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VIBRATIONAL SPECTROSCOPIC STUDIES OF SOME h^3-ALLYL COMPLEXES OF IRON

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Summary

Vibrational assignments have been proposed for a number of modes in the h^3-allyl complexes $(C_3H_5)Fe(CO)_3X$, where X = Br, NO_3 or $(C_3H_5)Fe(CO)_3$. The wavenumbers of the $(C_3H_5)Fe$ modes were all quite close to those of other h^3-allyl complexes. From the $\nu(CO)$modes it was clear that the net electron donating ability of X was in the sequence $NO_3 < Br < (C_3H_5)Fe(CO)_3$. Bands due to the NO_3 group were consistent with its behaving as a unidentate ligand.

Introduction

The vibrational spectrum due to a π-bonded allyl group is now reasonably well-established [1—7], but the only reported vibrational assignment for a π-allyl iron complex concerns $(C_3H_5)Fe(CO)_2(NO)$ and $(C_3D_5)Fe(CO)_2NO$ [6]. With the availability of the detailed information on these two molecules, it is now possible to offer as complete an assignment as possible for the related species $(C_3H_5)Fe(CO)_3X$, where X = Br, NO_3 or $(C_3H_5)Fe(CO)_3$. For these complexes, experimental difficulties limited the available vibrational data to IR results and a few Raman wavenumbers from solid-phase samples.

Experimental

The bromide complex $(C_3H_5)Fe(CO)_3Br$ was prepared by the method of Murdoch and Weiss [8], and the dimer $[(C_3H_5)Fe(CO)_3]_2$, by the method of Murdoch and Lucken [9], while the nitrato-species $(C_3H_5)Fe(CO)_3NO_3$ was prepared in good yield by the metathesis of $AgNO_3$ and $(C_3H_5)Fe(CO)_3Br$ [10].

IR spectra were obtained for solids (as KBr discs or halocarbon and nujol mulls) and solutions (for the bromo-complex only, in CS_2 and CCl_4) using a Perkin—Elmer 521 spectrometer (wavenumber range 4000—250 cm^{-1}, calibration using known absorptions of H_2O vapour, NH_3 and CO).

The Raman spectra of solid $(C_5H_5)Fe(CO)_3NO_3$ and $[(C_3H_5)Fe(CO)_3]_2$ were obtained using a Cary Model 81 Raman spectrophotometer. The excitation source was a Spectra-Physics Model 125 He—Ne laser (output ca. 60 mW at 632.8 nm). The spectrum of indene was used to calibrate the wavenumbers and (for the nitrato-complex) the sample was removed periodically because of slow decomposition in the laser beam.

Results

The IR and Raman wavenumbers observed for $(C_3H_5)Fe(CO)_3Br$, $(C_3H_5)Fe(CO)_3NO_3$ and $[(C_3H_5)Fe(CO)_3]_2$ are given in Tables 1—3 respectively, together with the assignments to be discussed below.

TABLE 1

VIBRATIONAL WAVENUMBERS AND PROPOSED ASSIGNMENT FOR (h^3-ALLYL) IRON TRICARBONYL BROMIDE (IN CM^{-1})

IR			Approx. assignment
Solid (KBr disc)	CS_2 soln.	CCl_4 soln.	
3158w			
3090m	3086w	3088w	CH$_2$ stretch, A''
3008m	3023w	3024w	CH stretch, A'
2963w		2967w	CH$_2$ stretch, A''
2916w		2917w	CH$_2$ stretch, A'
	2840w	2851w	
	2082s	2090s	CO stretch, A'
2000vvs(br)	2038s	2045s	CO stretch, A'
	2010s	2012vs	CO stretch, A''
1459s		1462w	CH$_2$ scissoring, A'', +
1390m		1396w	CCC antisymm. str., A''
1258w	1253vw		
1220s	1223m		O.o.p. CH def., A'
1110w	1093w		I.p. CH def., A''
1050s	1042m		CH$_2$ twist, A'
1014m	1015w		CCC symm. stretch, A'
945s	943m		CH$_2$ wag, A'
932m			CH$_2$ wag, A''
921m	918w		CH$_2$ twist, A''
790m	778m		CH$_2$ rock., A'
	626m	628m	Fe—C—O def., A''
600vs	611s	615s	Fe—C—O def., A'
	600s	608s	Fe—C—O def., A'
560vs	563 s	565s	Fe—C—O def., A''
	550m	550m	Fe—C—O def., A'
525vs	528m	530m	Fe—C—O def., A'' +
499vs	500m	500m	CCC def., A'
480m	480s	480s	Fe—(CO) stretch, A''
450m	440w	446m	Fe—(CO) stretch, A'
420m		426w	Fe—(CO) stretch, A''
390w		400vw	Fe—allyl stretch, A'
370w		358w	Fe—allyl stretch, A''
348w			
330w		329w	Fe—allyl stretch, A' (? + Fe—Br stretch, A')

