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VIBRATIONAL SPECTRA OF π-ALLYL- AND π-ALLYL-d_5-DICARBONYLNITROSYLIRON

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SUMMARY

Vibrational spectra of π-$C_3H_5Fe(CO)_2NO$ and π-$C_3D_5Fe(CO)_2NO$ have been studied in the liquid and solid states. The spectra have been interpreted on the basis of a C_s molecular symmetry. A reassignment of some bands is proposed for the allylic fragment based on ν_H/ν_D isotopic shifts. Examination of spectra of deuteriated derivatives has also allowed a reasonable assignment of all the modes involving the Fe–C–O and Fe–N–O groups.

INTRODUCTION

π-Allyl complexes of transition metals have assumed increasing importance in organometallic chemistry[1]. However, despite the extensive structural work carried out on them (NMR and X-ray)[2], little attention has been devoted to their vibrational behaviour and only recently have papers been published, dealing with the vibrational spectra of (π-Allyl–PdCl)$_2$[3,4] and of π-Allyl–Mn (CO)$_4$[5].

Assignments, based almost exclusively on polarization Raman data, are not yet definitive, essentially because a reference molecular structure having a similar electronic configuration for the organic fragment, cannot be found. In the present study we have studied the spectra of π-C_3D_5–$Fe(CO)_2NO$ with the aim of obtaining further vibrational data. Furthermore, an analysis of the oriented crystal spectra in polarized light allows the attribution of peaks to the proper symmetry species.

EXPERIMENTAL

Materials

π-$C_3H_5Fe(CO)_2NO$ (I), π-(2-$CH_3C_3H_4$)$Fe(CO)_2NO$, π-(1-ClC_3H_4)$Fe(CO)_2$-NO, π-(2-ClC_3H_4)$Fe(CO)_2NO$, π-(2-BrC_3H_4)$Fe(CO)_2NO$ were prepared by literature methods[6,7]. π-$C_3D_5Fe(CO)_2NO$ (II) was prepared utilizing allyl-d_5 chloride, obtained by reacting propene-d_6 and chlorine in a flow system at 650°[8]. After repeated distillation *in vacuo*, all complexes were finally purified by means of gas-chromatography 2 m column of SE 30 (10%) on Anachrom 60–80 mesh, column temperature 80°, injector temperature 120°.

Spectra

IR spectra between 4000 and 300 cm^{-1} were recorded on a Perkin–Elmer mod. 521 spectrophotometer. Far IR spectra were measured on a Beckman IR 11 spectrometer.

Solid state spectra were run on polycrystalline-oriented films obtained by slow crystallization of the liquid just below the melting point. The degree of crystal orientation was determined using crossed polaroids. A Perkin–Elmer grid-polarizer unit was used for the measurements with polarized radiation. The temperature of the sample, monitored by a thermocouple, was 100 K in all the experiments.

Raman spectra, either of liquids or solutions, could not be obtained due to rapid decomposition of the complexes. However, it was possible to obtain a Raman spectrum of (I) in the solid state at the liquid nitrogen temperature. The spectrometer used was a Jarrel–Ash He/Ne laser (60 mW, 632.8 nm).

Frequencies are accurate to ± 1 cm^{-1}.

RESULTS AND DISCUSSION

NMR results show that the allylic group in the complexes studied is planar[2]. If, as seems highly probable, the NO group lies in the plane containing the Fe atom and the methinic group, or if free rotation around the Fe–Allyl bond is possible, then the molecule has overall symmetry C_s. This symmetry is thus the same as the local symmetries of both organic and inorganic fragments. Also in the solid state the C_s symmetry of the molecule seems to be retained in the crystalline sites. In fact, the crystal spectrum in polarized light shows only two species of bands with opposite polarization character. Moreover, since all the bands in the crystal appear single [except the ν(C–O) and ν(N–O) modes], we infer that appreciable dynamic intermolecular coupling can be excluded. On the other hand, the anomalous complexity of the ν(C–O) and ν(N–O) bands is probably due to the strong polar character of

