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TRANSITION METAL CARBYNE COMPLEXES

LXII *. VIBRATIONAL STUDY OF $(\text{CO})_5\text{Re}-\text{M}(\text{CO})_4\text{CC}_6\text{H}_5$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) AND OF $(\text{CO})_5\text{Re}-\text{W}(\text{CO})_4\text{CCH}_3$

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Summary

IR ($2200-200\text{ cm}^{-1}$) and Raman ($2200-30\text{ cm}^{-1}$) spectra of $(\text{CO})_5\text{Re}-\text{M}(\text{CO})_4\text{CC}_6\text{H}_5$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) and $(\text{CO})_5\text{ReW}(\text{CO})_4\text{CCH}_3$ were recorded and interpreted. Polarized Raman spectra obtained with single crystals of some of the compounds permitted the assignment of the vibrational bands for these molecules. The vibrational features of the phenyl group and the $\text{M}\equiv\text{C}$ vibration are identical for this series and the $\text{XM}(\text{CO})_4\text{CPh}$ series ($\text{X} = \text{Cl}, \text{Br}, \text{I}$). A comparison of the frequencies of the C—O groups of various compounds permitted a classification of the acceptor/donor behaviour of other groups studied previously.

Introduction

As part of a study of transition metal carbyne complexes by vibrational spectroscopy and in order to permit a better understanding of their physico-chemical properties, particularly interesting because of the existence of the metal—(carbyne)carbon triple bond and the effect of back-bonding of the transition metal atom, we have examined methyl- [2–3] and phenyl-carbynes [4]. Thanks to the polarisation effect observed with single crystals, which is easy to interpret in the case of phenylcarbynes which crystallise in a high symmetry

* For part LXI see ref. 1.

crystal system, we were able to assign practically all the vibrational frequencies expected for these molecules.

In the present paper, we report studies of the Raman and IR spectra of $(\text{OC})_5\text{Re}-\text{M}(\text{CO})_4\text{CC}_6\text{H}_5$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) and of $(\text{OC})_5\text{Re}-\text{W}(\text{CO})_4\text{CCH}_3$ (abbreviated as ReCrPh, ReMoPh, ReWPh and ReWMe, respectively). These compounds have some interesting characteristics. They are carbyne complexes in which the halogen atom in the *trans* position has been replaced by the $(\text{CO})_5\text{Re}$ group to give rise to binuclear carbyne complexes with metal-metal bonding. They also have high molecular symmetry and their axes are oriented in the crystal cell parallel to the binary axis, and we can again use the polarisation effect observed in the Raman spectra of single crystals in assigning the vibrational spectra and comparing them to those of similar compounds, such as $\text{X}(\text{CO})_4\text{MCR}$ or $(\text{OC})_5\text{Re}-\text{M}(\text{CO})_5^-$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) anions.

Structural and theoretical considerations

Structural data

The crystal structure of ReMoPh was determined by Frank [5]. The compound crystallises in the monoclinic system, space group $B2/b$. The unit cell dimensions are $a = 1084.4$, $b = 1042.4$, $c = 1712.7$ pm, $\gamma = 91.2^\circ$, $Z = 4$. The ideal molecular structure (Fig. 1) is analogous to that of the *trans*-halogenophenylcarbynes [5] in which the halogen atom has been replaced by the nucleophilic group $(\text{CO})_5\text{Re}$. It can also be regarded as derived from the dimetallic anions $[\text{M}'\text{M}(\text{CO})_{10}]^-$ ($\text{M}' = \text{Re}, \text{M} = \text{Cr}, \text{Mo}, \text{W}$) [6] in which the axial CO group bonded to M has been replaced by the phenylcarbyne group. However, the phenyl plane in ReMoPh is not in the bisector plane of the equatorial carbonyl group as in the $\text{X}(\text{CO})_4\text{MCPH}$ compounds, but makes angles of 17° and 21° , respectively, with the direction MoC_7O_7 and ReC_2O_2 ; this means that the

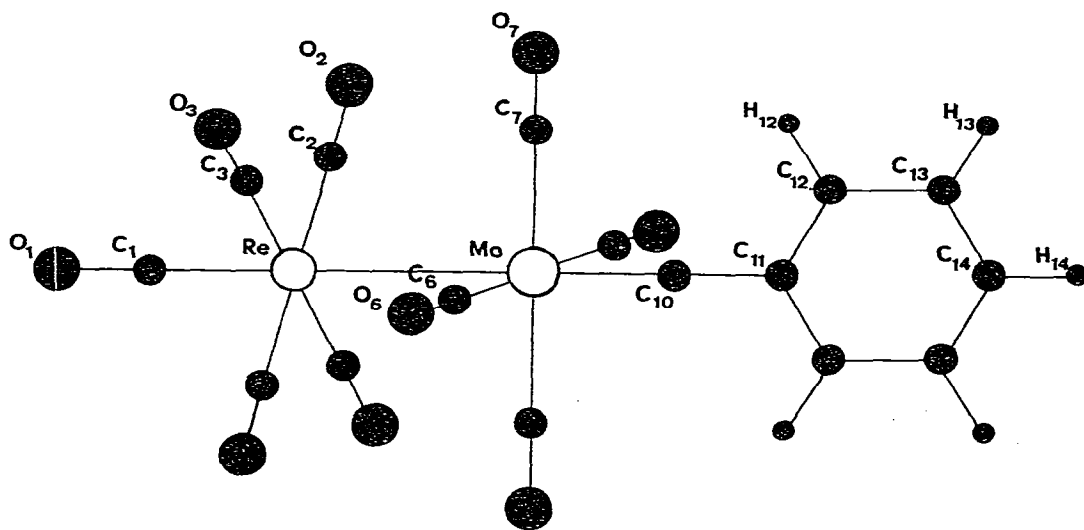


Fig. 1. The idealized molecular structure of $(\text{CO})_5\text{Re}-\text{Mo}(\text{CO})_4\text{CC}_6\text{H}_5$.

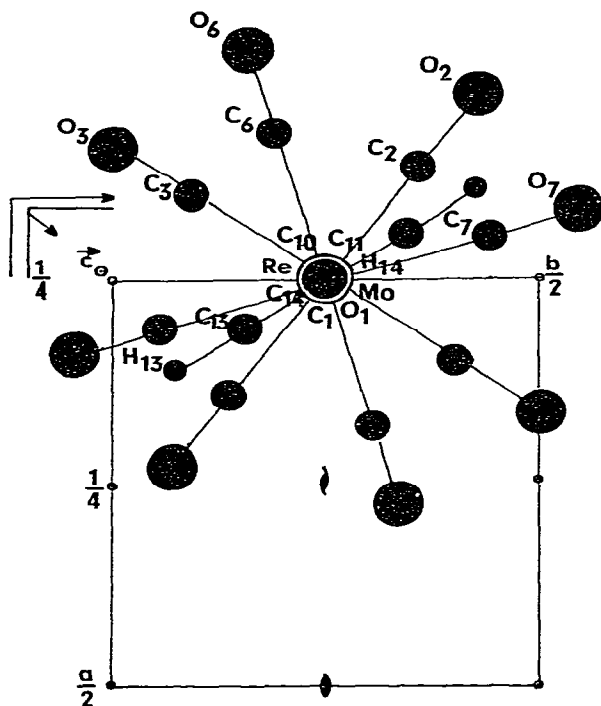


Fig. 2. The crystal structure of $(\text{CO})_5\text{Re}-\text{Mo}(\text{CO})_4\text{CC}_6\text{H}_5$ projected parallel to the binary axis c .