TABLE 2

VIBRATIONAL WAVENUMBERS AND PROPOSED ASSIGNMENT FOR (h^3-ALLYL) IRON TRICARBONYL NITRATE (IN CM^{-1})

IR solid (KBr disc)	Nujol mull	Halocarbon mull	Raman solid	Approx. assignment
3118w				
3026w				CH stretch, A'
2960vw				CH$_2$ stretch, A''
2921w		2936w		CH$_2$ stretch, A'
2858vw		2860w		
2100s(br) (2106s, CH$_2$Cl$_2$soln)	2100m	2100m	2110m 2071m	CO stretch, A'
2030vs(br) (2060s and 2024s, CH$_2$Cl$_2$ soln)	2035s	2020s(br)	2058m	CO stretch, A'
			2042m	CO stretch, A''
1720w	1750w(br)			
1475s		1475m	1476m	CH$_2$scissoring, A'', + NO$_2$ str., B_1
1458s		1458m		CH$_2$ scissoring, A'
1398m 1383s		1400w	1403m	CCC antisymm. stretch, A''
1280s	1281ms			NO$_2$ stretch, A
1230m	1228w		1234m	O.o.p. CH def., A'
1100m	1100w		1101w—m	I.p. CH def., A''
1055w				
1015(sh)			1016(sh)	CCC symm. str., A', + CH$_2$ twist, A'
1010s	1010m		1010s	NO stretch, A_1
960m	960w—m		958s	CH$_2$ wag, A'
940m	940w			CH$_2$ wag, A''
925w				CH$_2$ twist, A''
830w				
810m	800w		804w—m	CH$_2$ rock, A'', + NO$_2$ wag, B_2
718w	722m			CH$_2$ rock, A', + NO$_2$ def., A
617s	620m	620m	620vw	Fe—C—O def., A''
604s	608m	610m		Fe—C—O def., A'
570s	574m	569	568w	Fe—C—O def., A'
		555 MeNO$_2$		Fe—C—O def., A''
535s	540m	531 soln.	534m	I.p. C—C—C def., A', + Fe—C—O def., A'
496m	499w—m	491	496w	Fe—C—O def., A''
496m	470m		464w	Fe—(CO) stretch, A''
			443w—m	Fe—(CO) stretch, A'
426m	428w—m			Fe—(CO) stretch, A'
			416m	allyl—Fe stretch, A'
			354m	allyl—Fe stretch, A''
340m(br)			336s	allyl—Fe stretch, A'

Discussion

It will be convenient to divide this into three sections, dealing with vibrations of the Fe—(C_3H_5) unit, vibrations of the Fe(CO)$_3$ unit, and vibrations of Fe—X (for X = Br, NO$_3$ only) respectively.

(i) Vibrations of the Fe—(C_3H_5) fragment

A local symmetry of C_s will be assumed in each case, and the types of vibra-

TABLE 3

VIBRATIONAL WAVENUMBERS AND PROPOSED ASSIGNMENTS FOR THE (h^3-ALLYL) iron t IRON TRICARBONYL DIMER (IN CM^{-1})

IR (solid, ~ 100 K)	Raman (solid, ~ 100 K)	Approximate assignment
3080vw		CH_2 stretch, A''
3018w		CH stretch, A'
2930w(br)		CH_2 stretch, A
2845vw		
2040s		CO stretch, A'
1990vs		CO stretch, A'
1934vs(br)		CO stretch, A''
1500m		CH_2 scissoring, A''
1470m }		CH_2 scissoring, A'
1414m		
1395m		
1360m		CCC stretch, A''
1351m		
1225w		O.o.p. CH def., A'
1207w		I.p. CH def., A''
1015wm		CCC stretch, A', + CH_2 twist, A'
980vw		CH_2 twist, A''
945m		CH_2 wag, A'
910m		CH_2 wag, A''
878vw		CH_2 rock, A''
806wm		CH_2 rock, A'
630m	632w	Fe—C—O def., A''
620m	621vw	Fe—C—O def., A'
602m	612w	Fe—C—O def., A'
585m	580w	Fe—C—O def., A''
568m		Fe—C—O def., A'
536m	546w	Fe—C—O def., A''
499w	498s	I.p. C—C—C def., A'
430w		Fe—CO stretch, A''
	457m	Fe—CO stretch, A'
430m	422m	Fe—CO stretch, A'
390w	380mw(br)	Fe—allyl stretch, A'
361wm	350m(br)	Fe—allyl stretch, A''
330m(br)	326m	Fe—allyl stretch, A'

tion and their numbers and symmetry types, are summarized in Table 4. Assignments may be proposed using the published results for $(C_3H_5)Mn(CO)_4$ [3], $(C_3H_5)Co(CO)_3$ [4] and $(C_3H_5)Fe(CO)_2NO$, [6] and results for all three complexes will be considered together. It must be recognized that, in the absence of Raman polarisation data, discrimination between A' and A'' modes of a given type is likely to be arbitrary in many cases.

