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NATURE OF THE IRON—LIGAND BOND IN π-(HETERODIENE)TRICARBONYLIRON COMPLEXES

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Summary

The electric dipole moments of the complexes π-LFe(CO)$_3$, where L = *trans*-PhCH=CHCHO, *trans*-PhCH=CHCOMe, *trans*-PhCH=CHCOPh, *trans,trans*-PhCH=CH—CH=CHPh and CH$_2$=CHCHO, have been measured. The preparation of the last two complexes is also described. A vectorial analysis of the moments leads to the conclusion that the complexes are π in type, i.e. the aldehyde and ketone ligands bond to the iron via the olefinic and carbonylic bond and do not involve the oxygen lone pairs. The metal to ligand back-bonding is stronger in the aldehyde and ketone complexes than in the butadiene ones.

Introduction

In complexes of the type π-LFe(CO)$_3$, where L is an (α, β) unsaturated aldehyde or ketone, the organic moiety may bond to the iron using, apart from an olefinic bond, *(i)* the π electrons of the C=O bond or *(ii)* the oxygen lone pairs. Information as to the preferred mode of bonding has been obtained from X-rays [1] and IR and NMR spectra [2-4]. From the structural parameters obtained for π-(PhCH=CHCHO)Fe(CO)$_3$ it was deduced that the π-electrons of the organic carbonyl group participate in bonding to the metal in a manner similar to that suggested for the compounds π-(1,3-diene)Fe(CO)$_3$. IR and NMR spectra [2] of the same compound lead to the conclusion that the preferred configuration is *(i)*, although it was not possible to entirely exclude the existence of *(ii)*. For complexes with L = crotonaldehyde-n-butylimine [3], benzilideneacetone and chalcone, NMR measurements [4] gave, instead, the same results as were obtained from X-rays [1]. Since, the conformations *(i)* and *(ii)* have very different polarity, electric dipole moment measurements should contribute to a solution of the problem.

This article describes the dipole moments observed for complexes of the type π-LFe(CO)$_3$ having L = *trans*-PhCH=CHCHO, *trans*-PhCH=CHCOMe, *trans*-

PhCH=CHCOPh, CH_2=CHCHO and *trans,trans*-PhCH=CH—CH=CHPh, in benzene.

Experimental

Materials

Complexes π-(PhCH=CHCOR)Fe$(CO)_3$, with R = H, Me, Ph, were prepared as in the literature [4,5]. They were identified via m.p.'s and C=O stretching vibrations.

π-(CH_2=CHCHO)Fe$(CO)_3$ was prepared by reacting 10 g (27 mmole) $Fe_2(CO)_9$ suspended in benzene with 3.5 ml (52 mmole) CH_2=CHCHO at 60°C. The reaction went to completion after 24 h. The solution was filtered and dried at the water pump. The liquid residue was distilled in vacuo to give a volatile liquid having ν(C=O) (n-hexane) at 2080, 2020 and 1997 cm^{-1}.

π-(PhCH=CH—CH=CHPh)Fe$(CO)_3$ was prepared by the reaction between $Fe(CO)_5$ and *trans,trans*-PhCH=CH—CH=CHPh in benzene for 6 h under irradiation from a medium-pressure Hanovia UV lamp. During the course of reaction, the IR spectra showed the presence of π-(PhCH=CH—CH=CHPh)Fe$(CO)_4$ as intermediate, which was not isolated. The solution was filtered and dried and the residue recrystallised from benzene at 7°C to give a red solid of m.p. 158-161°C and ν(C=O) (n-hexane) = 2045, 1988, 1980 cm^{-1}.

Physical measurements

IR spectra were recorded on a Perkin—Elmer 257 spectrophotometer using 0.1 mm path length NaCl cells. Dielectric constants, densities and refractive in-

TABLE 1

PHYSICAL PROPERTIES OF BENZENE SOLUTIONS[a]

