

VIBRATIONAL SPECTRA AND SCCC MO STUDIES OF SUBSTITUTED ALLYLTRICARBONYLCOBALT COMPOUNDS

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(Received April 28th, 1972)

SUMMARY

A study of the vibrational spectra of $\text{XC}_3\text{H}_4\text{Co}(\text{CO})_3$ ($\text{X} = \text{H}, 1\text{-CH}_3, 2\text{-CH}_3, 1\text{-Cl}, 2\text{-Cl}$) is reported. Assignment of bands is proposed and carbonyl force constants are calculated. The trends in frequencies and force constants are compared with the results of Self-Consistent Charge and Configuration Molecular Orbital calculations (SCCCMO).

INTRODUCTION

Previous studies^{1,2} of the vibrational spectra of π -allyl complexes of transition metals include those on $(\text{XC}_3\text{H}_4\text{PdY})_2$ ($\text{X} = \text{H}, \text{CH}_3$; $\text{Y} = \text{Cl}, \text{Br}$) and $\pi\text{-C}_3\text{H}_5\text{Mn}(\text{CO})_4$.³ Partial infrared studies of palladium-allyl complexes have been reported by Fritz⁴ and by Dent *et al.*⁵ Some infrared data on $\text{C}_3\text{H}_5\text{Co}(\text{CO})_3$ has already been reported^{6,7} and recently the vibrational spectrum of σ -allylpentacarbonylmanganese has been studied⁸. Vibrational studies of complexes containing the tricarbonyl group have also been reported⁹⁻¹³. The electronic structures of the metal-allyl complexes A_2M and $(\text{AMCl})_2$, $\text{A} = \pi\text{-C}_3\text{H}_5$ and $\text{M} = \text{Ni}, \text{Pd}, \text{Pt}$, have been studied by the SCCC MO method¹⁴.

This study is divided into four parts: (I) The carbonyl stretching modes and Cotton-Kraihanzel¹⁵ force constants are considered. The trends occurring are explained in terms of electronic effects. (II) The other vibrational modes of the $\text{Co}(\text{CO})_3$ moiety, in C_{3v} symmetry, are considered. (III) The allyl-cobalt vibrations and (IV) the spectra of the allyl groups in $\text{XC}_3\text{H}_4\text{Co}(\text{CO})_3$ are discussed.

RESULTS AND DISCUSSION

I. Carbonyl stretching modes

In Table 1 the spectra of the five compounds studied are given in the carbonyl region along with Cotton-Kraihanzel force constants and C-O bond orders calculated by the SCCC method. The method of "local symmetry", proposed by Cotton *et al.*¹⁶, has been used to interpret the spectra of a range of organometallic compounds, including $\text{C}_5\text{H}_5\text{Mn}(\text{CO})_3$ ¹¹, $\text{C}_4\text{H}_6\text{Fe}(\text{CO})_3$ ¹², $\text{C}_5\text{H}_5\text{V}(\text{CO})_4$ ¹⁷ and $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$ ¹⁸. This approximation is valid if the $\text{M}(\text{CO})_n$ group is rotating freely with respect to the

TABLE 1

CARBONYL FREQUENCIES OF $\text{XC}_3\text{H}_4\text{Co}(\text{CO})_3$ (in cyclohexane), FORCE CONSTANTS, C-O BOND ORDERS AND CO ORBITAL POPULATIONS (SCCC)

<i>X</i>	<i>Vibrational mode (cm⁻¹)</i>		<i>Force constants (md/Å)</i>		<i>C-O bond order SCCC</i>	<i>CO orbital populations SCCC</i>	
	<i>E</i>	<i>A₁</i>	<i>k</i>	<i>k_i</i>		<i>5σ</i>	<i>π*</i>
H	2000 vs	2068 s	16.53	0.37	2.984	1.919	0.085
1-CH ₃	1995 vs	2064 s	16.45	0.38	2.980	1.923	0.091
2-CH ₃	1997 vs	2065 s	16.47	0.38	2.984	1.919	0.086
1-Cl	1995 vs 2010 vs 2017 vs 2022 (sh)	2077 s	16.74	0.34	2.995	1.908	0.074
2-Cl	2012 vs	2076 s	16.70	0.35	2.987	1.917	0.082

