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# DIPOLE MOMENTS AND MOLECULAR CONFORMATIONS OF $(C_6H_5)_3SnFe(CO)_2NOL$ AND RELATED COMPLEXES

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## SUMMARY

Dipole moment measurements on $(C_6H_5)_3SnFe(CO)_2NOL$ complexes [L = CO, $P(C_6H_5)_3$, $As(C_6H_5)_3$, $P(OC_6H_5)_3$] indicate that the ligand L is in a *cis* position relative to the axial $(C_6H_5)_3Sn$ grouping, in contrast to the situation with analogous Co and Mn complexes, for which both the ligands are in the axial positions of the trigonal bipyramidal structure. Similarly, it is found that the two $P(OC_6H_5)_3$ ligands in the trimetallic linear complex $Hg[Fe(CO)_2NOP(OC_6H_5)_3]_2$ do not both occupy axial positions and probably both occupy equatorial positions. There is evidence that in these compounds the metal–L-group dipole moments are more dependent on the electron density at the central metal, as determined by the presence of $\sigma$ or $\pi$ acceptor groupings, than on the nature of the central metals and the structures of the complexes.

## INTRODUCTION

Electron diffraction and dipole moment measurements have shown[1,2] that cobalt and manganese complexes such as $R_3MCo(CO)_4$, $(C_6H_5)_3PMn(CO)_3NO$, $[(C_6H_5)_3P]_2Mn(CO)_2NO$, $(C_6H_5)_3GeCo(CO)_3P(C_6H_5)_3$ and $R_3MMn(CO)_4PR_3$ (M = Si, Ge, Sn, Pb, P, As; R = H, Cl, F, $C_6H_5$), all have trigonal or tetragonal bipyramidal conformations; whenever two $MR_3$ groupings are present, the observed structure is a *trans* one. For the analogous iron complexes $(C_6H_5)_3SnFe(CO)_2NOL$ (L = phosphines, phosphites or arsines) direct structural information is not available. However, the chemical and spectral similarity of these compounds to those of Co and Mn indicates[3,4] for them a trigonal bipyramidal distribution of the ligands around the iron atom, with the tin atom in the axial position; the relative intensities of the two CO stretching IR bands indicates that the ligand L is *trans* to the $SnR_3$ group. Similarly, for the structurally related trimetallic linear compounds $Hg[Fe(CO)_2NOL]_2$, a trigonal bipyramidal structure around the iron atoms has been proposed[5], with the nitrosyl ligands in the equatorial planes at a dihedral angle of about 60°, and with the L ligands in axial positions. However, the number of CO bands observed for the di- and trimetallic iron complexes agrees also with a structure having the L ligands in equatorial positions.

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The present work aims at providing, through dipole moment measurements, additional structural information on these compounds, and at establishing whether the metal–ligand-group moments now estimated can be transferred from one complex to another with different structure and central metal.

## RESULTS AND DISCUSSION

In order to decide the preferred conformation of the $(C_6H_5)_3SnFe(CO)_2NOL$ complexes [$L = P(C_6H_5)_3$, $As(C_6H_5)_3$ and $P(OC_6H_5)_3$], their observed dipole moments were compared with those calculated. These were estimated for the *cis* and *trans* conformers [referred to the relative positions of the $(C_6H_5)_3Sn$ and L ligands] by assuming a trigonal bipyramidal structure[3,4] with the NO ligand in the equatorial plane. The Fe–CO (0.5 D) and Fe–NO (1.0 D) group moments used were taken from the literature[6]*. The $(C_6H_5)_3Sn$–Fe group moment (2.4 D) was deduced from the $\mu_{20\%}$1.86 D value observed for the $(C_6H_5)_3SnFe(CO)_3NO$ complex; for the metal–L-group moment two extreme values were used, *viz.* those obtained from tetra- and penta-coordinated molecules (Table 1).

The moments so estimated are listed in Table 2, and show that the molecules considered here have *cis* conformations independent of the nature of the ligand L

TABLE 1

EXPERIMENTAL DIPOLE MOMENTS AND M-M'R$_3$ GROUP MOMENTS (IN DEBYES)

| *Complex* | $\mu$ | $\mu_{20\%}$ | $\mu(M\text{-}M'R_3)$ |
|---|---|---|---|
| $Fe(CO)_4P(C_6H_5)_3$ | 5.03 | 4.90 | 4.4 |
| $FeCO(NO)_2P(C_6H_5)_3$ | 5.09[a] | 5.00 | 4.1 |
| $Co(CO)_2NOP(C_6H_5)_3$ | 4.61[a] | 4.50 | 3.8 |
| $Fe(CO)_4As(C_6H_5)_3$ | 5.28 | 5.20 | 4.7 |
| $Co(CO)_2NOAs(C_6H_5)_3$ | 4.55[a] | 4.40 | 3.7 |
| $Co(CO)_2NOP(OC_6H_5)_3$ | 2.27[b] | 1.95 | 1.2 |
| $(C_6H_5)_3SnFe(CO)_3NO$ | 2.20 | 1.86 | 2.3 |

[a] Ref. 6b. [b] Ref. 8.

