Preparation, Infrared Spectra, and Structures of some [(π-dienyl)FeCo(CO)$_4$(π-diene)] Compounds

By **A. R. Manning**, Department of Chemistry, University College, Belfield, Dublin 4, Ireland

The reactions of [(π-dienyl)FeCo(CO)$_6$] (dienyl = C_5H_5, MeC_5H_4, and C_9H_7) with various dienes give [(π-dienyl)-FeCo(CO)$_4$(π-diene)] complexes (diene = norbornadiene, cyclohexa-1,3-diene, or 2,3-dimethylbuta-1,3-diene). In the solid state these appear to exist as either *cis*- or *trans*-carbonyl-bridged tautomers with structures similar to those of the related [{(π-dienyl)Fe(CO)$_2$}$_2$] and [{(π-diene)Co(CO)$_2$}$_2$] compounds. In solution, the two isomers are in equilibrium. Their relative abundance depends on the solvent, temperature, the (π-diene) ligands, and, to a lesser extent, the (π-dienyl) ligands.

THE ability of various conjugated and non-conjugated dienes to act as bidentate ligands towards transition metals is well documented.[1] Previously it has been shown that [{(π-diene)Co(CO)$_2$}$_2$] derivatives of norbornadiene and various substituted buta-1,3-dienes are both isoelectronic and isostructural with [{(π-dienyl)-Fe(CO)$_2$}$_2$] complexes.[2] The two series of compounds exhibit a similar tautomeric behaviour with both *cis*- and *trans*-carbonyl-bridged species coexisting in solution.[2,3] Thus it seemed probable that if the mixed metal complexes [(π-dienyl)Fe(CO)$_2$Co(CO)$_2$(π-diene)] could be obtained, they, like their parent compounds, would be tautomeric. This supposition has been confirmed by the preparation of a series of such derivatives {dienyl = C_5H_5, MeC_5H_4, and C_9H_7(indenyl); diene = norbornadiene, cyclohexa-1,3-diene, and 2,3-dimethylbuta-1,3-diene} from the reactions of [(π-dienyl)FeCo(CO)$_6$] with dienes in heptane solution at *ca.* 100 °C.

---

[1] *E.g.*, E. O. Fischer and H. Werner, ' Metal π-Complexes,' Elsevier, Amsterdam, 1966, vol. 1; and ' Organic Syntheses *via* Metal Carbonyls,' eds. I. Wender and P. Pino, Interscience, New York, 1968, vol. 1.

[2] P. McArdle and A. R. Manning, *Chem. Comm.*, 1968, 1020; *J. Chem. Soc.* (*A*), 1970, 2123.

[3] A. R. Manning, *J. Chem. Soc.* (*A*), 1968, 1319.

EXPERIMENTAL

Most chemicals were purchased. The preparations of 2,3-dimethylbuta-1,3-diene,[4] and the [(π-dienyl)FeCo(CO)$_6$] complexes (dienyl = C_5H_5, MeC_5H_4, and C_9H_7) [5] have been described. All reactions were carried out under an atmosphere of nitrogen using dried and deoxygenated solvents at room temperature, unless it is stated otherwise.

TABLE 1

Colours, melting points, and analyses for the [(π-dienyl)FeCo(CO)$_4$(π-diene)] compounds

