Vibrational Spectrum of π-Allyltricarbonylcobalt

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The i.r. and Raman spectra of $Co(\pi-C_3H_5)(CO)_3$ are reported, and an assignment proposed. The vibrations of the $Co(CO)_3$ portion of the molecule can be assigned assuming a ' local symmetry ' of C_{3v}, in contrast to the molecule $Mn(\pi-C_3H_5)(CO)_4$, where the overall symmetry had to be used.

FEW detailed vibrational studies of π-allyl complexes of transition metals have been reported. The ' pure ' π-allyl complexes $Ni(\pi-C_3H_5)_2$ and $Pd(\pi-C_3H_5)_2$ have proved to be too unstable for detailed vibrational spectroscopic investigations;[1] where the complex contains other ligands (*e.g.* halogens or carbonyl groups), however, the stability is greatly increased, and the vibrational spectra can be studied. Thus, assignments have been proposed for $[Pd(\pi-C_3H_5)X]_2$ ($X = Cl, Br$), and the 2-methylallyl analogues,[2,3] and also for $Mn(\pi-C_3H_5)(CO)_4$.[4]

To extend the knowledge of π-allyl transition-metal carbonyl complexes, we have studied the i.r. and Raman spectra of π-allyltricarbonylcobalt, $Co(\pi-C_3H_5)(CO)_3$.

Selection Rules.—No *X*-ray- or electron-diffraction data are available for $Co(\pi-C_3H_5)(CO)_3$. However, the isoelectronic molecule $Co(CO)_3(NO)$ has been found to be pyramidal (C_{3v} symmetry).[5] Therefore we assume a pyramidal arrangement for the $Co(CO)_3$ group, with the C_3H_5 group situated so that the carbon skeleton of the allyl group lies in a plane parallel to the plane which contains the three carbonyl carbon atoms.

The overall symmetry of the molecule will, therefore, be C_s: if ' local symmetry ' is a valid approximation, however, the symmetry of $Co(CO)_3$ will be C_{3v}, with that of the allyl group still C_s. In Table 1 the numbers and types of modes of the allyl group and the (π-allyl)–Co unit are listed, assuming a symmetry of C_s. Table 2 gives the corresponding information for $Co(CO)_3$, assuming (i) C_{3v} and (ii) C_s symmetry. From the numbers of i.r. and Raman bands observed it should be possible to decide whether the assumption of ' local symmetry ' is valid.

TABLE 1

Numbers and symmetries of normal modes for the allyl group and the Co–(allyl) portion of $(\pi-C_3H_5)-Co(CO)_3$ (C_s symmetry)

ν(C–H)	A'
$\nu(CH_2)$	$2A' + 2A''$
$\delta(CH_2)$	$A' + A''$
π(CH)	A'
δ(CH)	A''
ν(C–C–C)	$A' + A''$
$\rho_t(CH_2)$	$A' + A''$
$\rho_w(CH_2)$	$A' + A''$
$\rho_r(CH_2)$	$A' + A''$
δ(C–C–C)	A'
ν[Co–(allyl)]	$2A' + A''$
τ[Co–(allyl)]	A''

All vibrations are i.r. and Raman active; A' vibrations will give polarised Raman scattering. (ν = Stretch; δ = in-plane deformation; π = out-of-plane deformation; ρ_t = twist; ρ_w = wag; ρ_r = rock; τ = torsion).

The Raman and i.r. frequencies for π-allyltricarbonylcobalt are listed in Table 3.

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TABLE 2

Numbers and symmetries of $Co(CO)_3$ vibrational modes

	C_{3v}	C_s
ν(C–O)	$A_1 + E$	$2A' + A''$
δ(Co–C–O)	$A_1 + A_2 + 2E$	$3A' + 3A''$
ν(Co–(CO))	$A_1 + E$	$2A' + A''$
δ(C–Co–C)	$A' + E$	$2A' + A''$
δ[(allyl)–Co–$(CO)_3$]	E	$A' + A''$

(All vibrations are i.r.- and Raman-active except the A_2 mode (C_{3v} symmetry). A_1 and A' vibrations will give polarised Raman scattering.)