TABLE 2

CALCULATED DIPOLE MOMENTS (DEBYES) FOR THE *cis* AND *trans* CONFORMATIONS OF THE $(C_6H_5)_3SnFe(CO)_2NOL$ COMPLEXES

| *Complex* | $\mu_{20\%\ obs.}$ | $\mu_{calcd.\ cis}$ | | $\mu_{calcd.\ trans}$ | |
|---|---|---|---|---|---|
| $(C_6H_5)_3SnFe(CO)_2NOP(C_6H_5)_3$ | 4.62 | 4.9[a] | 5.5[b] | 6.1[a] | 6.7[b] |
| $(C_6H_5)_3SnFe(CO)_2NOAs(C_6H_5)_3$ | 4.45 | 4.8 | 5.7 | 6.0 | 7.0 |
| $(C_6H_5)_3SnFe(CO)_2NOP(OC_6H_5)_3$ | 2.12 | 2.1 | | 3.6 | |

[a,b] Figures calculated by using the extreme values of each group moment from Table 1 respectively.

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* $Co(CO)_3NO$ and $Fe(CO)_2(NO)_2$ have dipole moments of 0.72 and 0.95 D respectively[7]. Assuming $P_a = 20\%\ P_e$ for these molecules, as found for $Fe(CO)_5$[7], the two group moments are found to differ by 0.4–0.5 D, which implies an Fe–NO-group moment of about 1.0 D.

and of the value chosen for the metal–L-group moment. Indeed, the values calculated for the *trans* structure are 1.5 to 2.5 D higher than those observed. It is noteworthy that the metal–L-group moment values which give the best agreement with the experimental results are those deduced from cobalt and iron tetrahedral complexes, rather than those obtained from iron trigonal bipyramidal complexes. This agreement must be at least partly fortuitous; it suggests that, in the complexes considered here, the presence of acceptor groupings in the molecule and their influence on the electron density at the central metal[9] is more important in determining the values of the group moments than the nature of the central metal itself or the structure of the complex. The ligand NO (which is known to be a better $\pi$-acceptor than CO[10]) and the $\sigma$-acceptor grouping $Sn(C_6H_5)_3$ can partly accept the electronic charge transferred to the metal by the $\sigma$-donor ligand L, so reducing the amount of charge separation in the Fe–L dipoles compared with that in the $Fe(CO)_4L$ complexes. The information gained on the conformation of $(C_6H_5)_3SnFe(CO)_2NOL$ compounds is of interest, also, because many structurally similar Co and Mn complexes have *trans* conformations (see above). In order to see whether this difference can be connected with the nature of the central metal, we have examined two trimetallic complexes $Hg[Fe(CO)_2NOL]_2$ [L=CO and $P(OC_6H_5)_3$]; it has been suggested[5] by analogy with similar cobalt compounds, that the L ligands are in axial positions in these complexes.

The dipole moment observed when L=CO (1.22 D) agrees with the literature value (1.25 D)[11]; assuming $P_a = 27\%\ P_e$, as deduced from the isoelectronic complex $Hg[Co(CO)_4]_2$[11], it is found that $\mu = 0.6$ D. This low value precludes the derivation of any reliable structural information; either a rigid structure with a dihedral angle, as mentioned, or one involving free rotation around the Fe–Hg–Fe axis is compatible with the experimental dipole moment value. They give a difference between the Fe–CO and Fe–NO group moments of about 0.4 D, in agreement with the above reported value.

The moment observed for the $Hg[Fe(CO)_2NOP(OC_6H_5)_3]_2$ complex (2.7 D) rules out the possibility that the two $P(OC_6H_5)_3$ ligands both occupy axial positions. Indeed, to reduce the moment to about 0.6 D (*i.e.*, to the value for the unsubstituted compound) $P_a$ would have to be set at about 55% $P_e$, an unlikely value; with $P_a = 27\%\ P_e$ (see above) one obtains $\mu = 1.97$ D. The arrangement of the $P(OC_6H_5)_3$ ligands in this molecule must therefore be one of the following: (*a*) one ligand in an axial and the other in an equatorial position, (*b*) both in equatorial positions; the second alternative is preferred for reasons of symmetry. Measurements at several temperatures may possibly give additional information on the matter.

