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η^1-Allylrhenium pentacarbonyl and η^3-allylrhenium tetracarbonyl; preparations, ^{1}H N.M.R., mass and vibrational spectra

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Summary

$(\eta^1\text{-}C_3H_5)Re(CO)_5$ has been prepared from $[Re(CO)_5]^-$ and photo-decarbonylated to give $(\eta^3\text{-}C_3H_5)Re(CO)_4$. Both allyl complexes have been characterised by ^{1}H n.m.r., mass spectrometry and liquid-phase infrared and Raman spectra. The vibrations of the $Re(CO)_5$ unit in the η^1-allyl compound can be assigned in terms of local C_{4v} symmetry, but such an approximation is not valid for the η^3-allyl compound which must be discussed in terms of overall C_s symmetry. The η^1- and η^3-allyl internal modes are discussed in terms of C_s symmetry

Introduction

The synthesis of $(\eta^1\text{-}C_3H_5)Mn(CO)_5$ from allyl chloride and $[Mn(CO)_5]^-$ and its subsequent photo or thermal decarbonylation to $(\eta^3\text{-}C_3H_5)Mn(CO)_4$ is widely regarded as a classic piece of organometallic synthesis [1]. Wishing to synthesise the two rhenium analogues we were surprised to find that not only was $(\eta^1\text{-}C_3H_5)Re(CO)_5$ [2] a poorly characterised species, but also that apparently it could not be successfully decarbonylated to $(\eta^3\text{-}C_3H_5)Re(CO)_4$ either by heat or by irradiation.

There has been only one previous report [2] of the preparation of $(\eta^1\text{-}C_3H_5)Re(CO)_5$. It was isolated, in a rather impure state, after chromatographic work-up of the reaction between allyl chloride and $Na[Re(CO)_5]$. The yield was only ca. 10%. Since decarbonylation was evidently not a useful route to $(\eta^3\text{-}C_3H_5)Re(CO)_4$, the η^3-allyl complex has been prepared [3,4] by reacting $(\eta^1\text{-}C_3H_5)Sn(CH_3)_3$ with either $Re(CO)_5Br$ in refluxing tetrahydrofuran or $Re_2(CO)_{10}$ in diglyme at 150° for 100 h. It appears that $(\eta^1\text{-}C_3H_5)Re(CO)_5$ is not involved as an intermediate in these reactions

We now report that, contrary to previous belief, pure samples of $(\eta^1\text{-}C_3H_5)Re(CO)_5$ can easily be prepared in at least 90% yield from the reaction of allyl chloride with $Na[Re(CO)_5]$, and that this complex can be conveniently photo-decarbonylated to give $(\eta^3\text{-}C_3H_5)Re(CO)_4$ in very reasonable (ca. 55%) yields. Having prepared these two allylrhenium carbonyls we decided to study their vibrational, n.m.r. and mass spectral features.

Experimental

Preparation of $(\eta^1\text{-}C_3H_5)Re(CO)_5$

A solution of $Na[Re(CO)_5]$ was prepared by stirring a solution of $Re_2(CO)_{10}$ (0.326 g, 0.5 mmol) in nitrogen-saturated anhydrous tetrahydrofuran (10 cm^3) with 0.5% sodium amalgam (2 cm^3) at 0° for 1 h, under dry nitrogen. After removal of the excess amalgam, allyl chloride (1.0 cm^3), saturated with dry nitrogen, was added. A colourless precipitate of sodium chloride formed quickly, and after 5 min. all the $[Re(CO)_5]^-$ had been consumed, (as shown by the absence of anion ν(CO) i.r. bands). Removal of solvent at 20°/15 mm., followed by distillation (30°/0.1 mm) gave a very pale straw coloured liquid product. (Yield: 0.340 g, 92%. Found: C, 26.4; H, 1.39. $C_8H_5O_5Re$ calc.: C, 26.2; H, 1.37%).

Preparation of $(\eta^3-C_3H_5)Re(CO)_4$

A solution of $(\eta^1-C_3H_5)Re(CO)_5$ (0.260 g) in anhydrous n-pentane ($75\ cm^3$) was irradiated for 1 h. under dry nitrogen in a conventional water-cooled quartz photochemical reactor. The irradiation source was a 100 watt medium pressure mercury lamp. The reaction was monitored by observing the decay of the i.r. ν(CO) bands of the pentacarbonyl and the growth of bands ascribed to the tetracarbonyl. Prolonged irradiation caused no further change. Removal of the solvent (20^o/15 mm) followed by two vacuum sublimations on to a cold finger cooled with solid CO_2 gave the product as fine colourless crystals. (Yield: 0.132 g, 55%. Found: C, 24.0; H, 1.38. $C_7H_5O_4Re$ calcd.: C, 24.8; H, 1.49%). A 37% yield of pure $Re_2(CO)_{10}$ could be obtained from the residue after sublimation.

Infrared spectra were recorded on a Perkin-Elmer 597 spectrophotometer as liquid films between CsI plates, or as solutions in CCl_4, C_6H_{12} or pentane. Raman spectra of liquid $(\eta^1-C_3H_5)Re(CO)_5$ or a solution in benzene and of $(\eta^3-C_3H_5)Re(CO)_4$ held just above its melting point of 32^o were recorded using a Spex 1401 spectrometer in conjunction with a Spectra-Physics 125 He-Ne laser having an output of ca. 50 mW at 632.8 nm. Spectra were calibrated by means of several lines of the neon gas emission spectrum and from known indene peaks. Depolarisation ratios were measured by examining the spectrum with the plane of the polarised light parallel and perpendicular, respectively, to the axis of an analyser. The vibrational frequencies quoted, apart perhaps from a few very weak or broad features, are accurate to at least $\pm 2\ cm^{-1}$. N.m.r. spectra in $CDCl_3$ were measured on a Jeol PS 100 spectrometer with tetramethylsilane as internal standard. Mass spectra were recorded using an A.E.I. MS 12 spectrometer. Samples were introduced via an all-glass inlet system, and an ionisation energy of 70 eV was employed. Ion abundances are expressed relative to a rhenium-containing base peak of 100 units.