None of the $(C_3H_5)Fe(CO)_3X$ species investigated gave values for all 5 of the C—H stretches predicted. Four were seen in the bromide, at 3086, 3023, 2967 and 2917 cm^{-1}. Comparison with other h^3-allyl systems suggests that these may be assigned as $A''CH_2$, $A'CH$, $A''CH_2$ and $A'CH_2$ stretches respectively. When X = NO_3, three features are seen, at 3026, 2960 and 2921 cm^{-1}, as is the case for the dimeric complex also (3080, 3018, 2930 cm^{-1}.)

Previous assignments of bands in the 1350—1500 cm^{-1} have been contradictory, but the isotopic shifts observed for $(C_3H_5)Fe(CO)_2(NO)$ and $(C_3D_5)Fe(CO)_2$-

TABLE 4

NUMBERS AND SYMMETRIES OF NORMAL MODES FOR THE Fe—(C_3H_5) FRAGMENT OF (C_3H_5)Fe$(CO)_3$X (C_s SYMMETRY) [a]

ν(C—H)	A'
$\nu(CH_2)$	$2A' + 2A''$
$\delta(CH_2)$	$A' + A''$
π(C—H)	A'
δ(C—H)	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 Fe—(C_3H_5)	$2A' + A''$
τ Fe—(C_3H_5)	A''

[a] All vibrations are IR 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).

NO by Paliani et al. suggests that the feature ca 1500 cm^{-1} is ν_{as} (C—C—C), with $\delta(CH_2)$ ca 1380 cm^{-1} (both of A'' symmetry), and the symmetric $\delta(CH_2)(A')$ at ca 1450 cm^{-1}. This assignment is accepted here, in preference to the other proposed assignment, which reverses the descriptions of the two A'' modes. It must always be remembered, however, that some mixing of modes will occur between the two vibrations so that each partakes of the character of the other. Solid state effects lead to splitting of these bands in the spectrum of $[(C_3H_5)Fe(CO)_3]_2$.

There is no ambiguity in the assignment of the out-of-plane and in-plane CH deformations to features ca 1225 cm^{-1} and between 1100—1200 cm^{-1} respectively.

Difficulties in assignment are again apparent, however, in the range 800—1050 cm^{-1}. Isotopic shifts led Paliani et al. to assign the symmetric C—C—C stretch to 966 cm^{-1}, in $(C_3H_5)Fe(CO)_2(NO)$ [6], while the band at 1018 cm^{-1} (ν_s (CCC) according to other workers [1—4,7] was described as the $A'CH_2$ twist. This modification to the previously accepted assignment cannot be made easily for the complexes at present under consideration, where the observed bands are at rather different wavenumbers. In any case the modes in this region are certain to be mixed extensively. Remembering, therefore, that the assignments are largely arbitrary, they were proposed using those given for $(C_3H_5)Mn(CO)_4$ [3].

The only remaining features in this section are the CCC deformation, found ca 500 cm^{-1} as in previous work, and the Fe—(C_3H_5) stretches, $2A' + A''$. These are seen in the range 330—420 cm^{-1} in each case, assignment to individual modes being made by comparison with data on $(C_3H_5)Co(CO)_3$ [4] and $(C_3H_5)Mn(CO)_4$ [3], where Raman polarisation data were available.

No feature assignable as a torsion, τFe—(C_3H_5) could be detected for any of the complexes.

A summary of the proposed Fe—(C_3H_5) assignments is given in Table 5. The NMR spectrum of the analogous iodo-complex has been interpreted assuming the presence of two isomers (due to restricted rotation of the C_3H_5 group) [11]. No evidence for such isomers could be found in the vibrational spectra reported here.