phenyl plane is almost situated in the bisector plane of the dihedral formed by the $\text{Mo}-\text{Re}-\text{C}_2\text{O}_2$ and $\text{Re}-\text{Mo}-\text{C}_7\text{O}_7$ planes (Fig. 2). The site symmetry of the molecule is C_2 . In the crystal the molecules are placed so as to have their axis parallel to the binary axis of the monoclinic cell. For the spectroscopic study, and in particular for the assignment of the observed frequencies, in order to use the group frequencies, the vibrational features of the phenyl group of local symmetry C_{2v} and the dimetallic carbonyl carbyne group $(\text{CO})_5\text{Re}-\text{Mo}(\text{CO})_4$ of local symmetry C_{4v} can be examined separately. The structures of ReWPh and ReCrPh have not been determined but since their IR and Raman spectra are very similar to those of ReMoPh we consider that the series is isostructural.

The compound ReWMe crystallises in the monoclinic system $a = 1831$, $b = 722$, $c = 1501$ pm, $\beta = 128.7^\circ$ Space group $C2/c$ or Cc [7]. We assume that the local symmetries of the dimetallic carbonyl carbyne group and of the Me group are C_{4v} and C_{3v} , respectively. The symmetry of the molecule is C_s by analogy to the known structures of the $\text{X}(\text{CO})_4\text{MCCH}_3$ series.

Numbering of the vibrations

The RePh molecule of C_2 symmetry presents 90 vibrations:

$$\Gamma^{C_2} = 42a + 48b$$

As in the case of the phenylcarbynes [4], we can consider the two parts of the molecule separately: (a) $= -\text{C}_6\text{H}_5$ (local symmetry C_{2v}) and (b) $= (\text{CO})_5\text{Re}-$

$(\text{CO})_4\text{M}\equiv\text{C}$ (local symmetry C_{4v}).

For part (a): $\Gamma_{(\text{Ph})}^{C_{2v}} = 11a_1 + 3a_2 + 6b_1 + 10b_2$

For part (b): $\Gamma_{(\text{b})}^{C_{4v}} = 12a_1 + 3a_2 + 6b_1 + 6b_2 + 15e$

If the symmetry of (b) is lowered to C_{2v} (which would be the case for the ideal molecular structure of ReMPh when the Ph group is situated in the plane of ReMoC_7C_7), we find by correlation:

$$\Gamma_{(\text{b})} = 18a_1 + 9a_2 + 15b_1 + 15b_2.$$

The junction of the two parts gives rise to three internal rotations defined by

$$\Gamma_{(\text{a}'/\text{b})}^{C_{2v}} = 1a_2 + 1b_1 + 1b_2.$$

a_2 is the rotation around the molecular axis; b_1 and b_2 are the other two rotations which can be called by analogy rocking and wagging modes of the Ph group and the rest of the molecule linked together. For ReWMe , we obtain the following results for the (a') = CH_3 group (symmetry C_{3v}): *

$$(\text{a}') : \Gamma_{(\text{Me})}^{C_{2v}} = 3a_1 + 3e$$

The vibrations of the (b) group and of the junction (a'/b) are the same as above. The different vibrational modes of the phenyl and methyl groups have already been described [3,4]. We summarize in Table 1 the various modes of the part (b). Table 2 gives the vibrations of the molecule in its C_2 site symmetry and in the space group C_{2h} for ReMPh . For ReWMe , since it is not possible to carry out the polarisation experiments and since the crystal structure is not known, it is not necessary to give the correlation table.

Experimental results

Recording of the spectra

The IR spectra were recorded with a Perkin-Elmer 580 spectrophotometer over the range $4000\text{--}180\text{ cm}^{-1}$. The samples in the solid state were pressed with CsI or KBr into pellets or mixed with Nujol. Solutions in n-hexane were studied over the range $2200\text{--}1800\text{ cm}^{-1}$ with a Perkin-Elmer 21 spectrometer.

Raman spectra were recorded with a Coderg PH1 spectrometer using the 647.1 nm exciting line of an $\text{Ar}^+\text{--Kr}^+$ Spectra-Physics Laser. The power was limited to 30 mW to avoid the decomposition of the compounds. Polarized Raman spectra were obtained with single crystals of ReMoPh and ReWPh having the form of small plates of dimensions $1 \times 1 \times 0,5\text{ mm}^3$. The morphology of the crystal was determined by the X-ray precession method. The direction perpendicular to the plane of the plate is the binary axis \vec{c} . The other faces frequently observed are (100), (010), (110) and ($1\bar{1}0$). Because of the sensitiv-

* In order to carry out the same analysis for ReMPh and ReMMe , we have divided the molecules at the level of the $\equiv\text{C}\text{--C}$ (Ph or Me) bond. In a previous article [3], on the contrary we included the C atom of the Me group in the carbyne moiety for the numbering of the vibrations. We can easily see that in the present article the junction movements correspond to $\tau(\text{CH}_3)$ (symmetry a_2) and the double degenerate δ^E ($\text{M}\equiv\text{C}\text{--C}$); The third vibration of a_1 symmetry of the --CH_3 group corresponds to $\nu_3^A(\text{C}\text{--CH}_3)$.

ity of the carbyne complexes, which had to be handled under N_2 and at low temperature, it was impossible to cut and polish the crystals. Four polarisations related to the crystal axes were registered: $X(ZZ)Y$, $X(ZX)Y$, $X(YZ)Y$ and $X(YX)Y$. For each compound, several single crystals were examined in order to determine the polarisation effect of each band. For the $ReCrPh$ compound, since we had only a very small quantity of microcrystalline material we could not obtain a good Raman spectrum. Only a few strong bands were observed. For $ReWMe$ the Raman diffusion is weak and no polarisation effect was obtained.

The polarisation effect is only partial; this is due to the fact that the molecules do not present the ideal structure represented in Fig. 1 and also that the x and y axes of the molecules do not coincide with the crystal axes \vec{a} and \vec{b} . Moreover, the crystals we used were imperfect and unpolished. However, the effect was good enough for use in interpretations.

Figures 3 and 4 show the IR spectra of the compounds $ReMoPh$, $ReWPh$ and $ReWMe$ respectively in the region of 2000 cm^{-1} and in the range $1600\text{--}200\text{ cm}^{-1}$. Figure 5 shows the polarized Raman spectra of $ReMoPh$ in different orientations from 2200 to 200 cm^{-1} . Figure 6 shows the polarized Raman spectra in the low-frequency region of $ReMoPh$ and $ReWPh$. Figure 7 shows the unpolarized Raman spectrum of $ReWMe$.

