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THE ELECTRIC DIPOLE MOMENTS OF 1,3-BUTADIENECARBONYLIRON COMPLEXES AND TWO CLUSTER COMPOUNDS

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Summary

Analysis of the electric dipole moments of di-1,3-butadienemonocarbonyliron, bis(2,3-dimethyl-1,3-butadiene)monocarbonyliron, di-1,3-cyclohexadienemonocarbonyliron, di-1,3-butadiene(trimethylphosphite)iron and (trimethylphosphite)tetracarbonyliron allows an assessment of the magnitude of the (iron—carbonyl) group moment in di-1,3-butadienemonocarbonyliron. For this group moment a tentative value of ca. 2 D (from Fe to CO) is suggested. The electric dipole moments of cyclobutadienetricarbonyliron, 1,2,3,4-*tetrahapto*-cyclooctatetraenetricarbonyliron, methyl 1,3-pentadienoate- and diethyl muconate- tricarbonylirons were also measured and interpreted, as well as those of methylnonacarbonyltricobalt and trifluoromethylnonacarbonyltricobalt. Molecular structures for bis(diethyl muconate)monocarbonyliron and bis(methyl sorbate)monocarbonyliron are discussed in relation to their dipole moments.

Introduction

Knowledge of the electric dipole moments has proved to be very useful for the elucidation of the electronic distribution and configuration of a large variety of molecules [1-3], including molecular π-complexes [4].

In the present study an attempt was made to determine the (iron—carbonyl) group moment from dipole moment analysis of chosen complexes, and to elucidate the conformations of bis(diethyl muconate)monocarbonyliron and bis(methyl sorbate) monocarbonyliron. 1,3-Butadiene tricarbonyliron, (methyl 1,3-pentadienoate)- and (diethyl muconate)tricarbonyliron were also studied, as well as two cluster cobalt compounds.

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Experimental

Di-1,3-butadiene-, bis(2,3-dimethyl-1,3-butadiene)-, bis(methyl sorbate)-, bis(diethyl muconate)- and di-1,3-cyclohexadiene-monocarbonylirons, as well as 1,3-butadiene-, methyl 1,3-pentadienoate- and diethyl muconate-tricarbonylirons were prepared by Koerner von Gustorf and his coworkers [5]. Di-1,3-butadiene(trimethylphosphite)iron and (trimethylphosphite)tetracarbonyliron were also synthesized by Koerner von Gustorf. Cyclobutadienetricarbonyliron and 1,2,3,4-*tetrahapto*-cyclooctatetraenetricarbonyliron were provided by Pettit [6].

Pure samples of methylnonacarbonyltricobalt and trifluoromethylnonacarbonyltricobalt were kindly supplied by Tominaga et al. [7] and Booth et al. [8], respectively.

The dipole moments were measured in benzene solution at 25.0°C. The value of the polarization of the solute, extrapolated to infinite dilution, was calculated from the ratios [9]:

$$\alpha = \frac{\Sigma(\epsilon - \epsilon_1)}{\Sigma w} \text{ and } \beta = \frac{\Sigma(v - v_1)}{\Sigma w}$$

obtained by least-squares analysis. In these equations w is the weight fraction of the solute and ϵ and v are, respectively, the dielectric constant and specific volume of the solutions (subscript 1 refers to the pure solvent as used).

All weighings were carried out using a Sartorius microbalance and due precautions were taken in the preparation of solutions to avoid contamination by air. The cell was dried by pure nitrogen.

In every case the $({}_{\mathrm{E}}P + {}_{\mathrm{A}}P)$ distortion term was assumed equal to molecular refraction of the solute, for the Na-D line.

The technique for the determination of dielectric constants, specific volumes and refraction indices has been described elsewhere [10].

TABLE 1

PHYSICAL DATA FOR MOLECULAR REFRACTION CALCULATIONS [a]

Compound	R_D (cm^3)
Carbon monoxide	5.08
Trimethylphosphite [b]	29.30
1,3-Butadiene [b]	21.42
2,3-Dimethyl-1,3-butadiene [b]	29.76
1,3-Cyclohexadiene [b]	26.86
Cyclobutadiene [c]	17.64
Cyclooctatetraene [d]	37.02
Methyl acrylate [e]	22.02
Methyl sorbate [e]	38.19
1,3-Butadienetricarbonyliron [c]	47.05
Methyl 1,3-pentadienoatetricarbonyliron [e]	60.86

[a] In liquid phase, except for carbon monoxide which was examined in the gaseous phase (and for white light). [b] From Beilsteins Handbuch, I, erg. 3, p. 1203. [c] Additive value, from bond refractions [13], with no allowance of 1,3-butadiene exaltation (1.73 cm^3) as cyclobutadiene is antiaromatic [14]. [d] Obtained by adding 1.73 cm^3 to the observed refraction (35.29 cm^3) of free cyclooctatetraene, as cyclooctatetraene residue in *tetrahapto*-1,2,3,4-cyclooctatetraenetricarbonyliron has its iron-united (C=C—C=C) group planar [15]. [e] This study.