Compound [a]	Colour	M.p. (°C) [b]	Found (%) C	Found (%) H	Required (%) C	Required (%) H
$(C_5H_5)FeCo(CO)_4(C_7H_8)$	Purple	138—140 (dec.)	49·5	3·6	50·0	3·4
$(C_5H_5)FeCo(CO)_4(C_6H_8)$	Red	dec. 152	48·1	3·5	48·4	3·5
$(C_5H_5)FeCo(CO)_4(C_6H_{10})$	Purple	119—121	47·7	3·9	48·1	4·0
$(MeC_5H_4)FeCo(CO)_4(C_7H_8)$	Purple	110—112	50·8	3·8	51·2	3·8
$(MeC_5H_4)FeCo(CO)_4(C_6H_8)$	Red	140—142 (dec.)	49·3	3·8	49·7	3·9
$(MeC_5H_4)FeCo(CO)_4(C_6H_{10})$	Purple	104—106 (dec.)	49·7	4·5	49·5	4·4
$(C_9H_7)FeCo(CO)_4(C_7H_8)$	Brown	dec. 130	55·2	3·4	55·4	3·5
$(C_9H_7)FeCo(CO)_4(C_6H_8)$	Red-brown	dec. 148	54·3	3·6	53·9	3·6
$(C_9H_7)FeCo(CO)_4(C_6H_{10})$	Red-brown	143—145 (dec.)	53·3	3·8	53·8	4·0

[a] C_7H_8 = norbornadiene, C_6H_8 = cyclohexa-1,3-diene, C_6H_{10} = 2,3-dimethylbuta-1,3-diene, and C_9H_7 = indenyl. [b] Determined in sealed tubes; dec. = decomposes without melting, and (dec.) = melts with decomposition.

TABLE 2

The i.r. spectra of [(π-C_5H_5)FeCo(CO)$_4$(π-diene)] complexes in the 1700—2100 cm^{-1} region at 25 °C

Solvent	Diene	Absorption bands [a]					
	A [b]	B	C [b]	D	E [b]	F	G [b]
	Norbornadiene						
Heptane	1800 (10)		1821 (sh)	1969 (0·6)	1982 (4·0)	1998 (0·5)	2014 (15·5)
	Cyclohexa-1,3-diene						
Heptane	1805 (10)	1810 (sh)	1825 (sh)	1976 (4·5)	1983 (2·9)	2001 (0·9)	2019 (8·6)
Carbon disulphide	1795 (10)	1800 (sh)	1823 (sh)	1972 (6·0)	1976 (sh)	1998 (sh)	2012 (14·1)
Xylene	1794 (10)	1800 (sh)	1821 (sh)	1971 (4·4)		1998 (sh)	2010 (9·4)
Tetrahydrofuran	1794 (10)	1798(sh)	1819 (sh)	1962 (sh)	1968 (3·5)	1993 (sh)	2004 (10·0)
	2,3-Dimethylbuta-1,3-diene						
Heptane	1799 (sh)	1802 (10)	1827 (sh)	1975 (11·8)	1984 (2·3)	2005 (3·6)	2024 (5·8)
Carbon disulphide	1789 (sh)	1794 (10)	1822 (sh)	1970 (9·3)	1977 (sh)	2000 (2·9)	2016 (6·3)
Xylene	1793 (10)	1797 (sh)	1821 (sh)	1967 (7·0)	1974 (sh)	1996 (2·0)	2014 (5·2)
Tetrahydrofuran	1791 (10)	1795 (sh)	1818 (sh)	1966 (5·7)	1973 (sh)	1998 (sh)	2008 (8·9)

[a] This and Tables 3—6 give peak positions (cm^{-1}) with relative peak-heights in parentheses. [b] These absorption bands are due to the *cis*-isomers. The others are due to the *trans*.

Substitutions of [(π-dienyl)FeCo(CO)$_6$] (*ca.* 2 g) with the dienes (*ca.* 2—5 ml) were effected by heating a mixture of the reactants in heptane solution (50 ml) to *ca.* 100° for 20—40 min. The reactions were monitored by i.r. spectroscopy. At suitable times, the solutions were filtered, and the filtrates chromatographed on alumina using hexane, benzene, or a mixture of the two as eluants. The desired products were isolated from the appropriate chromatographic fraction by removal of the solvent at reduced pressures, and purified by recrystallisation from pentane, hexane, toluene, toluene–hexane mixtures, or ethanol. Large quantities of the symmetrical compounds [{(π-dienyl)Fe(CO)$_2$}$_2$] and [{(π-diene)Co(CO)$_2$}$_2$] were invariably obtained. Consequently the yields of the [(π-dienyl)FeCo(CO)$_4$(π-diene)] derivatives were never greater than 15% and were usually *ca.* 5% or less. The colours, melting points, and analyses of the new compounds are summarised in Table 1.