Results and Discussion

Reaction between $Na[Re(CO)_5]$ and allyl chloride had previously been stated [2] to give a low yield (ca. 10%) of impure (n.m.r. evidence)

(η^1-C_3H_5)Re(CO)$_5$. Using basically the same method with variations in reaction times, but replacing a chromatographic purification step by vacuum distillation we have achieved at least a 90% yield of pure (η^1-C_3H_5)Re(CO)$_5$. As well as employing the established method of sodium amalgam cleavage of the metal-metal bond in $Re_2(CO)_{10}$, we have also explored the potential use of Li[$(C_2H_5)_3BH$] [5], potassium hydride [6]and sodium-potassium alloy [7] for this purpose. Only when the alloy is employed is $[Re(CO)_5]^-$ formed in appreciable concentration, but the reaction proceeds very slowly. None of the above reagents are therefore superior to sodium amalgam. The reaction conditions quoted in the literature for sodium amalgam cleavage of $Re_2(CO)_{10}$ [2,7,8] vary considerably, but we find that an optimum concentration of $[Re(CO)_5]^-$ is achieved after 1 h. at 0°. Extending the reaction time produces other unidentified carbonyl species (ν(CO) i.r. bands at 1969, 1920, 1885 cm^{-1}) and the $[Re(CO)_5]^-$ concentration declines.

(η^1-C_3H_5)Re(CO)$_5$ is a very air-sensitive liquid at room temperature, decomposing to a pale yellow solid within a few minutes. Although this solid has not been characterised, mass spectral evidence shows that it contains a component with Re_2 units. The η^1-allyl can be stored at room temperature in sealed ampoules under nitrogen for at least several weeks.

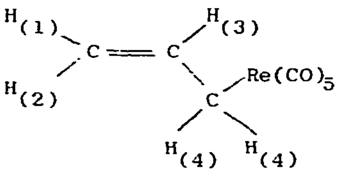
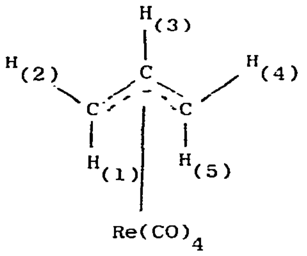
Previous workers [2] suggested that the pentacarbonyl could not be decarbonylated to give (η^3-C_3H_5)Re(CO)$_4$. We have now shown however that (η^3-C_3H_5)Re(CO)$_4$ (m.p. 32°) can be prepared in acceptable yield (*ca*. 55%) by photochemical decarbonylation of the η^1-allyl. Using the conditions described above decarbonylation appears to be in competition with allyl cleavage as $Re_2(CO)_{10}$ (*ca*. 37%) is also produced, presumably by coupling of $Re(CO)_5^{\bullet}$ radicals. Both allyl compounds have been fully characterised using ^{1}H n.m.r., mass and vibrational spectroscopic methods.

(a) N.m.r. results

The ^{1}H n.m.r. spectrum of (η^1-C_3H_5)Re(CO)$_5$, recorded in $CDCl_3$, although similar to that reported previously [2], is of superior quality in that all possible first order coupling constants are obtainable. The spectrum is of the expected $ABCX_2$ type and details are given in Table 1.

TABLE 1

^{1}H N.M.R. SPECTRA

Compound	Chemical shift (δ) (multiplicity)	Assignment (rel.intensity)	Coupling constants (Hz)
	6.34 (12)	$H_{(3)}$ (1)	J_{23} 16.5
	4.65 (10)	$H_{(2)}$ (1)	J_{13} 9.5
	4.34 (12)	$H_{(1)}$ (1)	J_{34} 8.5
	1.85 (8)	$H_{(4)}$ (2)	J_{12} 2.0
			J_{24} 1.0
			$J_{14} \sim 0.5$
	4.73 (tt)	$H_{(3)}$ (1)	J_{13} 12.0
	2.89 (dt)	$H_{(2)},H_{(4)}$ (2)	J_{23} 7.2
	1.90 (dt)	$H_{(1)},H_{(5)}$ (2)	$J_{12} = J_{14}$ 1.5

tt = triplet of triplets

dt = doublet of triplets

The ^{1}H n.m.r. spectrum of $(\eta^{3}-C_{3}H_{5})Re(CO)_{4}$ has previously been obtained [9], both in a nematic liquid-crystal and in an isotropic phase. It was concluded from a consideration of the dipolar coupling constants that the protons of the allyl group do not all lie in one plane. Our results (Table 1) agree well with those previously obtained in $CDCl_{3}$, the symmetrical η^{3}-allyl group giving a simple AM_2X_2 type of spectrum with spectroscopic equivalence of the syn and of the anti protons.