TABLE 2

PHYSICAL DATA FROM BENZENE DIPOLE MOMENT DETERMINATIONS (AT 25.0°C)

Solute	w_{max}	α	$-\beta$	$P_{2\infty}$	$R_{2\infty}$	R_D(add.)	μ(D)
Methyl acrylate	0.021	3.43	0.083	82.9	22.0 [a]	—	1.73 [d]
Diethyl muconate	0.016	3.03	0.183	169.5	—	53.1	2.39
L in L_2FeCO							
1,3-Butadiene	0.020	2.90	0.365	149.3	54	55.0 [b]	2.15
2,3-Dimethyl-1,3-butadiene	0.012	4.15	0.290	256.7	75	74.6	2.98
1,3-Cyclohexadiene	0.016	2.17	0.423	151.9	66	65.9	2.05
Methyl sorbate	0.018	1.26	0.410	153.4	—	88.5	1.78
Diethyl muconate	0.008	1.73	0.403	262.2	—	118.5	2.65
L in $LFe(CO)_3$							
1,3-Butadiene	0.036	3.00	0.414	151.7	47.0 [a]	—	2.26 [e]
Cyclobutadiene	0.029	4.15	0.462	188.8	43.0	43.2	2.67
tetrahapto-1,2,3,4-Cyclooctatetraene	0.018	1.70	0.453	128.2	—	62.5	1.79
Methyl 1,3-pentadienoate	0.021	3.38	0.405	215.7	60.9 [a]	—	2.75
Diethyl muconate	0.009	2.40	0.420	225.5	79.4	78.8	2.68
Miscellaneous complexes							
$(1,3\text{-Butadiene})_2FeP(OMe)_3$	0.005	1.94	0.403	168.8	79	78.5	2.10
$(MeO)_3PFe(CO)_4$	0.017	6.75	0.437	432.2	65	62.0 [c]	4.26
$MeC(Co)_3(CO)_9$	0.033	0.78	0.549	147.8	—	73.9	1.90
$F_3C(Co)_3(CO)_9$	0.015	1.42_4	0.530	229.8	—	73.3	2.77

[a] In liquid phase (see Table 1). [b] Taken equal to 2 × R_D(butadiene) + R(Fe) + R(CO). [c] From refractions of 1,3-butadienetetracarbonyliron, trimethylphosphite and 1,3-butadiene. [d] Lit. value [3]; μ 1.77 D. [e] Lit. value [12]: μ 2.15 D.

Light absorption makes some molecular refractions difficult to measure, and in special cases additive values should be preferred. Additive figures were derived from molar refractions measured on pure liquids which are, of course, much more accurate than those determined in solution. Physical data for molecular refraction calculations are given in Table 1. Also of interest are the atomic refractions [11] of iron (7.0 cm³) and cobalt (6.6 cm³) and the molecular refraction [12] of 1,3-butadienetetracarbonyliron (55.2 cm³).

For the solutes examined, w_{max} (only three decimals are reported), α, $-\beta$, $P_{2\infty}$, $R_{2\infty}$ (determined from β and $\gamma = (\Delta n)/w$ experimental ratios), R_D(add.) and μ calculated using R_D(add.), except in three cases, are given in Table 2.

Results and discussion

The electric dipole moments of 1,3-butadienetricarbonyliron and cyclobutadienetricarbonyliron

As indicated by X-ray analysis [16], in 1,3-butadienetricarbonyliron the tricarbonyliron group symmetry axis makes an angle of 61° with the planar (*s-cis* shaped) 1,3-butadiene residue. For cyclobutadienetricarbonyliron the tricarbonyliron symmetry axis is perpendicular to the planar (square-shaped) cyclobutadiene residue [17]. The same situation is observed for the iron-united butadiene group in 1,2,3,4-*tetrahapto*-cyclooctatetraenetricarbonyliron [15]. Electric dipole moments for these compounds are 2.26, 2.67 and 1.79 D, respectively, and the carbonyl stretching frequencies are nearly equal for the first two compounds [18] (2051 cm⁻¹) and somewhat greater [15] (2058 cm⁻¹) for the last compound. By analogy with the direction found for the di-1,3-butadienemonocarbonyliron electric moment (see later), we may safely infer that all these dipole moments are directed from Fe towards the geometrical centre of the three (nearly mutually perpendicular) CO groups.

In the following discussion we shall divide the dipole moment of $LFe(CO)_3$ into three terms:

$\mu(L) = A$, $\mu(L—Fe) = B$, $\mu(Fe(CO)_3) = X$.

Though *s-cis*-butadiene has not been examined, simple considerations do not support the view that it is polar *. This may not be true, however, of the coordinated 1,3-butadiene residue in 1,3-butadienetricarbonyliron, even though a theoretical calculation [21] gave $\mu(L) = 0$.