π -bonded moiety and if there is no strong coupling between the vibrational modes of the two groups¹⁶. Assuming these conditions the tricarbonyl group of $\text{XC}_3\text{H}_4\text{Co}(\text{CO})_3$ can be discussed in terms of C_{3v} symmetry. Thus two carbonyl stretching vibrations ($A_1 + E$) are expected in the 1850–2200 cm^{-1} region.

The symmetry coordinates of these stretches are:

$$A_1: \frac{1}{\sqrt{3}}(r_1 + r_2 + r_3)$$

$$E: \frac{1}{\sqrt{6}}(2r_1 - r_2 - r_3)$$

$$\frac{1}{\sqrt{2}}(r_2 - r_3)$$

Thus the A_1 mode represents the symmetrical stretching of all the carbonyls and this requires greater energy than the E stretches. Therefore the higher frequency bands are the A_1 bands.

The frequencies and force constants (k), calculated by the Cotton-Kraihanzel method, for the 1-Cl and 2-Cl compounds are greater than those of the unsubstituted molecule, while those of the methyl-substituted compounds are less. These results are in accord with chlorine being an electron-withdrawing agent, decreasing metal-carbonyl π -back-bonding, which in turn increases the C-O bond order. With a methyl substituent the cobalt has a more negative charge than with the parent unsubstituted compound, so back-bonding to the empty π^* orbitals of the carbonyl groups is facilitated (Table 1). This in turn lowers the C-O bond order and hence the frequencies and force constants. These results may be represented schematically $\text{ClC}_3\text{H}_4 \leftarrow \text{Co}-\text{C}\equiv\text{O}$, $\text{CH}_3\text{C}_3\text{H}_4 \rightarrow \text{Co}=\text{C}=\text{O}$. It is also apparent, from Table 1, that the effects due to the chlorine substituents are greater than those due to the methyl groups. Thus, as expected, the chlorine is a strong electron-withdrawing agent and the methyl is a weak electron donor.

The trends in carbonyl frequencies are in accord with Hammett's and Taft's¹⁹ σ parameters. For the methyl substituent σ_m and σ_o values are both -0.17 , while for the chloro substituent σ_m is 0.227 and $\sigma_o = 0.20$. Thus the decreases in force constants, frequencies and bond orders are expected for the methyl-substituted compounds, and the corresponding increases for the chloro compounds. Since the order of the carbonyl frequencies, force constants (k) and C-O bond orders is $H < 2-Cl < 1-Cl$ and $\sigma_o < \sigma_m$, the chloro in the 2 position has an "ortho" effect, and in the 1 position a "meta" effect.

In the most symmetrical unsubstituted compound the E band is degenerate, as it is in the 2-Cl compound, which is also symmetrical. However, the 2-CH₃ perturbs the symmetry so that two frequencies occur ($A' + A''$ in C_s symmetry), while the more unsymmetrical 1-Cl compound has the E mode split into a doublet and shoulder. The corresponding band is slightly asymmetric in the 1-CH₃ compound. In the spectra of $XC_6H_5Cr(CO)_3$ in cyclohexane no splitting of the E band occurred when $X = H, CH_3$ but when $X = F, Cl$ shoulders were observed²⁰. Thus the substituents on the allyl perturb the C_{3v} symmetry of the $M(CO)_3$ moiety because of the lower symmetry of the substituted allyl and because of tilting of the allyl group out of the plane defined by the carbons of the carbonyls.

The interaction force constants (k_i) also behave as expected in that the methyl values are slightly greater than the values for the unsubstituted compound and the chlorine values are appreciably less. This shows firstly the greater electronic perturbation of the chlorine than of the methyl, and secondly the smaller interaction between the carbonyls in the chloro compounds, due to the lengthening of the Co-C bond when the back-bonding from the metal to the carbonyl is lowered.