Assignment of the vibrational spectra

When we examine the polarized Raman spectra of both $ReMoPh$ and $ReWPh$ compounds, we notice that the two polarisations YZ and ZX are very similar

(Continued on p. 334)

TABLE 1

VIBRATIONAL MODES OF PART (b): $(CO)_5Re-M(CO)_4\equiv C-$ OF C_{4v} SYMMETRY ^a

Internal coord.	a_1	a_2	b_1	b_2	e
$\nu(C-O)_{eq,Re}$	I	—	—	XIX	XXV
$\nu(C-O)_{eq,M}$	II	—	XIII	—	XXVI
$\nu(C-O)_{ax,Re}$	III	—	—	—	—
$\nu(M\equiv C)$	IV	—	—	—	—
$\nu(Re-C)_{ax}$	V	—	—	—	—
$\nu(Re-C)_{eq}$	VI	—	—	XX	XXVII
$\nu(M-C)_{eq}$	VII	—	XIV	—	XXVIII
$\delta(Re-C-O)_{ax}$	—	—	—	—	XXXIX
$\delta(Re-C-O)_{op}$	VIII	—	—	XXI	XXIX
$\delta(M-C-O)_{op}$	IX	—	XV	—	XXX
$\delta(Re-C-O)_{ip}$	—	XL	XVI	—	XXXI
$\delta(M-C-O)_{ip}$	—	XLI	—	XXII	XXXII
$\delta(C-Re-C)_{eq}$	—	—	XVII	—	XXXIII
$\delta(C-M-C)_{eq}$	—	—	—	XXIII	XXXIV
$\delta(C_{eq}-Re-C_{ax})$	{X	—	—	{XXIV	XXXV
$\delta(C_{eq}-Re-M)$	—	—	—	—	XXXVII
$\delta(C_{eq}-M\equiv C)$	{XI	—	{XVIII	—	XXXVI
$\delta(Re-M-C)_{eq}$	—	—	—	—	XXXVIII
$\nu(M-Re)$	XII	—	—	—	—
$\tau[Re(CO)_4/M(CO)_4]$	—	XLII	—	—	—

^a eq, ax = related to equatorial or axial atoms. op, ip = out of plane, in plane. X = $\delta^{a_1}(C_{eq}-Re-C_{ax})-\delta^{a_1}(C_{eq}-Re-M)$. XI = $\delta^{a_1}(C_{eq}-M\equiv C)-\delta^{a_1}(Re-M-C_{eq})$. XVIII = $\delta^{b_1}(C_{eq}-M\equiv C)-\delta^{b_1}(Re-M-C_{eq})$. XXIV = $\delta^{b_2}(C_{eq}-Re-C_{ax})-\delta^{b_2}(C_{eq}-Re-M)$.

TABLE 2
CORRELATION TABLE FOR ReMPh

Part (b) C_{4v}	Part (a) C_{2v}	Site symmetry C_2	Factor group symmetry C_{2h}
a_1 ($xx + yy, zz$) (Tz)	a_1 (Tz) (xx, yy, zz)	a (Tz) (xx, yy, zz, xy)	A_g (XX, YY, ZZ, XY)
a_2	a_2 (xy)	a (Tz) (xx, yy, zz, xy)	A_u (TZ)
b_1 ($xx - yy$)	b_1 (Tx) (zx)	b (Tx, Ty) (yz, zx)	B_g (YZ, ZX)
b_2 (xy)	b_2 (Ty) (yz)	b (Tx, Ty) (yz, zx)	B_u (TX, TY)
e (Tx, Ty) (yz, zx)			

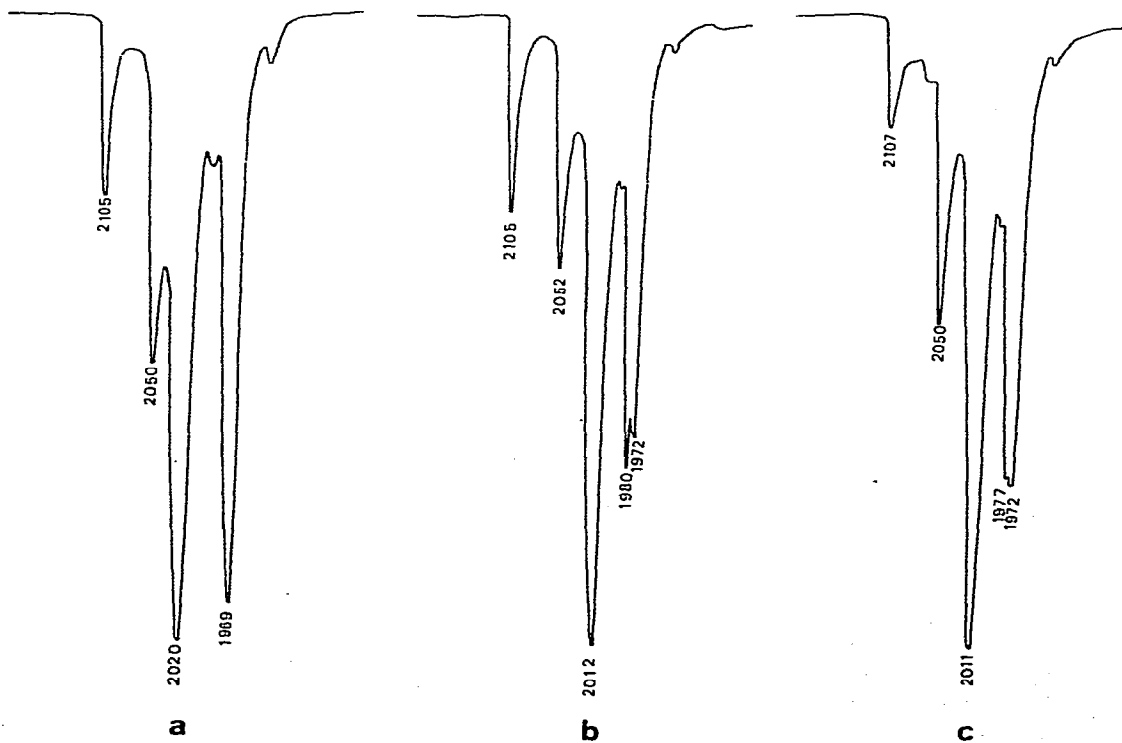


Fig. 3. The IR spectra of ReMoPh (a), ReWPh (b) and ReWMe (c) in n-hexane in the 2000 cm^{-1} region.

