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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 (C₃H₅)Fe(CO)₂(NO) and (C₃D₅)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 (C₃H₅)Fe(CO)₃X, where X = Br, NO₃ or (C₃H₅)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 AgNO₃ 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) CS₂ soln. CCl₄ soln. 3158w 3090m 3086w 3088w CH2 stretch, A" 3008m 3024w 3023w CH stretch, A 2963w 2967w CH2 stretch, A' 2916w 2917w CH2 stretch, A 2840w 2851w 2082s 2090s CO stretch, A' 2000vvs(br) 2038s 2045s CO stretch, A' 2010s 2012vs CO stretch, A" CH2 scissoring, A", + 1459s 1462w } 1390m CCC antisymm. str., A" 1258w 1253vw 1220s 1223m 0.o.p. CH def., A' 1110w 1093w I.p. CH def., A 1050s 1042m CH2 twist, A' 1014m CCC symm. stretch, A' 1015w 9455 943m CH2 wag, A' CH₂ wag, A" 932m CH2 twist, A" 921m 918w 790m 778m CH2 rock., A 626m 628m Fe-C-O def., A 600vs 611s 6155 Fe-C-O def., A 600s 608s Fe-C-O def., A Fe-C-O def., A 563 s 565s 560vs ſ 550m 550m Fe-C-O def., A 530m } 52515 Fe-C-O def., A" + 528m 499vs 500m CCC def., A' 480m 480s 480s Fe-(CO) stretch, A" 450m 440w 446m Fe-(CO) stretch, A 420m 426w Fe-(CO) stretch, A" 390. 400vw Fe-allyl stretch, A' 370w } 348w } 358w Fe-allyl stretch, A' 330w 329w Fe-ally] stretch, A' (? + Fe-Br stretch, A')

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TABLE 2

VIBRATIONAL WAVENUMBERS AND PROPOSED ASSIGNMENT FOR $(h^3$ -Allyl) iron tri-CARBONYL NITRATE (IN CM⁻¹)