Self-Consistent Charge and Configuration (SCCC) calculations have been useful in showing trends in series of compounds^{14,21}. The SCCC calculations on the substituted allyltricarboxylcobalt compounds show the expected results: the methyl compounds have the same or slightly smaller bond orders than the unsubstituted compound and with chloro compounds the bond orders are greater. These results parallel the order in the frequencies and force constants (k) and are in agreement with the rationalisation proposed above to explain the order in the experimental results. The results are also in agreement with the 5σ and π^* orbital populations (Table 1). The carbonyl wave-functions of Brown and Chambers²¹ and the wave-functions of Owens²² for the substituted allyls were employed. In the absence of crystallographic data, the allyl group was assumed parallel to the plane of the oxygen atoms and the OC-M-CO angle was considered a right angle. The bond lengths (Co-C = 1.85 \AA , C-O = 1.15 \AA , $C_3H_5-M = 2 \text{ \AA}$) were assumed constant throughout the series. Kettle's²³ formulae for the group overlap integrals of the $Co(CO)_3$ fragment were used.

II. Other $Co(CO)_3$ vibrational modes

The $\nu(M-C)$, $\delta(M-C-O)$ and $\omega(C-M-C)$ symmetry species are given in Table 2. In assigning bands to these modes some general considerations are useful¹⁷. Usually in $(\pi\text{-moiety})M(CO)_3$ compounds $\delta(M-C-O)$ bands are found^{11,12,18} at $500-700 \text{ cm}^{-1}$ while $\nu(M-C)$ bands are expected¹⁷ at $\approx 500 \text{ cm}^{-1}$ or less and $\omega(C-M-C)$ vibrations are $\approx 100 \text{ cm}^{-1}$. Separation into $\delta(M-C-O)$ and $\nu(M-C)$ bands is an approximation because of extensive interaction between modes of the same symmetry.

TABLE 2
 SYMMETRY OF MOIETIES OF $C_3H_5Co(CO)_3$

Vibration	Symmetry modes	Group
$\nu(C-O)$	$C_{3v} A_1 + E$	$C_3 2A' + A''$
$\nu(M-C)$	$A_1 + E$	$2A' + A''$
$\delta(M-C-O)$	$A_1 + A_2 + 2E^a$	$3A' + 3A''$
$\omega(C-M-C)$	$A_1 + E$	$2A' + A''$
$\nu(Co-Allyl)_{sym}$	$C_{3v} A_1$	$C_3 A'$
$\nu(Co-Allyl)_{asym}$	E	$A' + A''$
$\nu(C-H)$	$C_{2v} 3A_1 + 2B_1$	$C_3 3A' + 2A''$
$\nu(C-C)$	$A_1 + B_1$	$A' + A''$
$\delta(H-C-C)$ in-plane	$2A_1 + 3B_1$	$2A' + 3A''$
$\delta(H-C-C)$ out-of-plane	$3A_2 + 2B_2$	$3A' + 2A''$
$\delta(C-C-C)$	A_1	A'
Allyl-Co(CO) ₃	$C_{3v} E$	$A' + A''$
Angle deformation twist	A_1	A'

^a A_2 IR inactive.

TABLE 3

$Co(CO)_3$ VIBRATIONS (cm^{-1})

700–440 cm^{-1} , benzene solution, polythene cells.