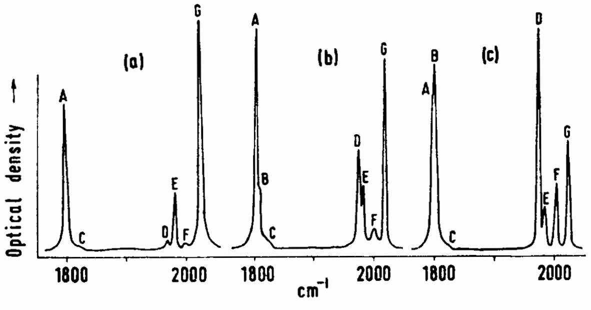

FIGURE 1 The i.r. spectra of [(π-C_5H_5)FeCo(CO)$_4$(π-diene)] between 1700 and 2100 cm^{-1} in heptane solution at 25 °C; diene = (a) norbornadiene, (b) cyclohexa-1,3-diene, and (c) 2,3-dimethylbuta-1,3-diene

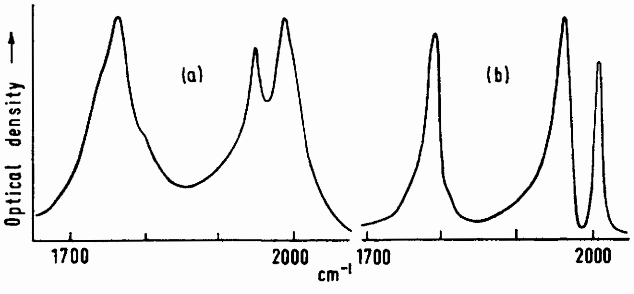

FIGURE 2 The i.r. spectra of (a) *cis*-[(π-C_5H_5)FeCo(CO)$_4$(π-C_6H_8)] and (b) *trans*-[(π-C_5H_5)FeCo(CO)$_4$(π-C_6H_{10})] as Nujol mulls between 1700 and 2100 cm^{-1}

I.r. spectra were obtained as described.[2,3,5] The investigation was limited to the 1700—2100 cm^{-1} region of

---

[4] C. F. H. Allen and A. Bell, *Org. Synth.*, 1955, Coll. Vol. 3, p. 312.

[5] A. R. Manning, *J. Chem. Soc.* (*A*), 1971, 2321.

TABLE 3

The i.r. spectra of [(π-MeC$_5$H$_4$)FeCo(CO)$_4$(π-diene)] complexes in the 1700—2100 cm^{-1} region at 25 °C unless it is stated otherwise

Solvent	Diene	Absorption bands[a]						
		A[b]	B	C[b]	D	E[b]	F	G[b]
	Norbornadiene							
Heptane		1796 (10)		1819 (sh)	1968 (1·0)	1979 (3·3)	1995 (0·6)	2013 (13·3)
	Cyclohexa-1,3-diene							
Heptane		1801 (10)	1804 (sh)	1825 (sh)	1973 (5·3)	1979 (2·5)	1998 (1·3)	2016 (8·5)
Carbon disulphide		1792 (10)	1797 (sh)	1822 (sh)	1969 (6·5)	1974 (sh)	1994 (2·2)	2010 (12·2)
Xylene		1793 (10)	1797 (sh)	1822 (sh)	1968 (4·7)		1991 (sh)	2008 (8·6)
Tetrahydrofuran		1791 (10)	1794 (sh)	1820 (sh)	1959 (sh)	1964 (3·8)	1993 (sh)	2003 (9·6)
	2,3-Dimethylbuta-1,3-diene							
Heptane		1793 (sh)	1796 (10)	1825 (sh)	1972 (11·3)	1980 (1·6)	2001 (3·7)	2021 (4·4)
Pentane		1792 (sh)	1797(10)		1971 (10·7)	1979 (1·6)	2001 (3·7)	2022 (4·1)
Pentane (−77 °C)		1792 (3·3)	1796 (10)		1970 (10·0)	1979 (sh)	2001 (3·0)	2022 (2·2)
Carbon disulphide			1791 (10)	1818 (sh)	1966 (10·8)	1972 (sh)	1996 (3·3)	2014 (4·5)
Xylene		1785 (sh)	1791 (10)	1819 (sh)	1964 (8·2)	1972 (sh)	1994 (2·5)	2012 (4·3)
Tetrahydrofuran		1788 (10)	1793 (sh)	1817 (sh)	1963 (6·5)	1966 (sh)	1993 (sh)	2007 (6·2)