Interview Interview <thinterview< th=""> <thinterview< th=""> <th< th=""><th>IR solid (KBr disc)</th><th>Nujol mull</th><th>Halocarbon mull</th><th>Raman solid</th><th>Approx. assignment</th></th<></thinterview<></thinterview<>	IR solid (KBr disc)	Nujol mull	Halocarbon mull	Raman solid	Approx. assignment
$\begin{array}{c c c c c c c c c c c c c c c c c c c $					p
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	3118w				
2921 w 2936 w CH2 stretch, A 2858 w 2860 w CH2 stretch, A 2109(str) 2100m $\left\{\begin{array}{c} 2110m \\ 2071m \end{array}\right\}$ C0 stretch, A' 2030s(br) 2035s 2020(str) 2058m C0 stretch, A' 2030s(br) 2035s 2020(str) 2058m C0 stretch, A' 2030s(br) 2035s 2020(str) 2058m C0 stretch, A' 1720w 1750w(br) 1475m 1476m CH2 scissoring, A', + N02 1475s 1475m 1476m CH2 scissoring, A', + N02 1383m 1458m CH2 scissoring, A' 1388m 1458m CH2 scissoring, A' 1383s 1400w 1403m CC antisymm. stretch, A'' 12800 1281ms NO, stretch, A NO 1230m 1228w 1234m 0.o.p. CH def., A'' 1010s 100w 1016(sh) CC symm. str., A', + CH2 1015sh 1010m 958s CH2 wag, A'' 940m 940w CH2 twist, A'' CH2 twist, A'' 810m 800w 804w-m CH2 rock, A', + NO2 wag, A'' <td>3026w</td> <td></td> <td></td> <td></td> <td>CH stretch, A</td>	3026w				CH stretch, A
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	230000		00.02		Ch ₂ stretch, A
2400w 2100m 2100m $\left\{ 2110m \\ 2071m \right\} \right\}$ CO stretch, A' (2106s, CH_2Cl_soln) 2035s 2020s(br) 2058m CO stretch, A' (2060s and 2024s. CO stretch, A' CO stretch, A' (2105w) 1475m 2042m CO stretch, A' (2105w) 1475m 1476m CH_3cissoring, A'', + NO2 1475s 1475m 1476m CH_3cissoring, A'', + NO2 1398m 1400w 1403m CCC antisymm.stretch, A'' 1393b 1281ms NO2 stretch, A NO2 stretch, A'' 1230m 1228w 1234m O.o.p. CH def., A'' 1010w 1101w-m Lp. CH def., A'' Wist, A' 1015sh 1016(sh) CCC symm.str., A', + CH2 Wist, A' 960m 960w-m 958s CH2 wag, A' CH2 wag, A' 925w CH2 rock, A', + NO2 wag, B B2 CH2 rock, A', + NO2 wag, B B2 718w 722m 620m 620vw Fe-C-0 def., A' S34m LP. CO stretch, A'', + Fe_dot, A'	2921W		7936W		CH ₂ stretch, A
1.100m 1.100m 1.2110m 2.010m 1.0100m 1.0105m 1.010m 1.010m 1.010m 1.010m 1.010m 1.010m 1.010s 1.010s <td>2100s(br)</td> <td>2100m</td> <td>2100m</td> <td>(9110m)</td> <td></td>	2100s(br)	2100m	2100m	(9110m)	
$ \begin{array}{c} 1001, 011, 011, 011, 011, 011, 011, 01$	(2106e CHaClasolp)	210011	210011	2071m	CO stretch, A'
Loose Loose <thloose< th=""> <thloose< th=""> <thl< td=""><td>2030vs(br)</td><td>20358</td><td>2020s(br)</td><td>2058m</td><td>CO strutch 4</td></thl<></thloose<></thloose<>	2030vs(br)	20358	2020s(br)	2058m	CO strutch 4
CH2Cl2 soln) 2042m C0 stretch, A'' 1720w 1750w(br) 1475s 1475m 138m 1458m 138m 1400w 138as 1281ms 1230m 1228w 1100m 101w-m 1100w 1010w-m 1101w-m 1.p. CH def., A' 1010s 1010m 960m 960w-m 958s CH2 wag, A' 940m 940w 940m 940w 940m 940w 940m 940w 958s CH2 wag, A' 940m 940w 940m 940w 940m 620m 620m 617s 620m 620m 617s 620m 620m 617s 620m 620w	(2060s and 2024s.	20333	20203(01)	200011	eo sueici, A