$w_2 \times 10^3$	ϵ_{12}	V_{12}	n_{12}^2	$w_2 \times 10^3$	ϵ_{12}	V_{12}	n_{12}^2
π-(PhCH=CHCHO)Fe(CO)$_3$				*π-(CH$_2$=CHCHO)Fe(CO)$_3$*			
0.68	2.2741	1.1437	2.2436	0.94	2.2762	1.1441	2.2438
1.42	2.2763	1.1434	2.2437	1.62	2.2786	1.1438	2.2439
2.23	2.2786	1.1431	2.2439	2.97	2.2833	1.1432	2.2440
3.43	2.2821	1.1425	2.2441	4.01	2.2869	1.1428	2.2441
4.51	2.2852	1.1421	2.2443				
6.09	2.2898	1.1414					
π-(PhCH=CHCOPh)Fe(CO)$_3$				*π-(PhCH=CHCOMe)Fe(CO)$_3$*			
0.72	2.2742	1.1443	2.2435	0.56	2.2740	1.1445	2.2425
1.43	—	1.1440	2.2437	1.24	2.2759	1.1442	2.2426
2.24	2.2779	1.1437	2.2439	2.17	2.2785	1.1439	2.2428
3.12	2.2801	1.1433	2.2441	3.21	2.2814	1.1435	2.2430
4.05	2.2823	1.1430	2.2444	4.14	2.2840	—	2.2432
5.74	2.2865	1.1423	2.2448	6.03	2.2894	1.1423	2.2436
π-(PhCH=CH—CH=CHPh)Fe(CO)$_3$							
1.01	2.2745	1.1436	2.2443				
1.94	2.2760	1.1432	2.2446				
2.61	2.2770	1.1429	2.2448				
3.43	2.2783	1.1426	2.2450				
4.47	2.2799	1.1422	2.2453				
6.00	2.2823	1.1415	2.2458				

[a] V_{12} in $cm^3\ g^{-1}$.

TABLE 2

OBSERVED DIPOLE MOMENTS AND PARAMETERS USED IN THEIR CALCULATION[a]

Complex	ϵ_1	α	V_1	β	n_1^2	γ	$P_{2\infty}$	R_D	μ
π-(PhCH=CHCHO)Fe(CO)$_3$	2.2722	2.903	1.1440	−0.438	2.2435	0.194	205.7	66.3	2.61
π-(CH$_2$=CHCHO)Fe(CO)$_3$	2.2730	3.476	1.1445	−0.430	2.2438	0.085	170.5	44.1	2.49
π-(PhCH=CHCOPh)Fe(CO)$_3$	2.2725	2.437	1.1445	−0.389	2.2434	0.250	237.5	93.7	2.65
π-(PhCH=CHCOMe)Fe(CO)$_3$	2.2724	2.820	1.1447	−0.397	2.2424	0.201	215.4	73.5	2.63
π-(PhCH=CH—CH=CHPh)Fe(CO)$_3$	2.2730	1.554	1.1440	−0.420	2.2440	0.302	175.7	93.2	2.01

[a] V_1 in cm^3 g^{-1}; $P_{2\infty}$ and R_D in cm^3; μ in D.

dices were measured at 25 ± 0.1°C using methods described previously [6]. The total polarization and molar refraction at infinite dilution were calculated by the method of Halverstadt and Kumler [7]. The atomic polarization was assumed to be zero. Table 1 reports the experimental results and Table 2 collects the observed dipole moments and parameters used in calculating them. The observed moments are accurate to ±0.02 D.

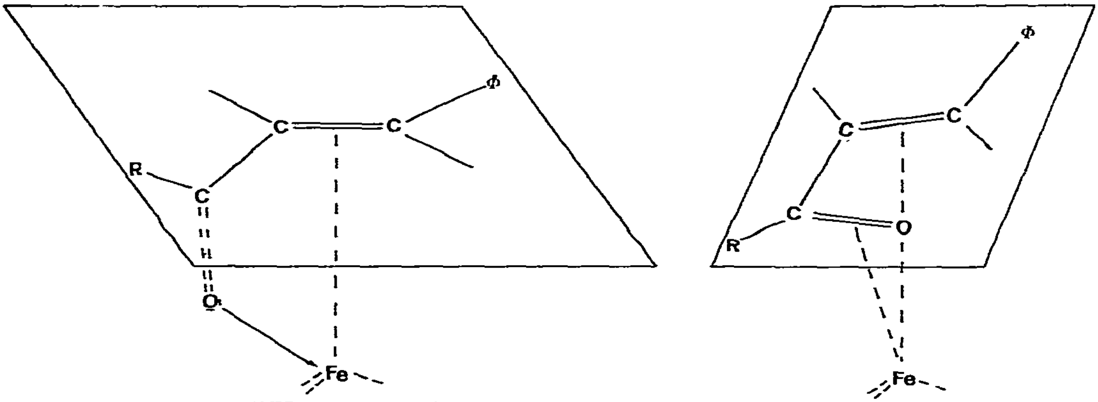
Discussion

Before discussing the results obtained, it is of relevance to note that the free (α,β) unsatured aldehydes and ketones may exist as the planar rotational forms, *s-cis* or *s-trans*, depending on whether the carbonyl bond is almost perpendicular or almost parallel, respectively, to the olefinic bond. Conformational studies have shown that, whilst aldehyde ligands exist in the *s-trans* form, ketone ligands prefer the *s-cis* form [8]. In π-LFe(CO)$_4$ complexes studied recently [9], the ketone ligands maintain the conformation of the free state, whilst the aldehydes show a conformational equilibrium between the two forms. For the π-LFe(CO)$_3$ complexes examined here, all the literature results [2,4] indicate that the ligands, both aldehyde and ketone, exist in the *s-cis* form. The discussion which follows will assume the presence of only this form.