(b) Mass Spectra

The metal-containing ions observed in the mass spectrum of $(\eta^1-C_3H_5)Re(CO)_5$ are listed in Table 2, such ions being clearly identified by the isotopic ratio $^{187}Re : ^{185}Re = 1 : 0.59$. The molecular ion is present and there are two

TABLE 2

MASS SPECTRA (^{187}Re-containing ions only)

Ion	$^m/_e$	$(\eta^1-C_3H_5)Re(CO)_5$ R.I.	$(\eta^3-C_3H_5)Re(CO)_4$ R.I.
$(C_3H_5)Re(CO)_5^+$	368	28	-
$(C_3H_5)Re(CO)_4^+$	340	81[b]	65
$(C_3H_5)Re(CO)_3^+$	312	50[b]	28[b]
$(C_3H_5)Re(CO)_2^+$	284	46[b]	44[b]
$(C_3H_5)Re(CO)^+$	256	15	14
$(C_3H_5)Re^+$	228	9.0	11
$(C_3H_3)Re(CO)_2^+$	282	100[a]	100[a]
$(C_3H_3)Re(CO)^+$	254	37[a]	34[a,b]
$(C_3H_3)Re^+$	226	52[a]	40[a]
$Re(CO)_5^+$	327	35	-
$Re(CO)_4^+$	299	65[b]	1.6
$Re(CO)_3^+$	271	61	6.0
$Re(CO)_2^+$	243	20	6.0
$Re(CO)^+$	215	11	3.0
Re^+	187	22	11

[a] Relative intensities also involve contributions from $(C_3H_5)^{185}Re\,(CO)_x$;

[b] Metastable supported

primary fragmentation pathways involving either stepwise loss of carbon monoxide with final cleavage of the allyl group or initial loss of allyl followed by stepwise loss of carbon monoxide. In this respect the spectrum is reminiscent of those of $Re(CO)_5X$ (X = Cl or I) [10] where initial CO or X loss are competing primary fragmentation processes. As expected, $[(C_3H_5)Re(CO)_4]^+$ is a very abundant ion in the spectrum. Several carbonyl fragmentation steps are supported by the observation of appropriate metastables, (see Table 2).

By a consideration of the rhenium isotopic ratio it is clear that peaks at $^m/e$ 284, 282 (base peak) and 280 are associated with the ions $[(C_3H_5)Re(CO)_2]^+$ and $[(C_3H_3)Re(CO)_2]^+$. The ions $[(C_3H_3)Re(CO)_x]^+$, (x = 2, 1 or 0), are of high abundance in the spectrum and must arise by loss of two hydrogens from the allyl group bound to the metal. Similar eliminations have been observed in the spectra of $[Rh(\eta^3\text{-}C_3H_5)(\mu\text{-}Cl)]_2$ [11], $[W(CO)_3(\eta^5\text{-}C_5H_5)(\eta^1\text{-}C_3H_5)]$ and $[W(CO)_2(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_3H_5)]$ [2] and $[Mo(CO)_2(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_3H_5)]$ [12]. Indeed for the last three complexes the most abundant metal-containing ion is $[M(\eta^5\text{-}C_5H_5)(C_3H_3)]^+$. In line with previous proposals [11] we believe that the abundance of such ions can be explained by their formulation as cyclopropenyl-metal species.

The mass spectrum of $(\eta^3\text{-}C_3H_5)Re(CO)_4$, run using similar operating conditions as employed for the η^1-allyl compound, shows that the fragmentation pathway of stepwise loss of carbon monoxide with retention of the allyl group is much favoured over that involving initial fragmentation of the allyl followed by stepwise carbon monoxide loss. Thus all $[Re(CO)_x]^+$ ions (x = 0-4) are of low abundance. Metal-containing ions are given in Table 2, together with observed metastables. Cyclopropenyl-rhenium ions containing two or less carbonyl groups are again prominent. The relative intensities given are those of a spectrum recorded soon after sample insertion, some minor changes being observed with time. In particular weak peaks are observed at $^m/e$ 654 and at [654-n(28)] (n = 1-10) associated with the formation of $[Re_2(CO)_x]^+$, (x = 0-10), in the spectrometer, ($^m/e$ for ^{187}Re isotope).

(c) Vibrational Spectra

It was surprising to find that vibrational data were not available for either allyl species, apart from a list of i.r. ν(CO) frequencies for the η^3-allyl complex in a supplementary publication associated with Ref.[3]. We have now obtained fairly extensive i.r. and Raman data on both compounds. As $(\eta^1\text{-}C_3H_5)Re(CO)_5$ is a liquid at room temperature and $(\eta^3\text{-}C_3H_5)Re(CO)_4$ has a melting point of only 32°, liquid phase spectra of these molecules with Raman polarisation measurements are easily obtained. The results are therefore amenable to analysis as correlation and factor-group splittings are eliminated.

$(\eta^1\text{-}C_3H_5)Re(CO)_5$

Although the vibrational spectra of few η^1-allyls have been examined, useful information is available for $M(\eta^1\text{-}C_3H_5)_4$ (M = Si or Sn) [13], $Hg(\eta^1\text{-}C_3H_5)_2$ [14] and the allyl halides [15]. The vibrational spectrum of $(\eta^1\text{-}C_3H_5)Mn(CO)_5$ has also been reported [16], but due in part to a lack of polarisation data some of the assignments, particularly in the δ(MnCO) and ν(MnC) region, seem erroneous. Some comments to this effect are made below.

In analysing the vibrational spectra of many organometal carbonyls the concept of local symmetry has been employed. For $(\eta^1\text{-}C_3H_5)Re(CO)_5$ the local symmetry of the isolated allyl group is C_s and that of the $Re(CO)_5$ unit C_{4v}. Table 3 lists the numbers and symmetries of the normal modes for the allyl group and for the $Re(CO)_5X$ unit (X = bonded C of the η^1-allyl group).

