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THE VIBRATIONAL SPECTRUM OF DIBUTADIENEIRON CARBONYL

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SUMMARY

A vibrational assignment has been proposed for $(C_4H_6)_2Fe(CO)$. The internal butadiene modes show that there is very little interaction between the two C_4H_6 molecules, and that electronically it is very similar to C_4H_6 in $(C_4H_6)Fe(CO)_3$.

INTRODUCTION

Two recent papers have been published[1,2] which report the preparation of a new π-bonded transition metal complex: dibutadieneiron carbonyl, $(C_4H_6)_2Fe(CO)$. Having previously studied the vibrational spectrum of the related complex, butadieneiron tricarbonyl[3], we were interested in the dibutadiene species chiefly for two reasons. We wished to study, first, the interactions between the two butadiene ligands, and second, whether the substitution of two CO molecules by one butadiene gave rise to any marked effects on the vibrational spectrum. In addition, it is worth noting that detailed vibrational studies of transition metal complexes containing two π-bonded non-cyclic hydrocarbon ligands have not hitherto been reported, although some recent studies on di-π-allylnickel and -palladium, have been made[4].

EXPERIMENTAL

Dibutadieneiron carbonyl was prepared by the original method of Carbonaro and Greco[1]. The product was obtained as dark-red crystals by vacuum sublimation.

IR spectra (of the solid, in a KBr disc, and of CS_2, C_6D_6 and C_6H_{12} solutions—the last only in the C≡O stretching region) were obtained using a Perkin–Elmer 521 spectrometer. The instrument was calibrated using known peaks of CH_4, HBr, CO, H_2O and NH_3; the frequencies are all expected to be accurate to $\pm 2\ cm^{-1}$.

Raman spectra were obtained using a Cary model 81 spectrometer, with a Spectra-Physics 125 He/Ne laser as excitation source (output approximately 50 mW at 632.8 nm). Spectra were observed for solid samples, and for solutions in C_6H_6 and C_6D_6; the latter were contained in capillary cells, i.d. approximately 1 mm. Depolarisation ratios were determined by observing the spectrum with the plane of the polarised incident light parallel and perpendicular, respectively, to the axis of the polaroid analyser. True values were not given directly, but the sample cell was calibrated using accurately known standards.

TABLE 1

OBSERVED VIBRATIONAL SPECTRUM OF DIBUTADIENEIRON CARBONYL

(All values in cm^{-1}.)

IR			*Raman*			*Assignment*
Solid	*CS_2 soln.*	*C_6D_6 soln.*	*Solid*	*C_6H_6 soln.*	*C_6D_6 soln.*	
	3066 m		3059 m			CH_2 str. (antisym.)
3052 m	3041 m				3045 w, pol.	CH_2 str. (sym.)
3001 m	3006 m		3001 m		3003 w, pol.	CH str. (sym.)+ CH_2 str. (antisym.)
2932 m	2931 s				2934 w	CH str. (antisym.)
					2901 w,? pol.	
	2658 vw					
2561 vw	2557 vw					
2416 vw	2452 vw					
1951 vs	1976 vs	(1982 vs, C_6H_{12})	1973 w			C≡O str.
	1932 w					
1480 w		1482 w	1483 w		1481 vw	C=C str. (sym.)
1471 m		1474 w				CH_2 scissors (sym.)
1431 m			1435 w			C=C str. (antisym.)
1372 m			1373 w(br)			CH_2 scissors (antisym.)
1216 m	1216 m		1227 w	1231 m, pol.	1225 m	CH bend or C–C str.
1191	1189 w					CH bend
1053 m	1053 w		1053 s	1056 m, pol.	1053 m	C–C str. or CH bend.
1021 vw						CH_2 twist
970 vw	969 vw					CH_2 rock
946 w	940 vw					CH_2 twist
916 m	915 w		925 w	925 m, pol.		CH_2 rock + wag
893 m	875 m					CH_2 wag
815 vw						
788 w						
773 m	766 w					CH wag
654 w	651 w					CH wag
580 s	576 s		588 w			δ(FeCO), B_2 or B_1
541 s 532 s	532 s		540 w			δ(FeCO), B_1 or B_2
488 m	483 w		478 w		473 w	i.p. skeletal bend
457 w			453 w			i.p. skeletal bend
					?427 vw	o.o.p. skeletal bend (A_2)
402 s		403 w				o.o.p. skeletal bend (B_1)
390 s		394 w				(C_4H_6)–Fe str. (B_2)
			364 vs	361 vs, pol.		Fe–(CO) str. (A_1)
			339 w	335 m, dp.	332 m	(C_4H_6)–Fe tilts
			301 vs	297 vs, pol.		(C_4H_6)–Fe str. (A_1)
			218 w			? torsion

RESULTS AND DISCUSSION

The observed IR and Raman frequencies for $(C_4H_6)_2Fe(CO)$ are listed in Table 1, together with the assignments, which will be discussed below.