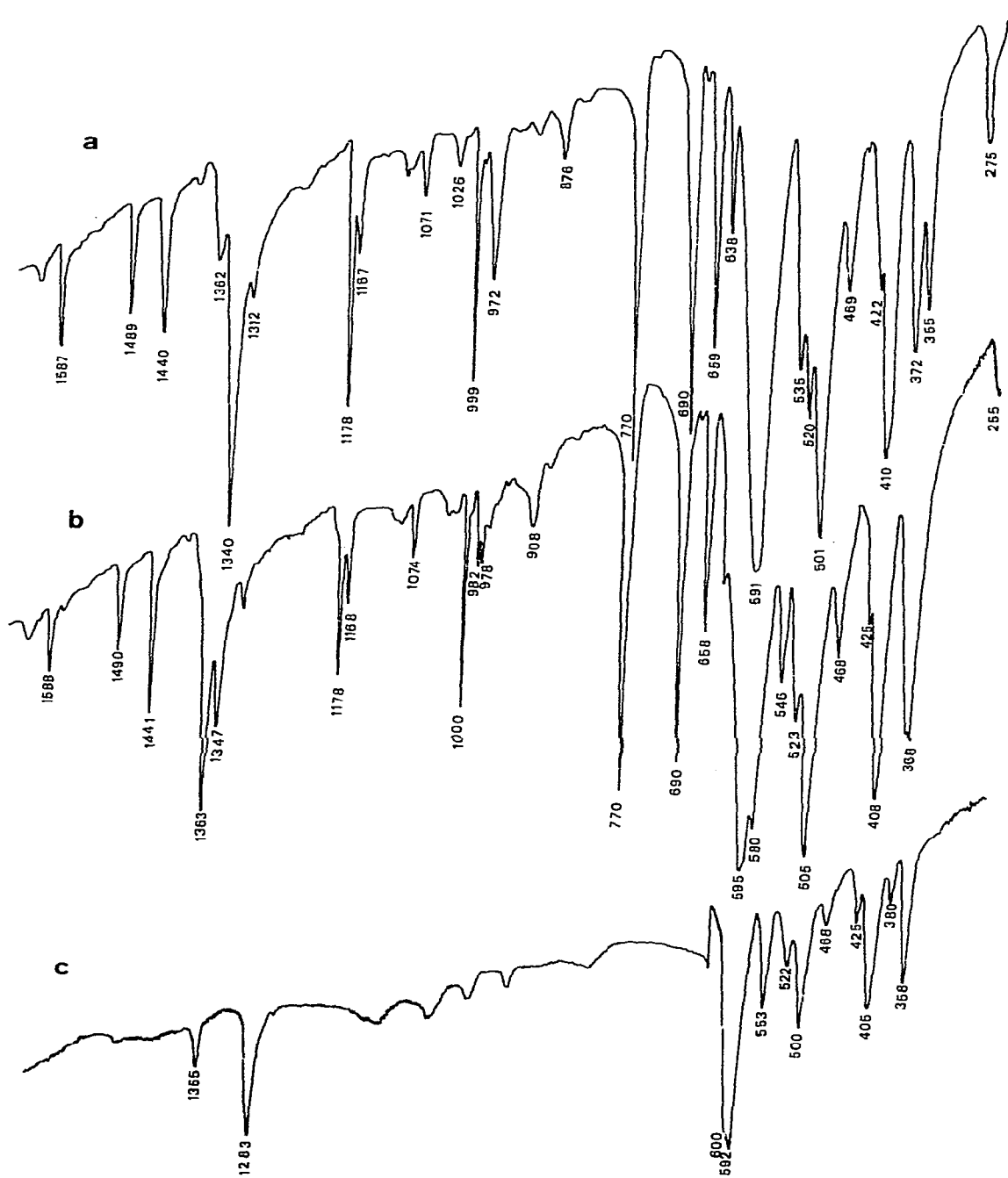


Fig. 4. The IR spectra of ReMoPh (a), ReWPh (b) and ReWMe (c) in ICs pellets in the range 1600–200 cm^{-1} .

TABLE 3

ASSIGNMENT OF THE RAMAN AND IR BANDS OF $(\text{CO})_5\text{Re}-\text{M}(\text{CO})_4\text{CC}_6\text{H}_5$ (M = Cr, Mo, W) AND OF $(\text{CO})_5\text{Re}-\text{W}(\text{CO})_4\text{CCH}_3$

ReCrPh	ReMoPh			ReWPh			ReWMe			Assign- ment	
	Raman	IR	Pol.	Raman	IR	Pol.	Raman	IR	Raman		IR
—	2105s	—	a ₁	2105m	2105s ^a	a ₁	2105m	2105s ^a	2108m	2107s	I
—	—	—	—	2063vv	—	—	—	—	—	—	—
—	2055(sh)	—	a ₁	2052m	2050s ^a	a ₁	2052m	2052s ^a	2052w	2050s ^a	II
—	—	—	b ₁ , b ₂	2022m	—	—	2022m	—	2015m	—	XIX
—	2011vs	—	—	2013vw(sh)	2020vs ^a	—	2013vw(sh)	2012vs ^a	—	2011vs ^a	XXV
—	—	—	—	—	1991vw ^a	—	—	1990vw ^a	—	1988vw ^a	—
—	—	—	b ₁ , b ₂	1983m	—	—	1989m	—	1997m	—	XIII
—	—	—	—	—	—	—	—	—	—	—	—
—	1977(sh)	—	—	1969vw(sh)	1969vs ^a	—	1973vw(sh)	1980vs ^a	—	1972s ^a	XXVI
—	—	—	a ₁	1952s	—	—	1966s	1972(sh) ^a	1979m	1977(sh) ^a	III
—	—	—	—	1948vw	1940vw	—	—	1942vw	—	—	—
—	—	—	—	—	—	—	1743vw	1738vw	—	—	—
—	—	—	—	—	—	—	1654vw	—	—	—	—
—	—	—	—	—	—	—	1639vw	—	—	—	—
—	—	—	—	1623m	1617vw	—	1622m	1620vw	—	—	—
—	—	—	—	—	—	—	1603vw	—	—	—	—
1586vs	1590s	—	a ₁	1587vs	1587m	—	1688vs	1568m	—	—	8a
—	—	—	—	—	1565vw	—	—	1570vw	—	—	8b
—	1580vw	—	—	—	1581vw	—	—	—	—	—	—
1486vs	—	—	a ₁	1489vs	1488m	—	—	1490m	—	—	19a
—	—	—	—	—	—	—	1490vs	19b	—	—	19b
—	1442s	—	—	—	1440m	—	1447vw	1441m	—	—	—
—	—	—	—	—	1393vw	—	1442vw	1395vw	—	—	—
—	—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	1371m	—	—	1379m	—	—	—	—
1344vs	1345s	—	a ₁	1362w	1362w	—	—	—	1355w	1354w	IV
—	—	—	—	1341vs	1340s	—	1368vs	1363vs	—	—	—
—	—	—	—	—	—	—	1364(sh)	—	—	—	—
—	—	—	—	—	—	—	1348vs	1347s	—	—	—
—	1330w(sh)	—	—	1331w	—	—	1334w	1334(sh)	—	—	—
—	—	—	—	1317vw	1312w	—	1319vw	1315w	—	—	14
—	—	—	—	1309vw	—	—	1313vw	—	—	—	—
—	—	—	—	1285vw	—	—	1284w	—	—	—	—
—	—	—	—	—	—	—	—	—	1283w	—	(CH ₃) + IV (ReWMe)
—	—	—	—	—	—	—	—	—	—	1280(sh) 1275m	—

