Conformational Study of π-Tetracarbonyl(mono-olefin)iron Complexes by Infrared Spectra and Dipole Moment Measurements

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The electric dipole moments of the complexes π-$LFe(CO)_4$, where L = *trans*-PhCH=$CHCOCH_3$, *trans*-PhCH=CHCOPh, *trans*-PhCH=CHCHO, CH_2=CHCHO, and CH_2=CHCN, have been determined. It is found that the ligand plane is never parallel to the axis of the trigonal bipyramid. The ligand CO group in the carbonyl derivatives is slightly out of the C=CC plane. The structure of the acrylonitrile complex in solution is the same as that found for the solid from *X*-ray studies. The ketone ligands have the same conformation in the complex as in the free ligand. The aldehyde ligands, present only as the *s-trans*-conformer in the free state, form both isomers when bonded to the metal. The enthalpy variation for the conformational equilibrium *s-cis* $\rightleftharpoons$ *s-trans* for the aldehyde complexes has been calculated from i.r. data, and an assignment of the CO stretchings has been proposed.

MUCH *X*-ray work has been performed on organometallic compounds[1] and also a certain amount for the gaseous state by the use of electron diffraction measurements.[2] For solutions, the information obtained to date from spectroscopic measurements has been mainly concerned with the symmetry of the compounds and less with the orientation of the organic part of the molecule.

The present study is concerned with the complexes π-$LFe(CO)_4$, L = *trans*-PhCH=$CHCOCH_3$, *trans*-PhCH=CHCOPh, *trans*-PhCH=CHCHO, CH_2=CHCHO, and CH_2=CHCN in solution, studied by means of i.r. spectra and electric dipole moments. The only structural information in the literature on these complexes relates to π-(PhCH-CHCHO)$Fe(CO)_4$ and π-(CH_2=CHCN)$Fe(CO)_4$. I.r. and n.m.r. measurements on the first compound[3] and *X*-ray diffraction measurements on the second[4] showed that the bonding between the metal and the organic ligand is π in nature and that only the two electrons of the double bond are involved.

From the present measurements we aimed to obtain information on (i) the conformation of the molecules in an apolar solvent, (ii) the distribution of the ligand between the two rotameric forms *s-cis* and *s-trans*, and possible interconversion between the two, and (iii) possible π back donation. Elucidation of point (iii) should allow the reasons for the differing stabilities of the olefinic compounds and their behaviour in the kinetics of substitution to be clarified.[5]

EXPERIMENTAL

Materials.—Benzylideneacetone and benzylideneacetophenone were commercial products and were purified by triple crystallisation from n-hexane. Literature methods were used to prepare π-(PhCH=$CHCOCH_3$)$Fe(CO)_4$,[6]

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π-(PhCH=CHCOPh)Fe(CO)$_4$,[7,8] π-(PhCH=CHCHO)Fe(CO)$_4$,[7] and π-(CH$_2$=CHCHO)Fe(CO)$_4$.[9] The last mentioned compound was purified by fractional distillation, and its n.m.r. spectrum agrees with that in the literature, τ(CS$_2$), 6·7 (2H, d, J 9·6 Hz, CH$_2$) 5·9 (m, =CH), and 0·45 (d, J 5·1 Hz, CHO). The i.r. spectrum of this complex shows four bands due to the stretching modes of the CO groups attached to the metal and a further band assigned to the stretching mode of the aldehyde CO. These bands split in some inert apolar solvents, *e.g.* $\nu_{\text{max.}}$ (C$_6$H$_6$): 2099, 2039, 2022, 1997, and 1688 cm^{-1}; $\nu_{\text{max.}}$ (C$_6$H$_{14}$): 2106, 2100, 2042, 2038, 2026, 2022, 2006, 2002, 1697, and 1684 cm^{-1}. This behaviour, similar to that found in π-(PhCH=CHCHO)-Fe(CO)$_4$,[7] indicates the presence of two rotamers, *s-cis* and *s-trans*. The two n.m.r. bands of CHO do not split even at −80°, although two conformers are observed by i.r. measurements: the high interconversion rate does not allow the observation of the conformers by n.m.r.