For inner and outer carbon atoms a marked increase in ^{13}C chemical shifts is found passing from free butadiene [22] (55.6 and 76.2 ppm, against CS_2) to complexed butadiene(s) in 1,3-butadienetricarbonyliron [23] (107.0 and 151.7 ppm) and di-1,3-butadienemonocarbonyliron [24] (113 and 155 ppm).

The theory of ^{13}C NMR shifts is still the subject of controversy [25], and several factors accompany electron density changes. Bond anisotropy, mobile bond order changes, changes in hybridization energy [26], etc., can contribute to upfield coordination shifts in cases where a downfield shift is expected on the basis of electron density, for instance in $C_6H_6Cr(CO)_3$ [27]. It is not easy, therefore, to explain the differences between C(2) and C(1) chemical shifts observed for butadiene (76.2 — 55.6 = 20.6 ppm) and coordinated butadienes (151.7 — 107.0 = 44.7 ppm; 155 — 113 = 42 ppm). Gain in electrons coming from the iron atom to inner and outer butadiene-carbon atoms may explain the increase if iron back-bonding is stronger with outer carbon atoms: this produces a term that contributes to *B*. Electron transfer from the inner to the outer carbon atoms in coordinated butadiene(s), giving rise to an *A* term, is unlikely because it would imply that the ^{13}C shift of the former would be decreased (i.e. less than 55.6 ppm) and that of the latter increased by the same amount. Though in free butadiene the carbon atoms are not π-charged, there is a difference of 20.6 ppm between the inner and outer carbon chemical shifts. This fact does not support the existence of a dipole moment in coordinated butadiene(s), due to unequal electronic charges (as related to chemical shifts) at C(2) (and C(3)) and C(1) (and C(4)). However such a hypothesis cannot be entirely precluded from these arguments.

The dipole moment of a system of two (both negative) unequal charges, proportional to (151.7 — 76.2) and (107.0 — 55.6), is expressed as $\mu = 2edK \times (44.7—20.6)/2$. Taking K as 370 [28], we calculate a dipole moment of $A = 0.3$ D for the butadiene moiety in 1,3-butadienetricarbonyliron. This value is probably very much overestimated as all contributing factors other than electronic charges have been ignored.

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* Actually 1,3-butadiene exists predominantly (95-98%) as the non-polar *s-trans* form [19], and its dipole moment was found to be zero (at 195 K and at room temperature) using molecular beam electric deflection technique [20].

It is known at present that free cyclobutadiene is square-shaped and exists as a singlet [29]. All carbon atoms being magnetically equivalent in coordinated cyclobutadiene [6], $\mu(L)$ is certainly zero in cyclobutadienetricarbonyliron. Despite this fact the dipole moment of cyclobutadienetricarbonyliron (2.67 D) is markedly higher than that of 1,3-butadienetricarbonyliron (2.26 D). Since X dipoles in these two compounds are close to each other, as shown by their nearly equal carbonyl stretching frequencies, this clearly confirms that $\mu(L)$ is negligible in 1,3-butadienetricarbonyliron.

Evaluation of $\mu(L—Fe) = B$ requires a knowledge of X. Taking as a trial X = ca. 2 D (see footnote, p. 118), one derives $\mu(L—Fe) = 0.3$ D.

Concerning $\mu(L—Fe) = B$ and $\mu(Fe(CO)_3) = X$ in 1.3-butadienetricarbonyliron, two theoretical calculations lead to quite divergent results. The all valence electrons SCF method [21] indicates $B = 0$ and X negative (from the geometrical center of carbonyl bonds to the iron atom), while the ab initio method [30] gives B negative (0.88 electron transferred from Fe to the butadiene residue) and X positive, equal to ca. $(3.2) \times \sqrt{3} = 5.6$ D.

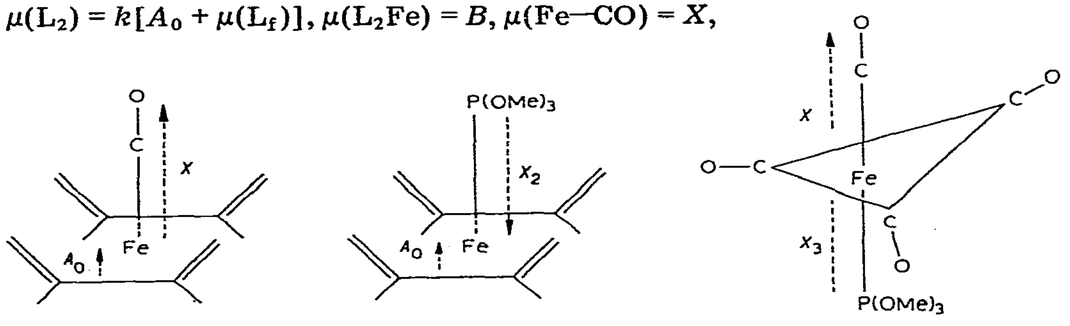
The electric dipole moment of di-1,3-butadienemonocarbonyliron