1180m	1254vw	1255vw	1178m	1178m	1178m	1178m	9a
1170(sh)	1180s	1180s	1167w	1167w	1168w	1168w	9b
1130vw	1171vw	1170vw	1130vw	1130vw	1140vw	1140vw	
1095w	1099w	1099w	1099w	1099w	1099w	1099w	1100, 1, vw
1070w	1071w	1071w	1071w	1071w	1074vw	1074vw	18b
1030w	1031vw	1032vw	1026w	1026w	1026vw	1026vw	18a
1002m	1000s	1000s	999m	999m	1000m	1000m	12
980m	980vw	980vw	989vw	989vw	990vw	990vw	5
972(sh)	981vw(sh)	983vw	980vw(sh)	980vw(sh)	982w	982w	17a
945vw	976vw	977vw	972m	972m	978w	978w	
925w	945vw	948vw	935vw, 1	935vw, 1	942vw	942vw	17b
845w	860vw	860vw	910vw	910vw	908w	908w	
770s	850vw	848vw	876w	876w	882vw	882vw	
690m(sh)	770s	770vs	848vw	848vw	848vw	848vw	
675sh	680s	680s	770vs	770vs	770vs	770vs	
668m	638w	638w	690vs	690vs	690vs	690vs	11
638s	610(sh)	610(sh)	672vw	672vw	672vw	672vw	4
606w	590vs	590vs	658s	658s	658m	658m	1
590vs	543vw	543vw	638w	638w	631vw	631vw	6b
560s	523vw	523vw	606w	606w	606w	606w	XXX
540(sh)	505vw	505vw	591vs	591vs	595vs	595vs	(Cz)
505vw	492vw	492vw	535s	535s	580(sh)	580(sh)	VIII
474m	467m	467m	520s	520s	527m	527m	XXXIX
467m	467m	467m	501vs	501vs	509w	509w	ν(C-CH ₃)
	505vw	505vw	504(sh)	504(sh)	557w	557w	XXXII
	492vw	492vw	b ₁ , b ₂	b ₁ , b ₂	546m	546m	IX (Cz)
	474m	474m	b ₁ , b ₂	b ₁ , b ₂	523m	523m	XXXI
	467m	467m	a ₁	a ₁	509w	509w	IX
	467m	467m	a ₁	a ₁	468m	468m	(Mo, W)
	467m	467m	a ₁	a ₁	476vs	476vs	XXI
	467m	467m	a ₁	a ₁	465(sh)	465(sh)	XV (Mo)
	467m	467m	a ₁	a ₁	468m	468m	VI + V
	467m	467m	a ₁	a ₁	468m	468m	V + VI

(continued)

TABLE 3 (continued)

ReCrPh		ReMoPh		ReWPh		ReWMc		Assign- ment
Raman	IR	Raman	Pol.	IR	Raman	Pol.	IR	
--	428m	446m	a ₁	--	--	--	--	VII (Cr, Mo)
--	--	--	--	422m	--	425(sh)	425m	XX
--	--	--	--	--	--	416s	423s	XIX (W)
--	395vs	416m	--	410vs	408vw(sh)	408vs	410m	XXIX
--	--	389m	b ₁ , b ₂	--	400vw	--	--	XIV (Mo)
--	380(sh)	383m	e	--	382m	--	387w	XXVII
--	370(sh)	360vw	--	370m	375w	375(sh)	--	16
--	--	--	--	355m	368vw	368vs	368m	XXVIII
--	--	--	--	--	--	360(sh)	--	--
--	--	281m	a ₁	275m	269m	265m	--	6a
--	--	139s	b ₁ , b ₂	--	137s	--	--	XVIII
--	--	129s	e	--	131s	--	131(sh)	XXXIII
--	--	121w	b ₁ , b ₂	--	121w	--	--	XXIV
--	--	114vs	a ₁	--	110vs	--	116vs	X + XI + XII
--	--	101m	e	--	101m	--	101(sh)	XXXIV
--	--	91vs	a ₁	--	90vs	--	80vs	X + XI + XII
--	--	75vs	e	--	76vs	--	77sh	XXXVI
--	--	61m	e	--	62m	--	62s	XXXVIII +
--	--	44vs	e	--	43vs	--	--	XXXVI
--	--	34vs	a ₁ ?	--	34vs	--	--	XXXVI +
--	--	--	--	--	--	--	--	XXXVIII
--	--	--	--	--	--	--	--	X + XI + XII

^a Values obtained in solutions of CH₂Cl₂ and in Nujol. vs = very very strong, vs = very strong, s = strong, w = weak, vw = very weak, sh = shoulder, l = large.