π-(CH$_2$=CHCN)Fe(CO)$_4$, described previously,[10] was prepared by reacting Fe$_2$(CO)$_9$ and CH$_2$=CHCN for 1·5 h at 35° using the ligand as solvent. The solvent was evaporated to dryness *in vacuo* and the pure product obtained by sublimation from the semi-solid paste at room temperature. Benzene and n-hexane were first dried over sodium and deaerated with nitrogen.

(a) *Dipole Moments*.—Dielectric constants, densities, and indices of refraction were measured at 25·0 ± 0·1°, using methods described previously.[11] The total polarisation and molar refraction at infinite dilution of the molecules were calculated by the method of Halverstadt and Kumler.[12]

The atomic polarisation was assumed to be zero. Moments are accurate to ±0·02 D, with the exception of π-(PhCH=CHCHO)Fe(CO)$_4$ in n-hexane for which the reproducibility is ±0·05 D, because of its low solubility in this solvent. To allow comparison with literature data the moments of PhCH=CHCOCH$_3$ and PhCH=CHCOPh were redetermined. The moments of the other ligands were taken from the literature, having been determined under the same experimental conditions.

(b) *Spectroscopic Measurements*.—N.m.r. measurements were carried out on a JEOL 60 CHL spectrometer using tetramethylsilane as reference. I.r. spectra were obtained on a Perkin-Elmer 257 spectrophotometer.

Conformational analysis based on the i.r. spectra was carried out by measuring the variation in relative intensity of the carbonyl groups bonded to the metal iron at 2106 and 2100 cm^{-1}, in n-hexane, for the complex π-(CH$_2$=CHCHO)Fe(CO)$_4$ and at 2103 and 1998 cm^{-1} for π-(PhCH=CHCHO)Fe(CO)$_4$. Despite the greater separation of the bands, measurements carried out on the stretching bands of the aldehyde carbonyl did not give reproducible results because of overlapping with the CO stretching band of the free ligand, present in small quantities at >40° due to slight decomposition of the complex. Since the two overlapping bands have a well defined minimum between them, a vertical line from this point to the base line was used to divide the areas of both conformers. This is the most accurate method in order to measure the enthalpy variation of a conformational equilibrium when the band intensities of interest are approximately the same.[13]

TABLE 1

Physical properties of solutions [a]

10^3w_2	ε_{12}	V_{12}	n^2_{12}
trans-PhCH=CHCOCH$_3$ [b]			
1·22	2·2830	1·1442	2·2434
2·47	2·2933	1·1440	2·2437
3·61	2·3027	1·1438	2·2439
5·03	2·3144	1·1436	
6·20	2·3240	1·1434	2·2444
7·38	2·3337	1·1432	2·2477
trans-PhCH=CHCOPh			
1·01		1·1445	2·2434
2·26	2·2846	1·1443	2·2438
3·45	2·2907	1·1440	2·2441
4·80	2·2976	1·1438	2·2446
6·09	2·3042	1·1435	2·2450
7·50	2·3115	1·1432	2·2454
π-(*trans*-PhCH=CHCOCH$_3$)Fe(CO)$_4$ [b]			
1·12	2·2753	1·1441	2·2437
2·20	2·2785	1·1438	2·2439
3·33	2·2819	1·1434	
4·06	2·2840	1·1431	2·2442
5·10	2·2872	1·1427	2·2443
6·72	2·2920	1·1423	2·2446
π-(*trans*-PhCH=CHCOPh)Fe(CO)$_4$ [b]			
1·22	2·2751	1·1441	2·2434
2·37	2·2778	1·1436	2·2438
3·24	2·2799		2·2440
4·52	2·2829	1·1428	2·2444
5·86		1·1423	2·2448
6·60	2·2879	1·1420	2·2451
π-(*trans*-PhCH=CHCHO)Fe(CO)$_4$ [b]			
0·62	2·2747	1·1443	2·2433
1·49	2·2778	1·1439	2·2434
2·76	2·2724	1·1434	2·2436
3·81	2·2862	1·1430	2·2438
5·29	2·2915	1·1424	2·2440
π-(*trans*-PhCH=CHCHO)Fe(CO)$_4$ [c]			
0·87	1·8748	1·5256	1·8825
2·03	1·8773	1·5251	1·8825
2·45	1·8782	1·5249	1·8826
π-(CH$_2$=CHCHO)Fe(CO)$_4$ [b]			
0·81	2·2755	1·1437	2·2431
1·75	2·2795	1·1432	2·2432
2·80	2·2841	1·1428	2·2432
4·63	2·2920	1·1420	2·2433
6·10	2·2983	1·1413	2·2434
6·95	2·3020	1·1409	2·2435
π-(CH$_2$=CHCHO)Fe(CO)$_4$ [c]			
1·36	1·8774	1·5243	1·8829
3·06	1·8819	1·5231	1·8831
3·94		1·5225	1·8832
5·63	1·8887	1·5212	1·8834
7·16	1·8927	1·5203	1·8836
7·91	1·8947		1·8837
π-(CH$_2$=CHCN)Fe(CO)$_4$ [b]			
0·90	2·2784	1·1440	2·2430
1·57	2·2832	1·1438	2·2430
2·81	2·2921	1·1433	2·2431
4·25	2·3024	1·1427	2·2432
5·62	2·3122	1·1421	
5·90			2·2432