The X-ray structures of di-1,3-butadienemonocarbonyliron [31] and di-1,3-cyclohexadienemonocarbonyliron [32] are known. The two butadiene units (both *s-cis* shaped) are situated in nearly parallel planes and the carbonyl group is close to the butadiene double bonds (Fig. 1). There is no reason why bis(2,3-dimethyl-1,3-butadiene)monocarbonyliron and di-1,3-butadieneiron(trimethylphosphite) should not have analogous structures. By analogy with (triphenylphosphine)tetracarbonyliron [33], we may infer that (trimethylphosphite)-tetracarbonyliron is trigonal-bipyramidal (Fig. 1). A C_3-symmetry model for its $(MeO)_3P—Fe$ group can be assumed, the best being obtained by putting each methyl group mid-way between the lone pairs of the neighbouring oxygen atoms [34].

The following arguments show the electric dipole moment of di-1,3-butadienemonocarbonyliron (I) to be directed along the Fe—CO axis, from Fe towards CO (Fig. 2).

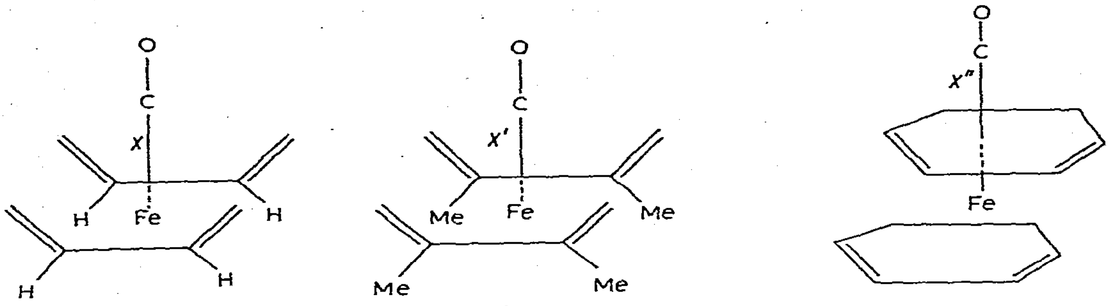
1. As before, let us divide the dipole moments of L_2FeCO complexes into three terms:

$\mu(L_2) = k[A_0 + \mu(L_f)]$, $\mu(L_2Fe) = B$, $\mu(Fe—CO) = X$,



(I) (II) (III)

Fig. 1. Analysis of the dipole moments of di-1,3-butadienemonocarbonyliron (I), di-1,3-butadieneiron-(trimethylphosphite) (II) and (trimethylphosphite)tetracarbonyliron (III).



(I)
ν(CO) = 1984.5 cm^{-1}
μ = 2.15 D

(I')
ν(CO) = 1975 cm^{-1}
μ = 2.98 D

(I'')
ν(CO) = 1964.5 cm^{-1}
μ = 2.05 D

Fig. 2. The X component of the dipole moments of di-1,3-butadienemonocarbonyliron (I), bis(2,3-dimethyl-1,3-butadiene)monocarbonyliron (I'), and di-1,3-cyclohexadienemonocarbonyliron (I'').

where k is a geometrical factor approximately equal to 2 cos 7.5° = 1.98 (15° is the angle between the two ligand planes), $A_0 \sim 0$ has the same meaning as A defined above and L_f is the dipole moment, if any, of the free ligands. $\mu(L_2Fe) = B$ is negligibly small for di-1,3-butadiene-, bis(2,3-dimethyl-1,3-butadiene)- and di-1,3-cyclohexadiene-monocarbonylirons, (I, I' and I''), and for di-1,3-butadiene(trimethylphosphite)iron (II), as diene moieties are nearly parallel in these molecules.

The dipole moment of 1,3-cyclohexadiene is 0.437 D [3], directed from the (CH_2—CH_2) mid-point to the geometrical centre of the ring. That of *s-cis*-2,3-dimethyl-1,3-butadiene is not known but, by analogy, it may be taken to be —0.4 D.

With these assumptions the electric moments of I, I' and I'' can be written as: $\mu(\mathrm{I}) = X$, $\mu(\mathrm{I}') = k(0.4) + X'$, $\mu(\mathrm{I}'') = k(-0.44) + X''$.

Increase in diene π-basicity is likely to occur going from 1,3-butadiene to 2,3-dimethyl-1,3-butadiene and 1,3-cyclohexadiene. This augments the electron density at the iron atom and brings to X an additional term (ΔX) directed from Fe to CO [35]. The observed order for the carbonyl stretching frequencies (1984.5 and 1964.5 cm^{-1} for I and I'', respectively [5]; 1975 cm^{-1} as deduced from ν(CO) of diisoprenemonocarbonyliron (1980 cm^{-1})) indicates: $\Delta X(\mathrm{I}) = 0.0$ D, $\Delta X(\mathrm{I}'') \gg \Delta X(\mathrm{I}')$.

