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PROTONATION OF METAL CARBONYL COMPLEXES

III. CYCLOPENTADIENYL CARBONYL COMPLEXES OF MANGANESE

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SUMMARY

Using IR spectroscopy, the phosphine derivatives of cyclopentadienylmanganese tricarbonyl have been shown to undergo protonation in solutions of trifluoroacetic acid and in mixtures of this solvent with methylene chloride, protonation at the metal atom being the most probable. Ease of protonation increases with increasing electron-releasing properties of both the π-ring substituents and the phosphine ligands attached to the manganese atom.

The basicity of manganese in these cyclopentadienylmanganese tricarbonyl compounds is less than that of chromium in the corresponding benzenechromium tricarbonyl derivatives.

INTRODUCTION

In the previous papers in this series[1] it has been shown through the use of IR spectroscopic methods that phosphine derivatives of benzenechromium tricarbonyl undergo protonation at the metal atom in trifluoroacetic acid media. The ease of protonation is apparently governed by the nature of benzene ring substituents, protonation occurring more readily with donor but less readily with acceptor groups. Benzenechromium tricarbonyl complexes are not protonated in trifluoroacetic acid but as shown by PMR spectroscopy, they tend to protonate more readily at the metal atom in a more acidic medium (*e.g.* in a mixture of trifluoroacetic acid and boron trifluoride hydrate). Thus the replacement of a CO group by a triphenylphosphine ligand also stimulates protonation due to an increase of negative charge at the metal atom.

Protonation of the isoelectronic analogue of benzenechromium tricarbonyl, namely, cyclopentadienylmanganese tricarbonyl (CMT) has not been studied. On solution in sulphuric acid, the formation of a red solution only was noted[2], and no signals corresponding to protons attached to the metal atom were observed in the PMR spectrum of such a solution. This observation was attributed by the authors to a rapid exchange of the Mn–H proton with the solvent.

In the present work the series of investigations into the mechanism of hydrogen–deuterium exchange of CMT and its derivatives in the acidic media[3-5] is con-

TABLE 1

STRETCHING MODE FREQUENCIES ν(CO) (cm^{-1}) FOR THE COMPLEXES CpMn(CO)$_2$L MEASURED IN DIFFERENT SOLVENTS

Cp	*L*	*In* CS_2	*In* CF_3COOH		*In* CF_3COOH/CH_2Cl_2 (1/4)		
			Non-prot. form	*Prot. form*	*Non-prot. form*	*Prot. form*	$D_{prot.}/D_{non\text{-}prot.}$
C_5H_5	CO	1939 2023	1957 2033		1936 2024		0
	$P(OPh)_3$	1900 1963	decompn.		1898 1962		0
	PPh_3	1875 1937	1937	2054	1867 1933	1967 2047	0.018
	$AsPh_3$	1874 1936	1937	2007 2052	1867 1931	2007 2049	
	$SbPh_3$	1875 1935	1937	2005 2049	1867 1930	1987 2039	
	$P(C_6H_4CH_3\text{-}p)_3$	1868 1936	1932	2009 2049	1862 1930	2002 2044	0.059
	$P(CH_2C_6H_5)_3$	1865 1929		2047	1861 1928	1962 2042	0.049
	$P(i\text{-}C_3H_7)_3$	1862 1927		2003 2044	1853 1921	1994 2039	0.177
	$P(C_6H_{11})_3$	1859 1925		2001 2041	1851 1920	1991 2035	0.408
Et_4HC_5	CO	1921 2007	1939 2014	2077	1922 2008	2072	
	PPh_3	1859 1924		1997 2036	1862 1917	1988 2029	0.645
Et_5C_5	CO	1918 2003	1917 2008	2075	1917 2003	2070	
	PPh_3	1865 1919		1995 2032	1847 1914	1986 2027	2.76

tinued. The IR spectra of the complexes $CpMn(CO)_2L$ (when $Cp=C_5H_5$. $L=CO$, tertiary phosphines, $AsPh_3$, $SbPh_3$, when $Cp=Et_4HC_5$ and Et_5C_5, $L=CO$, PPh_3), and $C_5H_5Mn(CO)L_2$, $L_2=(PPh_3)_2$ or $Ph_2P(CH_2)_nPPh_2 (n=1–3)$, have been studied over their CO stretching regions. Such spectra were obtained in a neutral medium (CS_2), in trifluoroacetic acid and in the mixtures CF_3COOH/CH_2Cl_2 (molar ratio 1/4) (system A).