[a,b] See Table 2.

TABLE 4

The i.r. spectra of [(π-C$_9$H$_7$)FeCo(CO)$_4$(π-diene)] complexes in the 1700—2100 cm^{-1} region at 25 °C

Solvent	Diene	Absorption bands[a]						
		A[b]	B	C[b]	D	E[b]	F	G[b]
	Norbornadiene							
Heptane		1800 (10)		1824 (0·4)	1965 (sh)	1980 (4·5)	1995 (sh)	2010 (19·0)
	Cyclohexa-1,3-diene							
Heptane		1807 (10)	1810 (sh)	1836 (0·4)	1971 (3·6)	1978 (3·1)	1999 (1·5)	2016 (11·5)
Carbon disulphide		1798 (10)	1804 (sh)	1830 (0·6)	1969 (5·3)	1973 (sh)	1995 (2·3)	2010 (13·4)
Xylene		1798 (10)	1803 (sh)	1828 (0·4)	1968 (5·0)		1993 (sh)	2009 (11·5)
Tetrahydrofuran		1797 (10)		1822(0·4)	1955 (sh)	1963 (2·3)	1991 (sh)	2003 (11·7)
	2,3-Dimethylbuta-1,3-diene							
Heptane		1801 (sh)	1806 (10)	1835 (0·5)	1969 (11·2)	1980 (1·5)	2003 (5·4)	2022 (5·4)
Carbon disulphide		1793 (sh)	1798 (10)	1830 (0·8)	1965 (11·1)	1974 (sh)	1999 (4·4)	2017 (5·9)
Xylene		1793 (sh)	1797 (10)	1829 (0·6)	1962 (9·0)	1971 (sh)	1995 (3·4)	2014 (5·3)
Tetrahydrofuran		1794 (10)	1798 (sh)	1825 (0·7)	1959 (5·8)	1968 (sh)	1992 (sh)	2009 (9·3)

[a,b] See Table 2.

TABLE 5

The i.r. spectra of [(π-dienyl)FeCo(CO)$_4$(π-diene)] complexes in the solid state as Nujol mulls

Dienyl	Diene	Absorption bands[a]			
C$_5$H$_5$	Norbornadiene	1768 (s)	1799 (sh)	1954 (m)	1991 (s)
C$_5$H$_5$	Cyclohexadiene	1768 (s)	1807 (sh)	1953 (m)	1993 (s)
C$_5$H$_5$	Dimethylbutadiene[b]	1791 (s)	1816 (sh)	1962 (vs)	2009 (m)
MeC$_5$H$_4$	Norbornadiene	1760 (s)	1807 (m)	1961 (m)	2001 (s)
MeC$_5$H$_4$	Cyclohexadiene	1770 (s)	1807 (sh)	1956 (m)	1991 (s)
MeC$_5$H$_4$	Dimethylbutadiene[b]	1772 (s)	1816 (w)	1955 (s), 1965 (s)	2002 (s), 2007 (s)
C$_9$H$_7$	Norbornadiene	1777 (s)	1805 (m)	1954 (m), 1969 (m)	1999 (m), 2017 (m)
C$_9$H$_7$	Cyclohexadiene	1773 (s)	1805 (w)	1960 (m)	2003 (s)
C$_9$H$_7$	Dimethylbutadiene[b]	1778 (s)	1809 (sh)	1947 (s)	1986 (m)

[a] See Table 1. [b] These are *trans* in the solid state, the other compounds are *cis*.

the spectrum. The frequencies and relative intensities of the observed absorption bands are summarised in Tables 2—5 and some are illustrated in Figures 1 and 2. The Tables do not include certain weak absorption bands which may be attributed to molecules containing one ^{13}CO ligand.