[a] V_{12} in cm^3 g^{-1}. [b] In benzene. [c] In n-hexane.

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[8] E. Koerner von Gustorf, F. W. Grevels, C. Kruger, G. Olbrich, F. Mark, D. Shultz, and R. Wagner, *Z. Naturforsch.*, 1972, **27b**, 392.

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[11] S. Sorriso, G. Cardaci, and S. M. Murgia, *Z. Naturforsch.*, 1972, **27b**, 1316.

[12] I. F. Halverstadt and W. D. Kumler, *J. Amer. Chem. Soc.*, 1942, **64**, 2988.

[13] A. W. Baker and M. D. Yeaman, *Spectrochim. Acta*, 1966, **22**, 1773.

The temperature range was between 9 and 59°. The band areas were measured by a planimeter and each measurement was repeated three times, the measurements being reproducible to within ±2%. The spectra were taken with a 0·5 mm cell, thermostatted to within ±1°.

RESULTS AND DISCUSSION

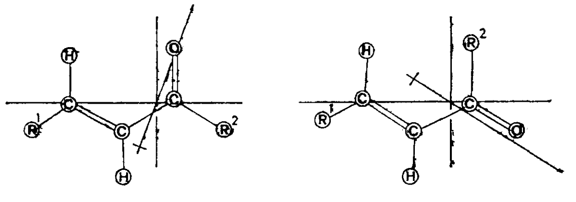
Table 1 reports the physical properties of solutions and Table 2 the calculated moments together with the parameters used to calculate them. As mentioned previously, there are no structural data extant for these molecules in solution. Consequently, wherever possible we have used the structural results obtained in the solid and gas. The structures of π-(CH_2=CHCN)Fe($CO)_4$,[4] in the solid state, and π-(CH_2=CH_2)Fe($CO)_4$,[2] in the gaseous state, are similar and are based on a trigonal bipyramid. It seems reasonable to assume that the structures of such complexes remain the same in solution, with two carbonyl groups in axial positions and hence not contributing to the molecular moment. There is an angle of 105—107° between the other two carbonyl groups. The moment obtained by the vector sum of two $\overrightarrow{\mu(\mathrm{Fe{-}CO})}$ and $\overleftarrow{\mu(\mathrm{Fe{-}L})}$, lying along the bisector of the $\mathrm{CO\widehat{Fe}CO}$ angle will be given by μ[LFe($CO)_2$]. We can now turn to the possible existence of *s-cis*/*s-trans*-conformers in the ligands of the complexes. It is known that the *trans*-isomers of benzylideneacetone, benzylideneacetophenone, and cinnamic and acrylic aldehydes may, in theory, exist as two conformers (Figure 1). Only the *cis*-form is present in the ketones and only the *trans*-form in the aldehydes.[14] I.r. measurements for π-LFe($CO)_4$ show that only a single conformer is present for the ketone derivatives whilst both are present in the aldehydes. The rotamer present in the ketone complexes may be deduced from the dipole moments. These moments are noticeably lower than those of the free ligands (Table 1). The presence of the *s-trans*-planar conformer alone may be immediately excluded since a high degree of rotation of the carbonyl out of the plane would be necessary to explain the observed dipole moment, because of the direction of the ligand moment in the *s-trans*-form. An intermediate situation between *s-cis* and *s-trans* may also be eliminated since this would not be possible because of strong steric interaction between the methyl and phenyl groups and the inorganic part of the molecule. This leaves the *s-cis*-configuration. In fact, for this structure, agreement is found between calculated and observed moments assuming a slight deviation of the ligand plane with respect to the axis of the bipyramid (as found experimentally in the solid acrylonitrile complex) together with a small rotation of the ketone carbonyl.