It is quite obvious that one can account for the experimental dipole moments of I' and I'' (2.98 and 2.05 D), starting from that of I (2.15 D), only if $\mu(\mathrm{I})$ (and consequently X) is positive, i.e. directed from Fe towards CO. Indeed, for plausible values of ΔX, $2.15 + \Delta X(\mathrm{I}') + 2 \times 0.4$ leads to $\mu(\mathrm{I}') = 2.98$ D, $2.15 + \Delta X(\mathrm{I}'') - 2 \times 0.44$ gives $\mu(\mathrm{I}'') = 2.05$ D. Hence $\Delta X(\mathrm{I}') = +0.03$ D [**],

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[*] The preferred conformation for uncomplexed trimethylphosphite may differ from that suggested for the $(MeO)_3P$ group of di-1,3-butadiene(trimethylphosphite)iron and (trimethylphosphite)tetracarbonyliron as the P—Fe link is not strictly comparable to the phosphorus lone pair.

[**] Reduction in the electric moment adopted for *s-cis*-2,3-dimethyl-1,3-butadiene, as this molecule cannot be quite planar for obvious steric reasons, leads to a somewhat higher $\Delta X(\mathrm{I}')$ value.

$\Delta X(\mathrm{I}'') = +0.78$ D. To obtain $\mu(\mathrm{I}')$ and $\mu(\mathrm{I}'')$ from $\mu(\mathrm{I}) = -2.15$ D, quite unreasonable values of $\Delta X(\mathrm{I}')$ and $\Delta X(\mathrm{I}'')$, 4.33 and 5.08 D, are required. $\Delta\mu$ values found for *p*-xylene- and durene-tricarbonylchromiums are 0.38 and 1.0 D, respectively [35].

2. Trimethylphosphite is plainly basic and, therefore, the electric dipole moment of di-1,3-butadiene(trimethylphosphite)iron (II) is certainly directed from P towards Fe (i.e. X_2 is negative). That the dipole moment found for (trimethylphosphite)tetracarbonyliron (4.26 D) is close to the sum $\mu(\mathrm{I}) + \mu(\mathrm{II}) = 2.15 + 2.10 = 4.25$ D strongly suggests that $\mu(\mathrm{I})$ is directed from Fe towards CO.

From this discussion it follows that the dipole moment of the (Fe—CO) group X is directed from Fe towards CO and is of the same order of magnitude as $\mu(\mathrm{I}) = 2.15$ D.

Such a high (and positive) value for the (Fe—CO) group moment indicates an overall electron transfer from metal to carbonyl and supports the idea that the (metal-d_π—π^*) (CO) interaction is stronger than the σ (CO)—metal interaction. Most semi-empirical calculations on mononuclear transition metal carbonyls indicate that the metal is positively charged, for instance in tetracarbonylnickel [36-38] (see however [39] and hexacarbonylchromium [40,41], a conclusion in accordance with photoelectron spectroscopy [42,43].

Comparison of μ(Fe—CO) with (M—CO) group moments indicated in literature

It is generally admitted that μ(M—C) does not depend strongly on the nature of the transition metal atom. For Mn, Fe, Co and Ni the electronegativities and the atomic covalent radii are of the same order of magnitude [44]: $\chi = 1.6$—1.7, $r = 1.15$ Å. The first factor determines the magnitude of the ionic component of the bond moment [45] and the second one its so-called overlap moment [46]. The carbonyl moment, however, depends on the nature of the ligands, as indicated by carbonyl stretching frequencies of metal carbonyl complexes [47].

Arguments [48] favouring a small M—CO group moment in cyclopentadienyl complexes $\mathrm{CyV(CO)_4}$, $\mathrm{CyMn(CO)_3}$ and $\mathrm{CyCo(CO)_2}$ have been criticized by Bigorgne and Messier [49].

Fischer [50] suggested $\mu[\mathrm{Cr(CO)_3}] = -0.8$ D (with the chromium atom negatively charged), from analysis of the benzenetricarbonylchromium moment, but no details are given in his paper. Chatt and Hart [51] derived μ(M—CO) = +0.5 D after examination of the dipole moment of *cis*-dichloroplatinum dichloride, and John [52] adopted μ(Ru—CO) = 0 D.

Let us consider now some results obtained by Hieber et al. [53] and by Beck, Hieber and Tengler [54].

