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Carbonyl Spectra of $L_2XMn(CO)_3$ Complexes

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Reaction of $Mn(CO)_5X$ (X = Cl, Br) with monodentate tertiary phosphorus and arsenic ligands gives the trans-*$L_2XMn(CO)_3$ species; for L = $SbPh_3$ the* fac-*isomers are obtained.*

CO stretching and interaction force constants have been derived. Scales of relative $\sigma \rightarrow \pi^*$ donor and π acceptor character have been calculated for ligands in fac-$L_2BrMn(CO)_3$ complexes.

Introduction

As part of a spectroscopic study of metal carbonyls we report the carbonyl spectra of complexes with the general formula $L_2XMn(CO)_3$ (X = Cl, Br; L = a trivalent derivative of the elements P, As, Sb, a monodentate Lewis base).

These compounds may exist in three distinct isomeric forms [1]: the *meridional trans*-L_2, the *meridional cis*-L_2 or the *facial* form. Throughout this report they will be referred to as the *trans-*, *cis-* or *fac*-isomers.

Results and Discussion

For both the *meridional* conformers of $L_2XMn(CO)_3$ one expects one weak and two strong CO bands in the infrared 5μ region. Except for the stibine substituted complexes the prepared compounds (Table I) are considered as *trans*-isomers having C_{2v} symmetry. This is clearly borne out by the correlation chart for the series $Mn(CO)_{5-n}\{P(OMe)_3\}_nBr$.

It is seen that if the disubstituted trimethylphosphite derivative had been assigned a *cis*-conformation one ought to observe an absorption near 2020 cm^{-1} instead of the band at 1936 cm^{-1} (dashed arrow in Fig. 1).

Due to cancellation of moments a symmetric stretching of the two equivalent CO groups *cis* to the halogen atom (A_1^b mode) gives rise to only a weak band, observed at the high frequency side of the spectrum. Considering that the local oscillating dipoles of the two kinds of CO groups should be equal, we would expect the B_1 fundamental to show an integrated intensity about twice that of the A_1^a mode [2]. Therefore the lowest frequency band is assigned to the latter mode, the intermediate band to the former (Fig. 2).

TABLE I. CO Stretching Frequencies (cm^{-1}) of $L_2XMn(CO)_3$ Species, X = Cl, Br.*

Complex	A_1^b	B_1	A_1^a
$\{PPh_3\}_2BrMn(CO)_3$	2036	1950	1917
$\{PPh_3\}_2ClMn(CO)_3$	2034	1952	1915
$\{AsPh_3\}_2BrMn(CO)_3$	2036	1952	1915
$\{AsPh_3\}_2ClMn(CO)_3$	2038	1951	1914
$\{PPh_2Cl\}_2BrMn(CO)_3$	2055	1974	1942
$\{PPhCl_2\}_2BrMn(CO)_3$	2076	2005	1963
$\{P(NEt_2)_3\}_2BrMn(CO)_3$	2038	1953	1917
$\{EtP(NEt_2)_2\}_2BrMn(CO)_3$	2034	1950	1911
$\{Et_2P(NEt_2)\}_2BrMn(CO)_3$	2033	1949	1909
$\{PMe_3\}_2BrMn(CO)_3$	2033	1944	1900
$\{PnBut_3\}_2BrMn(CO)_3$	2025	1939	1892
$\{PnBut_3\}_2ClMn(CO)_3$	2025	1934	1893
$\{PnBut_2Cl\}_2BrMn(CO)_3$	2054	1977	1933
$\{P(OMe)_3\}_2BrMn(CO)_3$	2056	1970	1936
$\{P(OMe)_3\}_2ClMn(CO)_3$	2058	1976	1935
$\{P(OPh)_3\}_2BrMn(CO)_3$	2068	1993	1949
$\{P(OPh)_3\}_2ClMn(CO)_3$	2070	1994	1948
	A'_b	A''	A'_a
$\{SbPh_3\}_2BrMn(CO)_3$**	2019	1951	1910
$\{SbPh_3\}_2ClMn(CO)_3$**	2024	1953	1912

*The relative intensities of the absorptions in the order given in the table are: (w), (vs), (s) unless otherwise indicated. **(s), (s), (s).