RESULTS AND DISCUSSION

The new complexes are crystalline solids. In the solid state they are more stable than their [{(π-diene)-Co(CO)$_2$}$_2$] counterparts. Their solutions in hydrocarbon solvents are stable, but they react slowly with carbon disulphide and rapidly with acetonitrile.

The i.r. spectra of the nine compounds in non-hydroxylic solvents show seven absorption bands and/or shoulders which may be assigned to their C–O stretching vibrations (Tables 2—4; Figure 1). Three, A—C, are due to the vibrations of bridging ligands whilst the four others, D—G, are attributed to terminal carbonyl groups. Although A/B cannot be resolved at room temperature, in most spectra there is a distinct shoulder to the principal peak. However, the two components may be separated for $[(\pi\text{-MeC}_5\text{H}_4)\text{FeCo(CO)}_4(\pi\text{-C}_6\text{H}_{10})]$ using pentane solution at *ca.* −77 °C (Table 3). It is only in the spectra of the three $[(\pi\text{-C}_9\text{H}_7)\text{FeCo(CO)}_4(\pi\text{-diene})]$ complexes (Table 4) that C is a separate absorption band rather than an ill resolved shoulder (*cf.* $[\{(\pi\text{-C}_9\text{H}_7)\text{Fe(CO)}_2\}_2]$ [6] and $[\{(\pi\text{-C}_5\text{H}_5)\text{-Fe(CO)}_2\}_2]$ [3]).

The variations of the relative intensities of the seven absorption bands with changes in (π-diene) and (π-dienyl) ligands, temperature, and solvent, allow them to be divided into two groups, A, C, E, and G, and B, D, and F. As the intensities of A/B are always comparable to those of D—G, it is probable that both of the tautomers which give rise to these two sets of ν(CO) vibrations have bridging carbonyl groups. Thus it is proposed that in solution, the $[(\pi\text{-dienyl})\text{FeCo(CO)}_4(\pi\text{-diene})]$ complexes exist as equilibrium mixtures of *cis*- and *trans*-carbonyl-bridged tautomers as do the $[\{(\pi\text{-dienyl})\text{Fe(CO)}_2\}_2]$,[3,6-8] and $[\{(\pi\text{-diene})\text{Co(CO)}_2\}_2]$ derivatives.[2]

The relative intensities of the four absorption bands A, C, E, and G are similar to those due to the ν(CO) vibrations of $[\{(\pi\text{-C}_7\text{H}_8)\text{Co(CO)}_2\}_2]$ and $[\{\pi\text{-C}_5\text{H}_4{\cdot}\text{CH(NMe}_2){\cdot}\text{CH(NMe}_2)\text{C}_5\text{H}_4\}\text{Fe}_2\text{(CO)}_4]$.[2,7,9] These two compounds exist in solution only as *cis*-isomers. This suggests that A, C, E, and G are due to the *cis*-$[(\pi\text{-dienyl})\text{FeCo(CO)}_4(\pi\text{-diene})]$ species (Figure 3) with a near-planar $\text{Fe(CO}_b)_2\text{Co}$ bridging system similar to that found by *X*-ray diffraction for *cis*-$[\{(\pi\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\}_2]$,[10] and *cis*-$[\{(\pi\text{-C}_6\text{H}_8)\text{Co(CO)}_2\}_2]$.[11] Deviations of the actual structure from the ideal shown in Figure 3 are possible, but it is unlikely that they would affect the appearance of the i.r. spectrum to any great extent, and so they are not considered further.