TABLE 2

Observed dipole moments and parameters used in their calculation [a]

Compound	ε_1	α	V_1	β	n_1^2	γ	R_D	$P_{2\infty}$	μ
trans-PhCH=CHCOCH_3 [b]	2·2730	8·228	1·1444	−0·165	2·2432	0·205	47·6	268·7	3·29
trans-PhCH=CHCOC_6H_5 [b]	2·2730	5·135	1·1447	−0·203	2·2431	0·310	69·7	259·5	3·05
π-(*trans*-PhCH=CHCOCH_3)Fe($CO)_4$ [b]	2·2720	2·980	1·1445	−0·340	2·2435	0·163	83·8	251·2	2·86
π-(*trans*-PhCH=CHCOPh)Fe($CO)_4$ [b]	2·2722	2·379	1·1445	−0·375	2·2431	0·300	106·3	254·5	2·69
π-(*trans*-PhCH=CHCHO)Fe($CO)_4$ [b]	2·2725	3·596	1·1445	−0·408	2·2432	0·156	73·6	268·7	3·09
π-(*trans*-PhCH=CHCHO)Fe($CO)_4$ [c]	1·8730	2·118	1·5260	−0·460	1·8835	0·020	74·5	265·7	3·06 [d]
π-(CH_2=CH=CHO)Fe($CO)_4$ [b]	2·2720	4·322	1·1440	−0·449	2·2430	0·056	47·9	228·4	2·97
π-(CH_2=CH=CHO)Fe($CO)_4$ [c]	1·8738	2·650	1·5253	−0·730	1·8828	0·121	48·5	221·2	2·91
π-(CH_2=CHCN)Fe($CO)_4$ [b]	2·2720	7·150	1·1444	−0·412	2·2430	0·040	49·1	345·2	3·81

[a] V_1 in cm³ g⁻¹; R_D and $P_{2\infty}$ in cm³; μ in D. [b] In benzene. [c] In n-hexane. [d] ±0·05 D.



s-cis *s-trans*

FIGURE 1 Models for *s-cis*- and *s-trans*-conformers of *trans*-R′CH=CHCOR² showing the orientation of the molecular dipole moments

To obtain information on the orientation of the ligand plane with respect to the axis of the bipyramid, and on the μ[LFe($CO)_2$] group moment, it is assumed that the latter is the same in the benzylideneacetone and benzylideneacetophenone complexes, and equations (1) and (2)

$$(\mu')^2 = \mu^2_{L'} + \mu^2_x + 2\mu_{L'}\mu_x \cos\theta \quad (1)$$

$$(\mu'') = \mu^2_{L''} + \mu^2_x + 2\mu_{L''}\mu_x \cos\theta \quad (2)$$

were used where μ' and μ'' are the observed moments for the above two complexes, $\mu_{L'}$ and $\mu_{L''}$ those for the analogous free ligands, $\mu_x = \mu$[LFe($CO)_2$], and θ is the angle between μ_x and μ_L. Given the direction of the molecular moment in the *s-cis*-form, it is reasonable to assume that θ is also the angle between the ligand plane and μ_x. The solution having physical significance gives θ 121° and $\overrightarrow{\mu[\mathrm{LFe(CO)_2}]}$ 2·3 D. This value of θ corresponds to an angle between the axis of the bipyramid and normal to the ligand plane of 59°, compared with an experimental value of 76° for solid (CH_2=CHCN)-Fe($CO)_4$. This difference is probably caused by a small rotation of the carbonyl out of the ligand plane, as mentioned above. Note that an angle of 76°, instead of one of 90°, in the acrylonitrile complex has been