1720w1750w(br)160 kmCH setsoring str. B_1 1475s1475m1476mCH setsoring str. B_1 1458s1458mCH setsoring setsoring A', + NO2 str. B_1 138as1400w1403mCCC antisymm. stretch A''138as1281msNO2 stretch A1280s1281msNO2 stretch A''1280m1228w1234mO.o.p. CH def., A''100m1100w1101w-mI.p. CH def., A''1055w1016(sh)CCC symm. str., A', + CH2 twist, A'1010s1010m958sCH2 wag, A''940m960w-m958sCH2 wag, A''925w800w804w-mCH2 rock, A', + NO2 wag, B2810m800w804w-mCH2 rock, A', + NO2 wag, B2718w722m620m620w617s620m620wFe-C-O def., A'535s540m531 soln.568w535s540m531 soln.568w496m499w-m491464w426m428w-m446w426m428w-mFe-(CO) stretch, A''426m428w-m416m340m(br)336sallyl-Fe stretch, A''	CH ₂ Cl ₂ soln)			904.9m	CO stretch 4"
1475s 1475m 1476m CH2scissoring, A'' , + NO2 1458s 1458m CH2 scissoring, A'' 1398m 1400w 1403m CCC antisymm. stretch, A'' 1380s 1281ms NO2 stretch, A 1230m 1230m 1228w 1234m O.o.p. CH def., A'' 100m 1100w 1101w-m I.p. CH def., A'' 1015(sh) 1016(sh) CCC symm. str., $A'_* + CH_2$ 1010s 1010m 958s CH2 wag, A'' 940m 960w-m 958s CH2 wag, A'' 925w CH2 rock, $A'_* + NO2$ wag, A''' 810m 810m 800w 804w-m CH2 rock, $A'_* + NO2$ wag, $A''''''''''''''''''''''''''''''''''''$	1720w	1750w(br)			
1458s 1458m str., B1 1458s 1458m CH2 scissoring, A' 1398m 1400w 1403m CCC antisymm. stretch, A" 1280s 1281ms NO2 stretch, A 1230m 1228w 1234m O.o.p. CH def., A' 1000m 1101w-m I.p. CH def., A' 1055w 100w 1101w-m I.p. CH def., A' 1015(sh) 1016(sh) CCC symm. str., A', + CH2 twist, A' 1010s 1010m 1010s NO stretch, A1 960m 960w-m 958s CH2 wag, A' 925w CH2 rock, A', + NO2 wag, B2 718w 722m 620m 620w 604s 608m 610m 568w Fe-C-0 def., A' 570s 574m 569 555 540m 531 535s 540m 531 soln. 568w Fe-C-0 def., A' 496m 499w-m 491 464w Fe-(CO) stretch, A' 426m 428w-m Fe-(CO) stretch, A' 443w-m Fe-(CO) stretch, A' 426m 428w-m <t< td=""><td>1475s</td><td></td><td>1475m</td><td>1476m</td><td>CHaseissoring, A", + NOa</td></t<>	1475s		1475m	1476m	CHaseissoring, A", + NOa
1458s 1458m CH 2 sitsoring, A' 1398m 1400w 1403m CCC antisymm. stretch, A'' 1383s 1280m 0.0.p. CH def., A'' 1230m 1228w 1234m 0.0.p. CH def., A'' 1100m 1100w 1101w-m 1.p. CH def., A'' 1055w 1016(sh) CCC symm. str., A', + CH2 twist, A'' 1010s 1010m 1010s NO stretch, A_1 960m 960w-m 958s CH2 wag, A'' 925w CH2 rock, A'', + NO2 wag, B'' CH2 rock, A'', + NO2 wag, B'' 810m 800w 804w-m CH2 rock, A'', + NO2 wag, B'' 718w 722m CH2 rock, A', + NO2 wag, B'' 604s 608m 610m 568w Fe-C-O def., A'' 570s 574m 569 Fe-C-O def., A'' 535s 540m 531 soln. 544m 196w 496m 499w-m 491 464w Fe-(CO) stretch, A'' 426m 428w-m 416m allyl-Fe stretch, A'' 416m allyl-Fe stretch, A'' 336s_ allyl-Fe stretch, A'' <td></td> <td></td> <td></td> <td></td> <td>str. Bi</td>					str. Bi