TABLE 3

Observed vibrational frequencies of $Co(\pi\text{-}C_3H_5)(CO)_3$ (all figures in cm^{-1})

I.r.		Raman	Approximate assignment
Pure liquid	Gas phase	Pure liquid	
3086w	3091w	3087w,?dp	$\nu(CH_2)$ (A'')
3022w	3028w	3023m,pol	ν(CH) (A')
2970sh		2971w,?pol	$\nu(CH_2)$ (A')
2940w	2940vw		$\nu(CH_2)$ (A')
2860vw			
~2060vs,br		2062m,pol	ν(C–O) (A_1)
(2065vs; C_6H_{12} soln)	2076s	(2064w,pol; C_6H_{12} soln)	
~1980vs,br		1989vs,dp	ν(C–O) (E)
(1998vs; C_6H_{12} soln)	2025s	(1996s,dp; C_6H_{12} soln)	
(1962w; C_6H_{12} soln)	1978w,br		
1485m	1481vw,br	1487vw,br	$\delta(CH_2)_{asym}$ (A'')
1476m		1473vw,br	$\delta(CH_2)_{sym}$ (A')
1388m	1390vw,br	1389m,dp	$\nu(C\text{–}C\text{–}C)_{asym}$ (A'')
1360w,br			
1320w,br			
1225m	1224w,br	1228m,pol	π(CH) (A')
1186m	1186vw,br	1189m,dp	δ(CH) (A'')
1071m	1021w	1020s,pol	$\nu(C\text{–}C\text{–}C)_{sym}$ (A') $+\rho_t(CH_2)_{sym}$ (A')
950m		951s,pol	$\rho_w(CH_2)_{sym}$ (A')
934m	935w,br		$\rho_w(CH_2)_{asym}$ (A'')
		927m,?dp	$\rho_t(CH_2)_{asym}$ (A'')
805w			$\rho_r(CH_2)_{asym}$ (A'')
775m	773w		$\rho_r(CH_2)_{sym}$ (A')
590s	592m	587w,pol	δ(Co–C–O) (A_1)
557s	560m	560w,dp	δ(Co–C–O) (E)
		525w,?pol	δ(C–C–C) (A')
515s	520m		δ(Co–C–O) (E)
480m	480m	482m,pol	ν(Co–C) (A_1)
455m	460w	455w,dp	ν(Co–C) (E)
410w		419m,pol	$\nu(Co\text{–}allyl)_{asym}$ (A')
375m			$\nu(Co\text{–}allyl)_{asym}$ (A'')
362m		362s,pol	$\nu(Co\text{–}allyl)_{sym}$ (A')
		93m,dp	δ(C–Co–C) (E + ?A_1)

RESULTS AND DISCUSSION

Assignment of Spectra.—It will be convenient to divide the discussion into two sections: (*a*) internal vibrations of the allyl group and those involving (π-allyl)–Co, and (*b*) vibrations of $Co(CO)_3$.

(a) *Vibrations of the allyl group and of* (π-allyl)–Co. The assignment is based upon those which have previously been made for $Mn(\pi\text{-}C_3H_5)(CO)_4$ [4] and for $[Pd(\pi\text{-}C_3H_5)X]_2$.[2,3]

(i) C–H *stretching vibrations.* Four i.r. and three Raman bands, all weak, were observed (in the pure liquid) between 2900 and 3100 cm^{-1}. In the i.r. of the vapour only three bands were detected. Due to the weakness of these bands, the polarisation data were somewhat uncertain. The observed frequencies were, however, closely analogous to those previously assigned for $Mn(\pi\text{-}C_3H_5)(CO)_4$, thus: 3086 cm^{-1} (?dp.), A'' CH_2 stretch; 3022 cm^{-1} (pol.), A' C–H stretch; 2970 cm^{-1} (pol.), A' CH_2 stretch; 2940 cm^{-1} (i.r. only), A' CH_2 stretch. It is worth noting that, unlike $Mn(\pi\text{-}C_3H_5)(CO)_4$, where all five fundamenatls were detected,[4] the A'' CH_2 stretch was not observed. A similar situation arose with the dimers $[Pd(\pi\text{-}C_3H_5)X]_2$.[2,3]

(ii) *Deformation and skeletal stretching vibrations.* The normal modes to which the observed frequencies must be assigned are approximations, since extensive coupling of vibrations of the same symmetry species will doubtless occur. The frequencies in the region 500—1600 cm^{-1} will be assigned, therefore, remembering this approximation.