The force constants (k_a, k_e, t and c) as calculated for the *trans*-$L_2BrMn(CO)_3$ derivatives are given in the first part of Table II. k_a refers to the axial CO group (*trans* to Br) and k_e to the equatorial CO's (*cis* to Br). t and c are the $CO_{eq} - CO_{eq}$ and $CO_{ax} - CO_{eq}$ interaction constants. The secular equations for the CO vibrations in *trans*-$L_2XMn(CO)_3$ species are given in the literature [3]. The force field, however, is undetermined with one degree of freedom. Therefore the calculations are done using a supplementary (CO stretching)–(CO-stretching) interaction relationship resulting from overlap theories developed by Jones [4]:

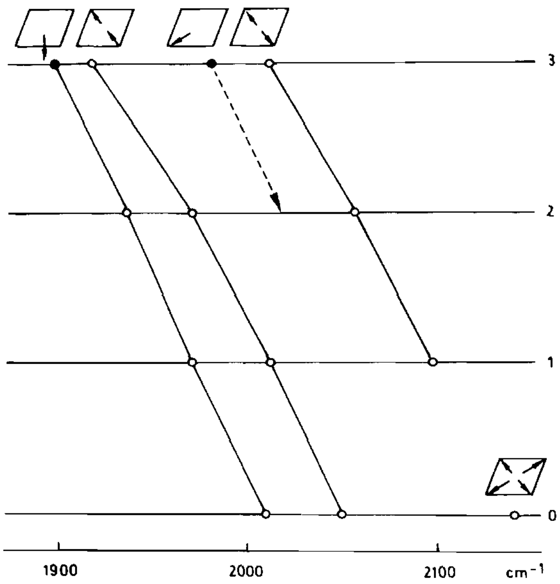

Figure 1. Correlation chart for the CO spectra of $\mathrm{Mn(CO)_{5-n}\{P(OMe)_3\}_nBr}$; for n = 1 the phosphite ligand stands *cis* to Br; for n = 2 the *trans*-isomer is considered; n = 3: (●) has all the three phosphite ligands *cis* to Br, (○) has one $\mathrm{P(OMe)_3}$ group *trans* to Br and both the other phosphites *cis* to Br but *trans* to each other.

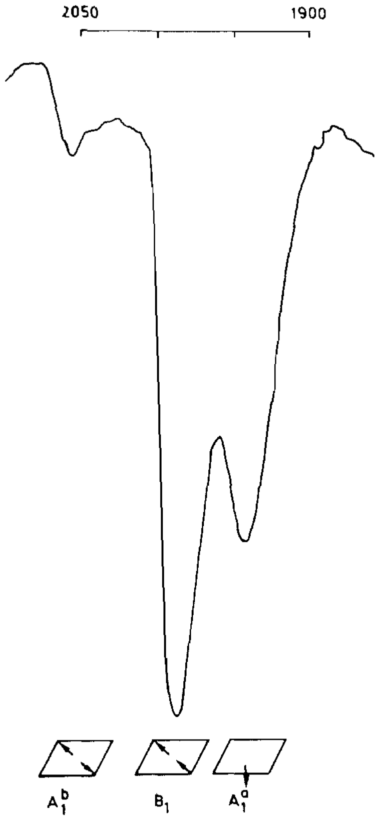

Figure 2. Infrared spectrum of *trans*-$\mathrm{(PnBut_2Cl)_2BrMn(CO)_3}$ in the presence of excess $\mathrm{PnBut_2Cl}$, in chloroform.

$\delta = t/c = (3 + 2y)/(1 + 2y)$.

The amount of Mn–X π bonding has been assumed to be unchanged by varying L. Since y varies from zero to one the above equation predicts a δ range of 1.67 to 3.00, centered around $\delta = 2.09$. Over this range k_a and k_e were found on average to vary by ±0.05 and ±0.02 mdynes/Å respectively.

The secular equations for *trans*-$\mathrm{L_2XMn(CO)_3}$ may also be used for the *fac*-conformers, c' taking the place of t. However, a new (CO stretching)-(CO stretching) interaction relationship has to be considered:

$$\rho = c'/c = (1 + y)/(1 + 2y)$$

which predicts a range of 0.67 to 1.00 for the ratio c'/c, centered around $\rho = 0.81$. The force constants for some selected *fac*-$\mathrm{L_2BrMn(CO)_3}$ complexes are given in Table II.

The series of *fac*-isomers considered is particularly interesting with regard to a separation of σ and π bonding effects. Changes in the π acceptor ability of L affect both k_a and k_e but in a different manner. L_1 interacts via the manganese $3d_{yz}$ orbital with the π_z^* orbital of $CO_{(2)}$ as well as with the π_y^* orbital of $CO_{(3)}$ (Fig. 3). Therefore each of these carbonyls feels only half the partial change $\Delta\pi_{yz}(\mathrm{Mn{-}L_1})$.

The same holds for $CO_{(1)}$ and $CO_{(3)}$ with respect to $\Delta\pi_{xz}(\mathrm{Mn{-}L_2})$. In the equatorial plane however the carbonyls $CO_{(1)}$ and $CO_{(2)}$ are affected twice; each of them feels half the changes $\Delta\pi_{xy}(\mathrm{Mn{-}L_1})$ and $\Delta\pi_{xy}(\mathrm{Mn{-}L_2})$. Assuming the various partial changes to be equal and summing them, we can write $\Delta k_a = 2(\Delta\pi/2)$ and $\Delta k_e = 3(\Delta\pi/2)$.