1398m 1383s1400w1403mCCC antisymm. stretch. A"1280s1281msNO2 stretch. A1230m1228w1234mO.o.p. CH def., A'1100m1100w1101w-mI.p. CH def., A"1055w1016(sh)CCC symm. str., A', + CH21015s1010m1010sNO stretch. A1960m960w-m958sCH2 wag, A'940m940w958sCH2 wag, A'940m940wCH2 rock, A', + NO2 wag, B2940m960w-m958sCH2 wag, A'940m960w-m958sCH2 rock, A', + NO2 wag, B2940m960w-m958sCH2 rock, A', + NO2 wag, B295wCH2 rock, A', + NO2 def., AB2718w722m620m620w604s608m610mFe-C-O def., A'570s574m569555535s540m531496m470m496w496m470m496w426m428w-mFe-CO def., A'416mally1-Fe stretch, A'416mally1-Fe stretch, A'340m(br)336s,ally1-Fe stretch, A'	1458s		1458m		CH ₂ scissoring, A'
1383s i 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 1016(sh) CCC symm. str., A', + CH ₂ 1010s 1010m 1010s NO stretch, A ₁ 960m 960w-m 958s CH ₂ wag, A' 940m 940w CH ₂ wag, A' CH ₂ wag, A' 925w CH ₂ wag, A'' CH ₂ wag, A'' Stretch, A'' 810m 800w 804w-m CH ₂ rock, A'', + NO ₂ wag, B B ₂ 718w 722m 617s 620m 620w Fe-C-O def., A'' 604s 608m 610m 568w Fe-C-O def., A' 570s 574m 569 Statm Fe-C-O def., A'' 496m 499w-m 491 496w Fe-C-O def., A'' 496m 470m 464w Fe-(CO) stretch, A' 426m 428w-m Fe-(CO) stretch, A' 554m 426m 428w-m 416m <td>1398m</td> <td></td> <td></td> <td></td> <td><u>-</u></td>	1398m				<u>-</u>
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1383s ⁷		1400w	1403m	CCC antisymm. stretch, A"
1230m1228w1234mO.o.p. CH def., A'1100m1100w1101w-mI.p. CH def., A'1055w1016(sh)CCC symm. str., A', + CH21015(sh)1016(sh)CCC symm. str., A', + CH21010s1010m1010sNO stretch, A1960m960w-m958sCH2 wag, A'940m940wCH2 wag, A'925wCH2 wag, A'830w800w804w-mCH2 rock, A'', + NO2 wag,810m800w804w-mCH2 rock, A'', + NO2 wag,718w722mCH2 rock, A', + NO2 def., A604s608m610mFe-C-O def., A'570s574m555540m531soln.568w496m499w-m491496m470m464wFe-CO def., A'426m428w-mFe-CO stretch, A''426m428w-mFe-CO stretch, A''340m(br)336sallyl-Fe stretch, A''	1280s	1281ms			NO ₂ stretch, A
1100m1100w1101 w-m1.p. CH def., A"1055w1015(sh)1016(sh)CCC symm. str., A', + CH2 twist, A'1010s1010m1010sNO stretch, A1 960m960m960w-m958sCH2 wag, A' CH2 wag, A'940m940wCH2 wag, A' CH2 wag, A'925wCH2 wag, A' CH2 twist, A''830w800w804w-m810m800w804w-m604s620m620w604s608m610m 555535s540m531 555540m531 491496m499w-m491426m428w-m443w-m426m428w-mFe-(CO) stretch, A' Fe-(CO) stretch, A'340m(br)336s_ allyl-Fe stretch, A'	1230m	1228w		1234m	0.0.p. CH def., A'
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	1100m	1100w		1101w-m	I.p. CH def., A"
1015(sh)1016(sh)CCC symm. str., A' , + CH2 twist, A' 1010s1010m1010sNO stretch, A_1 960m960w-m958sCH2 wag, A' 940m940w958sCH2 wag, A'' 925wCH2 twist, A'' CH2 twist, A'' 830w800w804w-mCH2 rock, A'' , + NO2 wag,810m800w804w-mCH2 rock, A'' , + NO2 wag,810m800w804w-mCH2 rock, A'' , + NO2 def, A'' 810m800w620m620vwFe-C-0 def, A'' 604s608m610mFe-C-0 def, A'' 570s574m569 555Soln.534mLp. C-C-C def, A'' 535s540m531 enderSoln.534mLp. C-C-C def, A'' 496m499w-m491464wFe-(CO) stretch, A'' 426m428w-mFe-(CO) stretch, A'' 443w-m416mallyl-Fe stretch, A'' 354mallyl-Fe stretch, A''	1055w				