TABLE 5

PROPOSED ASSIGNMENT OF THE Fe—(C_3H_5) VIBRATIONAL MODES IN (C_3H_5)Fe(CO)$_3$X (IN CM^{-1})

X	Br	NO$_3$	(C_3H_5)Fe(CO)$_3$
$\nu(CH_2)$, A''	3086		3080
$\nu(CH)$, A'	3023	3026	3018
$\nu(CH_2)$, A'			
$\nu(CH_2)$, A''	2967	2960	
$\nu(CH_2)$, A''	2916	2921	2930
$\nu_{as}(CCC)$, A''		1476	1500
$\delta_s(CH_2)$, A'	1462	1458	1470/1414
$\delta_{as}(CH_2)$, A''	1396	1400	1395/1360/1351
$\pi(CH)$, A'	1223	1228	1225
$\delta(CH)$, A''	1110	1100	1207
$\nu_s(CCC)$, A'	1015	1016	1015
$\rho_t(CH_2)(s)$, A'	1042	1016	1015
$\rho_w(CH_2)(s)$, A'	943	960	945
$\rho_w(CH_2)(as)$, A''	932	940	910
$\rho_t(CH_2)(as)$, A''	918	925	980
$\rho_r(CH_2)(as)$, A''		800	878
$\rho_r(CH_2)(s)$, A'	778	722	806
$\delta(CCC)$, A'	500	540	499
$\nu_{as}(Fe{-}C_3H_5)$, A'	400	416	390
$\nu_{as}(Fe{-}C_3H_5)$, A''	358	354	361
$\nu_s(Fe{-}C_3H_5)$, A'	329	336	330
$\tau(Fe{-}C_3H_5)$, A''			

(ii) Vibrations of the Fe(CO)$_3$ unit

It is immediately obvious that in all of the cases the strict "local symmetry" approach, giving C_{3v} symmetry to the Fe(CO)$_3$ unit is inapplicable. Thus each complex gives 3 CO bands (2 predicted for C_{3v}), even in solution, and so C_s symmetry must be used as a basis. The lack of data, especially Raman polarisation measurements, renders a detailed assignment impossible, however.

The relative positions of the ν(CO) bands in (C_3H_5)Fe(CO)$_3$X may be used to estimate the abilities of the various X ligands to build up electron density at the iron. Since corresponding ν(CO) values all fall in the sequence X = NO$_3$ > Br > (C_3H_5)Fe(CO)$_3$ it appears that the nitrato group is the most efficient of the 3 ligands at withdrawing electron density from the Fe, hence the possible extent of Fe → CO back-donation is restricted.

Another observation which can be made concerning the ν(CO) wavenumbers is that there is a close correspondence between the values in the solid phase and in solution. There is no evidence for the ionisation (giving X$^-$ and (C_3H_5)Fe(CO)$_3^+$) in solution postulated by some previous workers [12,13]. Also, no bands attributable to a second isomer were seen [14].

An appropriate number of bands in the 400—700 cm^{-1} range were seen, corresponding to the numbers of δ(Fe—C—O) and ν(Fe—CO) vibrations predicted by C_s symmetry. No detailed assignment can be put forward with any great confidence, however.

(iii) Vibrations of Fe—X

This discussion is only relevant for X = Br or NO$_3$. Fe—Br would be expected to occur below 300 cm^{-1} [15] and no feature which could be so assigned was seen.

TABLE 6

PROPOSED ASSIGNMENT OF VIBRATIONS OF THE NO_3 LIGAND IN $(C_3H_5)Fe(CO)_3NO_3$ (IN CM^{-1})

NO_2 stretches	A_1	1280
	B_1	1475
NO stretch	A_1	1010
NO_2 def.	A_1	718
NO_2 rock	B_2	801
Combination (1010 + 718)		1720

Several bands due to coordinated nitrate were, however, observed in the spectrum of $(C_3H_5)Fe(CO)_3NO_3$. The chief point of interest is whether the NO_3 is bound as a uni- or a bi-dentate ligand. The 18-electron rule suggests that the former is the more probable, and a number of well-established empirical rules are available to deduce the manner of attachment of a nitrate ligands from the vibrational spectrum [16,17].

The features at 1720, 1475, 1280, 1010, 801 and 718 cm^{-1} are thought to be associated with the nitrato ligand. The assignment of these is summarised in Table 6, using "local symmetry" of C_{2v} as a basis. From it we may deduce that the ligand is unidentate; thus the combination band at 1720 cm^{-1} is unsplit [15], and the band at 1280 cm^{-1} ("Band 2" according to the classification of Addison et al [16]) is not the weakest nitrato-band.

Conclusion

Partial vibrational spectroscopic data have been presented for the series of h^3-allyl complexes $(C_3H_5)Fe(CO)_3X$, where X = Br, NO_3 or $(C_3H_5)Fe(CO)_3$. The internal modes of the h^3-allyl group, and Fe—(C_3H_5) modes are very similar in wavenumbers to those in other h^3-allyl complexes. Detailed assignments could not be made for other modes, but it was possible to deduce that the effective electron donating ability of X varied in the sequence $NO_3 < Br < (C_3H_5)Fe(CO)_3$, and that the NO_3 group was unidentate.

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