Regarding the data for the f-(amine)$_2$BrMn(CO)$_3$ species (Table II) it is seen that k_a changes more than k_e. This is inconsistent with π bonding influences but may be explained in terms of a direct donor (*cis*) effect [5]. The σ_y bonding orbital of L_1 interacts directly with both the π_y^* orbital of $CO_{(1)}$ and the π_y^* orbital of $CO_{(3)}$. On the other hand the σ_x bonding orbital of the ligand L_2 interacts with the π_x^* orbital of $CO_{(2)}$ and of $CO_{(3)}$. So the axial CO group is affected twice, the equatorial CO's only once, and for this portion of the overall change in force constants, we obtain $\Delta k_a = 2\Delta(\sigma{\to}\pi^*)$, $\Delta k_e = \Delta(\sigma{\to}\pi^*)$.

For the overall changes in force constants in going from one ligand to another, we get:

$$\Delta k_a = 2\Delta(\sigma{\to}\pi^*) + 2(\Delta\pi/2),$$

$$\Delta k_e = \Delta(\sigma{\to}\pi^*) + 3\,(\Delta\pi/2).$$

This assumes that the changes in the ligand-to-metal σ bond are of minor importance in determining $\nu\{\mathrm{CO}\}$ [6, 7]. Determining Δ values relative to the aniline derivative, a scale of relative bonding parameters is build up and given in Table III.

Examining first the $\sigma{\to}\pi^*$ scale we notice that for the complexes with L = *o*-chloroaniline ($pK_a = 2.62$),

TABLE II.CO Force Constants for some $L_2BrMn(CO)_3$ Complexes (mdynes/Å).

Complex	k_a	k_e	(c')	c
tr-$\{PnBu^t_3\}_2BrMn(CO)_3$	14.55	15.82	0.64	0.31
tr-$\{PMe_3\}_2BrMn(CO)_3$	14.68	15.92	0.66	0.32
tr-$\{PEt_2(NEt_2)\}_2BrMn(CO)_3$	14.81	15.96	0.63	0.30
tr-$\{PEt(NEt_2)_2\}_2BrmN(CO)_3$	14.84	15.98	0.63	0.30
tr-$\{P(NEt_2)_3\}_2BrMn(CO)_3$	14.94	16.04	0.63	0.30
tr-$\{PPh_3\}_2BrMn(CO)_3$	14.94	15.99	0.64	0.31
tr-$\{AsPh_3\}_2BrMn(CO)_3$	14.91	16.01	0.63	0.30
tr-$\{PnBu^t_2Cl\}_2BrMn(CO)_3$	15.17	16.37	0.58	0.28
tr-$\{P(OMe)_3\}_2BrMn(CO)_3$	15.24	16.32	0.65	0.31
tr-$\{PPh_2Cl\}_2BrMn(CO)_3$	15.33	16.34	0.61	0.29
tr-$\{P(OPh)_3\}_2BrMn(CO)_3$	15.42	16.61	0.57	0.28
tr-$\{PPhCl_2\}_2BrMn(CO)_3$	15.64	16.78	0.55	0.26
f-$\{PPhCl_2\}_2BrMn(CO)_3$[a]	15.63	16.55	0.33	0.41
f-$\{P(OPh_3\}_2BrMn(CO)_3$[a]	15.56	16.47	0.32	0.40
f-$\{P(OMe)_2Ph\}_2BrMn(CO)_3$[b]	15.32	16.16	0.41	0.50
f-$\{PEt_2Ph\}_2BrMn(CO)_3$[c]	14.90	15.81	0.39	0.48
f-$\{PMe_2Ph\}_2BrMn(CO)_3$[b]	14.91	15.80	0.38	0.48
f-$\{SbPh_3\}_2BrMn(CO)_3$	15.05	15.75	0.38	0.48
f-$\{CH_3CN\}_2BrMn(CO)_3$[d]	15.59	15.91	0.45	0.56
f-$\{glu\}BrMn(CO)_3$[d]	15.52	15.91	0.45	0.55
f-$\{o\text{-}ClC_6H_4NH_2\}_2BrMn(CO)_3$[c]	15.59	15.77	0.47	0.59
f-$\{C_6H_5NH_2\}_2BrMn(CO)_3$[c]	15.47	15.76	0.47	0.58
f-$\{p\text{-}MeOC_6H_4NH_2\}_2BrMn(CO)_3$[c]	15.41	15.74	0.47	0.58
f-$\{EtOH\}_2BrMn(CO)_3$[e]	15.42	15.69	0.56	0.69