RESULTS AND DISCUSSION

The CO stretching frequencies for the compound investigated are listed in Tables 1 and 2. Two CO stretching bands observed for $CpMn(CO)_3$ type complexes may be attributed to the symmetric and degenerate CO vibrations in the $Mn(CO)_3$ moiety with C_{3v} local symmetry (A_1 and E symmetry classes respectively). For $CpMn(CO)_2L$ complexes, two $\nu(CO)$ bands were observed being the symmetric and antisymmetric CO modes (A' and A'' of local symmetry C_s). Only one $\nu(CO)$ band was detected for the diphosphine derivatives. The band positions depend upon both the nature of the cyclopentadienyl ring substituents and of the ligand L. Donor ring substituents decrease the $\nu(CO)$ frequencies in accordance with the known regularity[6] attributable to the greater $d_\pi(Mn)–p_\pi(CO)$ back donation and to the greater contribution of structure (I).

TABLE 2

STRETCHING MODE (FREQUENCIES $\nu(CO)$) (cm^{-1}) FOR MANGANESE DIPHOSPHINE COMPLEXES MEASURED IN DIFFERENT SOLVENTS

Complex	*In CH_2Cl_2*	*In CF_3COOH/CH_2Cl_2* 1/10		*In $CF_3COOH/CH_3COOH/CH_2Cl_2$* 0.1/0.9/10	
		Non-prot. form	*Prot. form*	*Non-prot. form*	*Prot. form*
$C_5H_5Mn(CO)(PPh_3)_2$	1827		1937	1825	1933
$C_5H_5Mn(CO)(Ph_2PCH_2PPh_2)$	1837		1957	1837	1965
$C_5H_5Mn(CO)(Ph_2PCH_2CH_2PPh_2)$	1837		1962	1836	1957
$C_5H_5Mn(CO)(Ph_2PCH_2CH_2CH_2PPh_2)$	1822		1947	1822	1947

$$\underset{(I)}{M{=}C{=}O} \leftrightarrow \underset{(II)}{\bar{M}{-}C{\equiv}O^+}$$

Replacement of a CO group with a phosphine ligand with greater donor properties leads to the same result. In a given series of monophosphine derivatives, the $\nu(CO)$ frequencies decrease as the phosphine basicity increases. A linear correlation[5] exists between $\nu(CO)$ and the Taft inductive constants σ^*: $\nu_{as}(CO)=1866.8+15.35\sigma^*$ (correlation coefficient $r=0.995$), $\nu_s(CO)=1931.3+14.44\sigma^*$ ($r=0.996$). This indicates that the electronic effect of substituents at the phosphorus atom is transmitted to the carbonyl groups via an inductive mechanism.

In the IR spectra of the compounds $CpMn(CO)_2L$ in CF_3COOH/CH_2Cl_2 (1/4), absorption bands for the neutral molecules were found in nearly the same region of the spectrum as in CS_2. Small shifts of the bands were found to be within the usual limits expected for solvent replacement. Except for L=CO and $P(OPh)_3$, all compounds exhibited two additional $\nu(CO)$ bands which were shifted by 100–150 cm^{-1} to the high frequency region. The same effect has been observed earlier for benzenechromium tricarbonyl compounds in acid media and has been explained in terms of an equilibrium between the neutral and protonated molecules.

$$CpMn(CO)_2L + H^+ \rightleftharpoons [CpMn(CO)_2LH]^+$$

It is interesting to note that in system A compound $C_6H_6Cr(CO)_2PPh_3$ was entirely protonated. Under the same conditions $C_5H_5Mn(CO)_2PPh_3$ was only partially protonated, the non-protonated form being predominant (Fig. 1). Full protonation of this complex was not observed even in pure CF_3COOH. Thus in cyclopentadienyl(triphenylphosphine)manganese dicarbonyl, the manganese atom has a much lower basicity than the chromium atom in the corresponding chromium compound.

The influence of ligands upon the protonation equilibria may be clearly seen

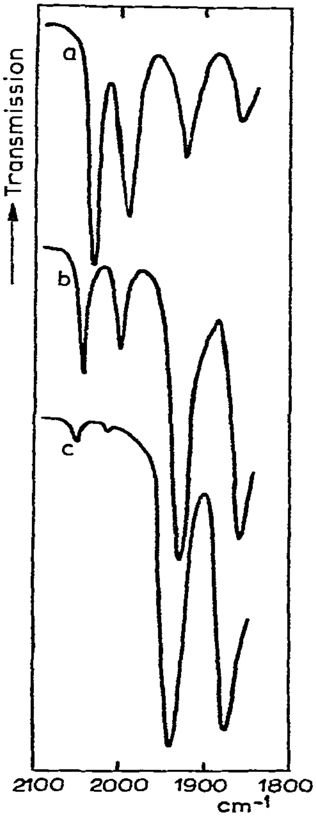

Fig. 1. Infrared spectra in CH_2Cl_2/CF_3COOH solution (4/1) in the spectral region 2100–1800 cm^{-1}: a. $Et_5C_5Mn(CO)_2PPh_3$; b. $C_5H_5Mn(CO)_2P(i\text{-}C_3H_7)_3$; c. $C_5H_5Mn(CO)_2PPh_3$.

by a comparison of the optical densities at the band maxima for the protonated and non-protonated forms. The ratios $D_{\text{prot}}/D_{\text{non-prot}}$ for symmetrical CO modes (high frequency component of the doublet) are given in Table 1. The low frequency band of the non-protonated form is distorted by overlap with the solvent band, and for this reason no measurement was made of the antisymmetric ν(CO) modes. Although the optical density ratios are not equal to the ratio of the concentrations due to the difference in the molar extinction coefficients, from the order of these values it is possible to arrive at the qualitative conclusion that the concentration of the protonated form in the solution increases with increasing donor properties of the ligand.