Trigonal bipyramidal $\mathrm{Ph_3PFe(CO)_4}$ and octahedral $\mathrm{HMn(CO)_4PPh_3}$ exhibit [54] the same dipole moment (5.1 D), indicating μ(Fe—CO) = μ(Mn—H). Now μ(Mn—H) is likely to be somewhat higher than μ(Si—H) = 1.4 D [55], from Si to H [56], as $\chi(\mathrm{Mn}) = 1.60$, $\chi(\mathrm{Si}) = 1.90$ [44] (or 2.30 [57] against $\chi(\mathrm{H}) = 2.20$, and $r(\mathrm{Mn}) \sim r(\mathrm{Si}) = 1.17$ Å [44].

Octahedral $\mathrm{CH_3Mn(CO)_5}$ and $\mathrm{HMn(CO)_5}$ exhibit small dipole moments [53] (0.79 and 0.70 D), which are directed from CO to methyl (or hydrogen) as shown by vector analysis of the dipole moments of $\mathrm{F_3CMn(CO)_5}$ (3.63 D) and

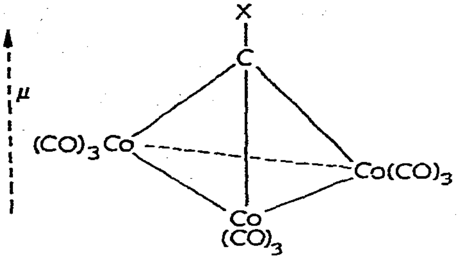

Fig. 3. The sign of the dipole moment of nonacarbonyl(methylcarbon)tricobalt.

$CH_3COMn(CO)_5$ (3.27 D), this latter being nearly equal to the vectional sum of the $CH_3Mn(CO)_5$ and acetone dipole moments. Hence we derive $\mu(Mn—CO) = \mu(Mn—H) — 0.7$ D. This may be due to the greater number of polar equatorial M—CO bonds (four instead of three) in the octahedral complex, increasing further the electronegativity of the central metal atom. That μ(Mn—CO) (in $CH_3Mn(CO)_5$) is smaller than μ(Fe—CO) (in $Ph_3PFe(CO)_4$) is supported by the carbonyl stretching frequencies (in KBr) of the complexes [54,53]: 2113, 2009 cm^{-1} and 2049, 1973, 1932, 1897 cm^{-1}. Note also that in $HMn(CO)_5$ and $Ph_3PFe(CO)_4$ the axial M—CO dipole moment is decreased by the presence of equatorial M—CO bonds whereas it must be (slightly) increased by the two electron-donating butadienes in di-1,3-butadienemonocarbonyliron.

In conclusion, a high value for the M—CO group moment is supported by these analyses of dipole moments (see Note added in proof, p. 123).

The electric dipole moment of nonacarbonyl(methylcarbon)tricobalt

Nonacarbonyl(methylcarbon)tricobalt is a pyramidal molecule [58] (angle CoCCo 81.1°). Its electric dipole moment (1.90 D) is directed along the A_3 symmetry axis, from the carbon atom to the methyl group since its trifluoro derivative (nonacarbonyl(trifluoromethylcarbon)tricobalt)) exhibits a dipole moment *higher* by 0.87 D (Fig. 3).

To calculate the dipole moment of the unsubstituted complex two angles are needed, the angle between the molecular symmetry axis A_3 and each Co—C bond and that between A_3 and the $Co(CO)_3$ group dipole moment. The former (48.5°) is easily derived from the known CoCCo angle, the latter (75°) is obtained by assuming $M = \mu(Co(CO)_3)$ along the resultant of three unit vectors lying on the C—Co and the two Co—Co bonds, respectively. Taking (as a trial) $M =$ 2 D *, one computes $\mu(Co—C) = 1.8$ D, directed from Co to C. Such a high value is quite plausible as cobalt and tetrahedral carbon electronegativities are 1.70 and 2.50 and their atomic covalent radii equal to 1.16 and 0.77 Å, respectively.

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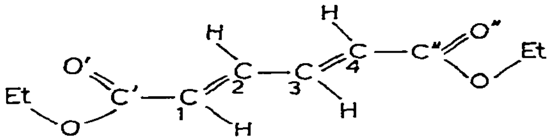
* Actually we should have $\mu[Co(CO)_3] \sim \mu(Co—CO) \times \sqrt{3}$. But there is very probably an important reduction factor due to mutual induction when three bond dipoles start from the same atom [59]. For instance, the dipole moments of chloroform (1.2 D) and methyl chloride (1.9 D) greatly differ in magnitude though their geometries are nearly identical and their carbon atoms tetrahedral. It is not unlikely, therefore, that $\mu(Co—CO) \sim \mu[Co(CO)_3]$. The carbonyl stretching frequencies in 1,3-butadienetricarbonyliron [12] (2000 cm^{-1}) and di-1,3-butadienemonocarbonyliron [5] (1964.5 cm^{-1}) support that $\mu(Fe(CO)_3) \leqslant \mu(Fe—CO) \times \sqrt{3}$.

The dipole moment found for nonacarbonyl(methylcarbon)tricobalt is not incompatible therefore with a positive and rather high value (ca. 2 D) for the $Co(CO)_3$ (and Co—CO) group moments.