Substituent	$\delta(M-C-O)$		$\nu(M-C)$	
	A_1	E	E	A_1
H	588 s	558 s, 517 s	482 ms	458 ms
1-CH ₃	580 s	558 m, 518 s	478 ms	445 ms
2-CH ₃	558 s	537 s, 518 s	482 ms	456 ms
1-Cl	571 s	553 s, 512 s	473 ms	449 ms
2-Cl	563 s	530 s, 512 s	470 ms	445 ms

In each of the compounds with $X=H$, 1-CH₃ and 2-CH₃ four bands occur between 500 and 600 cm^{-1} . Three of these are assigned to $\delta(M-C-O)$ vibrations on grounds of position and intensity (see Table 3). The remaining band is a (C-C-C) bend [see Section IV, (iii)]. When $X=1-Cl$ or 2-Cl three bands occur in this region all of which are assigned to $\delta(M-C-O)$. The $\delta(M-C-O)$ modes of the $X=H$, 1-CH₃ and 1-Cl compounds have similar patterns and frequencies which differ from those of the compounds with $X=2-Cl$ and 2-CH₃. This indicates the effect of substituents in the 2-position. For $X=2-CH_3$ each of the bands at 518 cm^{-1} and 537 cm^{-1} is slightly split. Thus these are assigned to the two E modes. The corresponding bands in the other compounds are shown in Table 3. The A_1 modes are assigned to the highest frequency bands, with the exception of the 2-CH₃ compound where the 558 cm^{-1} band is assigned A_1 by analogy with the 2-Cl compound and the conclusion of Adams and Squire¹ [see Section IV, (iii)].

The $\nu(M-C)$ bands in the compounds considered occur between 440 and 500 cm^{-1} . The higher frequency bands are assigned to the E mode, due essentially to their greater intensity caused by extensive mixing with $\delta(M-C-O)$ modes. In no case does

appreciable splitting of the E mode occur.

It is of interest to note that in general $\nu(\text{Co}-\text{C})$ for both the A_1 and E stretches for the methyl substituted compounds are greater than those for the chlorine compounds. This is in accord with less back-donation in the chloro compounds due to chlorine lessening, by electron withdrawal, the ability of the cobalt to donate electrons to the carbonyl π^* orbitals and the methyl group facilitating back-donation. SCCC calculations quantify this observation (Table 1).

The lack of trends in this region has been noted also for similar compounds²⁴.

There has been some disagreement among previous authors about the assignment of the $\nu(\text{M}-\text{C})$ modes in $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$. Fritz and Manchot⁹ suggested that the A_1 mode is at 533 cm^{-1} whereas Adams¹⁰ favoured 484 cm^{-1} for the A_1 and 306 cm^{-1} for the E mode. Brown and Carroll²⁴ did not find the 306 cm^{-1} band. Adams and Squire¹⁸ confirmed its "disappearance" and reassigned the bands using Raman and infrared spectra. The final assignments are: E mode at 488 cm^{-1} and A_1 mode at 483 cm^{-1} . Davidson and Riley¹³ assigned the bands at 499 cm^{-1} and at 483 cm^{-1} to the E and A_1 modes (respectively) in mesitylenetricarbonylchromium. Thus our assignment of the A_1 mode to a lower frequency than the E mode is in agreement with assignments in related compounds. For the CO stretches the symmetrical A_1 stretch is at higher frequency than the E stretch but this order is not necessarily valid for the $\nu(\text{M}-\text{C})$ stretches as these groups are not terminal and the effects of the oxygen atoms bonded to the carbons and mixing with $\delta(\text{M}-\text{C}-\text{O})$ modes of the same symmetry invalidate such a simple relationship.

The Mulliken overlap populations²⁸ of the $\text{M}-\text{CO}$ bond were essentially the same for all the compounds (≈ 0.21).

III. Allyl-cobalt vibrational modes

The allyl-cobalt vibrations have $A_1 + E$ modes under C_{3v} symmetry and $2A' + A''$ under C_s (Table 2). Three bands occur in the $350-430\text{ cm}^{-1}$ region when $\text{X} = \text{H}$, $1-\text{CH}_3$, $2-\text{CH}_3$ and $2-\text{Cl}$, and four bands when $\text{X} = 1-\text{Cl}$. Some shoulders occur in the chloro compounds. These bands are shown in Table 4 along with the proposed assignments.