	1015(sh)			1016(sh)	CCC symm. str., A', + CH ₂ twist, A'
960m960w-m958s $CH_2 wag, A'$ 940m940w $CH_2 wag, A''$ 925w $CH_2 twist, A''$ 830w $CH_2 twist, A''$ 810m800w $804w-m$ $CH_2 rock, A'', + NO_2 wag, B_2$ 718w722m $CH_2 rock, A', + NO_2 def, A$ 617s620m620m620w604s608m610mFe-C-O def, A''570s574m569568wFe-C-O def, A'535s540m531soln.534mLp. C-C-C def, A''496m499w-m491496wFe-C-O def, A''426m428w-m416mallyl-Fe stretch, A'340m(br)336s_allyl-Fe stretch, A'	1010s	1010m		1010s	NO stretch, A ₁
940m 940w $CH_2 wag, A''$ 925w $CH_2 twist, A''$ 830w $CH_2 twist, A''$ 810m 800w $804w-m$ $CH_2 tock, A'', + NO_2 wag, B_2$ 718w 722m $CH_2 rock, A'', + NO_2 def, A$ 617s 620m 620m 620w 604s 608m 610m Fe-C-O def, A'' 570s 574m 569 555 535s 540m 531 531 540m 499w-m 491 496w Fe-C-O def, A'' 496m 499w-m 491 496w Fe-C-O def, A'' 496m 470m 464w Fe-(CO) stretch, A'' 426m 428w-m Fe-(CO) stretch, A' 443w-m 354m< allyl-Fe stretch, A'	960m	960w-m		958s	CH ₂ wag, A
925w CH_2 twist, A'' 830w 80w 804w-m CH_2 rock, A'' , + NO ₂ wag, B_2 718w 722m CH_2 rock, A'' , + NO ₂ def., A'' 617s 620m 620m 620w 604s 608m 610m Fe-C-O def., A'' 570s 574m 569 568w Fe-C-O def., A'' 535s 540m 531 Soln. 534m Lp. C-C-C def., A'' 496m 499w-m 491 496w Fe-C-O def., A'' 496m 470m 464w Fe-(CO) stretch, A'' 426m 428w-m Fe-(CO) stretch, A' 416m allyl-Fe stretch, A'' 354m allyl-Fe stretch, A''	940m	940w			CH ₂ wag, A"
830w 800w 804w-m $CH_2 \operatorname{rock}, A^{''}, + NO_2 \operatorname{wag}, B_2$ 718w 722m $CH_2 \operatorname{rock}, A^{''}, + NO_2 \operatorname{def}, A$ 617s 620m 620m 620vw 604s 608m 610m Fe-C-0 def., A'' 570s 574m 569 MeNO2 568w Fe-C-0 def., A' 535s 540m 531 soln. 534m Lp. C-C-C def., A' 496m 499w-m 491 496w Fe-C-0 def., A' 496m 470m 464w Fe-(CO) stretch, A' 426m 428w-m Fe-(CO) stretch, A' 416m allyl-Fe stretch, A' 354m allyl-Fe stretch, A'	925w				CH ₂ twist, A"
810m 800w 804w-m $CH_2 \operatorname{rock}, A'', + NO_2 \operatorname{wag}, B_2$ 718w 722m $CH_2 \operatorname{rock}, A', + NO_2 \operatorname{def}, A'$ 617s 620m 620m 620w 604s 608m 610m Fe-C-O def, A'' 570s 574m 569 568w Fe-C-O def, A'' 535s 540m 531 soln. 534m I.p. C-C-C def, A'' 496m 499w-m 491 464w Fe-(CO) stretch, A'' 496m 470m 464w Fe-(CO) stretch, A'' 426m 428w-m Fe-(CO) stretch, A' 340m(br) 336s_ allyl-Fe stretch, A'	830w				
718w722m B_2 $CH_2 rock, A', + NO2 def., ACH_2 rock, A', + NO2 def., A''617s620m620m620wFe-C-O def., A''604s608m610mFe-C-O def., A'570s574m569555MeNO2568wFe-C-O def., A'535s540m53180ln.534mI.p. C-C-C def., A'496m499w-m491496wFe-C-O def., A'496m470m464wFe-(CO) stretch, A''426m428w-mFe-(CO) stretch, A'416mallyl-Fe stretch, A'340m(br)336s_allyl-Fe stretch, A'$	810m	800w		804w-m	CH_2 rock, A'' , + NO_2 wag,