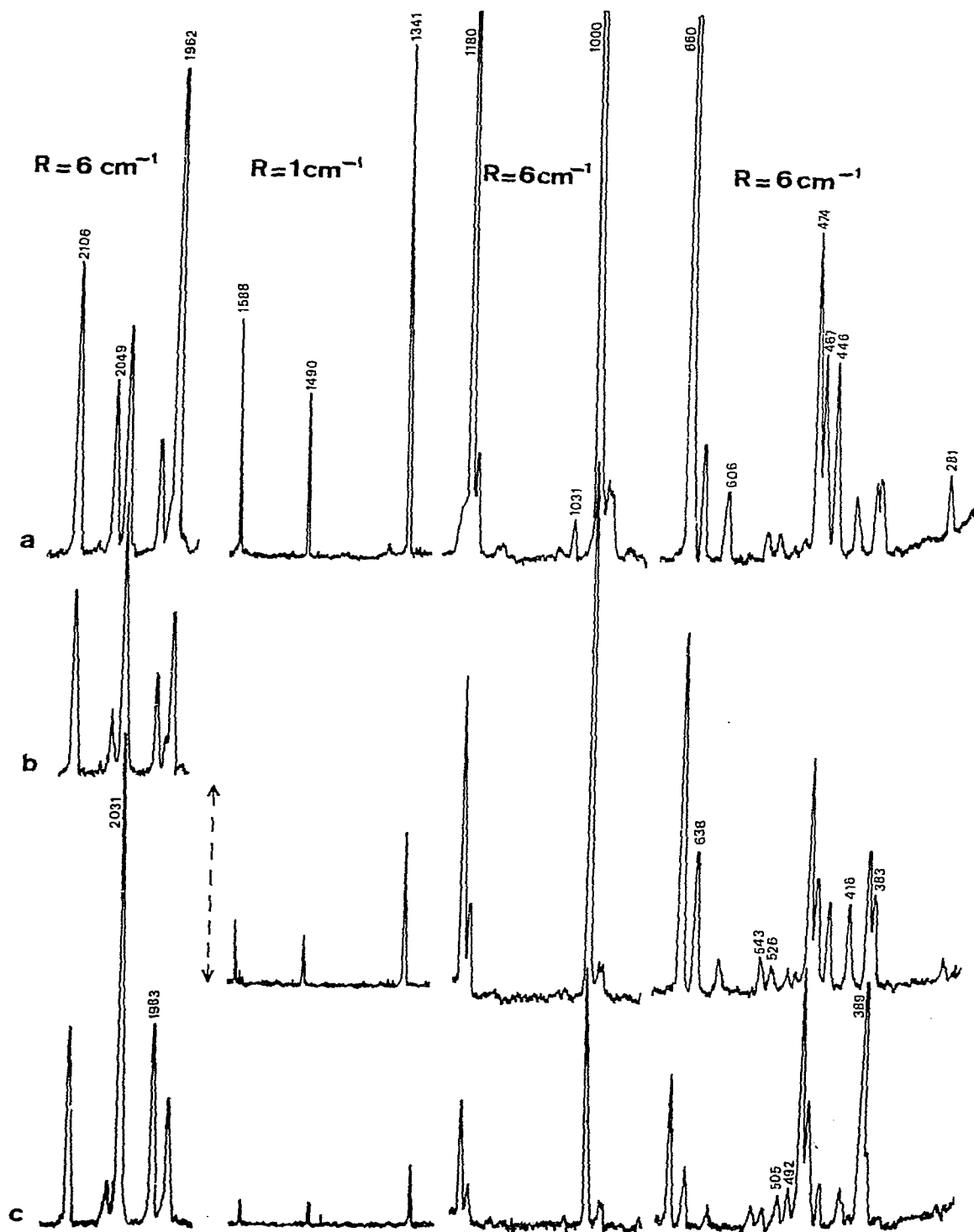


Fig. 5. The polarized Raman spectra of ReMoPh in the range of 2200–200 cm⁻¹: (a) = X(ZZ)Y, (b) = X(ZX)Y and (c) = X(YX)Y polarisations. X, Y, Z are parallel to a, b, c axes of the crystal, respectively. The polarisation X(YZ)Y is very similar to X(ZX)Y and is not shown.

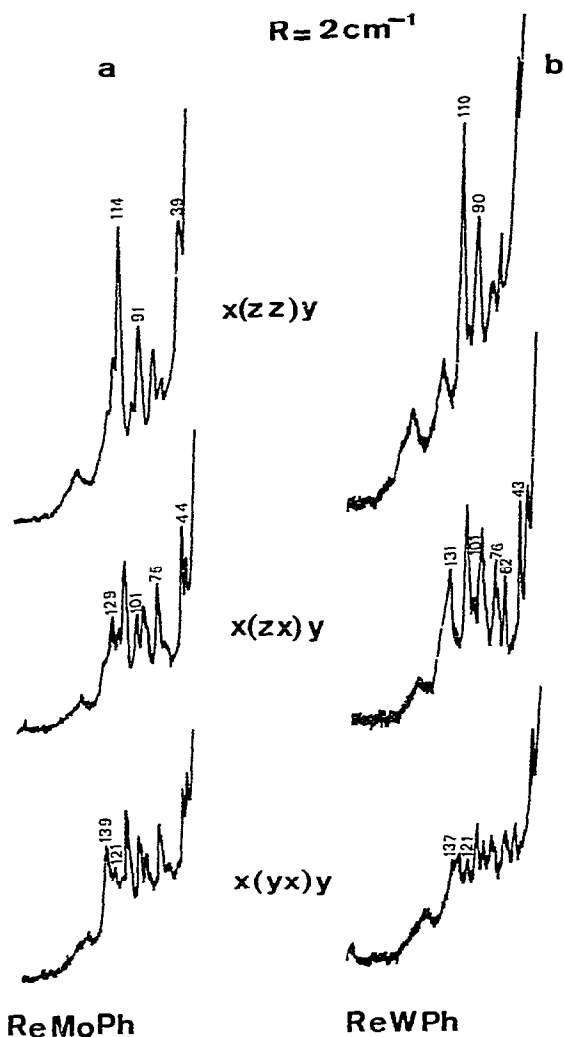


Fig. 6. The polarized Raman spectra of ReMoPh (a) and ReWPh (b) in the low frequency region.

but different from the polarisation XY , which in turn is different from the polarisation ZZ . In addition, the IR and Raman frequencies generally have the same value and the double degenerate vibrations predicted for the local symmetry have only very small splittings. These observations lead us to conclude that the polarisation effects can be interpreted in terms of the local symmetry of the two moieties (a) and (b) for the whole molecule. This is understandable if we notice that the \bar{a} and \bar{b} axes have practically the same length and that the corresponding angle is not very different from 90° (Fig. 2). If the intermolecular interaction is negligible, the \bar{c} axis can be considered as a pseudo-fourfold axis. This is the reason why we shall approximate the symmetry of the crystal to the symmetry of the molecule in the following discussion. The assignment of the vibrational bands can be made by using the polarisation effect and comparing

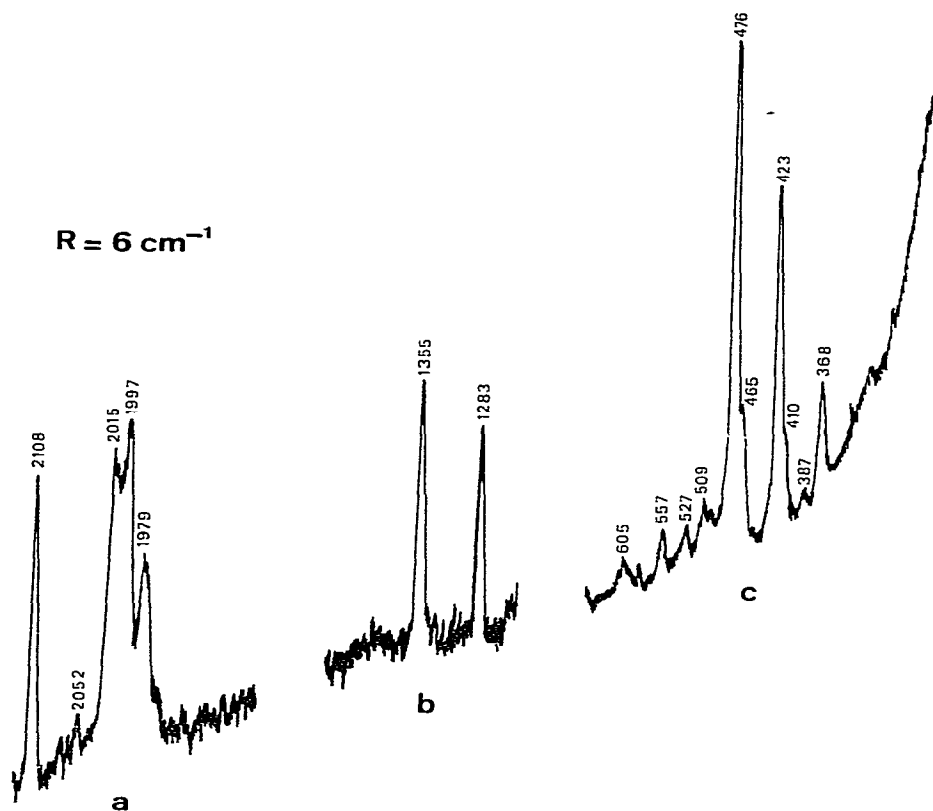


Fig. 7. The unpolarized Raman spectrum of ReWMe in the range 2200–200 cm^{-1} . The scale in (a) and in (b) is 2.5 times smaller than in (c).

the results with the *trans*-halogenocarbonyne series and data from the literature.