The new dipole moment data show that, in contrast to the situation in analogous cobalt and manganese complexes, the $R_3M$ groupings prefer to occupy equatorial positions in the iron complexes examined; the reasons for this difference in behaviour when the central metal is iron must remain uncertain until further data are available. The nature and stability of the tin–metal bond is somewhat influenced by the metal involved: Thus, (*a*), with M=Mn, Re and Co, the Sn–M bond length and the IR and NMR spectra indicate the effective presence of $(d \rightarrow d)\pi$ bonding superposed on the $\sigma$-bonding[12] but in the $(C_6H_5)_2ClSn–Fe(CO)_3NO$ and $C_6H_5Cl_2Sn–Fe(CO)_3NO$ complexes there is some evidence for restricted rotation at the Sn–Fe bond[3]; (*b*), when M=Fe, the complexes are less stable with respect to air,

TABLE 3

PARAMETERS FOR THE CALCULATION OF THE DIPOLE MOMENTS

| *Compound* | $\varepsilon_1$ | $\alpha$ | $V_1 (cm^3)$ | $\beta$ | $n^2$ | $\gamma$ | $P_{2\infty}$ | $R_D$ | $\mu_{20\%}$ (D) | $\mu_{20\%}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| $(C_6H_5)_3SnFe(CO)_3NO$ | 2.2718 | 1.370 | 1.1454 | −0.460 | 2.2438 | 0.370 | 240.2 | 141.2 | 2.20±0.03 | 1.86 |
| $(C_6H_5)_3SnFe(CO)_2NOP(C_6H_5)_3$ | 2.2719 | 3.660 | 1.1446 | −0.360 | 2.2446 | 0.300 | 695.3 | 216.4 | 4.84±0.04 | 4.62 |
| $(C_6H_5)_3SnFe(CO)_2NOAs(C_6H_5)_3$ | 2.2724 | 3.355 | 1.1452 | +0.456 | 2.2442 | 0.374 | 667.7 | 218.1 | 4.69±0.04 | 4.45 |
| $(C_6H_5)_3SnFe(CO)_2NOP(OC_6H_5)_3$ | 2.2719 | 1.168 | 1.1445 | −0.415 | 2.2449 | 0.285 | 350.4 | 215.1 | 2.57±0.04 | 2.12 |
| $Hg[Fe(CO)_3NO]_2$ | 2.2727 | 0.523 | 1.1444 | −0.746 | 2.2439 | 0.227 | 117.2 | 86.5 | 1.22±0.04 | 0.6[a] |
| $Hg[Fe(CO)_2NOP(OC_6H_5)_3]_2$ | 2.2726 | 1.060 | 1.1445 | −0.573 | 2.2432 | 0.352 | 408.2 | 259.1 | 2.70±0.05 | 1.97[a] |
| $Fe(CO)_4As(C_6H_5)_3$ | 2.2726 | 6.587 | 1.1438 | −0.450 | 2.2442 | 0.208 | 684.8 | 115.2 | 5.28±0.04 | 5.17 |
| $Fe(CO)_4P(C_6H_5)_3$ | 2.2724 | 6.745 | 1.1445 | −0.366 | 2.2435 | 0.364 | 645.4 | 127.9 | 5.03±0.04 | 4.93 |

[a] $\mu_{27\%}$.

light and temperature; (*c*), the stability of the tin–metal bond in the $R_3Sn$–M entities with M = Mn, Re or Co, increases on varying R in the order $CH_3$, $C_6H_5$, Hal[12]; in contrast, the $Hal_3Sn$–Fe bond is weaker than the $(C_6H_5)_3Sn$–Fe bond[3]. Furthermore, IR evidence for hexacoordinated iron complexes $Fe(CO)_4L_2$ [L = HgHal, HgR, $SnR_3$, $PbR_3$] suggests that the L ligands are always *cis* to one another[13].

## EXPERIMENTAL

### (*a*). *Physical measurements*

They were performed at 25 ± 0.1°, under the conditions previously described[14]. The electronic polarization $P_e$ was taken as equal to $R_D$, and evaluated from refractive index measurements; these were obtained with a Bausch and Lomb refractometer, the uncertainty is being estimated to be ±0.0001 units. The atomic polarization $P_a$ was inferred in each case as specified, by analogy with structurally similar complexes. The observed dipole moments were evaluated by the method of Halverstadt and Kumler[15]; Table 3 shows the parameters employed.

### (*b*). *Materials*

The complexes were prepared by published methods[1–3], except for $Fe(CO)_4P(C_6H_5)_3$ and $Fe(CO)_4As(C_6H_5)_3$, which were obtained by subjecting a mixture of $Fe(CO)_5$ and L (2/1) to UV irradiation in benzene solution. The solution, filtered to remove $Fe_2(CO)_9$, was concentrated under vacuum; the complexes were precipitated with n-hexane, and recrystallized from the same solvent. The purities of the compounds were checked by analysis. The solvents used for the synthesis and measurements were previously saturated with nitrogen.

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