718w 722m $CH_2 \operatorname{rock}, A', + NO_2 \operatorname{def}, A'$ 617s 620m 620m 620w $Fe-C-O \operatorname{def}, A''$ 604s 608m 610m $Fe-C-O \operatorname{def}, A''$ 570s 574m 569 555 $Fe-C-O \operatorname{def}, A''$ 535s 540m 531 soln. $534m$ $I.p. C-C-C \operatorname{def}, A''$ 496m 499w-m 491 $496w$ $Fe-C-O \operatorname{def}, A''$ $496w$ 496m 470m 464w $Fe-(CO) \operatorname{stretch}, A''$ $443w-m$ $Fe-(CO) \operatorname{stretch}, A''$ 426m 428w-m $Fe-(CO) \operatorname{stretch}, A''$ $416m$ $\operatorname{allyl-Fe \operatorname{stretch}, A''$ 340m(br) 336s_ allyl-Fe \operatorname{stretch}, A' A''					B ₂
617s 620m 620m 620w $Fe-C-O \ def., A''$ 604s 608m 610m $Fe-C-O \ def., A'$ 570s 574m 569 555 535s 540m 531 $568w$ $Fe-C-O \ def., A''$ 536m 499w-m 491 $534m$ $I.p. \ C-C-C \ def., A''$ 496m 470m 496w $Fe-C-O \ def., A''$ 496m 470m 464w $Fe-(CO) \ stretch, A''$ 426m 428w-m $Fe-(CO) \ stretch, A''$ 416m allyl-Fe \ stretch, A'' 340m(br) 336s_ allyl-Fe \ stretch, A'	718w	722m			CH_2 rock, A' , + NO ₂ def., A
604s 608m 610m $Fe-C-O \ def., A'$ 570s 574m 569 555 535s 540m 531 soln. 534m 1.p. C-C-C \ def., A' 496m 499w-m 491 496w Fe-C-O \ def., A' 496m 470m 496w Fe-C-O \ def., A'' 426m 428w-m 464w Fe-(CO) stretch, A'' 416m allyl-Fe stretch, A' 354m allyl-Fe stretch, A'' 340m(br) 336s_ allyl-Fe stretch, A' 364m	617s	620m	620m	620vw	Fe-C-O def., A"
570s 574m 569 555 MeNO2 568w Fe-C-O def., A' 535s 540m 531 soln. 534m Lp. C-C-C def., A' 496m 499w-m 491 534m Lp. C-C-C def., A' 496m 470m 496w Fe-C-O def., A' 496m 470m 464w 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'	604s	608m	610m	í .	Fe-C-O def., A
535s 540m 555 MeNO2 $Fe-C-O def., A'$ 535s 540m 531 soln. 534m Lp. C-C-C def., A' 496m 499w-m 491 496w $Fe-C-O def., A'$ 496m 470m 464w $Fe-(CO)$ 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'	570s	574m	569	568w	Fe-C-O def.
535s 540m 531 soln. 534m 1.p. C-C-C def., A, 496m 499w-m 491 496w Fe-C-O def., A'' 496m 470m 464w Fe-(CO) stretch, A'' 426m 428w-m Fe-(CO) stretch, A'' 416m allyl-Fe stretch, A' 340m(br) 336s_ allyl-Fe stretch, A'	5.05		555 MeNO ₂	1	Fe-C-O def., A
496m 499w-m 491 496w Fe-C-O def., A'' 496m 470m 464w Fe-(CO) stretch, A'' 426m 428w-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'	5355	540m	531 soln.	534m	I.p. $C = C = C$ def. A , + Fe=C = O def A'
496m 470m 464w Fe-(CO) stretch, A" 426m 443w-m Fe-(CO) stretch, A' 426m 428w-m Fe-(CO) stretch, A' 426m 416m allyl-Fe stretch, A' 340m(br) 336s allyl-Fe stretch, A'	496m	499w-m	491	(496w	Fe-C-O def., A''
426m 428w-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'	496m	470m	-	464w	Fe-(CO) stretch, A"
426m Fe-(CO) stretch, A' 416m allyl-Fe stretch, A' 340m(br) 336s allyl-Fe stretch, A'				443w-m	Fe-(CO) stretch, A'
416mallyl-Fe stretch, A'354mallyl-Fe stretch, A''340m(br)336s_allyl-Fe stretch, A'	426m	428w-m			Fe-(CO) stretch, A'
$354m$ $allyl-Fe$ stretch, A'' $340m(br)$ $336s_{2}$ $allyl-Fe$ stretch, A'				416m	allyl—Fe stretch, A
340m(br) 336s_ ally1-Fe stretch, A'				354m	allyi—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, NO₃ 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