Concerning the vibrational features of the phenyl group, we observe that their intensities and frequencies in the XMPH and ReMPH series are identical to within the experimental error. The assignment of the vibrations of the methyl and phenyl groups has been already discussed in previous papers [3,4]; here we examine only the assignment of the bands of the part (b).

In the carbonyl stretching region (2000 cm^{-1}), we expect 7 vibrations: $3a_1 + 1b_1 + 1b_2 + 2e$ corresponding respectively to the modes I, II, III, XIII, XIX, XXV and XXVI (Table 1). In the polarized Raman spectra of ReMoPh (ReWPh), the bands at 2106 (2105), 2049 (2052) and 1962 (1966) cm^{-1} are definitively of a_1 symmetry. They all have their corresponding IR bands except for the band at 1962 cm^{-1} of ReMoPh, which is too near to the very strong IR band at 1969 cm^{-1} to be observed clearly. The band at 1962 (1966) cm^{-1} can be assigned as III, which is usually lower in frequency than the equatorial stretching modes. For the other two bands, the first, with a constant value for the whole series, is assigned as I, while the second, varying with M, is due to the mode II. The doubly degenerate frequencies XXV and XXVI are usually very strong in IR spectra and very weak in Raman spectra. We observe, in fact, two very strong IR bands at 2020 (2012) and 1969 (1980) cm^{-1} . They can be

$$R = 6 \text{ cm}^{-1}$$

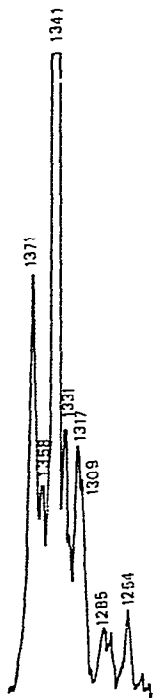


Fig. 8. The satellite Raman bands near the very strong ($\text{Mo}\equiv\text{C}$) peak in the region of 1350 cm^{-1} .

assigned as XXV and XXVI, respectively. In contrast, the respective modes XIII and XIX of b_1 and b_2 -symmetry must be very weak in IR and strong in Raman. The two bands at 2031 (2022) and at 1983 (1989) cm^{-1} correspond to these symmetries. The usual sequence $\nu^{a_1} > \nu^{b_{1,2}} > \nu^e$ of metal carbonyl complexes allow us to assign the high frequency band unambiguously as XIX and the second as XIII. The above assignment is more precise than that made previously for the C—O stretching region [8].

The range $1600\text{--}630 \text{ cm}^{-1}$ is chiefly concerned with the vibrational features of the phenyl group, except for one very strong band due to the vibration IV. As for the previously studied phenyl carbyne complexes [4], the most intense band of the Raman spectrum of ReMPh (two times stronger than the strongest band of the Ph group and about 40 times the C—O stretching vibrations) corresponds to the $\text{M}\equiv\text{C}$ vibration. These bands are situated at $1368\text{--}1348$, 1341 and 1344 cm^{-1} , respectively, for ReWPh, ReMoPh and ReCrPh. The splitting of vibration IV for the complex of tungsten remains unexplained. When we used a high sensitivity to record this range of the Raman spectrum of ReWPh and ReMoPh, we found a series of weak bands (Fig. 8) (about $1/100$ th in intensity of the band IV) near the strong band. They are probably combination bands of IV and very low frequencies of the molecule and the lattice vibrations. This fea-

ture is characteristic of the phenylcarbyne complexes. For the complex ReWMe, we again observe an important coupling between IV and the deformation $\delta_s(\text{CH}_3)$ situated in the same region. The bands at 1355 and 1283 cm^{-1} are assigned as a mixture of IV and of $\delta_s(\text{CH}_3)_4$ modes. As we have seen previously [3], deuteration of XWMe complexes shows that the $\text{M}\equiv\text{C}$ vibration (IV) is, in fact, situated at ca. 1315 cm^{-1} .

In the region 650–300 cm^{-1} appear the stretching vibrations $\nu(\text{Re}-\text{C})$, $\nu(\text{M}-\text{C})$ and the deformation vibrations $\delta(\text{Re}-\text{C}-\text{O})$ and $\delta(\text{M}-\text{C}-\text{O})$. We assume that the vibrations of the same symmetry class are strongly coupled, and only an approximate assignment can be made. In making this assignment, we assume that there are bands which vary with M and others which remain constant for the whole series. In general we assign the first type to the vibration of the $\text{M}(\text{CO})_4$ group, and the second to the vibration of the $\text{Re}(\text{CO})_5$ group. We start with the out of plane deformation $\delta(\text{M}-\text{C}-\text{O})_{\text{op}}$. This deformation gives rise to 3 vibrations IX(a_1), XV(b_1) and XXX(e). For the vibration IX, by analogy with the XMPH (M = Cr, W) series [4], we assign the shoulder at 540 cm^{-1} and the strong bands at 509 cm^{-1} and at 500 cm^{-1} observed in the IR spectra in ReCrPh, ReWPh and ReWMe, respectively, to IX. The corresponding Raman band for ReWPh is found at 509 cm^{-1} and the polarisation is effectively of the a_1 type. The nearest band for ReMoPh is found at 501 cm^{-1} and we assign it as IX (Mo). The band at 492 (496) cm^{-1} found for ReMoPh (ReWPh) is of b_2 or b_1 symmetry. The same value has been observed for $\delta^{b_2}(\text{Cr}-\text{C}-\text{O})_{\text{op}}$ in XCrPh. Consequently we assign it as XV (Mo). The corresponding vibration for ReWPh at ca. 460 cm^{-1} is perhaps hidden by the two strong Raman bands at 472–460 cm^{-1} . The vibration XXX is probably too weak to be observed in our spectra.

The in-plane deformation gives rise to 3 vibrations XLI(a_2), XXII(b_2) and XXXII(e). If the symmetry is rigorously C_{4v} , XLI should be IR and Raman inactive. In fact, only XXXII can be clearly observed at 543 (552) cm^{-1} for ReMoPh (ReWPh) which has the e symmetry. Similarly, a strong IR band is expected at 535 (546) cm^{-1} as for the XMPH series [4]. The IR band at 560 cm^{-1} observed for ReCrPh is by analogy with ReMoPh and ReWPh tentatively assigned as XXXII, although we did not observe the corresponding band in the XCrPh series. If this is so, the shoulder at 610 cm^{-1} found in ReCrPh, and which has its equivalent in the spectrum of XCrPh, can be assigned as XXX.