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[14] J. B. Bentley, K. B. Everard, R. B. Marsden, and L. E. Sutton, *J. Chem. Soc.*, 1949, 2957.

explained by invoking repulsion between the CN group and the apical ligand. If the $\mu(\overrightarrow{\text{Fe–CO}})$ contributions are subtracted from $\mu[\overrightarrow{\text{LFe(CO)}_2}]$ this gives $\mu(\overleftarrow{\text{Fe–L}}) = 1{\cdot}7$ D in good agreement with that of 1·6 D suggested previously for $\mu[\overrightarrow{(\text{C}_3\text{H}_5)\text{–Fe}}]$ in allyl complexes such as π-$(C_3H_5)Fe(CO)_2NO$.[11] In addition, such a low value for $\mu(\overleftarrow{\text{Fe–L}})$ supports other evidence[15] suggesting that the inorganic portion bonds to the metal *via* a σ bond between a full orbital of the olefinic ligand and an empty metal orbital. Superimposed on this is π back donation from a full iron orbital to an empty antibonding orbital of the ligand. Given the low basic character of the ethylenic ligand, such complexes are stabilised by a strong π back bonding[15] which increases with increase in the electron-attracting power of the ligand substituents. The moment of the complex π-$(CH_2{=}CHCN)Fe(CO)_4$ has been determined to support these conclusions. This is a convenient molecule for this purpose since the moment of the ligand almost coincides with the $\mu(\overrightarrow{\text{C–CN}})$ vector, which in turn lies in the C=CC plane. A $\text{C}\hat{\text{C}}\text{C}$ ligand angle of 116°, as found by *X*-ray studies,[4] and $\mu[\overrightarrow{\text{LFe(CO)}_2}]$ group moment of 2·3 D, as found above, were used in the vector analysis, and the ligand moment of 3·54 D[16] was split into the two components μ_p and μ_o, parallel and orthogonal, respectively, to the ethylene bond (Figure 2). Equation (3) may then be

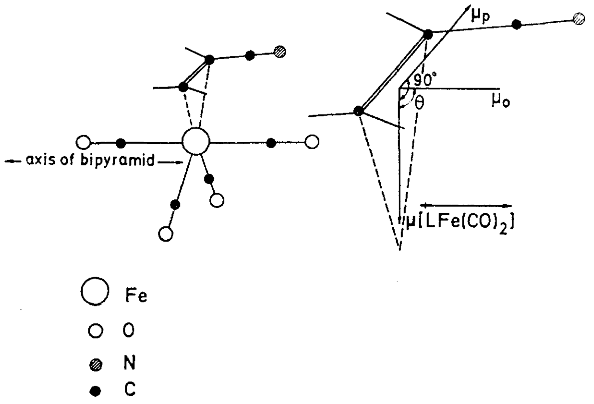

FIGURE 2 Vector diagram of the molecular dipole moment for π-$(CH_2{=}CHCN)Fe(CO)_4$

$$\mu^2_{\text{obs}} = \mu^2_R + \mu^2_p = \mu^2_x + 2\mu_o\mu_x\cos\theta + \mu^2_p \qquad (3)$$

written, where μ_{obs} is the observed moment for the complex and θ the angle between the ligand plane and the μ_x vector. The solution gives θ 102°, from which an angle between the perpendicular to the ligand plane and the axis of the bipyramid of 78° is obtained. This good agreement with the experimental value in the solid state (76°) supports the values calculated for the ketone complexes.

As pointed out above, there are two conformers, corresponding to the ligand *s-cis-* and *s-trans*-forms, present for the complexes π-$(PhCH{=}CHCHO)Fe(CO)_4$ and π-$(CH_2CHCHO)Fe(CO)_4$. Two methods have been used to obtain information on the equilibrium between the two rotamers.