TABLE 1

SYMMETRY OF NORMAL MODES FOR THE ALLYL–Fe AND –Fe(CO)$_2$NO FRAGMENTS UNDER C_s SYMMETRY[a]

π-Allyl–Fe		–Fe(CO)$_2$NO	
ν(C–H)	A'	ν(C–O)	$A'+A''$
ν(CH$_2$)	$2A'+2A''$	ν(N–O)	A'
δ(CH$_2$)	$A'+A''$	ν(Fe–C)	$A'+A''$
δ(C–H)	A''	ν(Fe–N)	A'
π(C–H)	A'	δ(Fe–C–O)	$2A'+2A''$
ν(C–C–C)	$A'+A''$	δ(Fe–N–O)	$A'+A''$
ρ_t(CH$_2$)	$A'+A''$	δ(C–Fe–C)	$A'+A''$
ρ_w(CH$_2$)	$A'+A''$	δ(C–Fe–N)	A''
ρ_r(CH$_2$)	$A'+A''$	δ(Allyl–Fe–C)	A''
δ(C–C–C)	A'	δ(Allyl–Fe–N)	A'
ν(Fe–Allyl)	$2A'+A''$		
τ(Fe–Allyl)	A''		

[a] All vibrations are IR active; ν stretch; δ deformation; π deformation out of C–C–C plane; ρ_t twist; ρ_r rock; ρ_w wag; τ torsion.

vibrations of this type, which may lead to long-range intermolecular coupling such as to cause additional splittings[9,10]. Therefore the observed polarization effects are only attributable to the local symmetry of the molecule.

Table 1 lists the number and symmetry species of the normal motions predicted for the organic and inorganic fragments under C_s symmetry. The vibrational frequencies for the compounds (I) and (II) are collected in Tables 2 and 3 respectively. Figure 1 shows the IR spectra of (I) and (II) as liquids and Fig. 2 the IR crystal spectrum of (I) in polarized light. Since the orientation of the crystal axes in the samples is unknown, the intensity of the fundamental at 1387 cm^{-1} has been chosen as reference. Therefore, we term "α" the spectrum where this band has the lower intensity and "β" that obtained upon 90° rotation of the polarizer.

A detailed examination of the spectra of complexes (I) and (II), compared with the Raman polarization data reported by Davidson for π-Allyl–Mn(CO)$_4$[5], clearly shows that the "α" bands belong to the A' symmetry species while the "β" bands belong to the A'' symmetry species.

(continued on p. 162)

TABLE 2

VIBRATIONAL SPECTRUM OF π-$C_3H_5Fe(CO)_2NO$

IR			*Raman*	
Liquid	*Oriented crystal* *T*=100 *K*	*Pol.*	*Solid* *T*=100 *K*	*Assignment*
3973 m	3966 m			2030+1962, 2012+1950
3936(sh)	3920 w			2×1962
3774 vw				2030+1734
3452 s	3460 ms			2×1734
3082 ms	3100 vw	β		$\nu(CH_2)\ A''$
3048 w	3052 vw	α		$\nu(C{-}H)\ A'$
3016 ms	3020 w	α		$\nu(CH_2)\ A'$
2968 ms	2973 w	α		$\nu(CH_2)\ A'$
2932 w	2925 vw	β?		$\nu(CH_2)\ A''$?
2870 w				1492+1387
2690 vw				1466+1229
2666 vw	2676 w			1466+1202
2592 w	2585 vw			1962+627
2524 mw	2526 w			2030+500
2508 mw	2502 vw			2030+475
2462 m	2472 w			1962+500
	2450 w			2028+419
2378 ms	2370 w			2030+348, 1762+611
	2348 w			2012+341
2302 vw				1962+348
	2083(sh)			1950+138
2030 vvs	2050 vs 2028 vs 2012 vs	α	2024 m	$\nu(C{-}O)\ A'$
	1999 mw			$\nu(^{13}C{-}O)\ A'$

(Continued)

TABLE 2 (*continued*)

