text{MX})$ than does triphenylphosphine.

¹⁸ W. R. Angus, C. K. Ingold, and A. H. Leckie, *J.*, 1936, 925.¹⁹ R. J. H. Clark and C. S. Williams, *Chem. and Ind.*, 1964, 1317; R. J. H. Clark and C. S. Williams, *Inorg. Chem.*, submitted for publication.

TABLE 6.
Absorption bands of octahedrally substituted derivatives of $\text{Mn}(\text{CO})_5\text{X}$ in the 700—200 cm.^{-1} region.

	$\nu(\text{MX})$		$\nu(\text{MC}), \text{Ligand and } \delta(\text{MCO}) \text{ Vibrations}$															
	$\nu(\text{MX})$	$\nu(\text{MX})$	425w	448m	467m	468m	474m	488m	498m	513m	523s	530w	548w	614sh	619s	633s	642s, br	658s, br
$\text{Mn}(\text{CO})_4(\text{AsPh}_3)\text{Cl}$	312s	396m																
$\text{Mn}(\text{CO})_4(\text{AsPh}_3)\text{Br}$	211w ^b	398w	414w	448m		463m	474s	474s	474s	498m	513m	523s	530w	614sh	619s	633s	642s, br	658s, br
AsPh_3						468m	474s	474s	474s	498m	513m	523s	530w	614sh	619s	633s	642s, br	658s, br
$\text{Mn}(\text{CO})_4(\text{PPh}_3)\text{Cl}$	293w	398m	420sh	427w	467m	490m	498m	498m	498m	513m	523s	530w	548w	614sh	619s	633s	642s, br	658s, br
$\text{Mn}(\text{CO})_4(\text{PPh}_3)\text{Br}$	215m	405w	422w	432m	467m	499w	498m	498m	498m	513m	523s	530w	548w	614sh	619s	633s	642s, br	658s, br
$\text{Mn}(\text{CO})_3(\text{PPh}_3)_2\text{Cl}$	289w	274w	421m	443m	476w ^c	499w	498m	498m	498m	513m	523s	530w	548w	614sh	619s	633s	642s, br	658s, br
$\text{Mn}(\text{CO})_3(\text{PPh}_3)_2\text{Br}$	208w	257w	421m	444w	479w ^c	499w	498m	498m	498m	513m	523s	530w	548w	614sh	619s	633s	642s, br	658s, br
PPh_3	249w	397w	419m	427m		492s	499s	499s	499s	513m	523s	530w	548w	614sh	619s	633s	642s, br	658s, br
$\text{Mn}(\text{CO})_3\text{py}_2\text{Cl}$	279s	350w	385w	433m	469m	496m	498m	498m	498m	513m	523s	530w	548w	614sh	619s	633s	642s, br	658s, br
$\text{Mn}(\text{CO})_3\text{py}_2\text{Br}$	< 200		385w	433m	468m	493m	498m	498m	498m	513m	523s	530w	548w	614sh	619s	633s	642s, br	658s, br
Pyridine				403s														
$\text{Mn}(\text{CO})_3(\text{bipy})\text{Cl}$	262s		418s	441w	472m	530s	530s	530s	530s	530s	530s	530s	530s	530s	530s	530s	530s	530s
$\text{Mn}(\text{CO})_3(\text{bipy})\text{Br}$	284s																	
2,2'-bipyridyl ^d	< 200		418s	439w	473m ^e	531s	531s	531s	531s	531s	531s	531s	531s	531s	531s	531s	531s	531s
$\text{Mn}(\text{CO})_3(p\text{-tol})_2\text{Cl}$	286s	308m	392m	419w	458w	472w	488m	488m	488m	508vs	531s	530s	530s	530s	530s	530s	530s	530s
$\text{Mn}(\text{CO})_3(p\text{-tol})_2\text{Br}$	< 200	304m	390m	418w	456w	470w	487m	487m	487m	503vs	530s	530s	530s	530s	530s	530s	530s	530s
<i>p</i> -toluidine	311m	334m	374s	410w						504vs								

^a Obscured by AsPh_3 band at 312 cm.^{-1} . ^b Ill-defined band. ^c Corrsin, Fax, and Lord, *J. Chem. Phys.*, 1953, 21, 1170. ^d Clark, *J.*, 1963, 1377. ^e Multiple peaks.