In system A, a solution of $C_5H_5Mn(CO)_2P(OPh)_3$ is virtually completely unprotonated while in the same solution the complex $C_5H_5Mn(CO)_2P(C_6H_{11})_3$ has a ratio $D_{\text{prot}}/D_{\text{non-prot}}$ equal to 0.408. In the series $CpMn(CO)_2PPh_3$, the concentration of the protonated form increases as Cp changes from C_5H_5 to Et_5C_5 (equivalent to an increase of $D_{\text{prot}}/D_{\text{non-prot}}$ from 0.018 to 2.76). Fig. 1 shows the dependence of these equilibria upon the nature of the phosphine ligand.

In pure CF_3COOH the equilibria are displaced towards the protonated form. Practically complete protonation was observed under such conditions for compounds with $L = P(CH_2Ph)_3$, $P(i\text{-}Pr)_3$ and $P(C_6H_{11})_3$, while both forms were present in such solutions for $L = P(C_6H_4Me\text{-}p)_3$, PPh_3, $AsPh_3$ and $SbPh_3$. It is important to note that $C_5H_5Mn(CO)_3$ undergoes no protonation in pure CF_3COOH while the compounds $Et_4HC_5Mn(CO)_3$ and $Et_5C_5Mn(CO)_3$ are partially protonated not only in pure CF_3COOH but also in system A.

Substitution of two carbonyl groups for phosphine ligands in the complex increases the basicity of the manganese atom and allows the full protonation of complexes $C_5H_5Mn(CO)(PPh_3)_2$ and $C_5H_5Mn(CO)[Ph_2P(CH_2)_nPPh_2]$ ($n = 1$–3) not only in system A, but also at very low concentrations of CF_3COOH, *e.g.* in a mixture CF_3COOH/CH_2Cl_2 at a molar ratio of 1/25 (Table 2). In those cases where both forms were capable of existence in solution, partial protonation was only observed in systems of much lower acidity, *e.g.* in a $CF_3COOH/CH_3COOH/CH_2Cl_2$ mixture at a molar ratio of 0.1/0.9/10.

Our results clearly show that the compounds $CpMn(CO)_2L$ and $CpMn(CO)L_2$ undergo protonation in acid media, and that such protonation probably occurs at the metal atom. The protonation reaction is reversible, the initial compound being isolated if water is added to the system. The position of the protonation equilibrium depends upon the acidity of the medium, the type of ligands at the metal atom and the nature of the cyclopentadienyl ring substituents. Increasing the donor properties of the ligands increases the basicity of the metal and shifts the equilibrium towards the protonated form.

By comparison with the data in ref. 1 it may be shown that the manganese atom in the CMT molecule and its derivatives has a lower basicity in comparison to that of the chromium atom in the corresponding benzenechromium tricarbonyl compounds.

EXPERIMENTAL

The IR spectra were measured on a Zeiss UR-20 spectrometer using an LiF prism. The instrument was calibrated using the DCl vibration–rotation spectrum. The compounds $C_5H_5Mn(CO)_2L$ were prepared by the methods of Strohmeier[7] and

Nyholm[8] using the photochemical reaction of $C_5H_5Mn(CO)_3$ with L in benzene.

The complexes $Et_4RC_5Mn(CO)_2PPh_3$ (R = H, Et) were obtained by reaction of equimolar quantities of the respective compounds $Et_4RC_5Mn(CO)_3$[9] with PPh_3 in benzene under UV irradiation (PRK-4 lamp) and in an argon atmosphere for 30 h. After the cessation of CO evolution, the mixture was filtered, the solution concentrated *in vacuo*, the residue dissolved in a small quantity of benzene (generally after heating) and the complex reprecipitated by addition of excess heptane. The crystals were washed with concentrated HCl, H_2O, alcohol and dried. Yield 50–70%. The complexes obtained were yellow crystalline products stable in air. Their m.p.'s and analyses are given in Table 3.