(i) The ν(CO) region

The bands observed are listed in Table 4. The assignments are in line with those reported for other $LM(CO)_5$ systems in that the ν(CO) frequencies decrease in the order A_1 (eq) > B_1 > E > A_1 (ax), where A_1 (eq) is an in-plane motion of the four equatorial CO groups and A_1 (ax) relates to the stretching of the unique CO group. In the i.r. spectrum the band intensities decrease in the expected [17] order E > A_1 (ax) >> A_1 (eq) >> B_1, the B_1 mode being formally inactive. Its appearance is indicative of a small

TABLE 3

VIBRATIONS OF AN ISOLATED η^1-ALLYL LIGAND (C_s) AND OF AN $XRe(CO)_5$ UNIT (C_{4v})

$\nu(CH_2)$ vinyl	2 A'	δ_r (CH) vinyl in-plane	A'
ν(CH) vinyl	A'	δ_w (CH) vinyl out-of-plane	A''
$\nu(CH_2)$ methylene	A' + A''	δ_s (CH_2) methylene	A'
ν(C=C)	A'	ρ_w (CH_2) methylene	A'
ν(C-C)	A'	ρ_t (CH_2) methylene	A''
$\delta_s(CH_2)$ vinyl	A'	ρ_r (CH_2) methylene	A''
$\rho_r(CH_2)$ vinyl	A'	(C-C=C) in-plane def.	A'
$\rho_t(CH_2)$ vinyl	A''	(C-C=C) out-of-plane def.	A''
$\rho_w(CH_2)$ vinyl	A''		

All modes i.r. and Raman active; A' polarised in the Raman.

ν(CO)	$2A_1 + B_1 + E$	ν(ReX)	A_1
ν(ReC)	$2A_1 + B_1 + E$	δ(CReX)	E
δ(CReC)	$A_1 + B_1 + B_2 + 2E$	δ(ReCO)	$A_1 + A_2 + B_1 + B_2 + 3E$

X = bonded C of η^1-C_3H_5 ligand; A_1 and E modes i.r. active;
A_1, B_1, B_2 and E modes Raman active, of which the A_1 are polarised.

perturbation from C_{4v} symmetry due to the presence of the allyl group. In the Raman spectrum the intensity order is A_1 (eq) > B_1 > A_1 (ax) >> E. The polarised nature of the A_1 vibrations confirms their assignments.

These results confirm the view that the local symmetry concept is a reasonable approach since if C_{2v} symmetry were more appropriate (pairs of equatorial CO groups being perturbed by the allyl) five ν(CO) bands should be observed in both the i.r. and Raman ($3A_1 + B_1 + B_2$; A_1 polarised). Likewise if C_s symmetry were appropriate five ν(CO) bands would be allowed in both the

TABLE 4

$\nu(CO)$, $\delta(ReCO)$ AND $\nu(ReC)$ BANDS (cm^{-1}) OF $(\eta^1-C_3H_5)Re(CO)_5$ AND SYMMETRY CORRELATION WITH $[Re(CO)_6]^+$

$[Re(CO)_6]^+$ [18]				$(\eta^1-C_3H_5)Re(CO)_5$		
Band	Assignment (O_h)			Assignment (C_{4v})	I.r. (liquid)	Raman (liquid)
				A_1 (eq)	2129 s	2127 vs,pol
				B_1	2050 m,sh	2051 s,dp
				E	2020 vs,br	2020 vw
				A_1 (ax)	1970 vs	1970 m,pol
441	A_{1g}	$\nu(ReC)$	→	A_1 (eq)	465 w,sh	463 vs,pol
426	E_g	$\nu(ReC)$	→	A_1 (ax)	446 ms	445 ms,pol?
			↘	B_1	430 w,sh	430 m,dp?
356	T_{1u}	$\nu(ReC)$	→	E	373 vs[a]	
584	T_{1u}	$\delta(ReCO)$	→	A_1	600 vs	603 w
			↘	E	585 vs	590 vw
522	T_{2u}	$\delta(ReCO)$	→	B_1		522 vw
			↘	E	531 ms	533 vw
486	T_{2g}	$\delta(ReCO)$	→	B_2	505 vw	503 vw
354	T_{1g}	$\delta(ReCO)$	→	A_2	inactive	
			↘	E	350 m	
				A_1 $\nu(Re-C_{allyl})$		370 s,pol[a]

[a] see text

i.r. and Raman (4A' + A"; A' polarised). The results are obviously only in line with the predictions of C_{4v} symmetry.

The $\nu(CO)$ frequencies obtained from n-pentane solutions have been used to calculate simple Cotton-Kraihanzel force constants. Values obtained are k_{ax}, 16.09; k_{eq}, 17.07; k_i, 0.29 mdyne/Å. Using literature $\nu(CO)$

frequencies we have also calculated C-K force constants for $(\eta^1\text{-}C_3H_5)Mn(CO)_5$ (k_{ax}, 16.20; k_{eq}, 16.88; k_i, 0.24) and for comparison those of $CH_3Re(CO)_5$ (k_{ax}, 16.02; k_{eq}, 16.93; k_i, 0.29) and $CH_3Mn(CO)_5$ (k_{ax}, 16.13; k_{eq}, 16.83; k_i, 0.25). The k_{ax} values are marginally lower and the k_{eq} and k_i values marginally higher for the rhenium compounds than for the manganese compounds when like pairs are considered, but the variations are barely significant. The results suggest that manganese and rhenium atoms in these compounds show very similar σ-acceptor and π-donor abilities and that the σ-bonding abilities of the methyl and η^1-allyl groups and their inductive effects are indistinguishable. Finally it is noticeable that although the A_1 (eq), E, and A_1 (ax) ν(CO) frequencies alter by +21, +6 and -8 cm^{-1} on moving from $(\eta^1\text{-}C_3H_5)Mn(CO)_5$ to $(\eta^1\text{-}C_3H_5)Re(CO)_5$, the B_1 frequency only changes by +1 cm^{-1}. This is in line with the symmetry requirement that the B_1 mode should be insensitive to changes in the mass of the metal atom.