(i) *Dipole Moments.*—The value of $\mu[LFe(CO)_2]$ for the ketone complexes was used in calculating the distribution of the two species and also θ for the *s-cis*-isomer. These assumptions seem reasonable since the orientation of the ligand plane in the complex is determined by repulsion between the aldehyde carbonyl and the CO group in the apical position and by the attraction between the olefinic π-system and iron. The angle θ in the *s-trans*-isomer is not known. However, given the expected lower repulsion between the aldehyde CO and the inorganic part and the fact that the moment lies almost along the possible rotation axis of the ligand plane, we assume that the angle between $\mu[LFe(CO)_2]$ and the ligand moment is 90°. The following results were obtained.

(a) π-$(PhCH{=}CHCHO)Fe(CO)_4$. Theoretical moments of the free ligand[14] are $\mu_{s\text{-}cis}$ 3·01 and $\mu_{s\text{-}trans}$ 3·55 D. Calculated moments for the complex are $\mu'_{s\text{-}cis}$ 2·6 and $\mu'_{s\text{-}trans}$ 4·2 D. From equation (4) the distribution 77% *s-cis* and 23% *s-trans* is obtained.

$$\mu^2_{\text{obs}} = X\mu'^2_{s\text{-}cis} + (1 - X)\mu'^2_{s\text{-}trans} \qquad (4)$$

(b) π-$(CH_2{=}CHCHO)Fe(CO)_4$. Theoretical moments for the ligand are $\mu_{s\text{-}cis}$ 2·44 and $\mu_{s\text{-}trans}$ 2·78 D.[14] Calculated moments for the complex are $\mu'_{s\text{-}cis}$ 2·3 and $\mu'_{s\text{-}trans}$ 3·6 D giving the distribution 59% *s-cis* and 41% *s-trans*.

(ii) *I.r. Spectra.*—Since the complex concentration, due to some decomposition, was not constant at different temperatures it was not possible to measure the ratio between the molar extinction coefficients of conformers by the method of ref. 17. Therefore only the enthalpies of the interconversion (ΔH) were obtained: π-$(CH_2{=}CHCHO)Fe(CO)_4$ 943 ± 200 and π-$(PhCH{=}CHCHO)Fe(CO)_4$ 1066 ± 200 cal mol^{-1}. For the same reason it was not possible to assign the CO stretching bands to the rotamers by means of integrated area measurements. Nevertheless, in order to assign these bands the following points may be considered: (a) the effect of the temperature on the two bands is the same, *i.e.* the integrated area of the band at lower frequency increases with temperature in both aldehyde complexes, and (b) the increase of the *s-cis* : *s-trans* ratio for π-$(CH_2{=}CHCHO)Fe(CO)_4$ is associated with an increase in the integrated area ratio between the higher frequency band and the lower. Therefore, the extinction-coefficient ratio being probably the same in both complexes, it can be suggested that the *s-cis*-species absorbs at higher frequency. Consequently the positive sign of the ΔH values refers to the *s-cis* $\longrightarrow$ *s-trans* interconversion.

Conclusions.—Both sets of measurements show that

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[16] M. T. Rogers, *J. Amer. Chem. Soc.*, 1947, **69**, 2544.

[17] K. O. Hartman, G. L. Carlson, R. E. Witkoski, and W. G. Fateley, *Spectrochim. Acta*, 1968, **24A**, 157.

the ketones retain the same configuration in the complex as in the free state, *s-cis*, whilst the aldehydes have both *s-cis-* and *s-trans*-forms. Since the height of the energy barrier is lower than 15 kcal mol^{-1} [18] the observation of a single conformer in the free ligands indicates that the difference between the energies of the two rotamers is sufficiently large. In the complexes this difference is lowered and both conformers are present. This is the case for the aldehyde complexes, in which the hydrogen atom, as its steric hindrance is very small, can rotate by passing ' inside ' the molecule and the *s-cis* $\rightleftharpoons$ *s-trans* equilibrium is restored. On the contrary, in the ketone complexes the high steric hindrance of the methyl and phenyl groups is a serious restriction on rotation. On the other hand, for electrostatic reasons rotation with the oxygen atom passing ' inside ' the molecule is not possible. Therefore, even if the difference between the free energies of the two conformers is small, only the *s-cis*-conformer formed as initial product should be observed.

[4/1594 *Received*, 31*st July*, 1974]

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