TABLE 3

ANALYTICAL DATA FOR $Et_4RC_5Mn(CO)_2PPh_3$ COMPLEXES

R	*M.p.* (°C)	*C* (%)		*H* (%)		*P* (%)		*Mn* (%)	
		Found	*Calcd.*	*Found*	*Calcd.*	*Found*	*Calcd.*	*Found*	*Calcd.*
H	142–143	70.40	70.03	6.71	7.05	5.73	6.02	10.56	10.68
Et	211–215	70.52	70.84	7.03	7.43	5.48	5.71	10.41	10.12

The structures of the compounds were confirmed by their NMR spectra (60 MHz) in CS_2: R = H $\delta = 0.85$ and 1.07, 12H, two triplets of non-equivalent CH_3 groups; $\delta = 1.74$ and 2.23, 8H, two quadruplets of non-equivalent CH_2 groups; $\delta = 3.40$, 1H, doublet $J = 4$ Hz, Cp–H; $\delta = 7.2$, 15H, multiplet, C_6H_5. R = Et, $\delta = 1.09$, 15H, triplet CH_3; $\delta = 1.94$, 10H, quadruplet CH_2; $\delta = 7.2$, 15H, multiplet C_6H_5. The complexes $C_5H_5Mn(CO)[Ph_2P(CH_2)_nPPh_2]$ were prepared by previously reported methods[8,10].

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THE CRYSTAL STRUCTURE OF BUTADIENE(CYCLOOCTATETRAENE)IRON MONOCARBONYL, $FeCO(C_4H_6)(C_8H_8)$, DETERMINED BY X-RAYS

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SUMMARY

The crystal and molecular structures of butadiene(cyclooctatetraene)iron monocarbonyl $(C_4H_6)(C_8H_8)Fe(CO)$ have been determined from an X-ray diffraction study performed with a Stoe-automated Weissenberg apparatus. The hydrogen atoms have been located and included in the least-squares refinement. The iron atom is bonded to the four coplanar carbon atoms of the butadiene ligand and to four coplanar carbon atoms of a butadiene-type residue of the cyclooctatetraene (COT) ligand. The hydrogen atoms linked to the four carbon atoms of butadiene are out of the plane defined by the carbon atoms, while the hydrogen and carbon atoms linked to the four coplanar carbon atoms of the butadiene-like residue of the COT ring are out of the plane defined by these four carbon atoms. The crystals of $(C_4H_6)(C_8H_8)Fe(CO)$ have symmetry $P2_1/m$, within experimental error, with two molecules in a unit cell defined by the parameters $a=6.95$ Å, $b=10.82$ Å, $c=7.28$ Å and $\beta=98°38'$. The final value of $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$ is 0.067 for 1792 independent observed reflections.

Two new coordination compounds of zerovalent iron have been recently synthesized in our laboratories, namely dibutadieneiron carbonyl $(C_4H_6)_2FeCO$, (I), and butadiene(cyclooctatetraene)iron carbonyl $(C_4H_6)(C_8H_8)FeCO$, (II)[1]. Both are crystalline solids, and exhibit a low catalytic activity in the dimerization of butadiene. We describe below some structural features of (I) and the crystal structure of (II).

Orange needle-like crystals of (I) were examined in Lindemann glass capillaries filled with dry nitrogen and flame-sealed. The X-ray analysis was performed with a Weissenberg camera by the equiinclination technique (Fe-$K\alpha$). The crystals of (I) are tetragonal with the following parameters: $a=b=7.73\pm0.03$ Å, $c=7.21\pm0.02$ Å; $z=2$; $d_{calc.}$ 1.48 g/cm^3, $d_{obs.}$ 1.46 g/cm^3; space group $P\bar{4}2_1m$.

These parameters are very similar to those listed by Immirzi and Allegra[2] for $Rh^ICl(C_4H_6)_2$, (III): $a=b=7.90\pm0.03$ Å, $c=6.92\pm0.02$ Å; $z=2$; space group $P\bar{4}2_1m$

The similarity in the unit cell parameters and symmetries suggests very similar crystal structures for (I) and (III). These conclusions are supported by a two-dimensional X-ray analysis of (I) and by packing considerations. By considering each butadiene group as a bidentate ligand, linked to iron through its outer C–C bonds, the coordination around the metal approximately corresponds to a square pyramid as in the case of (III). The three-dimensional X-ray study of (I) was not undertaken because Davis, Cupper and Simpson[3] had in the meantime announced the completion of a three-dimensional analysis of (I).

Dark-brown, needle-like, crystals of (II) were also scanned in Lindemann glass capillaries filled with dry nitrogen and flame sealed. Equiinclination Weissenberg photographs indicated that the crystals of (II) are monoclinic with the following unit cell parameters: $a=6.95\pm0.02$ Å, $b=10.82\pm0.03$ Å, $c=7.28\pm0.02$ Å; $\beta=98°38'\pm20'$; $z=2$; $d_{\text{calc.}}$ 1.49 g/cm^3, $d_{\text{obs.}}$ 1.43 g/cm^3; $F(000)$ 252.