(ii) The δ(ReCO) and ν(ReC) region

Assignments of δ(ReCO) and ν(ReC) vibrations have been attempted by a consideration of the relationships between these vibrations and those of an appropriate metal hexacarbonyl for which assignments are unequivocal. $[Re(CO)_6]^+$ [18] has been chosen for comparison, although $W(CO)_6$ could have been used. Symmetry correlations of this type have, for example, previously been applied successfully to assignment of δ(MCO) and ν(MC) vibrations of $Mn(CO)_5Br$ (correlation with $Cr(CO)_6$ [19] and $[M(CO)_5(PH_3)]$ (correlation with $M(CO)_6$; M = Cr, Mo, or W) [20]. One of the problems in assigning such bands is that extensive mixing of modes of the same symmetry will occur owing to the small frequency differences between δ(MCO) and ν(MC) fundamentals. As a guide it is well known that δ(MCO) bands are normally much more intense in the i.r. than in the Raman, the reverse situation applying to ν(MC) bands. Bands associated with δ(MCO) modes are generally, but not invariably, of higher frequencies than those of ν(MC) modes. The assignments and the symmetry correlation between $Re(CO)_5X$, C_{4v}, (X = bonded C of the $\eta^1\text{-}C_3H_5$ group) and $[Re(CO)_6]^+$, O_h, are given in Table 4.

Using the assignment of the Raman inactive T_{1u} δ(ReCO) mode of $[Re(CO)_6]^+$ to a band at 584 cm^{-1}, it follows that the two highest energy very strong i.r. bands for $(\eta^1-C_3H_5)Re(CO)_5$ are the A_1 + E δ(ReCO) vibrations. The A_1 band is too weak in the Raman for a polarisation measurement. The B_1 and B_2 δ(ReCO) vibrations should be Raman-active only and are assigned to weak bands at 522 and 503 cm^{-1}. The weakness of the B_1 vibration is expected as it is correlated with the formally inactive T_{2u} δ(ReCO) mode of $[Re(CO)_6]^+$. The two remaining bands assigned to δ(ReCO) vibrations are the E modes associated with an out-of-plane bend and an axial bend. These are, as expected, of high intensity in the i.r. but at best very weak in the Raman. One of these bends appears at the very low frequency of 350 cm^{-1} in line with the T_{1g} mode of $[Re(CO)_6]^+$ found at 354 cm^{-1}.

Correlation with $[Re(CO)_6]^+$ also allows a sensible assignment of the ν(ReC) modes of the η^1-allyl complex. The Raman-active A_{1g} mode of the cation correlates with the A_1(eq) mode of the C_{4v} allyl and this can readily be assigned to the very strong, polarised, Raman band at 463 cm^{-1} which appears only as a weak shoulder in the i.r. spectrum. The A_1(ax) mode is assigned to a moderate intensity Raman and i.r. band at 445 cm^{-1}. We have not been able to accurately test the polarisation of this band owing to the closeness of the very intense A_1(eq) band. However the intensity relationships of these two bands assigned to A_1 modes are in agreement with the prediction that the equatorial mode should develop nearly zero change in dipole moment but a very large change in polarisability. The B_1 mode assigned to a band at 430 cm^{-1} and the A_1(ax) band are not easily observed in the unpolarised Raman spectrum due to the intensity of the 463 cm^{-1} A_1(eq) band, but are clearly visible in parallel polarisation. Using the assignments for $[Re(CO)_6]^+$ and correlating E_g (R) → B_1 and T_{1u} (i.r.) → E, we expect the remaining E mode to occur as a strong i.r. band, but a weak Raman band at lower energy than the B_1. The only remaining very strong i.r. band is found at 373 cm^{-1} and so is assigned accordingly. However the Raman spectrum also contains a strong polarised band at 370 cm^{-1} which cannot be assigned to the E ν(ReC) vibration. We suggest that these bands cannot arise from the same vibration but are accidentally degenerate. The Raman band is tentatively assigned to the A_1 ν(Re-C_{allyl}) vibration, an analogous strong, polarised band in the Raman spectrum of [$W(CO)_3(\eta^5-C_5H_5)-(\eta^1-C_3H_5)$] at 353 cm^{-1} being similarly assigned to ν(W-C_{allyl}) [21]. A further difficulty is that both $Sn(\eta^1-C_3H_5)_4$ [13] and $Hg(\eta^1-C_3H_5)_2$ [14] display a band in this region associated with the A" C-C=C out-of-plane deformation. Such a vibration may also contribute to the intensities of the i.r. and Raman bands found for $(\eta^1-C_3H_5)Re(CO)_5$ at *ca.* 370 cm^{-1}.

Other workers have reported the vibrational spectra of the related molecules $Re(CO)_5(GeH_3)$ [22] and $Re(CO)_5(EMe_3)$ (E = Si, Ge, or Sn) [23] in this region. Although relatively few bands were detected there is agreement with the present work in that the two high energy intense i.r. bands at *ca.* 600 cm^{-1} are assigned to the A_1 and E δ(ReCO) vibrations and that the A_1(eq) ν(MC) band is always found at higher energy than the A_1(ax) ν(MC) band. Of most interest from a comparative point of view is the reported [16] spectrum of $(\eta^1-C_3H_5)Mn(CO)_5$. Again all bands observed have been assigned to A_1 or E modes but even though benzene solution spectra were recorded no polarisation data were included. Some of the assignments appear to us to be questionable. Thus a Raman band at 479 cm^{-1} is listed as coincident with an i.r. band at 456 cm^{-1} and the energy order of the ν(MC) bands is given as E > A_1(ax) > A_1(eq) when a more acceptable order for a $Mn(CO)_5$ derivative would be A_1(ax) > E > A_1(eq). Although the assignment of the two highest energy δ(MnCO)bands to A_1 + E is reasonable no regard has been paid to the fact that a A' C-C=C deformation of the allyl group should appear in this region.