The 378 cm^{-1} band in $\text{C}_3\text{H}_5\text{Co}(\text{CO})_3$ is assigned to the $\nu(\text{Co}-\text{Allyl})_{\text{asym}} E$ mode. Similar assignments have been made for the 397 cm^{-1} band in $(\text{C}_3\text{H}_5\text{PdCl})_2$ ^{1,2}, the 362 cm^{-1} band in $\text{C}_4\text{H}_6\text{Fe}(\text{CO})_3$ ¹², the 375 cm^{-1} band in $\text{C}_5\text{H}_5\text{Mn}(\text{CO})_3$ ¹¹, the 330 cm^{-1} band in $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$ ¹⁸, the 358 cm^{-1} band in $(\text{Mesitylene})\text{Cr}(\text{CO})_3$ ¹⁸

TABLE 4

$\text{XC}_3\text{H}_4-\text{Co}$ Vibrations (cm^{-1})

440-350 cm^{-1} , benzene solution, polythene cells.

Substituent	$\nu(\text{Co}-\text{Allyl})_{\text{sym}}$	$\nu(\text{Co}-\text{Allyl})_{\text{asym}}$	Ligand
H	365 m	378 m	418 w
1-CH ₃	364 ms	380 m	409 m
2-CH ₃	360 m	391 ms	428 wm
1-Cl	370 m	392 w, 408 w	419 w, 362 m (sh)
2-Cl	369 m	380 w	411 w (sh), 407 m

and the 333, 352 cm^{-1} bands in $\text{ClC}_6\text{H}_5\text{Cr}(\text{CO})_3$ ²⁵. The 365 cm^{-1} band in the unsubstituted allyltricarbonylcobalt is assigned to the $\nu(\text{Co-Allyl})_{\text{sym}} A_1$ vibrational mode. Similar assignments in other compounds have been reported, *e.g.*, in $(\text{C}_3\text{H}_5\text{-PdCl})_2$ (367 cm^{-1}), $\text{C}_5\text{H}_5\text{Mn}(\text{CO})_5$ (350 cm^{-1}), $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$ (298 cm^{-1}) and (Mesitylene) $\text{Cr}(\text{CO})_3$ (328 cm^{-1}).

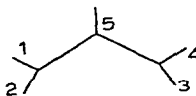
It is probable that the band at 418 cm^{-1} is due to a ligand vibration since 2,3-dichloro-1-propene has a band at 412 cm^{-1} . This is in accord with the assignment of the 420 cm^{-1} band in $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$ ¹⁸ to a ligand vibration corresponding to the 405 cm^{-1} band in benzene and Parker²⁶ has reported a band of 414 cm^{-1} in $\text{C}_3\text{H}_5\text{Fe}(\text{CO})_2\text{Cl}$ which is also probably a ligand vibration. In $(\text{C}_3\text{H}_5\text{PdCl})_2$ ¹ it has been found that the $\nu(\text{M-Allyl})_{\text{asym}} E$ mode is unsplit except at low temperature. The 418 cm^{-1} band in $\text{C}_3\text{H}_5\text{Co}(\text{CO})_3$ is therefore unlikely to be due to a splitting of the $\nu(\text{Co-C}_3\text{H}_5)_{\text{asym}} E$ mode. The 392, 408 cm^{-1} bands in 1- $\text{ClC}_3\text{H}_4\text{Co}(\text{CO})_3$ are assigned to the $\nu(\text{Allyl-Co})_{\text{asym}}$ vibrations [*cf.* $\text{ClC}_6\text{H}_5\text{Cr}(\text{CO})_3$]. The corresponding bands for the other substituted compounds are given in Table 4.