IR	Raman	Approximate	
(solid, ~ 100 K)	(solid, ~ 100 K)	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 ;	-		
1414m ^j		CH2 seissonng, A	
1395m			
1360m		CCC stretch, A"	
1351m			
1225w		O.o.p. CH def., A	
1207w		Lp. CH def., A"	
1015wm		CCC stretch, A'_1 + CH ₂ twist, A'_2	
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	$Fe-C-O def., A^{T}$	
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	
361 wm	350m(br)	Fe-allyl stretch, A"	
3.30m(br)	326m	re-allyl stretch, A	

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

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 = NO₃, 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 $1350-1500 \text{ cm}^{-1}$ have been contradictory, but the isotopic shifts observed for $(C_3H_5)Fe(CO)_2(NO)$ and $(C_3D_5)Fe(CO)_2^{-1}$

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TABLE 4	та	в	LE	4	
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NUMBERS AND SYMMETRIES OF NORMAL MODES FOR	R THE Fe-(C3H5) FRAGMENT OF
(C ₃ H ₅)Fe(CO) ₃ X (C _s SYMMETRY) ^a	

ν(C−H)	A
v(CH ₂)	2A' + 2A''
à(CH2)	A' + A''
π(C-H)	A'
ծ(C-H)	A″
₽(C−C−C)	A' + A''
$\rho_t(CH_2)$	A' + A''
$\rho_{w}(CH_{2})$	A' + A''
$\rho_{r}(CH_{2})$	$A' \neq A''$
ċ(C−C−C)	A^{*}
r Fe-(C3H5)	2A' + A''
7 Fe-(C3H5)	$A^{''}$

^{*a*} All vibrations are IR and Raman active: A' vibrations will give polarised Raman scattering ($v \approx$ stretch, b = in-plane deformation, $\pi =$ out-of-plane deformation, $\rho_{t} =$ twist, $\rho_{w} =$ wag, $\rho_{r} =$ rock, $\tau =$ torsion).

NO by Paliani et al. suggests that the feature ca 1500 cm⁻¹ is v_{as} (C–C–C), with δ (CH₂) ca 1380 cm⁻¹ (both of A'' symmetry), and the symmetric δ (CH₂)(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 $1100-1200 \text{ cm}^{-1}$ 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, $\tau Fe^{-}(C_3H_5)$ 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.

TA	BL	E	5

PROPOSED ASSIGNMENT OF THE $Fe-(C_3H_5)$ VIBRATIONAL MODES IN $(C_3H_5)Fe(CO)_3X$ (IN CM^{-1})

Х	Br	NO3	(C3H5)Fe(CO)3	
r(CH2), A"	3086		3080	
r(CH), A'	3023	3026	3018	
r(CH2), A				
r(CH2), A"	2967	2960		
$v(CH_2), A''$	2916	2921	2930	
$\nu_{as}(CCC), A''$		1476	1500	
δ _s (CH ₂), A'	1462	1458	1470/1414	
6as(CH2), A"	1396	1400	1395/1360/1351	
$\pi(CH), A'$	1223	1228	1225	
δ(CH), Α¨	1110	1100	1207	
r _s (CCC), A'	1015	1016	1015	
ρ _t (CH ₂)(s), A	1042	1016	1015	
ρ _w (CH ₂)(s), A'	943	960	945	
ρ _w (CH ₂)(as), A ["]	932	940	910	
ρ _t (CH ₂)(as), A"	918	925	980	
$\rho_{\mathbf{r}}(CH_2)(as), A''$		800	878	
$\rho_r(CH_2)(s), A'$	778	722	806	
b(CCC), A'	300	540	499	
Las (Fe-C3H5), A	400	416	390	
ras(Fe-C3H5), A"	358	354	361	
ν _s (Fe-C3H5), Α' τ(Fe-C3H5), Α"	329	336	330	

(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 $\nu(CO)$ bands in $(C_3H_5)Fe(CO)_3X$ may be used to estimate the abilities of the various X ligands to build up electron density at the iron. Since corresponding $\nu(CO)$ 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 \rightarrow CO back-donation is restricted.

Another observation which can be made concerning the $\nu(CO)$ 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 (C₃H₅)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 NO₃. Fe-Br would be expected to occur below 300 cm⁻¹ [15] and no feature which could be so assigned was seen.

TABLE 6

DDODOCED ACCIONNENT	OF 1755 ATLONE OF	THE NO. LICAND	N (C.U.)Es(CO). N	0. <u>08 CM 1</u>	
LUCLOSED ASSIGNMENT	OF VIDRATIONS OF	THE NO3 LIGAND	1. (03n5)re(00)3.	$o_3 u \circ c_{s_1}$	ŕ,

NO ₂ stretches	A_{1}	1280
-	BI	1475
NO stretch	Al	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 NO₃ 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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