IR			*Raman*	
Liquid	*Oriented crystal* $T = 100$ *K*	*Pol.*	*Solid* $T = 100$ *K*	*Assignment*
1962 vvs	1964 vs 1950 vs	β	1988 m 1953 m	ν(C–O) A''
	1937 ms			ν(^{13}C–O) A''
1850 w(br)	1870 m			2 × 926
1734 vvs	1762 vs	α		ν(N–O) A'
1528 w	1528 m			2 × 752
1492 s	1493 ms	β		ν(C–C–C) A''
1466 s	1465 s	α		δ(CH$_2$) A'
1387 s	1387 ms	β		δ(CH$_2$) A''
1340 vw				778 + 561
	1302 vw			736 + 561
1270(sh)	1274 vw	α		926 + 348
1257 w	1259 w			?
1229 s	1237 s	α	1240 w	π(C–H) A'
1202 s	1198 ms	β	1200 w	δ(C–H) A''
1080 w(br)	1075(br)			2 × 540
1018 s	1026 s	α	1030 w	ρ_t(CH$_2$) A'
	1016 w	α		603 + 419
966 ms	978 ms	α	978 w	ν(C–C–C) A'
926 s	940 s	α	939 w	ρ_w(CH$_2$) A'
	937 w			500 + 436
916 s	930 ms	β		ρ_w(CH$_2$) A''
	896 w	α		477 + 419
(812) w	(810) w			Impurity
778 ms	800 ms	α		ρ_r(CH$_2$) A'
752 ms	773 ms	β		ρ_t(CH$_2$) A''
722 w	736 m	β		ρ_r(CH$_2$) A''
627(sh)	640 vs	α	643 s	ν(Fe–N) A'
	611 s	β		δ(Fe–N–O) A''
605 vs	603 mw	α	601 ms	δ(Fe–N–O) A'
561(sh)	561 vs	α	564 w	δ(C–C–C) A'
540 vs	529 s	β	535 m	δ(Fe–C–O) A''
500 m	500 m	β	500 w	δ(Fe–C–O) A''
475 m	477 s	α	480 m	δ(Fe–C–O) A'
	465 vw			367 + 96
446 m	449 ms	β	450 w	ν(Fe–C) A''
			436 mw	δ(Fe–C–O) A'
417 ms	419 s	α	417 w	ν(Allyl–Fe) A'
365 ms	367 vs	α?	372 vs	ν(Allyl–Fe) A'
348 m	353 s	α	358 vs	ν(Fe–C) A'
335 m	341 ms	β		ν(Allyl–Fe) A''
			287 mw	2 × 138?
			232 w	138 + 96
			204 mw	δ(C–Fe–C)
132(br)			138 mw	δ(C–Fe–N)
106(br)			110 w	δ(Allyl–Fe–C)
			96 w	δ(Allyl–Fe–N)
				τ(Allyl–Fe)