Adams and Squire¹⁸ note a close similarity between the spectra of $\text{C}_6\text{H}_6\text{Cr}(\text{CO})_3$ and $\text{C}_5\text{H}_5\text{Mn}(\text{CO})_3$. There is also a similarity between the spectra of the isoelectronic $\text{C}_4\text{H}_6\text{Fe}(\text{CO})_3$ and $\text{C}_3\text{H}_5\text{Co}(\text{CO})_3$; *e.g.* The former has bands at 416, 378 and 362 cm^{-1} while the latter has bands at 418, 378 and 365 cm^{-1} . However, the assignments are not parallel. In $(\text{C}_4\text{H}_7\text{PdCl})_2$ Adams and Squire¹ assign the highest band in the 400 cm^{-1} region to $\nu(\text{M-Allyl})_{\text{asym}}$ or $\delta(\text{C-C-C})$, while Shobatake and Nakamoto's² assignments differ. Thus the assignments in this spectral region must be viewed with caution.

IV. Allyl vibrations

The proposed assignments are given in Table 5 for the allyl vibrations.

(i). *C-H stretching modes.* In unsubstituted π -allyl compounds there are five possible C-H stretches, two sets of which are coincident:

$$\left. \begin{aligned} \nu_1(\text{C-H}) &= \frac{1}{\sqrt{2}}(r_1 + r_4) \\ \nu_2(\text{C-H}) &= \frac{1}{\sqrt{2}}(r_2 + r_3) \end{aligned} \right\} 2A_1 \text{ terminal in-phase}$$


$$\left. \begin{aligned} \nu_3(\text{C-H}) &= \frac{1}{\sqrt{2}}(r_1 - r_4) \\ \nu_4(\text{C-H}) &= \frac{1}{\sqrt{2}}(r_2 - r_3) \end{aligned} \right\} 2B_1 \text{ terminal out-of-phase}$$

$$\nu_5(\text{C-H}) = r_5 \quad A_1$$

Three $\nu(\text{C-H})$ bands are therefore expected in $\text{C}_3\text{H}_5\text{Co}(\text{CO})_3$. Two are expected in the 2- CH_3 and 2- Cl compounds and four in the 1- CH_3 and 1- Cl compounds. The methyl substituted allyltricarbonylcobalt compounds will also have $\nu(\text{CH}_3)$ bands ($2A' + A''$ in C_s symmetry). From Table 5 by comparing the spectra of $\text{XC}_3\text{H}_4\text{Co}(\text{CO})_3$, when $\text{X} = \text{H}$ and when $\text{X} = 2\text{-CH}_3$, it is seen that $\nu_5(\text{C-H})$ is missing in the former. The three bands of approximately the same frequency in the methyl-substituted compounds are assigned to $\nu(\text{CH}_3)$. In the 1- Cl compound the expected four bands occur whereas

only two C-H vibrations are found in the 1-CH₃ compound as well as the $\nu(\text{CH}_3)$ vibrations.

(ii). *C-H bending modes.* Bands which occur in the unsubstituted and 1-substituted but not in the 2-substituted compounds are due to the central C-H. Thus bands at 1227 cm⁻¹ and 1189 cm⁻¹ in C₃H₅Co(CO)₃ are assigned to $\pi(\text{C-H}) (B_2)$ and to

TABLE 5

ALLYL VIBRATIONS (cm⁻¹)CCl₄ solution, KBr cells.