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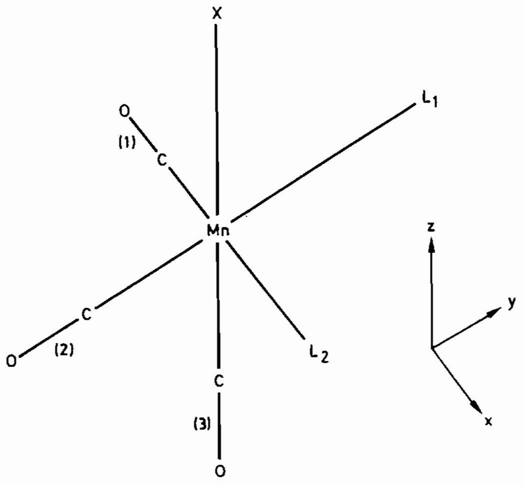

Figure 3. Coordinates used to label orbitals in the *fac* isomers.

TABLE III. Bonding Parameters for some *f*-$L_2BrMn(CO)_3$ Complexes (mdynes/Å).

L	$\Delta(\sigma\rightarrow\pi^*)$	$\Delta\pi$
CO[a]	0.14	1.05_5
$PPhCl_2$	-0.27_5	0.71
$P(OPh)_3$	-0.29	0.66_5
$P(OMe)_2Ph$	-0.31	0.47_5
PEt_2Ph	-0.45	0.33_5
PMe_2Ph	-0.44	0.32
$SbPh_3$	-0.31	0.20
CH_3CN	0.01_5	0.09
Glutaronitrile[b]	-0.04	0.12_5
$p\text{-}ClC_6H_4NH_2$	0.08_5	-0.05
$C_6H_5NH_2$	0.00	0.00
$p\text{-}MeOC_6H_4NH_2$	-0.03_5	0.01
EtOH	0.00_3	-0.04_5

[a] Calculated from frequencies given by H. B. Gray, E. Billig, A. Wojcicki and M. Farona, *Can. J. Chem., 41,* 1281 (1963).
[b] Bidentate.

aniline (pK_a = 4.58), *p*-anisidine (pK_a = 5.29) $\Delta(\sigma\rightarrow\pi^*)$ varies linearly with the pK_a value of the ligand considered. The gradient of this correlation however is negative (slope = –0.045). It follows that algebraically decreasing values of the $\sigma\rightarrow\pi^*$ parameters are associated with increasing $\sigma\rightarrow\pi^*$ donation by L. The $\sigma\rightarrow\pi^*$ ability of a ligand bonded through phosphorus obviously exceeds that of a ligand bonded through carbon, nitrogen or oxygen (all second row elements). This may result from the greater diffuseness of the requisite σ bonding orbital on phosphorus with regard to that on a second row element. An analoguous result has been obtained by Dobson, comparing (amine)$W(CO)_5$ with (phosphine)$W(CO)_5$ [6]. Another feature to be noted is that the substitution of alkyl groups on phosphorus by electronegative substituents such as $-Cl$ or $-OR$ results in a decrease in the amount of direct donor interaction, as expected.

Considering next the π scale some qualitative views are indicated. It is known that phosphines have significant ability to accept d_π electrons by the use of their $3d_\pi$ orbitals.

Aliphatic amines however have no such ability, except by a hyperconjugation mechanism [8]. Comparing the π parameters obtained for phosphine and amine substituted complexes we consequently assume the π parameter to increase algebraically with increasing π withdrawal capacity of the ligand under study. So it is seen that carbon monoxide is the best π acceptor, as is generally accepted and further that nitriles possess a small but real ability to accept π electrons in competition with CO groups. A similar conclusion has been drawn by Cotton on the basis of force constants alone [9]. Finally the π parameters indicate the phosphite ligands to be better acceptors than the phosphines.

With the aim of comparing the behaviour of phosphine and nonphosphine ligands in *trans*-$L_2BrMn(CO)_3$ complexes we tried to prepare compounds where L is an aliphatic or heterocyclic amine. Our attempts, however, were not successful. On grounds of their infrared absorption spectra the corresponding *fac*-isomers were obtained. Even upon heating no rearrangement to the *trans*-structure occurred as was the case for the phosphine complexes. In surveying the literature on manganese tricarbonyl halides no *trans*-isomers containing nonphosphine ligands were found either.

Experimental

The starting materials $Mn(CO)_5X$ were synthesized using procedures known in the literature [10]. The compounds $L_2XMn(CO)_3$ are prepared by the direct reaction between the ligand and the manganese pentacarbonyl halide. 0.1 g carbonyl halide was heated to 90 °C under reduced pressure with a tenfold excess of ligand. Heating was continued until the CO evolution ceased (*ca.* 1 hr). Except when using triphenyl stibine or amines *trans*-isomers are obtained. The spectra were recorded on chloroform solutions in the presence of excess ligand with a Perkin Elmer Model 225 double beam grating spectrometer.

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