Two Raman bands are found at 1487 and 1473 cm^{-1} for which no polarisation data were obtained, but it is reasonable, by analogy with previous work, to assign these to the $\delta(CH_2)_{asym}$ (A'') and $\delta(CH_2)_{sym}$ (A') respectively. The next-highest frequency is a medium-intensity, depolarised Raman band at 1389 cm^{-1}, which is assigned to $\nu(C\text{–}C\text{–}C)_{asym}$.

The in- and out-of-plane C–H deformations are assigned as follows: δ(CH) (in-plane, A''), 1189 cm^{-1}; π(CH) (out-of-plane, A'), 1228 cm^{-1}. The δ(CH) mode is at an appreciably higher frequency than in $Mn(\pi\text{-}C_3H_5)(CO)_4$.[4]

The polarised Raman band at 1020 cm^{-1} (with a corresponding i.r. band at 1017 cm^{-1}) can be assigned to $\nu(C\text{–}C\text{–}C)_{sym}$. This is very close to the values found in other π-allyl complexes.

Due to the lack of polarisation data, and also substantial mixing of modes, the assignment of bands in the 700—1100 cm^{-1} region must be regarded as somewhat tentative. The out-of-plane twisting (ρ_t) and wagging (ρ_w) of the CH_2 group give rise to bands in the 900—1100 cm^{-1} region, which are assigned as follows: $\rho_t(CH_2)_{sym}$ (A'), 1020 cm^{-1} (pol., see below); $\rho_w(CH_2)_{sym}$ (A'), 951 cm^{-1} (pol.); $\rho_w(CH_2)_{asym}$ (A''), 934 cm^{-1} (i.r. only); $\rho_t(CH_2)_{asym}$ (A''), 927 cm^{-1} (dp?). The symmetric twisting mode has been assigned previously to bands at 989 cm^{-1} (ref. 3) and 1009 cm^{-1} (ref. 4) in the i.r. There is, however, no i.r. band in that region, and the most likely explanation is that this vibration has shifted to become accidentally degenerate with $\nu(C\text{–}C\text{–}C)_{sym}$ (A') at 1020 cm^{-1}. The in-plane rocking modes (ρ_r) of the CH_2 groups give rise to bands at 805 cm^{-1} (i.r. only), $\rho_r(CH_2)_{sym}$ (A'); and at 775 cm^{-1} (i.r. only) $\rho_r(CH_2)_{asym}$ (A'').

The one vibrational mode remaining for the allyl group is the (in-plane) skeletal deformation, δ(C–C–C) (A'), which is assigned to a band which is only observed in the Raman spectrum, at 525 cm^{-1} (pol.). The out-of-plane skeletal deformations are equivalent to Co–(allyl) stretches (see below).

(iii) *The vibrations of* (π-allyl)–Co. From Table 1 we would expect to see three Co–(allyl) stretches ($2A' + A''$), which could also be expressed in terms of a Co–(allyl) stretch (A') and two non-degenerate allyl tilting vibrations ($A' - A''$). The torsional mode (A'') of the allyl group would be expected to give very weak i.r. and Raman bands, and no assignable feature was observed.

In the 300—400 cm^{-1} region, where (π-hydrocarbon)-metal stretches generally occur,[3,4,6-9] three bands were seen in the i.r. and two in the Raman. The two polarised Raman bands are assigned to the A' symmetric (all-in-phase) Co–(allyl) stretch (362 cm^{-1}) and to the A' Co-(allyl) stretch which has the ' terminal ' carbon atoms moving out-of-phase with the ' central ' carbon atom (419 cm^{-1}). The third band was observed only in the i.r., at 375 cm^{-1}, and is assigned to A'' Co–(allyl) stretch (attempts to resolve the Raman band at 362 cm^{-1} into 2 components proved to be impossible).

The (allyl)–Co–$(CO)_3$ deformations will be discussed below, together with the $Co(CO)_3$ vibrations.

The frequencies for the allyl part of the molecule $Co(\pi\text{-allyl})(CO)_3$ are summarised, and compared with those in $Mn(\pi\text{-allyl})(CO)_4$ and $[Pd(\pi\text{-allyl})X]_2$ (where X = Cl), in Table 4.