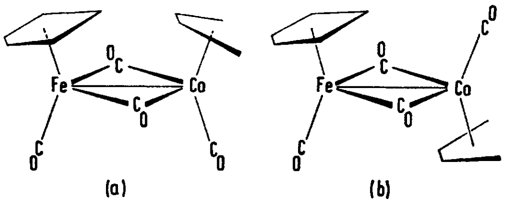

FIGURE 3 The two isomers of the $[(\pi\text{-dienyl})\text{FeCo(CO)}_4(\pi\text{-diene})]$ compounds, (a) *cis*, and (b) *trans*

The remaining three absorption bands, B, D, and F, are attributed to the *trans*-tautomers (Figure 3). If these isomers were centrosymmetric, only one absorption band due to the vibrations of the bridging and one due to the terminal CO ligands would be expected. However, the *trans*-$[(\pi\text{-dienyl})\text{FeCo(CO)}_4(\pi\text{-diene})]$ molecules are not centrosymmetric and so the separation of symmetric and antisymmetric ν(CO) modes is not complete. Furthermore, the $\angle\text{Co–Fe–CO}_t$ and $\angle\text{Fe–Co–CO}_t$ are probably not equal (in *trans*-$[\{(\pi\text{-C}_5\text{H}_5)\text{Fe(CO)}_2\}_2]$, $\angle\text{Fe–Fe–CO}_t = 95{\cdot}2^\circ$;[12] and in *trans*-$[\{(\pi\text{-C}_6\text{H}_{10})\text{Co(CO)}_2\}_2]$, $\angle\text{Co–Co–CO}_t = 106{\cdot}6^\circ$.[13] CO_t is a terminal carbonyl ligand), and the dipole gradient change due to the symmetric vibration would be different from zero. Consequently these molecules should give rise to two absorption bands due to their $\nu(\text{CO}_t)$ vibrations. That at highest frequency would be due primarily to the symmetric mode and would be expected to be less intense than that due primarily to the antisymmetric vibration. Similarly, one might also expect two absorption bands at *ca.* 1800 cm^{-1} due to the $\nu(\text{CO}_b)$ modes of the *trans*-isomers. It is worth noting that the intensity ratio A/B : C does not change markedly for the $[(\pi\text{-C}_9\text{H}_7)\text{FeCo(CO)}_4(\pi\text{-diene})]$ compounds where C is separate from A/B even though the *cis*-tautomer is the most important for the norbornadiene complex, and the *trans* predominates in the dimethylbutadiene derivative. This suggests that there are two components to C which are due to the *cis*- and *trans*-isomers respectively. Thus, in the *trans*-compound, it is unlikely that the $\text{O}_b\text{–C}_b \cdots \text{C}_b\text{–O}_b$ system is linear. The non-linearity may arise from a non-planar $\text{Fe(CO}_b)_2\text{Co}$ bridge, from differing Fe–C_b and Co–C_b distances, or from deviations from the ideal similar to those found for $[(\pi\text{-C}_9\text{H}_7)\text{FeCo(CO)}_6]$.[11]

Although absorption bands due to *trans*-tautomers are very weak in the i.r. spectra of the norbornadiene complexes, they are the more important for the dimethylbutadiene derivatives. Thus the proportions of the *cis*-isomers decrease along the series diene = $\text{C}_7\text{H}_8 > \text{C}_6\text{H}_8 > \text{C}_6\text{H}_{10}$. Similar, but more extreme, effects have been observed for the $[\{(\pi\text{-diene})\text{Co(CO)}_2\}_2]$ compounds where $[\{(\pi\text{-C}_7\text{H}_8)\text{Co(CO)}_2\}_2]$ exists solely as the *cis*-isomer and $[\{(\pi\text{-C}_6\text{H}_{10})\text{Co(CO)}_2\}_2]$ as the *trans*.[2] It was suggested that they were due to intermolecular diene–diene steric interactions which tend to destabilise the *cis*-species. In the present series of complexes, the variations are attributed to weaker dienyl–diene interactions.

