Dipole Moments and Molecular Conformation of Allylcarbonylnitrosyl Iron Complexes

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The dipole moments of the complexes \( \pi \left( \text{CH}_2\left(\text{CXCH}_3\right) \text{Fe(CO)}\left(\text{NO}\right)\right)_2 \), with \( X \) and \( L \) equal, respectively, to \( H, \text{CO}; \ H, \text{P(C})_3\text{H}_5\); \( \text{CH}_3, \text{CO}; \ Cl, \text{CO}; \ Br, \text{CO} \), have been measured. From the results it is concluded that:

1. The value of the group moment \( \pi \text{C}_6\text{H}_5-\text{Fe} \) is ca. 1.6 D, if \( \mu(\text{Fe-CO}) = 0.5 \) D, \( \mu(\text{Fe-NO}) = 1.3 \) D and \( \text{CO-Fe-CO(NO)} = 98^\circ \).
2. A trans structure appears most likely in the \( \pi \left( \text{CH}_2\text{CHCH}_3\right) \text{Fe(CO)}_2\text{NO} \) (Y = Cl, Br, \( \text{CH}_3 \)).
3. Qualitative comparison between \( \pi \text{C}_6\text{H}_5-\text{Cr} \) and \( \pi \text{C}_6\text{H}_5-\text{Mn} \) group moments confirms that the \( \text{C}_6\text{H}_5 \) group bonds to manganese as \( \left( \text{C}_6\text{H}_3 \right)^6 \). In a previous note \(^1 \) we reported the dipole moments of several carbonylnitrosyl complexes of iron and cobalt. The \( M-\text{NO} \) moment was calculated from the observed dipole moments for \( \text{Co(CO)}_2\text{NO} \) and \( \text{Fe(CO)}_2\left(\text{NO}\right) \), assuming a dipole moment of 0.5 D for \( M-\text{CO} \). Use of these moments in some substituted derivatives allowed group moments for \( M-\text{R-P(C}}_3\text{H}_5 \), \( \text{As(C}_3\text{H}_5) \), \( \text{Sb(C}_3\text{H}_5) \) to be deduced and confirmed the presence of back-donation in the \( M-\text{R} \) bond.

This paper presents dipole moments for the complexes \( \left( \text{CH}_2\text{C}X\text{CH}_3\right) \text{Fe(CO)}_L \text{NO} \), \( X = H, \text{CH}_3, \text{Cl}, \text{Br} \); \( L = \text{CO}, \text{P(C}}_3\text{H}_5 \). From these measurements, and the above-mentioned group moments, an attempt is made to calculate metal-allyl group moments and to deduce the molecular conformation of the halogenated derivatives.

The molecules investigated are reported in Table I.

### Experimental

**Materials**

The allyl complexes were prepared using a general method described in the literature.\(^4\) Purity was checked by experimental analysis, and the \( \pi \)-structure confirmed using NMR spectra.\(^3\) The benzene used for physical measurements was first de-aerated. Compounds were stable in benzene solution during the measurements.

**Physical Methods**

Dielectric constants were determined at 25 °C using a WTW DM 01 dipolmeter. The sensitivity, \( \Delta e/e \) for the cell used, was \( 4 \times 10^{-5} \) at a frequency of 2 MHz. Densities were determined to an accuracy of \( \pm 0.00008 \) g/cc. Refraction indices were measured on a Bausch and Lomb refractometer, with an uncertainty in measurement of \( \pm 0.00007 \). The total polarisation of solute at infinite dilution (\( P_{\infty} \)), and its electronic polarisation (\( P_e \), assumed to be equal to the molar refraction (\( R_H \)) for the sodium D line, were calculated using H a l v e r s t a d t and K u m l e r’s method.\(^8\) Atomic polarisation was assumed to be zero.

Table II reports the dipole moments obtained and parameters used in calculating them.

Because of their relevance the unpublished data for \( \pi \text{C}_6\text{H}_5\text{FeCONOP(C}_3\text{H}_5) \) and \( \pi (2 \text{CH}_2\text{C}_3\text{H}_4)\text{FeCONOP(C}_3\text{H}_5) \) are added.