Vibration	H	1-CH ₃	2-CH ₃	1-Cl	2-Cl	Assignment
C-H stretch	3082 mw	3075 w	3075 m	3090 w, 3074 w	3090 w	2B ₁
	3019 s	3019 m	3020 m	3024 w, 3050 w	3019 wm	2A ₁
		2973 m	2981 ms			} $\nu(\text{CH}_3)$ } 2A' + A''
		2921 ms	2922 ms			
		2857 m	2858 m			
C-H bends in-plane	1487 m	1462 m	1483 ms	1480 m	1462 s (sh)	$\delta(\text{CH}_2)$
	1471 m			1417 s	1454 s	$\delta(\text{CH}_2)$
	1388 m	1382 m	1386 ms	1400 w		+ $\nu(\text{C-C-C})_{\text{asym}}$
		1448 m	1448 s			} $\delta(\text{CH}_3)$ } + $\nu(\text{C-C-C})_{\text{sym}}$
		1438 m	1430 m (sh)			
			1351 w			
	1189 mw	1184 w		1200 mw		$\delta(\text{C-H}) B_1$
C-H bends out-of-plane	1227 m	1239 m		1308 s or 1239 vs		$\pi(\text{C-H}) B_2$
	951 m	983 m (sh)	953 vw		926 mw	$\rho_w(\text{CH}_2)_{\text{sym}} A_2$
	933 m	967 m	943 vw		899 mw	$\rho_w(\text{CH}_2)_{\text{asym}} B_2$
			929 w			$\rho(\text{CH}_3)$
			907 w			
		892 w				
"C-C-C" vibrations	1019 ms	1031 ms	1038 ms	1005 ms	1052 w	$\nu(\text{C-C-C}) A_1$
	526 s (sh)	520 s (sh)	583 m	621 ms		$\delta(\text{C-C-C}) A_1$
C-X and other vibrations				1643 w (sh)	1242 s	} Ligand
				1635 w	1651 w (sh)	
					1636 w	
		877 mw	842 ms			$\nu(\text{C-CH})_3$
			720 s		670 vs	$\nu(\text{C-Cl})$

$\delta(\text{C-H}) (B_1)$. The corresponding bands in the 1-CH₃ and 1-Cl compounds are shown in the Table. Similarly bands appearing only when methyl substituents are present are due to the methyl group, the CH₃-C bond or to a breakdown of C_{2v} symmetry due to the methyl group. In the unsubstituted compound ten C-H bends are expected; not all are seen in the spectra. The 1350-1500 cm⁻¹ spectral region is difficult to assign^{1,2}. However, our assignments are generally in accord with those of Adams and Squire¹.

(iii). *C-C-C vibrations.* The $\nu(\text{C-C-C})_{\text{sym}} (A_1)$ can be assigned to the 1019 cm⁻¹

band in $C_3H_5Co(CO)_3$ and to analogous bands in the remaining compounds^{1,2}. The $\nu(C-C-C)_{\text{asym}} (B_1)$ bands are expected in the 1350–1500 cm^{-1} region already discussed. The $\delta(C-C-C) A_1$ mode is assigned to the strong shoulder at 526 cm^{-1} in $C_3H_5Co(CO)_3$. A similar assignment (511 cm^{-1}) has been made in $(C_3H_5PdCl)_2$ ¹. Substitution by CH_3 in this latter compound shifts the $\delta(C-C-C)$ to 562 cm^{-1} and lowers its intensity. Accordingly the band at 583 cm^{-1} is assigned to $\delta(C-C-C) A_1$ in $2-CH_3C_3H_4Co(CO)_3$. The $\delta(C-C-C)$ bands in the other compounds are assigned as in Table 5.

(iv). Table 5 also shows C-X vibrations where X=Cl or CH_3 .

EXPERIMENTAL

The experimental method has been reported previously^{7,27}. The products were purified by distillation. The compounds, which are red oils, are extremely air sensitive. Analyses for cobalt were satisfactory in all cases.

In the 4000–400 cm^{-1} region spectra of CCl_4 solutions were obtained using a Perkin-Elmer 457 spectrophotometer and KBr cells. In the 2200–1900 cm^{-1} region spectra of cyclohexane solutions in KBr cells were obtained using a Perkin Elmer 337 spectrophotometer with a Hitachi-Perkin-Elmer recorder-readout. The 600–250 cm^{-1} region was examined using benzene solutions in polythene cells in the PE 457. The spectra in this region were also obtained using dichloromethane as a solvent and agreement with the benzene spectra was obtained.

The spectra were calibrated using H_2O , DCl and indene. Accuracy of ± 1 cm^{-1} is expected above 700 cm^{-1} and ± 2 cm^{-1} below 700 cm^{-1} .

ACKNOWLEDGEMENT

We are very grateful to Professor D. A. Brown for his advice and encouragement.

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