(iii) η^1-Allyl vibrations

Bands attributed to the allyl group and possible assignments are listed in Table 5 using as a basis C_s symmetry, (Table 3). The A' and A" modes of the allyl group have been assigned using the reported spectra of $Si(\eta^1-C_3H_5)_4$ [13] and the allyl halides [15] as a guide. The three ν(CH) and ν(CH_2) stretches of the vinyl part of the allyl group give rise

TABLE 5

ALLYL BANDS (cm^{-1}) OF (η^1-C_3H_5)Re(CO)$_5$

Band (cm^{-1})		Assignment	
Infrared	Raman		
3078 m	3075 vw,br	ν_{asym} (CH_2) vinyl	(A')
3027 w	3033 vw		
2989 w	2987 m	ν(CH) vinyl	(A')
2964 m		ν_{sym} (CH_2) vinyl	(A')
2925 m		ν_{asym} (CH_2) methylene	(A")
2911 m	2909 vw		
2854 w	2855 m	ν_{sym} (CH_2) methylene	(A')
2823 w			
2500 w			
2434 w			
1750 w		(2 x 875)	
1616 s	1617 s	ν(C=C)	(A')
1463 vw			
1434 m	1430 vw?	δ_s (CH_2) methylene	(A')
1398 m	1397 m	δ_s (CH_2) vinyl	(A')
1366 m		(2 x 678)	
1295 m	1293 m	δ_r (CH) vinyl	(A')
1268 w			
1200 ms	1202 w	ρ_w (CH_2) methylene	(A')
1095 m	1099 vs	ρ_r (CH_2) vinyl	(A')
1037 ms	1041 vw	ρ_t (CH_2) methylene	(A")
991 ms		ρ_t (CH_2) vinyl	(A")
954 ms	961 w	ν(C-C)	(A')
933 w	935 mw	(2 x 465)	
912 w			
875 s	874 w	ρ_w (CH_2) vinyl	(A")
755 m	752 w	ρ_r (CH_2) methylene	(A")
678 ms	678 m,pol	C=C-C in-plane def.	(A')
637 w		δ_w (CH) vinyl	(A")

to the highest energy fundamentals, two lower energy bands being assigned to the $\nu(CH_2)$ methylene stretches. The $\nu(C{=}C)$ stretch is convincingly assigned to the intense band at 1616 cm^{-1}, being found at 1617 cm^{-1} for the manganese analogue [16] and at 1614 cm^{-1} for $(\eta^5\text{-}C_5H_5)W(CO)_3(\eta^1\text{-}C_3H_5)$ [21]. These values are some 30 cm^{-1} lower than $\nu(C{=}C)$ of allyl halides. The observation of this band is a simple diagnostic test for the presence of a η^1- rather than a η^3-allyl group.

The methylene and vinyl scissors deformations at 1434 and 1398 cm^{-1} respectively are assigned by analogy with the allyl halides as are most of the other vibrations. The $\nu(C\text{-}C)$ stretch is assigned to a medium-strong i.r. band at 954 cm^{-1} rather than to the weak band at 933 cm^{-1} which we believe to be an overtone of an A_1 $\nu(ReC)$ vibration. This leaves strong i.r. bands with weak Raman counterparts at 875 and 755 cm^{-1} to be assigned to the vinyl CH_2 wag and the methylene rocking mode. The latter vibrations occur over a wide range (720-800 cm^{-1}) depending on the nature of the compound. The C=C-C in-plane deformation is assigned to a medium intensity band at 678 cm^{-1}, polarised in the Raman. Since the vinyl CH wag is also expected below 800 cm^{-1} it is assigned to the only remaining band above the $\delta(ReCO)$ region at 637 cm^{-1}. Finally the C=C-C out-of-plane deformation has not been found but it may possibly contribute to the intense band at 373 cm^{-1}, (Table 4), since this deformation for $Sn(\eta^1\text{-}C_3H_5)_4$ [13] appears at 389 cm^{-1}.

$(\eta^3\text{-}C_3H_5)Re(CO)_4$

The vibrational spectra of several η^3-allyls of the transition metals have been reported, extensive studies being carried out, for example, on $[Pd(\eta^3\text{-}C_3H_5)X]_2$ (X = Cl or Br) [24] and $(\eta^3\text{-}C_3H_5)Co(CO)_3$ [25]. A recent study of the low frequency vibrations of $[M(\eta^3\text{-}C_3H_5)X]_2$ (M = Ni, X = Br; M = Pd, X = Cl) is of interest in that incoherent inelastic neutron scattering has been used to obtain spectroscopic information [26]. However the most relevant study is that on $(\eta^3\text{-}C_3H_5)Mn(CO)_4$ [27]. We find that unlike $(\eta^1\text{-}C_3H_5)Re(CO)_5$, but in line with $(\eta^3\text{-}C_3H_5)Mn(CO)_4$, the concept of local symmetry cannot be applied to the assignment and interpretation of