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Table II. Experimental results and parameters used in calculating the observed dipole moments.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\mu_{calc}$</th>
<th>$\mu_{obs}$</th>
<th>$\mu_{(arene-)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\pi\text{C}_3\text{H}_5\cdot\text{Fe}($CO$)_2\text{NO}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$W_2 \cdot 10^5$</td>
<td>$\rho_{12}$</td>
<td>$V_{12}(cc/g)$</td>
<td>$n_i$</td>
</tr>
<tr>
<td>1.08</td>
<td>2.2775</td>
<td>1.1439</td>
<td>2.2444</td>
</tr>
<tr>
<td>2.19</td>
<td>2.2828</td>
<td>—</td>
<td>2.2446</td>
</tr>
<tr>
<td>3.28</td>
<td>2.2880</td>
<td>1.1429</td>
<td>2.2449</td>
</tr>
<tr>
<td>4.86</td>
<td>2.2955</td>
<td>1.1423</td>
<td>2.2452</td>
</tr>
<tr>
<td>6.05</td>
<td>2.3012</td>
<td>1.1418</td>
<td></td>
</tr>
</tbody>
</table>

$\alpha = 6.480$; $\beta = -0.386$; $\gamma = 0.570$; $P_{2oo} = 662.8$ cc; $\mu = 4.85 \pm 0.04$ D.

**Discussion**

1. The values $\mu(C - Cl) = 1.55$ D, $\mu(C - CH_2) = 0.4$ D, $\mu(M - CO) = 0.5$ D, and $\mu(M - NO) = 1.3$ D were used to calculate the theoretical moments independent of the type of complex. The angles Cr - C - O = 180° and CO - Cr - CO = 88°, as found by Corradini and Allegra, were assumed for the chromium compounds.

For the complex $\pi\text{C}_3\text{H}_5\text{Mn}($CO$)_3$ the angles: CO - Mn - CO = 92° and Mn - C - O = 178° were assumed, as found from the X-ray structure determination.

The structure of the complex $\pi(\text{CH}_2\text{CXCH}_2)\text{Fe}($CO$)_2\text{NO}$, not known to date, is assumed to be the same as that of butadiene-Fe($CO$)$_3$, found from electron diffraction measurements in the gas phase (angles: Fe - C - O = 180°; CO - FeCO(NO) = 96°). The uncertainty arising from this assumption most affects the absolute value of the iron-allyl group moment and is almost negligible when considering the structure of the halogenated complexes. The calculated moments are shown in Table III.

Table III. Calculated dipole moments.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\mu_{calc}$</th>
<th>$\mu_{obs}$</th>
<th>$\mu_{(arene-)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\pi\text{CH}_2\text{CH}_2\text{Cr}($CO$)_3$</td>
<td>4.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\pi\text{CH}_2\text{H}_4($CO$)_3$</td>
<td>4.0</td>
<td></td>
<td></td>
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<tr>
<td>$\pi\text{ClCH}_2\text{Cr}($CO$)_3$</td>
<td>3.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\pi\text{CH}_2\text{Mn}($CO$)_3$</td>
<td>2.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\pi\text{CH}_2\text{Fe}($CO$)_2\text{NO}$</td>
<td>1.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\pi\text{C}_3\text{H}_5\text{Fe}($CO$)_2\text{NO}$</td>
<td>cis</td>
<td>2.62</td>
<td>1.8</td>
</tr>
<tr>
<td>trans</td>
<td>2.84</td>
<td>3.03</td>
<td>1.7</td>
</tr>
<tr>
<td>$\pi\text{C}_3\text{H}_5\text{Fe}($CO$)_2\text{NO}$</td>
<td>cis</td>
<td>3.44</td>
<td>-1.1</td>
</tr>
<tr>
<td>gauche</td>
<td>3.28</td>
<td>-0.1</td>
<td></td>
</tr>
<tr>
<td>$\pi\text{C}_3\text{H}_5\text{Fe}($CO$)_2\text{NO}$</td>
<td>trans</td>
<td>2.75</td>
<td>2.22</td>
</tr>
<tr>
<td>free rot.</td>
<td>3.12</td>
<td>0.3</td>
<td></td>
</tr>
</tbody>
</table>

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$a$ Dipole moments calculated assuming $\mu(C_3H_5 - Fe) = 1.6$ D.