The consequences of changing the π-dienyl ligands are far less marked. It is clear that the *trans*-isomers increase in importance for the norbornadiene complexes along the series dienyl = $\text{C}_9\text{H}_7 < \text{C}_5\text{H}_5 < \text{MeC}_5\text{H}_4$. If the intensity ratio of D : G is a reasonable measure of the *trans* : *cis* isomer ratio then a similar series is also applicable for the cyclohexa-1,3-diene compounds in heptane solution, but for the dimethylbutadiene derivatives the series becomes dienyl = $\text{C}_5\text{H}_5 < \text{C}_9\text{H}_7 < \text{MeC}_5\text{H}_4$.

Solubility and stability problems have meant that a study of the effects of temperature upon the i.r. spectra of the compounds has been limited to solutions

---

[6] P. McArdle and A. R. Manning, *J. Chem. Soc.* (*A*), 1969, 1498.

[7] P. McArdle and A. R. Manning, *J. Chem. Soc.* (*A*), 1970, 2119.

[8] J. G. Bullitt, F. A. Cotton, and T. J. Marks, *J. Amer. Chem. Soc.*, 1970, **92**, 2155.

[9] P. McArdle, A. R. Manning, and F. S. Stephens, *Chem. Comm.*, 1969, 1310; F. S. Stephens, *J. Chem. Soc.* (*A*), 1970, 1722.

[10] R. F. Bryan, P. T. Greene, M. J. Newlands, and D. S. Field, *J. Chem. Soc.* (*A*), 1970, 3068.

[11] F. S. Stephens, personal communication.

[12] R. F. Bryan and P. T. Greene, *J. Chem. Soc.* (*A*), 1970, 3064.

[13] F. S. Stephens, *J. Chem. Soc.* (*A*), 1970, 2745.

of $[(\pi\text{-MeC}_5\text{H}_4)\text{FeCo(CO)}_4(\pi\text{-C}_6\text{H}_{10})]$ in pentane. The absorption bands due to the *cis*-isomer of this compound decline in importance with decreasing temperature (the intensity ratio D : G increases). Similarly, the *cis–trans* equilibrium for solutions of $[\{(\pi\text{-MeC}_5\text{H}_4)\text{Fe(CO)}_2\}_2]$ in pentane appears to be shifted towards the centrosymmetric tautomer on lowering of the temperature.[14]

An increase in solvent polarity along the series heptane < carbon disulphide < xylene < tetrahydrofuran brings about a decrease in the D : G intensity ratio due to the increasing importance of the *cis*-tautomers. Thus absorption bands due to the *trans*-isomers cannot be detected in solutions of the norbornadiene compounds in solvents other than heptane. Increases in solvent polarity have similar consequences for $[\{(\pi\text{-dienyl})\text{Fe(CO)}_2\}_2]$ and $[\{(\pi\text{-diene})\text{Co(CO)}_2\}_2]$ complexes.[2,3,6,7]

TABLE 6

The i.r. spectra of $[(\pi\text{-MeC}_5\text{H}_4)\text{FeCo(CO)}_4(\pi\text{-diene})]$ complexes in hydroxylic solvents between 1700—2100 cm^{-1} at 25 °C