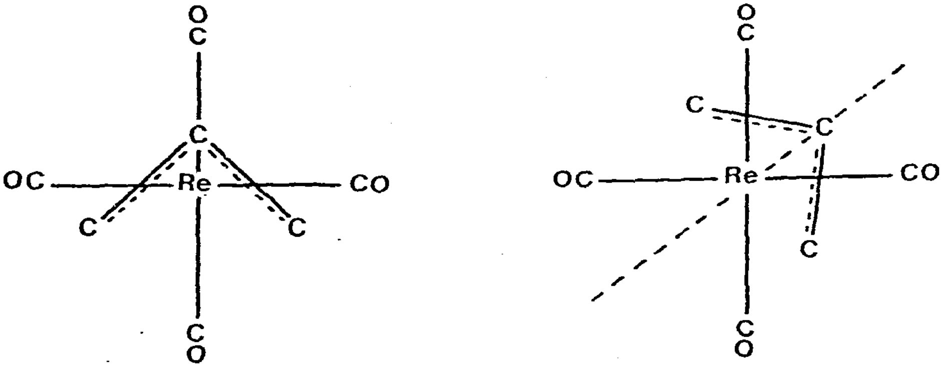


FIGURE 1

(a) symmetry plane derived from σ_v of C_{4v}

(b) symmetry plane derived from σ_d of C_{4v}

TABLE 6

VIBRATIONS OF (η^3-C_3H_5)Re(CO)$_4$, (C_s SYMMETRY WITH σ_v PLANE)

ν(CH)	A'	ν(Re-allyl)	2A' + A"
ν(CH_2)	2A' + 2A"	τ(Re-allyl)	A"
δ(CH_2) in-plane	A' + A"	ν(CO)	3A' + A"
π(CH) out-of-plane	A'	ν(ReC)	3A' + A"
δ(CH) in-plane	A"	δ(ReCO)	4A' + 4A"
ν(CCC)	A' + A"	δ(CReC)	2A' + 2A"
ρ_t (CH_2)	A' + A"	δ(CRe-allyl)	2A' + A"
ρ_w(CH_2)	A' + A"		
ρ_r(CH_2)	A' + A"		
δ(CCC)	A'		

All modes active in both i.r. and Raman;

A' are polarised in the Raman

TABLE 7

ν(CO), δ(ReCO), ν(ReC) AND ν(Re-allyl) BANDS (cm^{-1}) OF (η^3-C_3H_5)Re$(CO)_4$

Infrared (melt)	Raman (melt)	Assignment	
2094 s	2091 ms, pol	ν(CO)	A'
1994 vs	1990 m, pol	ν(CO)	A'
1980 vs	1979 mw, dp	ν(CO)	A"
1959 vs	1953 mw, pol	ν(CO)	A'
610 vs	608 vw, pol	δ(ReCO)	A'
591 vs	594 w, pol	δ(ReCO)	A'
547 s	546 mw, pol	δ(ReCO)	A'
	501 vw, dp?	δ(ReCO)	A"
471 s	477 vs, pol	ν(ReC)	A'
455 vw, sh	459 vs, pol	ν(ReC)	A'
442 m		ν(ReC)	A'
395 m, sh	394 m, pol	$\nu(\text{Re-allyl})_{asym}$	A'
377 vs	377 w, dp	$\nu(\text{Re-allyl})_{asym}$	A"
332 m	331 s, pol	$\nu(\text{Re-allyl})_{sym}$	A'
	314 ms, dp	ν(ReC)	A"
	217 ms, pol		
	142 m, dp	δ(CReC)	A"
	100 s, pol	δ(CReC)	A'

the vibrational spectrum of (η^3-C_3H_5)Re$(CO)_4$. Evidence presented below clearly shows that the vibrations of the Re$(CO)_4$ unit cannot be assigned using C_{4v} local symmetry but only by using overall C_s symmetry, the conformation of the molecule being that shown in Fig.1.a with a σ_v plane of symmetry rather than the alternative conformation shown in Fig.1.b. This situation is exactly that pertaining to $(\eta^3\text{-}C_3H_5)Mn(CO)_4$ [27]. Table 6 lists the symmetry types of the allyl group and the Re-allyl moiety in terms of C_s symmetry and the $Re(CO)_4$ in terms of C_s (σ_v) symmetry.

(i) The ν(CO) region

The bands observed and their assignments are listed in Table 7. Using a C_{4v} local symmetry approach to the $Re(CO)_4$ unit a total of three ν(CO) bands $(A_1 + B_1 + E)$ are predicted of which the A_1 should be polarised in the Raman and only $A_1 + E$ i.r. active. Alternatively a C_s symmetry approach predicts four bands, all i.r. and Raman active. If the conformation is that depicted in Fig.1.a three of the four (3A' + A") bands should be polarised, whereas if the conformation is that shown in Fig.1.b only two (A') of the four (2A' + 2A") bands should be polarised. The results listed are in agreement with the selection rules for the structure shown in Fig.1.a, four bands being found in both the i.r. and Raman spectra, the latter having three polarised bands and one depolarised band. The i.r. results are in good agreement with those given in a supplementary publication associated with ref.[3], (2091, 1996, 1982, and 1963 cm^{-1}).

We have also calculated Cotton-Kraihanzel force constants and find k_1 = 15.83, k_2 = 16.76 and k_i = 0.33 mdyne/Å. Using literature ν(CO) frequencies for $(\eta^3\text{-}C_3H_5)Mn(CO)_4$ we calculate k_1 = 15.78, k_2 = 16.64, and k_i = 0.27 mdyne/Å. As for the $(\eta^1\text{-}C_3H_5)M(CO)_5$, (M = Mn or Re), pair, there is obviously little significant difference in the electron availability at the two metal centres.