TABLE 4

Assignments of π-allyl vibrations in $(\pi\text{-}C_3H_5)\text{–}Co(CO)_3$, $(\pi\text{-}C_3H_5)\text{–}Mn(CO)_4$[4] and $[Pd(\pi\text{-allyl})X]_2$ (where X = Cl) assignments

	Frequencies (cm^{-1})		
Assignments	$(\pi\text{-}C_3H_5)Co\text{-}(CO)_3$	$(\pi\text{-}C_3H_5)Mn\text{-}(CO)_4$	$[(\pi\text{-}C_3H_5)\text{-}PdX]_2$
$\nu(CH_2)$, A''	3087	3078	3079
$\nu(CH)$, A'	3023	3025	3048
$\nu(CH_2)$, A'	2971	2973	3008
$\nu(CH_2)$, A''		2964	
$\nu(CH_2)$, A'	2940	2948	2955
$\delta(CH_2)_{asym}$, A''	1487	1503	1488
$\delta(CH_2)_{som}$, A'	1473	1462	1456
$\nu(C\text{–}C\text{–}C)_{asym}$, A''	1389	1397	1380
$\pi(CH)$, A'	1228	1214	1225
$\delta(CH)$, A''	1189	1155	1197
$\nu(C\text{–}C\text{–}C)_{sym}$, A'	1020	1017	1019
$\rho_t(CH_2)_{sym}$, A'	1020	1007	993
$\rho_w(CH_2)_{sym}$, A'	951	920	954
$\rho_w(CH_2)_{asym}$, A''	934	883	937
$\rho_t(CH_2)_{asym}$, A''	927	980	
$\rho_r(CH_2)_{asym}$, A''	805	788	766
$\rho_r(CH_2)_{sym}$, A'	775	774	755
$\delta(C\text{–}C\text{–}C)$, A'	525	521	510

(b) *Vibrations of the* $Co(CO)_3$ *group*. Two points of interest arise from a study of these vibrations. First, whether the concept of ' local symmetry ' is applicable to $Co(\pi\text{-}C_3H_5)(CO)_3$, and secondly to assign as fully as possible the normal vibrational modes of the $Co(CO)_3$ fragment, which has only been studied in detail in the molecule $Co(CO)_3(NO)$.[10]

Considering the C–O stretches, two bands ($A_1 + E$) are predicted for C_{3v} symmetry (both being i.r. and Raman active). For C_s symmetry, however, three bands ($2A' + A''$) would be seen in both the i.r. and the Raman spectra. Both the i.r. and Raman spectra of $Co(\pi\text{-}C_3H_5)(CO)_3$ in dilute solutions in cyclohexane show two bands assignable to fundamentals in the ν(C–O) region (2065 and 1997 cm^{-1}). This is in agreement with the predictions for C_{3v} symmetry. In the Raman spectrum the polarisations of the two bands were as expected for an $M(CO)_3$ system:[3,6,11] 2064 cm^{-1} (pol., A_1), 1996 cm^{-1} (dp., E). The weak i.r. band at 1962 cm^{-1} (in solution) was too weak and broad to have been derived from a split E mode, and it is probably a combination band.

Further evidence for the validity of C_{3v} symmetry is obtained from the number of Co–(CO) stretches and Co–C–O deformations. The relatively small number of bands observed between 400 and 600 cm^{-1} is inconsistent with effective C_s symmetry. The two Co–(CO) stretches are assigned as follows: 482 cm^{-1} (R, pol.; i.r.), A_1; 455 cm^{-1} (R, dp; i.r.), E. It is rather unusual for the degenerate mode to be at a lower frequency than the symmetric mode. Only three ($A_1 + 2E$) of the four ($A_1 + A_2 + 2E$) Co–C–O deformations should be observed, since the A_2 mode is totally inactive under C_{3v} symmetry. The most likely assignment is as follows: 587 cm^{-1} (R., pol.; i.r.), A_1; 560 cm^{-1} (R., dp.; i.r.), E; 515 cm^{-1} (i.r. only), E.