Concerning the deformation of the $\text{Re}(\text{CO})_5$ group, in addition to the vibrations of the equatorial CO groups, we have a doubly degenerate vibration XXXIX of the axial CO group. The band at 606 (606) cm^{-1} of a_1 symmetry can be assigned as VIII. The band at 505 (504) cm^{-1} of b_1 or b_2 symmetry is due to XXI. The doubly degenerate vibration XXIX must be situated at lower frequency. A band of e symmetry, observed in Raman spectra at 416(408) cm^{-1} , corresponds to a strong IR band at 410 (408) cm^{-1} and can reasonably be assigned to it. This vibration is probably coupled with the doubly degenerate vibration XXXIX which is found at 590 cm^{-1} and also with XXX situated at ca. 460 cm^{-1} .

For the in-plane deformation vibrations, three frequencies are expected. Here again, only the vibration XXXI is clearly observed in IR at 520 (523) cm^{-1} .

while the other two modes (XL and XVI) are too weak to be observed. In the same region, are the stretching vibrations of the Re—C and M—C groups. For the M—C_{eq} stretching vibrations, we expect 3 modes VII(*a*₁), XIV(*b*₁) and XXVIII(*e*). For the Re—C groups, four modes are expected: V(*a*₁), corresponding to Re—C_{ax}, and VI(*a*₁), XX(*b*₂) and XXVII(*e*) corresponding to (Re—C)_{eq}. The vibrations of the same symmetry must couple strongly. So we assign the two bands of *a*₁ symmetry at 474 and 467 cm⁻¹, practically constant for the series, as VI and V. The medium IR band at 422 cm⁻¹ observed for the whole series can reasonably be assigned as XX. The corresponding band in the Cr compound is probably concealed by the band at 428 cm⁻¹ which is assigned as VII (Cr) as we see later. The band at 383 (382) cm⁻¹ can be assigned as XXVII. For the vibration VII, the band at 446 cm⁻¹ of *a*₁ symmetry, observed only for ReMoPh can be assigned to it. The corresponding vibration in the Cr compound was found at ca. 427 cm⁻¹ in XCrPh. Consequently, the band observed at 428 cm⁻¹ for ReCrPh may be due to both XX and VII (Cr). As for XWPh, the mode VII (W) has not been observed in ReWPh.

In the low-frequency region (under 150 cm⁻¹), we expect the various deformations of C—M—C and C—Re—C groups and also the metal—metal stretching mode XII. For the last mode, the very strong and *a*₁-polarized Raman band at 114 (110) cm⁻¹ can be assigned to it, although there must be strong coupling with other modes of *a*₁ symmetry i.e. the deformations X and XI, which are found at 91 (90) cm⁻¹ and at 34 cm⁻¹. The other bands are assigned according to their experimental symmetry types and a provisional assignment is given.

In Table 3, we summarize the assignments of the Raman and IR bands of the compounds studied.

Discussion

Thanks to the polarisation effect observed in single crystals and by comparison with previous reports, we are able to assign the different vibrational bands of the ReMPh series and of the ReWMe compound. Concerning the metal—carbyne bond, we note that the frequency of the series varies in the order W > Cr > Mo, but the small difference between the force constants of the M≡C bond in the Cr and Mo complexes can be in the reverse order, due to heavy atomic mass of Mo. This difference can only be estimated by a complete normal coordinate analysis [9]. The frequency of the W≡C vibration is higher for the ReMPh (1368—1348 cm⁻¹) than for the ReMMe (1355—1283 cm⁻¹) as previously found for the XMPH and XMMe series. However, this frequency remains the same for the XMPH and ReMPh series. The M≡C bond is strong and this is probably the reason why it is not significantly charged by the replacement of the *trans* acceptor. As for XMPH, the vibrational features of the Ph group in ReMPh are independent of the rest of the molecule. This can be attributed to the fact that the single bond C—C(Ph) is weak compared to the triple bond M≡C and consequently the phenyl group can bend or rotate quite easily around the axis of the molecule. This has been observed for the IWPh compound where the angle of the phenyl group with the molecular axis is not 180° but 162° [10].

If we now examine the symmetric frequency of the C—O groups in the

XMPH series and compare them to the same frequency in the ReMPH series, we find that the $\nu(\text{CO})$ in BrWPh for example, is situated at 2129 cm^{-1} and is higher than the same frequency in ReWPh (2052 cm^{-1}). This means that the M—C bond is weaker in the XMPH series than in the ReMPH series and consequently X is a stronger acceptor than the $\text{Re}(\text{CO})_5$ group. If we now compare the different frequencies of the C—O group in the two series ReMPH and $\text{ReM}(\text{CO})_{10}^-$, we see that for the $(\text{Re}-\text{C}-\text{O})_{\text{ax}}$ group, the frequency appears at 1962 cm^{-1} for ReMoPh and at 1925 cm^{-1} for $\text{ReMo}(\text{CO})_{10}^-$ [6]. The $\text{Re}-\text{C}_{\text{ax}}$ bond is weaker in ReMPH than in $\text{ReM}(\text{CO})_{10}^-$. For the equatorial CO groups, the same conclusion is reached, that the $\text{Re}-\text{C}_{\text{eq}}$ bond is weaker in the first series than in the second. For the other CO groups bonded to the M atom, a similar phenomenon is observed. However, we also notice that the frequency $\text{Re}-\text{M}$ is of the same order or even lower in the ReMPH series than in the $\text{ReM}(\text{CO})_{10}$ series ($120[8], 114, 110 \text{ cm}^{-1}$ compared with $146, 130, 109 \text{ cm}^{-1}$ [6]). It thus appears that the carbyne group is much a stronger acceptor than the CO group, and the triple bond $\text{M}\equiv\text{C}$ can weaken not only the *trans* metal—metal bond but also the four equatorial CO bonds situated in the *cis* position.

From the better acceptor character of the carbyne group, we note that the metal carbyne moiety is an even better acceptor than the $\text{M}(\text{CO})_5$ moiety, as can be seen by the weakening of the $\text{Re}-\text{C}_{\text{eq}}$ and $\text{Re}-\text{C}_{\text{ax}}$ bonds in ReMPH compared to $\text{ReM}(\text{CO})_{10}^-$. However, the metal carbyne group is a weaker acceptor than the CO group ($\nu(\text{CO})_{\text{ax}}$ and $\nu(\text{CO})_{\text{eq}}$ in $\text{Re}(\text{CO})_5$ of the ReMPH series are notably weaker than in $[\text{Re}(\text{CO})_6]^+$: 1962 and 2106 cm^{-1} against 2200 cm^{-1} [11]).

Preparative section

ReMPH (M = Cr, Mo, W) were prepared according to ref. 8. Single crystals were obtained by slow crystallisation of the compounds in CH_2Cl_2 or in ether.

ReWMe was prepared in the same way as ReMPH. From 1.75 g (5 mmol) of $\text{NaRe}(\text{CO})_5$ and 1.79 g (5 mmol) of $\text{ClW}(\text{CO})_4\text{CCH}_3$, 2.3 g of yellow-orange crystals (yield: 72%) were obtained. Found: C, 20.38; H, 0.50; Re, 29.70. $\text{C}_{11}\text{H}_3\text{O}_9\text{ReW}$ calcd.: C, 20.35; H, 0.47; Re, 28.68%. Mol. mass: 650 (Mass spec. cf. ^{184}W and ^{187}Re). calcd.: 649.2.

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