The reciprocal lattice symmetry and the absence of ($0k0$) reflections with k odd suggested either $P2_1/m$ or $P2_1$ as possible space groups.

By means of a Stoe-automated Weissenberg camera, with the equiinclination technique, the intensities of 2675 independent reflections, with l ranging from 0 to 9, were collected (Mo-$K\alpha$, graphite monochromatized radiation).

The moving-crystal moving-counter technique was used, with an ω scan rate of 1°/min, and an ω scan range of 2.5°; the background counts were performed for 1 min each at the extremes of each scan. The examined crystal was nearly cylindrical, 0.30–0.20 mm as maximum and minimum diameter; the μR value was 0.35, therefore the absorption corrections were neglected.

The measured intensities were scaled to a common basis and corrected for the Lorentz and polarization factors. The intensities of 833 out of the 2675 measured reflections were lower than 2 times the calculated standard deviations; these reflections were considered as not observed and an arbitrary intensity equal to 0.50, the observable limit, was assigned to them.

The structure of (II) was solved by a three-dimensional Patterson and successive Fourier maps. The iron atoms were located in the mirror plane of the $P2_1/m$ space group[4]. This assumption, later proved to be correct within standard deviations, implies that the mirror of the $P2_1/m$ space group bisects the FeCO unit, the C_8H_8 ring and the C_4H_6 molecule. A three dimensional electron density map, based on the phases of the Fe atoms, clearly showed the whole molecule and all the remaining non-hydrogen atoms were easily located. The refinement of the structure was carried out by the least-squares method with the aid of a general program prepared by Immirzi[5]. The atomic scattering factors were calculated according to Vand, Eiland and Pepinsky[6] using the values suggested by Moore[7] for the constants A_j, B_j, C_j, a_j, b_j. The weighting scheme suggested by Cruickshank[8] was used. After eight full-matrix cycles performed with isotropic thermal parameters, anisotropic thermal parameters for all atoms were introduced. After eight full-matrix cycles the final shifts were less than 10% of the corresponding standard deviations for the atomic coordinates and less than 50% for the thermal parameters. The disagreement factor $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$ was 0.078 for the 1792 observed reflections with $d>0.60$ Å.

From a three-dimensional F_o–F_c map, definite indications of the positions of the H atoms were derived. The H atoms in this map were 100–140 units in height while the average background was 40 units. No unassigned peak was higher than 80 on the same scale (C atoms peaks $\simeq$900 units). Some cycles of full-matrix least-squares refinement varying the positional and thermal parameters of all atoms including hydrogen gave convergence to a final R of 0.067. The total R is 0.10. Tables 1 and 2 report the final fractional coordinates of the atoms of the independent unit with their thermal parameters and standard deviations. A list of the observed and calculated structure factors can be obtained by application to the authors.

TABLE 1

FINAL FRACTIONAL COORDINATES OF THE INDEPENDENT UNIT OF $(C_4H_6)(C_8H_8)FeCO$.
The e.s.d., in parentheses, in this and in the following tables, occur in the last significant digit.

Atom	*x/a*	*y/b*	*z/c*	*B* (*Å*^{2})
Fe	0.11483(8)	0.25000(0)	0.29784(9)	
O	0.1539(9)	0.25000(0)	−0.0959(7)	
C	0.1408(7)	0.25000(0)	0.0605(8)	
C_1	−0.1167(5)	0.1858(5)	0.4081(6)	
C_2	−0.1051(6)	0.1105(4)	0.2520(7)	
C_3	−0.2297(7)	0.1022(5)	0.0705(8)	
C_4	−0.3296(6)	0.1839(5)	−0.0428(7)	
C_5	0.3177(5)	0.1840(5)	0.5101(6)	
C_6	0.3498(6)	0.1204(5)	0.3507(8)	
H_1	−0.105(9)	0.163(6)	0.526(9)	2.7(12)
H_2	−0.046(7)	0.020(5)	0.277(7)	1.0(8)
H_3	−0.235(9)	0.025(7)	0.027(9)	3.1(14)
H_4	−0.421(9)	0.145(7)	−0.142(9)	3.6(14)
H_5	0.280(7)	0.141(5)	0.620(7)	1.6(10)
H_6	0.447(9)	0.147(6)	0.291(9)	2.8(13)
H_{61}	0.324(8)	0.040(6)	0.322(8)	1.8(10)

TABLE 2

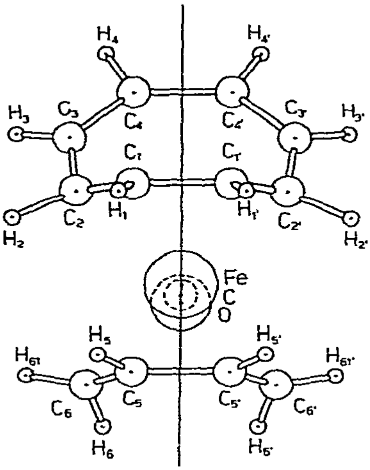
ANISOTROPIC THERMAL PARAMETERS (Å^2) FOR THE NON-HYDROGEN ATOMS OF THE INDEPENDENT UNIT OF $(C_4H_6)(C_8H_8)FeCO$