The electric dipole moments of (methyl 1,3-pentadienoate)tricarbonyliron and (diethyl muconate)tricarbonyliron

Methoxycarbonyl (or ethoxycarbonyl) substitution should greatly diminish the diene π-basicity in (methyl 1,3-pentadienoate)tricarbonyliron (IV) and (diethyl muconate)tricarbonyliron (V). Such an effect reduces by 0.9 or 2.47 D the vertical component of the dipole moments of (methyl benzoate)tricarbonylchromium and (dimethyl terephthalate)tricarbonylchromium [35].

In the solid phase *trans—trans*-diethyl muconate exists under the (C(1)C(4))-*trans*—(O'C(2))-*cis*—(O"C(3))-*trans* conformation [60]:



In dilute benzene solution, it probably exists in a number of conformations. The observed dipole moment (2.39 D) is in accord with that calculated for an equimolecular mixture of all (C(1)C(4))-*trans* conformers (*cis—cis, cis—trans, trans—cis* and *trans—trans*), being nearly equal [61] to the dipole moment of diethyl terephthalate (2.42 D).

The only known methyl-sorbate isomer probably exists (predominantly) in the (C(1)C(4))-*trans*—(MeC(3))-*trans*—(C(3)O")-*trans* conformation. Its dipole moment makes an angle of 56° with the C(2)—C(3) axis (situated in the diene plane), as obtained [61] by writing $2.42 = (2.07) \times \sin\theta\sqrt{2}$. Almost the same result would be obtained by adding the moment of propene (0.37 D) to that of methyl acrylate (1.73 D).

The dipole moment of methyl 1,3-pentadienoate is not known. It can be readily deduced from that of methyl sorbate as 1.9 D, inclined at 65° on the C(2)—C(3) axis.

1. We shall assume that (methyl 1,3-pentadienoate)tricarbonyliron (IV) is a mixture of two conformers * (I and II), shaped as 1,3-butadienetricarbonyliron, having their carbonyl oxygen atom near to, or away from, the (Fe—CO) group (Fig. 4).

It is easy to show that for I and II, $\mu(L) = 1.9$ D. With the assumption that methoxycarbonyl substitution reduces by $\Delta\mu$ the component along the $Fe(CO)_3$ symmetry axis of the total dipole moment (equal to 2.26 D in case of no substitution), we can calculate $\Delta\mu$ in three cases: (a) the molecule exists as I, (b) the molecule exists as II, (c) the compound is an equimolecular mixture of I and II. From $\mu(IV) = 2.75$ D, we derive —0.94, —3.58 and —0.27 D, respectively. The first value is improbable as the complex cannot exist as I (see later) and the second is too high to be accepted; hence we shall adopt $\Delta\mu = -0.3$ D.

2. The problem is more complicated for (diethyl muconate)tricarbonyliron

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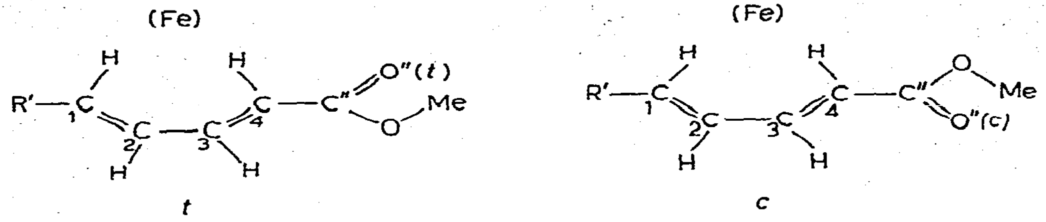
* See footnote, p. 120.



(I) R' = H (II) R' = H

Fig. 4. The *trans* and *cis* conformers of (methyl 1,3-pentadienoate)tricarbonyliron (IV) (R' = H).

(V), as the number of conformers is four *, two symmetric conformers I and II and two mixed conformers (*ct* and *tc*) (Fig. 5).

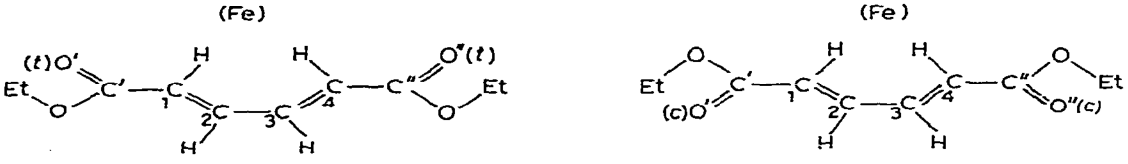
Assuming the complex as I,II, a 1 : 1 mixture of I and II or an equimolecular mixture of I, II and the two mixed conformers leads to no solution in the three first cases and to −1.1 D in the last case.