EXPERIMENTAL

The following compounds were prepared by literature methods: $\text{Mn}(\text{CO})_5\text{Cl}$; $\text{Mn}(\text{CO})_5\text{Br}$;^{20b} $\text{Mn}(\text{CO})_5\text{I}$;²¹ $\text{Re}(\text{CO})_5\text{X}$ (X = Cl, Br and I);²² $[\text{NEt}_4]^+[\text{M}(\text{CO})_5\text{X}]^-$ (M = Cr, Mo and W; X = Cl, Br and I);^{9, 23} $\text{Re}_2(\text{CO})_{10}$ ²⁴ (starting from ReO_2); $\text{Mn}(\text{CO})_4\text{LX}$ (L = PPh_3 , AsPh_3 ; X = Cl, Br);²⁵ $\text{Mn}(\text{CO})_3(p\text{-toluidine})_2\text{X}$ (X = Cl, Br);²⁵ $\text{Mn}(\text{CO})_3\text{L}_2\text{X}$ (L = $\text{C}_5\text{H}_5\text{N}$, PPh_3 ; X = Cl, Br);²⁰ $\text{Mn}(\text{CO})_3(\text{bipy})\text{X}$ (X = Cl, Br);²⁰ $\text{Mn}(\text{CO})_3[\text{P}(\text{OPh})_3]_2\text{Br}$.²⁰

The compounds, $\text{Fe}(\text{CO})_4\text{Br}_2$, and $\text{Fe}(\text{CO})_4\text{I}_2$ were prepared from iron pentacarbonyl and the appropriate halogen by the literature method,²⁶ isolated quickly from solution, and their infrared spectra measured immediately. The infrared spectrum of a sample of iron carbonyl iodide that had been sublimed ($50^\circ/0.1$ mm.) was identical with that of a sample crystallised from the reaction mixture. The literature method²⁶ of preparing iron carbonyl chloride by passing a slow stream of chlorine into a well-cooled solution of iron pentacarbonyl caused ignition of the latter and was therefore modified. A solution of chlorine in carbon tetrachloride (ca. 2 g. in 20 ml.) was added dropwise under nitrogen to a well-stirred solution of iron pentacarbonyl (ca. 5 ml.) in carbon tetrachloride (30 ml.) at -10° . The yellow-orange product was filtered, washed with light petroleum ($40-60^\circ$), dried in a stream of nitrogen and its infrared spectrum recorded immediately.

The infrared spectra were recorded with a Grubb-Parsons double-beam grating spectrophotometer, type D.M.2 serial number 28, over the range $200-455$ cm^{-1} at 25° . The calibration was carried out at twelve frequencies by reference to the rotational spectrum of water vapour in this region,²⁷ the spectrophotometer being used as a single beam instrument. With standard starting techniques, the correction to the frequency recorded in the chart was less than ± 1 cm^{-1} over the whole range. Spectra above 400 cm^{-1} were recorded on a Grubb-Parsons double-beam grating spectrometer, type GS2A and on a Perkin-Elmer 337 double-beam grating spectrometer, calibrated by reference to the spectrum of indene.²⁸

The spectra of the solid compounds were recorded as Nujol mulls between polythene discs, of up to 0.1 cm. in thickness. The spectra of the manganese carbonyl halides in solution were obtained by sealing the solutions in polythene bags (made from polythene 0.011 cm. thick) in such a way as to ensure that no air bubbles were trapped in the bag. Air bubbles should be removed from the path of the infrared radiation, because they lead to the appearance of interference bands. A compensating polythene bag of pure solvent may be used in the reference beam if necessary; this is, of course, of no value if the solvent itself absorbs in the spectral region under study, owing to loss of sensitivity of the instrument. Polythene itself is transparent in the spectral region under study, except for a weak band at ca. 228 cm^{-1} . Several scans of each spectrum were taken, so that the frequencies quoted should be accurate to ± 2 cm^{-1} .

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