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Fe	1.53(2)	2.50(2)	2.30(2)		0.10(2)	
O	5.05(24)	7.79(37)	3.30(20)		1.59(18)	
C	2.39(14)	3.44(20)	3.24(19)		0.36(13)	
C_1	2.29(11)	6.27(25)	3.71(17)	−0.45(13)	0.59(11)	1.55(16)
C_2	3.07(13)	2.75(13)	4.94(19)	−0.53(11)	−0.25(13)	0.82(13)
C_3	3.42(15)	3.20(16)	5.80(24)	−0.60(12)	−0.60(15)	−0.69(16)
C_4	3.22(14)	4.91(22)	4.46(19)	−0.41(14)	−0.99(14)	−0.94(17)
C_5	2.27(10)	4.84(20)	3.47(15)	0.48(12)	−0.40(10)	0.74(14)
C_6	2.74(12)	4.79(22)	4.60(19)	1.28(14)	0.02(13)	−0.27(17)

Since there was such good correspondence between calculated and observed data and the molecular geometry was in very good agreement with the data reported for many similar compounds[2,9–11] no structure refinement was carried out in the $P2_1$ space group. Moreover any distortion of the geometry of the molecule, lowering the *m* molecular symmetry, within the limits of the reported standard deviations, must be very small.

RESULTS AND DISCUSSION

The molecules of $FeCO(C_8H_8)(C_4H_6)$ are represented in Figs. 1–3 as obtained



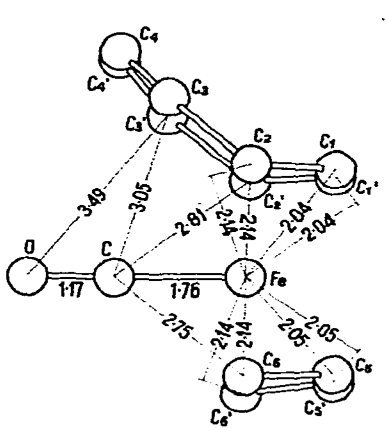


Fig. 1. Projection along the *c* axis of the $(C_4H_6)(C_8H_8)FeCO$ molecule, indicating the atom labelling scheme.

Fig. 2. Schematic representation of $(C_4H_6)(C_8H_8)FeCO$ molecule; some of the most significant intramolecular contact distances are indicated.

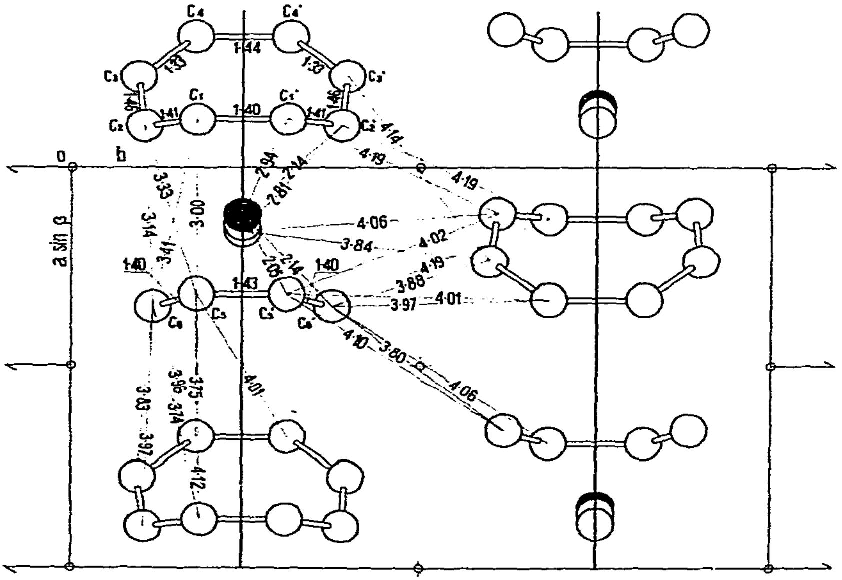


Fig. 3. The packing arrangement in $(C_4H_6)(C_8H_8)FeCO$, as viewed down the *c* axis. Some of the most significant contact distances are indicated.

from the coordinates reported in Table 1. The geometrical parameters of the molecules with their standard deviations are reported in Table 3.