TABLE 3: IR SPECTRUM OF π-$C_3D_5Fe(CO)_2NO$

Liquid	*Oriented crystal* $T=100$ *K*	*Pol.*	*Assignment*
3970 m			2030+1962
3924(sh)			2 × 1962
3769 vw			2030+1734
3454 s			2 × 1734
3380 vw			2326+1051
3340 w			2326+1014
2654 w			1414+1242
2586 vw	2584 vw		1962+622
2524 w			2030+500
2503 vw	2500 vw		2030+470
2464 w	2468 vw		1962+500
2440(sh)			1962+470
	2385 vw		2032+350
2367 w			1734+640
2326 mw	2332 vw		$\nu(CD_2)$ A''
	2296 vw		$\nu(C{-}D)$ A'?
2268 vw	2268 vw		$\nu(CD_2)$ A'
2202 mw	2205 w		$\nu(CD_2)$ A'
2030 vvs	2032 vs	α?	$\nu(C{-}O)$ A'
	2010 w		1239+778
	1998 mw		$\nu(^{13}C{-}O)$ A'
1962 vvs	1984 m	β	$\nu(C{-}O)$ A''
	1970 m	β	
	1950 w		1239+708
	1937 w		$\nu(^{13}C{-}O)$ A''
	1810 w		1414+396
1734 vvs	1754 vs	α	$\nu(N{-}O)$ A'
1538 w	1553 w		2 × 771
1476 w			771+704
	1437 w		854+590
1414 s	1414 w	β	$\nu(C{-}C{-}C)$ A''
	1335 vw		708+626
1258 w	1251 m	α	2 × 626
1242 m	1239 m	α	$\delta(CD_2)$ A'
1068(br)			603+470
1051 ms	1050 vw		$\delta(CD_2)$ A''
1014 ms	1018 ms	α	$\pi(C{-}D)$ A'
980 mw	983 w	β?	$\delta(C{-}D)$ A''
912 m	919 w		$\nu(C{-}C{-}C)$ A'
849 ms	854 s	α	$\rho_t(CD_2)$ A'
(807)w	(808) w		Impurity
771 mw	778 ms	α	$\rho_w(CD_2)$ A'
704 s	708 m	β	$\rho_w(CD_2)$ A''
689(sh)			$\rho_r(CD_2)$ A'
640 s	649 s	α	$\nu(Fe{-}N)$ A'
622 m	626 s	β	$\rho_t(CD_2)$ A''
	612 w		$\delta(Fe{-}N{-}O)$ A''
	603 w		$\delta(Fe{-}N{-}O)$ A'
582(sh)	590 s	β	$\rho_r(CD_2)$ A''
564 s	557 vs	α	$\delta(C{-}C{-}C)$ A'
522 s	528 m	β	$\delta(Fe{-}C{-}O)$ A''
500 (sh)	500 w		$\delta(Fe{-}C{-}O)$ A''
470 m	475 s	α	$\delta(Fe{-}C{-}O)$ A'
443 m	446 ms	β	$\nu(Fe{-}C)$ A''
397 m	396 s	α	ν(Allyl–Fe) A'
346 m	350 m	α?	ν(Allyl–Fe)A', $\nu(Fe{-}C)$ A'
322 m	312 m	β?	ν(Allyl–Fe) A''

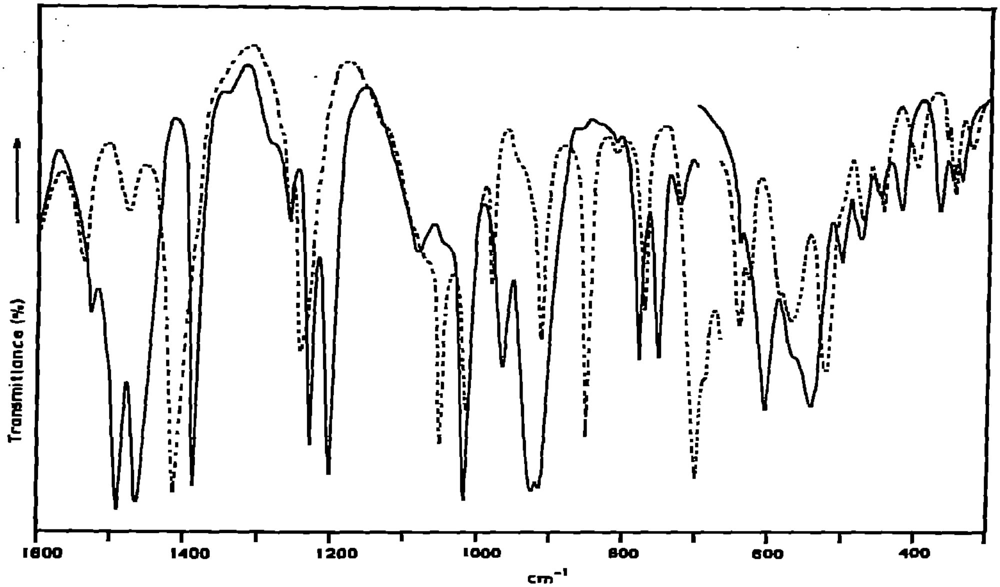

Fig. 1. Infrared spectra of liquid π-$C_3H_5Fe(CO)_2NO$ (——) and π-$C_3D_5Fe(CO)_2NO$ (---).