As regards the molecular geometry of π-LFe(CO)$_3$ complexes, electron diffraction [10] and X-ray [10] studies have shown, in good agreement with one another, that the carbon atoms form a considerably distorted square pyramid about the metal. One of the bonded CO groups lies on the pyramidal axis and the other two occupy two corner sites. The remaining corner sites are occupied by the two terminal carbon atoms in the butadiene-type derivative, and by the first olefinic carbon and the oxygen atoms in complexes with aldehydes and ketones.

We may now discuss the observed moments on the basis of *(i)* and *(ii)* above, shown schematically in Fig. 1, and indicated by "mixed" *(ii)* and "π-complexes" *(i)*. Rigorous vectorial analysis leading to information as to the configuration of the molecules is not possible since the group and bonding moments required are not known and there is no way of calculating them. Nevertheless, a qualitative vector analysis is capable of allowing a choice between forms *(i)* and *(ii)* to be made since they give rise to very different dipole moments.

For the "mixed" complex, the molecular moment arises, principally, from



MIXED COMPLEX

π COMPLEX

Fig. 1. Conformations of (PhCH=CHCOR)Fe group in π-(PhCH=CH—COR)Fe(CO)$_3$ complexes.

the vector sum of the moments: $\mu(\overrightarrow{\text{Fe—CO}})$, (0.50) [11]; $\mu(\overrightarrow{\text{L—Fe}})$, the iron—olefin moment, which may be assumed equal to that calculated previously for π-LFe(CO)$_4$ complexes [9], i.e. 1.6 D; $\mu(\overrightarrow{\text{C=O}})$, (2.7 D) [12], the moment of the organic carbonyl, which in this conformation has almost the same direction and sense as $\mu(\overrightarrow{\text{L—Fe}})$, and $\mu(\overrightarrow{\text{O—Fe}})$, the moment indicating the charge distribution of the two oxygen lone pairs between the oxygen atom and the iron atom. The moment $\mu(\overrightarrow{\text{O—Fe}})$ is not known and thus cannot be allowed for in the calculation. Nevertheless, since the sense of the moment $\mu(\overrightarrow{\text{O—Fe}})$ is about the same as the resultant of the other group moments of this configuration, the total theoretical moment, calculated without taking it into account, will represent the minimum value. Since the observed moments are all considerably lower than that calculated ($\mu_{\text{obs.}}$ = 2.45-2.65 compared to $\mu_{\text{calc.}}$ = 4.9 D) it is reasonable to exclude the presence of the "mixed" complex.

The theoretical moment of the π-complex may be calculated from the vector sum of $\mu(\overrightarrow{\text{LFe(CO)}_3})$, a moment which reflects the charge distribution between the two double bonds of the ligands, the iron atom and the three carbonyl groups, and of $\mu(\overrightarrow{\text{C=O}})$, (2.7 D) [12]. Now, if we assume, as a first approximation, that $\mu(\overrightarrow{\text{LFe(CO)}_3})$ in ketone and aldehyde complexes of this type are equal to the moment found for π-(PhCH=CH—CH=CHPh)Fe(CO)$_3$, (2.01 D), we obtain $\mu_{\text{calc.}}$ = 3.3 D. This allows us to conclude that the π-LFe(CO)$_3$ complexes examined are π in type, in agreement with most of the X-ray [1], IR and NMR data in the literature [2,3]. It is probable that this configuration is preferred because of the larger resonance energy, and hence greater stability, of the organic ligand when it is in a planar situation, in which delocalisation of the four π electrons of the two double bonds in a position suitable for conjugation occurs, compared to that in which such planarity does not exist ("mixed" type).