The molecular structures of bis(diethyl muconate)monocarbonyliron and bis(methyl sorbate)monocarbonyliron

1. With our preceding assumptions bis(diethyl muconate)monocarbonyliron can exist in eight conformations:

$(tt)_2$, $(cc)_2$, $(ct)_2$, $(tc)_2$, (tt,ct), (tt,tc), (cc,ct), (cc,tc). It is obvious that [61] $\mu(\mathrm{L}(tt)) = \mu(\mathrm{L}(cc)) = 2.42 \times \sqrt{2} = 3.42$ D, and $\mu(\mathrm{L}(ct)) = \mu(\mathrm{L}(tc)) = 0$ D and the data of Table 3 follow.

The $\Delta\mu_2$ vector is not known, but it can attain a value of −2.2 D, i.e. twice the value found for (diethyl muconate)tricarbonyliron. In spite of its high negative value, predicted moments for $(tt)_2$ and $(cc)_2$ conformers are still much higher than the experimental dipole moment of the complex (2.65 D). Conformer $(tt)_2$ would be unstable having four oxygen atoms (two O' and two O'') near the negatively-charged (as a whole) carbon monoxide group. Mixed conformers $(ct)_2$ and $(tc)_2$ are also energetically unfavoured and their dipole moments are too low. Conformers (tt,ct) and (tt,tc) have three carbonyl oxygen atoms near the carbon monoxide group. Hence the most abundant conformers must be $(cc)_2$, (cc,ct) and (cc,tc). An alternative, probably better, solution is to consider a unique conformation of the $(cc)_2$ type distorted in such a manner that the moment is reduced to the experimental value. This can be done rotating in its own



(I) (*tt*) (II) (*cc*)

Fig. 5. The *trans—trans* and *cis—cis* conformers of (diethyl muconate)tricarbonyliron.

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* More hindered conformers with mutually *cis* C—C(ester) and C(2)—C(3) bonds have been discarded.

TABLE 3

CALCULATED DIPOLE MOMENTS FOR THE RETAINED CONFORMERS OF BIS(DIETHYL MUCONATE)MONOCARBONYLIRON

Conformer	Dipole moment
$(tt)_2$	$2 \times (3.42) \times \cos 7.5^\circ + (2.15 + \Delta\mu_2)$
$(cc)_2$	$-2 \times (3.42) \times \cos 7.5^\circ + (2.15 + \Delta\mu_2)$
$(ct)_2$ and $(tc)_2$	$2.15 + \Delta\mu_2$
(tt,ct) and (tt,tc)	ca. $[3.4 + (2.15 + \Delta\mu_2)]$
(cc,ct) and (cc,tc)	ca. $[-3.4 + (2.15 + \Delta\mu_2)]$

plane each diethyl muconate moiety by opposite angles of, say, + and —60°. Such a distorted model is roughly in agreement with that found by X-ray analysis of the complex [62]. These rotations probably occur to make oxygen atoms (O′ and O′, O″ and O″) sufficiently more apart.

2. For bis(methyl sorbate)monocarbonyliron we shall consider four (Me, Me)-*cis* and four (Me,Me)-*trans* conformers (see Fig. 4, R′ = Me):

(C,cc), (C,tt), (C,ct), (C,tc); (T,cc), (T,tt), (T,ct), (T,tc).

The $\Delta\mu_2$ vector can attain twice the value derived for (methyl 1,3-pentadienoate)tricarbonyliron, i.e. $2 \times (-0.3) = -0.6$ D. The low figure found for the dipole moment of the complex (1.78 D) supports T structures. Moreover, C models are more unstable, especially (C,cc) and (C,tt), and conformer (T,tt) has too high a dipole moment (ca. 5 D). Though a mixture of (T,cc), (T,ct) and (T,tc) can fit the results we prefer to retain (T,cc) as the predominant conformer, because mixed T conformers still have a carbonyl oxygen atom near the carbon monoxide group. The dipole moment of (T,cc) is $\mu(T,cc) = 3.42 - (2.15 + \Delta\mu_2)$. By writing $\mu(T,cc) = 1.78$ D, one derives $\Delta\mu_2 = -0.51$ D.

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Note added in proof (15-12-1975). From the electric dipole moment of $Me_3SnCo(CO)_4$, L.F. Wuyts and G.P. van der Kelen (J. Organometal. Chem., 97 (1975) 453) derived $\mu(Sn—Co—(CO)_4) = 1.97$ D, directed from the metals to the axial CO group. This value compares well with our Fe—CO group moment as the $SnCo(CO)_3CO$ is trigonal-bipyramidal by analogy with the $SnCo(CO)_4$ in $ClSn(Co(CO)_4)_3$ (see B.P. Bir'Yukov, E.A. Kukhtenkova, Yu.T. Struchkov, K.N. Anisimov, N.E. Kolobova and V.I. Khandozhko, J. Organometal. Chem., 27 (1971) 237), and the Sn—Co bond moment is certainly very small.