The only feature observed in the Raman spectrum of pure liquid $Co(\pi\text{-}C_3H_5)(CO)_3$ below 300 cm^{-1} was a strong depolarised band at 93 cm^{-1}. Whether this is assignable as a C–Co–C deformation or as a (π-allyl)–-Co–$(CO)_3$ deformation (E symmetry) is questionable. The C–Co–C deformations in $Co(CO)_3(NO)$,[10] however, lie at 91 cm^{-1} (A_1) and 76 cm^{-1} (E), and so there would be no inconsistency in assigning the 93 cm^{-1} band as a C–Co–C deformation (E, with the A_1 mode possible accidentally degenerate). The (π-allyl)–Co–$(CO)_3$ deformation would be expected at a lower frequency, and it was not observed.

TABLE 5

Assignments of the (allyl)–Co and $Co(CO)_3$ vibrations for $(\pi\text{-}C_3H_5)Co(CO)_3$, with the $Co(CO)_3$ frequencies for $Co(CO)_3(NO)$

	Frequencies (cm^{-1})	
Assignment	$(\pi\text{-}C_3H_5)Co(CO)_3$ (liq)	$Co(CO)_3(NO)$ (liq) (Ref. 10)
$\nu(C\text{–}O)$, A_1	2065 (2076 vap.)	2105 (2108 vap.)
$\nu(C\text{–}O)$, E	1998 (2025 vap.)	2037 (2047 vap.)
$\delta(Co\text{–}C\text{–}O)$, A_1	587	484
$\delta(Co\text{–}C\text{–}O)$, E	560	602
$\delta(Co\text{–}C\text{–}O)$, E	515	466
$\nu(Co\text{–}C)$, A_1	482	392
$\nu(Co\text{–}C)$, E	455	441
$\nu(Co\text{–allyl})_{asym}$, A	410	627 [ν (Co–N)]
$\nu(Co\text{–allyl})_{asym}$, A''	375	
$\nu(Co\text{–allyl})_{sym}$, A'	360	
$\delta(C\text{–}Co\text{–}C)$, A_1	?93	91
$\delta(C\text{–}Co\text{–}C)$, E	93	76
$\delta[(allyl)\text{–}Co\text{–}(CO)_3]$, E		

Table 5 summarises the frequencies for the (allyl)–Co and $Co(CO)_3$ units, and compares the latter with those from the isoelectronic $Co(CO)_3(NO)$ molecule.

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Conclusions.—The assignment of the allyl group vibrations is in good agreement with previous work. The 'local symmetry' of C_{3v} assumed for $Co(CO)_3$ was adequate to assign the observed frequencies. The latter finding is in marked contrast to the situation found for $Mn(\pi\text{-}C_3H_5)(CO)_4$,[4] where C_s symmetry was necessary to assign the $Mn(CO)_4$ frequencies.

EXPERIMENTAL

π-Allyltricarbonylcobalt was prepared by the method of Heck and Breslow.[12,13] $Na[Co(CO)_4]$ was treated with allyl bromide in diethyl ether, and the π-complex formed was purified by fractional distillation *in vacuo*.

I.r. spectra (4000—250 cm^{-1}) were run in both the vapour phase and as liquid films of varying thickness on a Perkin-Elmer 521 spectrometer. The spectra were calibrated using the known bands of H_2O vapour, NH_3, and CO. Spectra of solutions in cyclohexane (2200—1900 cm^{-1}) were also recorded, and calibrated using bands of DCl.

Raman spectra of the pure liquid and a solution in cyclohexane (2200—1900 cm^{-1}) were obtained using a Cary model 81 Raman spectrophotometer. The liquid $Co(\pi\text{-}C_3H_5)(CO)_3$ is air-sensitive, and it was, therefore, distilled *in vacuo* into a capillary cell, *ca.* 1·5 mm i.d., which was subsequently sealed off. A Spectra-Physics 125A He–Ne laser was used as an excitation source (output *ca.* 50 mW at 632·8 nm). The spectra were calibrated using known indene peaks, and depolarisation ratios were determined by observing the spectrum with the plane of the polarised incident light parallel and perpendicular, respectively, to the axis of a polaroid analyser. True ρ values were not given directly, but the sample cell was calibrated using accurately known standards.

All reported frequencies are accurate to ± 2 cm^{-1} with the exception of weak and/or broad bands.

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