	Diene	Absorption bands [a]					
Solvent	A_l	A/B	A_h	D	E	F	G
	Norbornadiene						
Ethanol	1758 (2·5)	1789 (10)	1810 (sh)		1968 (4·1)		2002 (16·4)
m-Cresol	1730 (sh), 1738 (10)	1782 (5·8)	1807 (4·0)		1970 (8·2)		2003 (27·9)
o-Chlorophenol	1741 (sh), 1755 (10)	1776 (6·4)	1803 (3·3)		1967 (8·3)		2002 (28·9)
	Cyclohexa-1,3-diene						
Ethanol	1764 (2·2)	1795 (10)	1820 (1·1)	1970 (6·1)	1977 (sh)	1996 (sh)	2006 (13·7)
m-Cresol	1740 (10·6), 1751 (10·6)	1787 (10)	1816 (3·7)	1962 (sh)	1971 (13·7)		2007 (31·4)
o-Chlorophenol	1742 (sh), 1765 (10)	1783 (8·3)	1815 (2·4)	1962 (sh)	1969 (12·5)		2007 (25·0)
	2,3-Dimethylbuta-1,3-diene						
Ethanol	1767 (2·2)	1791 (10)	1821 (1·0)	1967 (10·0)	1976 (sh)	1997 (sh)	2012 (9·2)
m-Cresol	1764 (8·0, broad)	1788 (10)	1817 (3·9)	1968 (16·1)	1978 (sh)	1997 (sh)	2010 (16·1)
o-Chlorophenol	1747 (sh), 1763 (10)	1780 (9·5)	1816 (2·4)	1966 (17·6)	1976 (sh)	1998 (sh)	2010 (15·2)

[a] See Table 2.

The i.r. spectra of solid samples of the $[(\pi\text{-dienyl})\text{FeCo(CO)}_4(\pi\text{-diene})]$ derivatives (Table 5) may be divided into two classes; a typical example of each is shown in Figure 2. In the spectra of the norbornadiene and cyclohexadiene derivatives, there are two absorption bands due to $\nu(\text{CO}_t)$ modes with that of lower frequency being the less intense. This suggests that these compounds exist solely as *cis*-bridged isomers in the solid state. For the dimethylbutadiene complexes, the intensity ratio is reversed, which is consistent with *trans*-bridged structures. For all compounds there are two absorption bands due to $\nu(\text{CO}_b)$ vibrations (CO_b is a bridging carbonyl group). In some instances, solid-state effects increase the complexity of the spectra.

When the compounds are dissolved in alcohols or various phenols, their i.r. spectra are more complex than in non-hydroxylic solvents. Similar effects are observed for all nine complexes, but Table 6 summarises the i.r. spectra of the $[(\pi\text{-MeC}_5\text{H}_4)\text{FeCo(CO)}_4(\pi\text{-diene})]$ derivatives only, as these are typical. In the 1800 cm^{-1} region of the spectra, two extra absorption bands appear, one, A_l, at lower frequencies than A/B and the other, A_h, at higher. They are attributed to solute molecules which are hydrogen-bonded to the solvent. The interaction occurs between the oxygen atoms of the bridging carbonyl groups of both *cis*- and *trans*-$[(\pi\text{-dienyl})\text{FeCo(CO)}_4(\pi\text{-diene})]$ molecules and the hydroxyl protons of the solvent. This hypothesis has been advanced previously to account for similar effects observed for $[\{(\pi\text{-dienyl})\text{Fe(CO)}_2\}_2]$ and $[\{(\pi\text{-diene})\text{Cl(CO)}_2\}_2]$ complexes.[15] In some instances A_l clearly has a low frequency shoulder and in others it is an extremely broad absorption band which probably has more than one component. These may be due to more highly solvated solute molecules than those which are responsible for A_h and A_l.

There is no evidence for non-bridged isomers of any of the $[(\pi\text{-dienyl})\text{FeCo(CO)}_4(\pi\text{-diene})]$ compounds. This is not surprising as in many series of complexes, replacement of a $(\pi\text{-C}_5\text{H}_5)\text{Fe}$ by a $(\pi\text{-diene})\text{Co}$ moiety causes a bridged–non-bridged equilibrium to be shifted towards the carbonyl-bridged tautomers. For example, although $[(\pi\text{-C}_5\text{H}_5)\text{FeCo(CO)}_6]$ exists largely as the non-bridged form in solution,[5] only carbonyl-bridged forms of the isoelectronic $[(\pi\text{-diene})\text{Co}_2(\text{CO})_6]$ have been observed.[14]

[1/1899 *Received*, 15*th October*, 1971]

---

[14] A. R. Manning, unpublished observations.

[15] P. McArdle and A. R. Manning, *J. Chem. Soc.* (*A*), 1970, 2133.