$b$ Group dipole moments calculated from the observed dipole moments.

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$a$ Solute weight fraction (g sol./g soln).

$b$ Dielectric constant of the solution.

$c$ Specific volume of the solution.

$d$ Refractive index square of the solution.

$e$ Dielectric constant of the solvent, obtained by extrapolating to infinite dilution the solution values.

$f$ Specific volume of the solvent, obtained by extrapolating to infinite dilution the solution values.

$g$ Refractive index square of the solvent, obtained by extrapolating to infinite dilution the solution values.
The complex $\pi(CH_2CClCH_2)Fe(CO)_2NO$ may exist as different conformers according to the relative positions of halogen and nitrosyl. Free, or partially hindered, internal rotation about the allyl-iron bond is possible or trans, gauche and cis rotational isomers. To decide which is present, we have assumed, in a first attempt, that the allyl-group moment deduced from the parent compounds is, to a reasonable approximation, transferable to the halo- 

cyclic (cis, trans) the structures of allo.

3. The cyclopentadiene-Mn group moment is rather low when compared with the benzene-chromium group moment. This may indicate a residual negative charge on the cyclopentadiene ring. Although we cannot draw more conclusive deductions, we note that it has been suggested in the literature that the $C_5H_5$ group bonds to manganese as $(C_5H_5)^{-}$.
The Stability Increasing Effect of the Pyridyl and Imidazole Groups
on the Formation of Mixed Amine-Copper(II)-Adenosine
5'-monophosphate Complexes

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Adenosine 5'-monophosphate complexes, Complexes with amines and adenosine 5'-monophosphate, Copper(II) complexes, Mixed-ligand Cu(II) complexes, Stability of ternary complexes

The stability constants of the ternary Cu
2+
complexes containing adenosine 5'-monophosphate (AMP) and as a second ligand, 2,2'-bipyridyl, 4-(2'-pyridyl)imidazole, 2-picolylamine, 4-aminomethylimidazole, and ethylenediamine were determined by potentiometric titration in water containing 10% dioxane (\( \ell = 0.1 \); 25 °C). For the equilibrium, \( \text{Cu(amine)}^{2+} + \text{Cu}(\text{AMP}) = \text{Cu}(\text{amine})(\text{AMP}) + \text{Cu}^{2+} \), the corresponding constants are (in the order of the above amine ligands), \( \Delta \log K = \log K_{\text{Cu(amine)(AMP)}} - \log K_{\text{Cu}(\text{AMP})} = 0.53, 0.20, 0.04, -0.35, \) and \(-0.45\); hence, in the first cases the equilibrium is considerably on the side of the mixed-ligand complex. The importance of the \( \pi \)-system of the amine for the stability of the mixed-ligand Cu
2+
complexes is obvious from the given series. The imidazole group, an important binding site for metal ions in biological systems, has clearly qualities similar to the pyridyl group (Inorg. Chem. 9, 1238 [1970]), i.e. the stability of ternary Cu
2+
complexes containing these groups is increased.

Ternary complexes can be considered as models for enzyme-metal ion-substrate complexes as well as for mixed-ligand complexes occurring in biological fluids. Therefore, investigations of the stability of ternary complexes may help toward understanding the driving forces which lead to the formation of such complexes in biological systems.

From earlier studies \(^3,^4\) it is known that ligands containing oxygen as donor atoms, such as malonate or pyrocatecholate, form ternary complexes with Cu
2+
-2,2'-bipyridyl which are more stable than the corresponding binary Cu
2+-O-ligand 1:1 complexes \(^5\). The same phenomenon is observed in mixed-ligand Cu
2+
systems containing 2,2'-bipyridyl and a phosphate, e.g. hydrogen phosphate, adenosine 5'-monophosphate or -triphosphate \(^6\).

Recently, the stability of the mixed-ligand Cu
2+
complexes containing pyrocatecholate and one of the following N-ligands was determined: 2,2'-bipyridyl, 4-(2'-pyridyl)imidazole, 2-picolylamine, 4-aminomethylimidazole, and ethylenediamine \(^7\). It became apparent that the stability of the ternary N-ligand-Cu
2+-pyrocatecholate complexes is strongly...