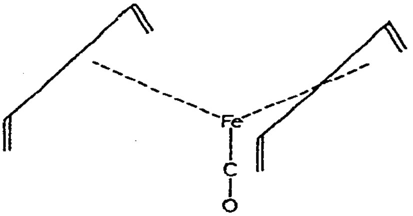

Fig. 1. Most probable molecular structure of $(C_4H_6)_2Fe(CO)$.

Vibrational analysis

An X-ray crystallographic study of the related complex, di-1,3-cyclohexadieneiron carbonyl[5], suggests that the structure of the butadiene analogue should be as depicted in Fig. 1.

The overall symmetry of the molecule is C_{2v}, and the following numbers and types of vibration are predicted:

(*i*) CH_2 stretches: $2A_1+2A_2+2B_1+2B_2$
(*ii*) CH stretches: $A_1+A_2+B_1+B_2$
(*iii*) C–C stretches: A_1+B_2
(*iv*) C=C stretches: $A_1+A_2+B_1+B_2$
(*v*) CH_2 and HCC (of CH_2) in-plane deformations: $2A_1+2A_2+2B_1+2B_2$
(*vi*) HCC (of CH) and skeletal in-plane deformations: $2A_1+2A_2+2B_1+2B_2$
(*vii*) CH_2 out-of-plane deformations: $2A_1+2A_2+2B_1+2B_2$
(*viii*) CH out-of-plane deformations: $A_1+A_2+B_1+B_2$
(*ix*) C_4 out-of-plane deformations: A_2+B_1
(*x*) C≡O stretch: A_1
(*xi*) Fe–(CO) stretch: A_1
(*xii*) Fe–C–O deformations: B_1+B_2
(*xiii*) Fe–(C_4H_6) stretches: A_1+B_2
(*xiv*) C_4H_6 tilts: $A_1+A_2+B_1+B_2$
(*xv*) C_4H_6 torsions: A_2+B_1
(*xvi*) (C_4H_6)–Fe–(CO) deformations: $A_1+B_1+B_2$.

(All of these will be Raman-active with A_1 polarised, while A_1, B_1 and B_2 modes will also be IR active.)

It will be convenient to discuss the assignment of frequencies to these modes in two sections, *i.e.* those which are "internal" vibrations of the two butadiene molecules [(*i*)–(*ix*)], and those which involve motions of the whole molecule [(*x*)–(*xvi*)].

Assignment of internal butadiene modes

As will be seen from the above listing, the presence of two butadiene molecules should give rise to a very complicated spectrum, with different frequencies expected for the in-phase and out-of-phase combinations of all of the vibrations of a single butadiene molecule. A close inspection of the observed spectrum, however, reveals a striking similarity, in the region above 500 cm^{-1}, with that seen for $(C_4H_6)Fe(CO)_3$[3]. This can be explained by the presence of only weak interactions between the two butadiene molecules—if this is so, then in-phase and out-of-phase vibrations would be degenerate, and the resulting spectrum would be very similar to that of a single, isolated butadiene molecule, possessing a "local" symmetry of C_s.

As a first approximation, we shall attempt the assignment on that basis. A single butadiene molecule should give 6 CH stretching modes, two would give 12, whereas 4 are seen. They cannot be assigned exactly by analogy with $(C_4H_6)Fe(CO)_3$ to specific modes but the following assignment fits the observed polarisation data for an isolated C_4H_6 molecule: 3063 cm^{-1}, $A'+A''(CH_2)$ stretch; 3043 cm^{-1}, A'-(CH_2) stretch; 3002 cm^{-1}, $A'(CH)$ stretch$+A''(CH_2)$ stretch; 2934 cm^{-1} $A''(CH)$ stretch. These are all reasonably close to the corresponding values for $(C_4H_6)Fe(CO)_3$[3], except that one A' and one A'' CH_2 stretch are slightly higher in frequency.

The remaining butadiene modes appear at frequencies very close indeed to those found in $(C_4H_6)Fe(CO)_3$[3], and in no case are there more bands than can be accounted for on the basis of effectively non-interacting butadiene molecules. The proposed assignments, together with those for the $(C_4H_6)Fe(CO)_3$ system, are listed in Table 2; it should be noticed that these assignments are likely to be approximate, with appreciable mixing of modes occurring, especially involving the C=C and C–C stretches, and the CH_2 scissors deformations.

TABLE 2

INTERNAL VIBRATIONS OF BUTADIENE IN $(C_4H_6)Fe(CO)_3$ AND $(C_4H_6)_2Fe(CO)$

(Local symmetry of C_s in each case; all figures in cm^{-1}.)