Within the standard deviations, the molecule of (II) lies about a mirror that bisects the FeCO group as well as the C_8H_8 ring and the C_4H_6 molecule. Because of the presence of the mirror, the four carbon atoms of butadiene (C_6,C_5,$C_{5'}$,$C_{6'}$) are

TABLE 3

MOST SIGNIFICANT INTRAMOLECULAR BOND LENGTHS AND ANGLES IN $(C_4H_6)(C_8H_8)$-FeCO

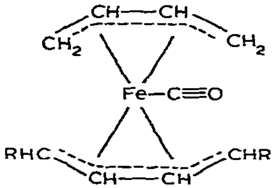
The molecule is bisected by the mirror plane at $y\ \frac{1}{4}$.

Bond lengths (Å)		*Bond angles (deg.)*		*Relevant distances between non-bonded atoms (Å)*	
Fe–C	1.766(6)	Fe–C–O	178.7(5)	$C_2 \cdot C_{2'}$	3.02(1)
$Fe–C_2$	2.138(4)	$Fe–C_2–C_1$	66.3(3)	$C_6 \cdot C_{6'}$	2.80(1)
$Fe–C_1$	2.033(4)	$Fe–C_1–C_2$	74.3(2)	$C_2 \cdot C_6$	3.14(1)
$Fe–C_6$	2.142(5)	$Fe–C_1–C_{1'}$	70.0(2)	$C_1 \cdot C_5$	3.00(1)
$Fe–C_5$	2.048(5)	$Fe–C_6–C_5$	66.9(3)	$C_1 \cdot C_{5'}$	3.31(1)
C–O	1.157(8)	$Fe–C_5–C_6$	74.2(3)	$C_{2'} \cdot C_3$	3.44(1)
$C_1–C_2$	1.412(7)	$Fe–C_5–C_{5'}$	69.6(3)	$C_{1'} \cdot C_3$	3.62(1)
$C_1–C_{1'}$	1.388(16)	$C_2–C_1–C_{1'}$	125.3(3)	$C \cdot C_2$	2.81(1)
$C_2–C_3$	1.463(8)	$C_1–C_2–C_3$	131.4(3)	$C \cdot C_1$	3.40(1)
$C_3–C_4$	1.328(8)	$C_2–C_3–C_4$	134.1(3)	$C \cdot C_6$	2.75(1)
$C_4–C_{4'}$	1.430(16)	$C_3–C_4–C_{4'}$	131.8(3)	$C \cdot C_5$	3.38(1)
$C_2–H_2$	1.07(5)	$C_{1'}–C_1–H_1$	106(1)	$O \cdot C_6$	3.61(1)
$C_1–H_1$	0.87(7)	$C_1–C_2–H_2$	117(3)	$O \cdot C_2$	3.67(1)
$C_3–H_3$	0.90(7)	$C_2–C_3–H_3$	112(4)	$O \cdot C_3$	3.49(1)
$C_4–H_4$	0.95(7)	$C_3–C_4–H_4$	111(4)	$O \cdot C_4$	3.53(1)
$C_6–C_5$	1.397(7)	$C_6–C_5–C_{5'}$	119.5(2)	$Fe \cdot H_6$	2.57(6)
$C_5–C_{5'}$	1.429(14)	$C_{5'}–C_5–H_5$	118(1)	$Fe \cdot H_{61}$	2.69(6)
$C_6–H_6$	0.91(6)	$C_5–C_6–H_6$	118(4)	$Fe \cdot H_5$	2.71(6)
$C_6–H_{6'}$	0.91(6)	$C_5–C_6–H_{6'}$	128(5)	$Fe \cdot H_1$	2.60(6)
$C_5–H_5$	1.00(6)	$C_2–Fe–C_6$	94.2(1)	$Fe \cdot H_2$	2.72(6)
		$C_2–Fe–C_{2'}$	89.8(1)	$H_1 \cdot H_{1'}$	1.89(12)
		$C_6–Fe–C_{6'}$	81.8(1)	$H_6 \cdot H_{6'}$	2.24(13)
		$C–Fe–C_2$	91.7(1)	$H_5 \cdot H_{5'}$	2.36(11)
		$C–Fe–C_6$	89.0(1)		
		$C–Fe–C_1$	126.7(1)		
		$C–Fe–C_5$	124.9(1)		

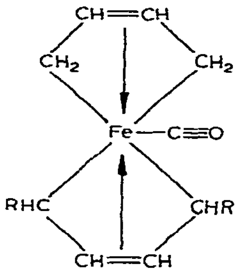
in a *cisoid* form and strictly coplanar. This happens also for the C_4H_4 butadiene-type residue of the C_8H_8 ring. The carbon atoms of the C_8H_8 ring are placed on two planes one defined by the four atoms $C_2,C_1,C_{1'},C_{2'}$ the other by the six atoms $C_2,C_3,C_4,C_{4'},C_{3'},C_{2'}$ (r.m.s. distance 0.06 Å); the dihedral angle between the two planes being 43°. The overall shape and coordination of the butadiene ligand resemble those found in $(C_4H_6)Fe(CO)_3$[9] while those of the cyclooctatetraene ligand are very similar to those found in $(C_8H_8)Fe(CO)_3$[10].