Assignment for the Fe–Allyl framework

The infrared spectra of complex (I) shows five bands in the region 3100–2900 cm^{-1}. The band at 3048 cm^{-1} is assigned to the A' C–H stretch because it is the only absorption which disappears in the spectra of the 2-halogenoallylic complexes. The remaining four bands are attributed to CH_2 stretching vibrations (see Table 2), in view of their symmetry characters. In the deuteriated complex only three satellite bands at 2326, 2268 and 2202 cm^{-1} were found which, on the basis of isotopic shifts and relative intensities, are assigned as in Table 3.

The spectrum of (I) in the region 1500–1300 cm^{-1} is very similar to those of π-$C_3H_5Mn(CO)_4$ and $(\pi$-$C_3H_5PdCl)_2$. They are characterised by three rather intense bands, assigned in refs. 4 and 5 as $\delta(CH_2)_{asym.}$, $\delta(CH_2)_{sym.}$ and $\nu(C\text{–}C\text{–}C)_{asym.}$ and by Nakamoto as $\nu(C\text{–}C\text{–}C)_{asym.}$, $\delta(CH_2)_{sym.}$ and $\delta(CH_2)_{asym.}$ respectively. Examination of the spectrum of the deuteriated complex indicates that Nakamoto's assignment is the correct one. In fact, the bands at 1492, 1466 and 1387 cm^{-1} in the spectrum of complex (I) should be, on the basis of their symmetry character (A'', A' and A'' respectively), correlated with the bands at 1414, 1242 and 1051 cm^{-1} of the deuteriated molecule.

We presume that the band at 1492 cm^{-1}, which is scarcely influenced by deuteriation ($\nu_H/\nu_D = 1.06$), must correspond to the skeletal ν(C–C–C) mode. The bands at 1466 and 1387 cm^{-1} consequently remain assigned as CH_2 scissoring vibrations.

In the region 1300–700 cm^{-1}, nine fundamental motions are expected. The attribution of IR bands to the relative symmetry species can be reasonably made on the basis of their polarization character in the infrared solid state spectrum. However, the substantial interaction between these modes and the lack of certain distinctive criteria among the deformation modes of the methylenic groups, does not allow a definite frequency assignment. The proposed assignment, reported in Table 2,