	A'		A''	
	$(C_4H_6)Fe(CO)_3$	$(C_4H_6)_2Fe(CO)$	$(C_4H_6)Fe(CO)_3$	$(C_4H_6)_2Fe(CO)$
CH_2 stretch	3067	3063	3067	3063
CH_2 stretch	3012	3043	2950	3002
CH stretch	3012	3002	2929	2934
C=C stretch	1477	1481	1439	1435
CH_2 scissors	1499	1474	1370	1373
C–C stretch	1205	1220		
CH i.p. bend	1060	1054	1174	1189
CH_2 twist	954	940	1048	1021
CH_2 rock	926	920	968	969
CH_2 wag	926	920	896	875
CH wag	669	651	791	766
C–C=C i.p. bend	493	481	417	453
C_4 o.o.p. bend		[a]	Not obs.	[a]

[a] Discussed under "Skeletal vibrations".

Two conclusions may be drawn from the assignment, first that coupling between the two butadiene molecules is rather weak, and second, that the similarity of the actual frequencies associated with internal C_4H_6 motions suggests that the replacement of 2 CO's by C_4H_6 in going from $(C_4H_6)Fe(CO)_3$ to $(C_4H_6)Fe(CO)$ has relatively little effect upon the (C_4H_6)–Fe bonding.

Assignment of skeletal modes

Here we must use C_{2v} overall symmetry for the system. One C≡O stretch is expected, and found, showing an appreciable phase shift, at 1951 (IR) and 1973 cm^{-1} (R) in the solid, and at 1982 cm^{-1} in C_6H_{12} solution. The presence of two bands in the solid phase spectrum, suggests that there are at least two molecules in the crystalline unit cell which must be centrosymmetric, since the mutual exclusion rule is obeyed.

Two bands which can be assigned to Fe–C–O deformations are found at 582 and 536 cm^{-1}. As usual for this type of vibration they are strong in the IR and weak in the Raman spectrum, and in the expected range (*e.g.* ref. 6). It is not possible, on present evidence, to assign these to the specific B_1 and B_2 modes.

M–(CO) stretches commonly give rise to intense Raman bands, ca. 350–500 cm^{-1}, and the Fe–(CO) stretching mode in $(C_4H_6)_2Fe(CO)$ is assigned to such a feature at 361 cm^{-1} (polarised), *cf.* 379 cm^{-1} for the A_1 mode in $(C_4H_6)Fe(CO)_3$[3].

M–(hydrocarbon) stretches usually occur[3,6–8] ca. 300 cm^{-1}. Two (A_1+B_2) should be found in the present case. The symmetric stretch clearly gives rise to the very strong, and strongly polarised Raman band at 297 cm^{-1}, while the most reasonable assignment for the B_2 mode is to an IR band at 394 cm^{-1} (no Raman counterpart).

Three (C_4H_6)–Fe–(CO) deformations $(A_1+B_1+B_2)$ are expected, below 150 cm^{-1}, but no features were observed in that region.

The only remaining vibrations are the out-of-plane C_4 deformations (A_2+B_1), (C_4H_6)–Fe tilts $(A_1+A_2+B_1+B_2)$ and C_4H_6 torsion (A_2+B_1). Of the first pair, the B_1 mode is assigned to a weak IR band at 403 cm^{-1}, and it is possible that the formally forbidden A_2 mode gives rise to the very weak Raman band at 427 cm^{-1}. (Hydrocarbon)–M tilting frequencies are generally at a slightly higher frequency than the symmetric (hydrocarbon)–M stretch (297 cm^{-1}). Only one otherwise unassigned band is seen in this region, at 334 cm^{-1}, and this is assigned to all of the (C_4H_6)–Fe tilts. A weak Raman band at 215 cm^{-1} is tentatively assigned to the B_1 (C_4H_6) torsion.

The assignments of skeletal vibrations are summarised in Table 3.

TABLE 3

SKELETAL VIBRATIONS OF $(C_4H_6)_2Fe(CO)$

(All figures in cm^{-1}.)

(*a*)	C≡O stretch	(A_1)	1982
	Fe–(CO) stretch	(A_1)	361
	Fe–C–O deformations	(B_1)	582
		(B_2)	536
(*b*)	Fe–(C_4H_6) stretch	(A_1)	297
		(B_2)	394
	(C_4H_6)–Fe–(CO) defs.	(A_1) (B_1) (B_2)	Not observed
(*c*)	o.o.p. C_4 defs.	(A_2)	?427
		(B_1)	403
	(C_4H_6)–Fe tilts	(A_1) (A_2) (B_1) (B_2)	334
	(C_4H_6) torsions	(A_2)	—
		(B_1)	218

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