The difference between the observed and calculated moment for the π-complex is very meaningful. It is due to the fact that the $\mu(\overrightarrow{\text{LFe(CO)}_3})$ group moment used to calculate the theoretical moment is lower in the ketone and aldehyde complexes than it is in π-(PhCH=CH—CH=CHPh)Fe(CO)$_3$. The doublet of the organic C=O bond is less available for bonding to the iron than is that of the olefinic bond in the butadiene-type derivative. Besides, it is known that the strength of metal-to-ligand back-donation largely depends on the groups present in the organic moiety. Consequently, when the ligand contains an electron-attracting substituent (in the present case —COR) the back-donation is greater than in butadiene-type complexes. Hence, remembering that the $\mu(\overset{+\!\!\longrightarrow}{\mathrm{L{-}Fe}})$ moment has the sense indicated and is the resultant of two contributions, $\mu_1(\overset{+\!\!\longrightarrow}{\mathrm{L{-}Fe}})$ derived from the passage of electrons from the double bonds to the empty *d* iron orbitals and $\mu_2(\overset{\longleftarrow\!\!+}{\mathrm{L{-}Fe}})$ indicating back-coordination from the metal to the ligand, it is clear that an increase in ligand electron-attracting power will give rise to a decrease in $\mu(\overset{+\!\!\longrightarrow}{\mathrm{L{-}Fe}})$. Evidence for this result may be obtained by comparing the IR bands of the CO groups bonded to the iron (see Table 3).

There is a clear increase in the carbonyl stretching frequency in the aldehyde and ketone complexes compared to those in the butadiene derivative. This indicates a decrease in "back-donation" from the metal to the CO and hence lower availability of the valence electrons of the iron in aldehyde and ketone complexes than in those of the (1,3-diene) type (Table 3). This lower availability of the iron electrons is due to a lower total charge transferred from the organic moiety to the metal, in agreement with the conclusions obtained from the dipole moments.

The chemical consequences of a stronger back coordination in complexes with ligands containing an electron-attracting atom compared to those where such an atom is not present are of interest. In fact, since the back-coordination seems to be responsible for the thermodynamic stability of these complexes [13], it is reasonable to conclude that the complexes with aldehyde and ketone ligands are more stable than those of the (1,3-butadiene) type.

A last comment on the results obtained regards the identical (within the limits of reproducibility) moments obtained for the complexes of cinnamic aldehyde, benzilideneacetone and chalcone (2.61, 2.63 and 2.65 D, in that order). This may at first sight appear surprising given that the moment of the free ligands are sensibly different from one another (3.71, 3.25 and 3.05 D for cinnamic aldehyde, benzilideneacetone and chalcone, respectively) [8]. The reason for the difference between the free ligands moments may be found, essentially, in the conjugation between the phenyl group linked to the olefinic bond and the carbonyl. The contribution to the molecular moment of extreme forms

TABLE 3

IR BANDS OF THE CO-GROUPS BONDED TO IRON

Complex	ν(C=O) (cm^{-1})^a		
π-(PhCH=CH—CH=CHPh)Fe(CO)$_3$	2045	1988	1980
π-(CH$_2$=CHCHO)Fe(CO)$_3$	2080	2020	1997
π-(PhCH=CHCHO)Fe(CO)$_3$	2074	2010	1992
π-(PhCH=CHCOMe)Fe(CO)$_3$	2067	2010	1992
π-(PhCH=CHCOPh)Fe(CO)$_3$	2067	2010	1997

^{a} In n-hexane

having a positive charge on the phenyl group and a negative charge on the oxygen atom is expected to be considerable, given the large distance between these two charges. Hence, the fact that the moments of the corresponding complexes are almost identical indicates that in these the phenyl—carbonyl conjugation is greatly reduced because the four π electrons of the heterodiene system are already involved in bonding to the metal. However, there is still a cetain amount of conjugation present, as shown by the fact that the moments of these three complexes are slightly higher than of the complex π-($CH_2{=}CHCHO)Fe(CO)_3$, which has no phenyl group.

Conclusions

A comparison of the theoretical moments (though calculated only approximately) for the "mixed" complex and for the π-type complex with the observed moments suggests that the structure present is the π structure, in agreement with experimental data in the literature. The reason for this resides, very probably, in the greater resonance stability of the planar form of the ligand compared to the distorted form which would be present in the "mixed" complex. This resonance arises only marginally from contributions of extreme forms having a positive charge on the phenyl group and negative charges on the oxygen atom. It mainly arises from the delocalisation of the four electrons of the C=C—C=O system over all three bonds, as observed for the C=C—C=C system [14]. Although the main contribution to the iron—heterodiene bond is due to the orbital comprised of the four delocalised electrons, the presence of substituents may partially alter the planar structure of the organic ligand, giving the extreme atoms of the conjugated system partial sp^3 character, as observed in other olefinic complexes [15].

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