(ii) The δ(ReCO), ν(ReC) and ν(Re-allyl) region

The i.r. and Raman spectra in the 600–300 cm^{-1} region are, as anticipated, very rich in bands, but it is again clear that C_{4v} local symmetry for the $Re(CO)_4$ unit is inappropriate. For example, three polarised Raman bands at 608, 594 and 546 cm^{-1} must be assigned to A' δ(ReCO) modes whereas for C_{4v} symmetry only the single A_1 vibration of the $A_1 + A_2 + B_1 + B_2 + 2E$ δ(ReCO) set should be polarised. Likewise the presence of at least two polarised Raman bands (477 and 459 cm^{-1}) assignable to ν(ReC) vibrations rules out C_{4v} symmetry since only the single A_1 vibration of the $A_1 + B_1 + E$ ν(ReC) set should be polarised. Although data from this region points to the appropriateness of C_s symmetry it is not possible to differentiate between conformations with σ_v or σ_d planes. However since evidence from the ν(CO) region clearly favours the conformation involving a σ_v plane, the results have been analysed from this standpoint. The total number of modes for δ(ReCO) + ν(ReC) + ν(Re-allyl) is therefore 9A' + 6A". Eleven bands have been observed of which seven are polarised so clearly A' in type.

Four δ(ReCO) bands are observed, (three only in the i.r.), whereas eight are predicted for C_s symmetry. As anticipated, they are strong in the i.r. but weak in the Raman. Three are polarised so must be assigned to A' modes. The Raman bands at 477 and 459 cm^{-1} are very intense and polarised so are assigned to A' ν(ReC) vibrations. The three ν(Re-allyl) stretches (2A' + A") have been assigned by a consideration of polarisation data and also in the knowledge that these bands are found between 300 and 400 cm^{-1} in such compounds as $(\eta^3-C_3H_5)Mn(CO)_4$ [27], $[Pd(\eta^3-C_3H_5)X]_2$ (X = Cl or Br) [24], $(\eta^3-C_3H_5)Co(CO)_3$ [25] and $[Ni(\eta^3-C_3H_5)Br]_2$ [26]. These vibrations are sometimes described as one stretch (A') and two tilting vibrations (A' + A"). Analysis of the spectra of several η^3-allyl-metal compounds has shown [28] that the frequency of the A" vibration can occupy any of the three possible positions in relation to the other two vibrations. On these grounds we have therefore assigned bands at 394, 377 and 331 cm^{-1} to these vibrations, the highest and lowest in energy being polarised and hence A' in type. This assignment is by no means secure however as a further depolarised Raman band at 314 cm^{-1}, tentatively assigned to the only A" ν(ReC) vibration, could be the A" ν(Re-allyl) stretch. The band at 377 cm^{-1} would then alternatively be assigned as ν(ReC). A final A" Re-allyl torsion has not been assigned but would be of low energy and weak intensity in both the i.r. and Raman. It is possible that the depolarised Raman band at 142 cm^{-1} could be so assigned but we believe it to be more likely a δ(CReC) vibration. One other Raman band at 100 cm^{-1} can be assigned to a δ(CReC) vibration, bands

TABLE 8

ALLYL BANDS (cm^{-1}) OF (η^3-C_3H_5)Re(CO)$_4$

Infrared (melt)	Raman (melt)	Assignment	
3075 w	3077 vw, dp	$\nu(CH_2)$	A"
3015 w	3019 w, pol	$\nu(CH)$	A'
2965 vw	2964 vw, pol	$\nu(CH_2)$	A'
2935 vw		$\nu(CH_2)$	A'
2675 vw			
2568 vw			
2465 w			
2418 w			
1495 m	1495 vw, dp	$\delta(CH_2)_{asym}$	A"
1463 m	1463 vw, pol	$\delta(CH_2)_{sym}$	A'
1397 w	1396 w, dp	$\nu(CCC)_{asym}$	A"
1323 vvw	1326 vw, dp?		
1214 m	1219 m, pol	$\pi(CH)$	A'
1140 w	1138 vw, dp?	$\delta(CH)$	A"
	1101 vw, dp?		
1090 w	1087 vw, pol?		
1047 w			
1025 vw	1023 m, pol	$\nu(CCC)_{sym}$	A'
1004 m	1003 ms, pol	$\rho_t(CH_2)_{sym}$	A'
978 vw		$\rho_t(CH_2)_{asym}$	A"
923 m	923 m, pol	$\rho_w(CH_2)_{sym}$	A'
872 m	871 vw, dp	$\rho_w(CH_2)_{asym}$	A"
797 w	791 mw, pol	$\rho_r(CH_2)_{sym}$	A'
774 vw	762 mw, dp	$\rho_r(CH_2)_{asym}$	A"

associated with δ(CRe-allyl) not being observed but would be expected at very low frequencies.

(iii) The η^3-allyl vibrations

Table 6 shows that for an allyl group of C_s symmetry there are 10A' + 8A" modes. In Table 8 nine A' and seven A" vibrations have been assigned for $(\eta^3\text{-}C_3H_5)Re(CO)_4$, no bands being found in the 2950 and 520 cm^{-1} regions which could be assigned to the A" $\nu(CH_2)$ and A' δ(CCC) vibrations respectively. The A" $\nu(CH_2)$ vibration could likewise not be found for either $(\eta^3\text{-}C_3H_5)Co(CO)_3$ [25] or $[Pd(\eta^3\text{-}C_3H_5)X]_2$ (X = Cl or Br) [24]. The assignments, which are approximate in view of coupling between vibrations of the same symmetry species, are based largely on those presented for $(\eta^3\text{-}C_3H_5)Mn(CO)_4$ [27] and $[Pd(\eta^3\text{-}C_3H_5)X]_2$ [24]. The rationale for the assignments need not therefore be repeated here.

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