The planes defined by the carbon atoms of the two butadiene residues $C_2,C_1,C_{1'},C_{2'}$ and $C_6,C_5,C_{5'},C_{6'}$ are nearly parallel (~6.5°) and are nearly perpendicular to the plane defined by the Fe atom and the terminal carbon atoms of both the butadiene residues. The C–C bond lengths of the carbon atoms of the two butadiene residues involved in the bonding with metal are nearly equal (1.41 ± 0.02 Å).

As found in many similar compounds, the electronic structure of these conjugated diene–transition metal complexes can be represented by two limiting bonding schemes:



(A)



(B)

In the limiting structure (A) all carbon atoms of the two butadiene residues have sp^2 hybridization and the bonding to iron is via the delocalized π electrons. In the limiting structure (B) the terminal carbon atoms of both butadiene residues are σ bonded to the iron atoms and hence are closer to sp^3 hybridization.

By assuming that the iron atom is bonded to the terminal carbon atoms of the butadiene residues, the five fold coordination around the metal is approximately a square pyramid, having the carbonyl group at the apex and the atoms C_2, $C_{2'}$, C_6, $C_{6'}$ being approximately at the vertices of a square. The C_2, $C_{2'}$, Fe, C_6, $C_{6'}$ atoms lie nearly on a plane (r.m.s. distance 0.008 Å). The basal bond lengths $Fe–C_2$=$Fe–C_{2'}$ and $Fe–C_6$=$Fe–C_{6'}$ are 2.14 ± 0.01 Å. The bond lengths $Fe–C_1$=$Fe–C_{1'}$ 2.03 ± 0.01 Å and $Fe–C_5$=$Fe–C_{5'}$ 2.04 ± 0.01 Å are slightly shorter than 2.14 ± 0.01 Å as found for the bonds between the metal and the terminal carbon atoms. The carbon atoms of the two butadiene residues are coplanar four by four and the values of the angles involved are near to 120° ($\angle C_2C_1C_{1'} = \angle C_{2'}C_{1'}C_1$ $125.3 \pm 0.3°$ and $\angle C_6C_5C_{5'} = \angle C_5C_{5'}C_{6'}$ $119.5 \pm 0.2°$). The carbon and hydrogen atoms linked to the carbon atoms of both butadiene residues are out of the planes defined by these atoms, and this is true both for the COT ligand and for butadiene. The most significant torsional angles are reported in Table 4.

For the butadiene ligand, within the limits of standard deviations, the hydrogen atoms in *anti* position (H_6 and $H_{6'}$) are 0.56 Å above the butadiene plane away from iron, the hydrogen atoms in *syn* position (H_{61} and $H_{61'}$) are 0.21 Å below the

TABLE 4

MOST SIGNIFICANT TORSIONAL ANGLES INVOLVING HYDROGEN ATOMS FOR THE BUTADIENE-LIKE RESIDUE OF COT AND FOR THE BUTADIENE LIGAND

The torsional angles are measured clockwise; the *cis* position corresponds to 0°.

Torsional angles (deg.)			
$C_{2'}C_{1'}C_1H_1$	170	$C_{5'}C_5C_6H_{61}$	197
$C_{1'}C_1C_2H_2$	154	$C_{5'}C_5C_6H_6$	44
$C_{1'}C_1C_2C_3$	−58	$H_{6'}C_6C_5H_5$	−10
$H_2C_2C_1H_1$	−14	$H_6C_6C_5H_5$	217
$C_{6'}C_{5'}C_5H_5$	186		

butadiene plane toward iron. The H_5 and $H_{5'}$ atoms are slightly below the butadiene plane toward the Fe atom (0.10 Å). For the butadiene-like residue of the COT ligand the carbon atoms in *anti* position (C_3 and $C_{3'}$) are 0.93 Å above the butadiene residue plane away from iron and the hydrogen atoms in *syn* position (H_2 and $H_{2'}$) are 0.42 Å below the butadiene residue plane toward iron. The H_1 and $H_{1'}$ atoms are slightly below the butadiene residue plane toward iron (0.14 Å). The picture is essentially similar both for the butadiene ligand and for the butadiene-like residue of the COT ring. The deviations from planarity of the atoms linked to the four carbon atoms of the butadiene residues are in good agreement with the data reported by other authors[12,13]. These distortions may be justified in order to provide an increased overlap between the butadiene residues π-electron orbitals and the iron *d*-electron orbitals.

The molecular packing of $(C_8H_8)(C_4H_6)FeCO$ consists in the arrangement of up and down molecules around each inversion center of the unit cell. No C–C intermolecular distance is shorter than 3.7 Å; the shortest O–C intermolecular distance between molecules superposed along the *c* axis is 3.35 Å (the corresponding O–H distance is 2.65 Å).

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