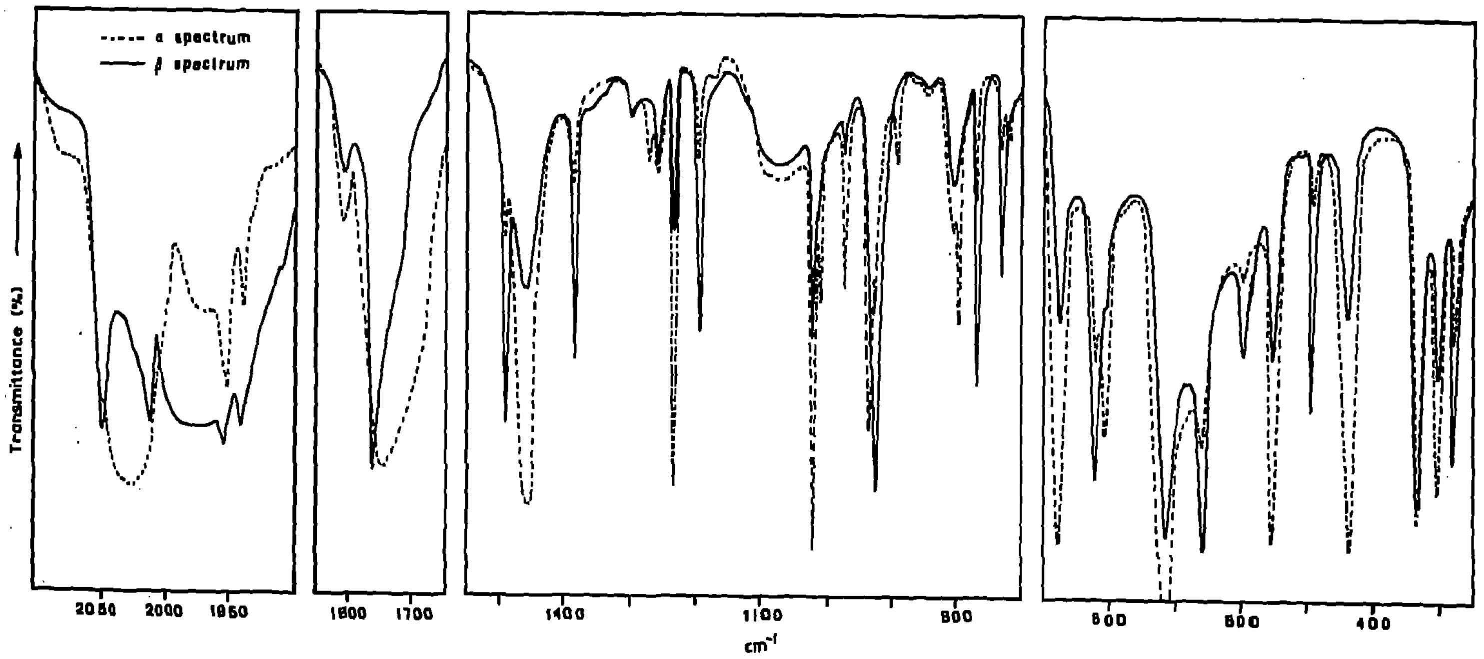

Fig. 2. Infrared crystal spectrum in polarized light of π-$C_3H_5Fe(CO)_2NO$ at 100 K.

disagrees from those previously quoted[3–5], as regards just the position of the ν(C–C–C)$_{\text{sym.}}$ mode, which, on the basis of its isotopic shift, must be localized, in our opinion, at 966 cm^{-1} (912 cm^{-1} in the deuteriated compound, $\nu_H/\nu_D = 1.06$).

Finally, we assign δ(C–C–C)$_{\text{sym.}}$ to the band at 560 cm^{-1}, essentially because, within this spectral zone, it is the only absorption which is influenced by the presence of substituents on the allylic group (2-CH$_3$: 580; 2-Br: 583; 2-Cl: 578 cm^{-1}).

Deuteriation and comparison with other known organometallic complexes in the literature[3,5] allows assignment of the bands at 417, 365 and 331 cm^{-1} in complex (I) to ν(Fe–Allyl) vibrations. The corresponding bands in the deuteriated complex are found at 397, 346 and 322 cm^{-1} ($\nu_H/\nu_D = 1.05$, 1.06 and 1.04 resp.).

Assignments for the –Fe(CO)$_2$NO framework

Absorptions at 2030, 1962 and 1734 cm^{-1}, which remain unchanged on deuteriation, are easily assigned as ν(C–O), A'; ν(C–O), A'' and ν(N–O)[11,12]. In the region 700–300 cm^{-1}, where Fe–N and Fe–C stretches, and Fe–N–O and Fe–C–O bendings are expected, assignment was carried out by comparison with previously investigated carbonylnitrosyl systems[9,11,13]. In these systems, the normal modes involving the nitrogen atom are found at higher frequencies than those involving the carbon atom. The band at 627 cm^{-1} (640 cm^{-1} in the spectrum of the solid) is assigned to the Fe–N stretch by comparison with Co(CO)$_3$NO[9,13], which has a ν(Co–N) band at 602 cm^{-1} (612 cm^{-1} when solid). The increase in frequency found for π-Allyl–Fe-(CO)$_2$NO is attributed to greater π-bonding capacity of the CO group compared to the allyl group[7]. Absorptions at 610 and 601 cm^{-1} in the crystal are then assigned to Fe–N–O bending modes. The remaining absorptions are tentatively attributed as reported in Table 2. Raman peaks at 138 (IR 132 cm^{-1}), 110 and 95 cm^{-1} (IR 96 cm^{-1}) are assigned to deformation modes at the central metal.

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