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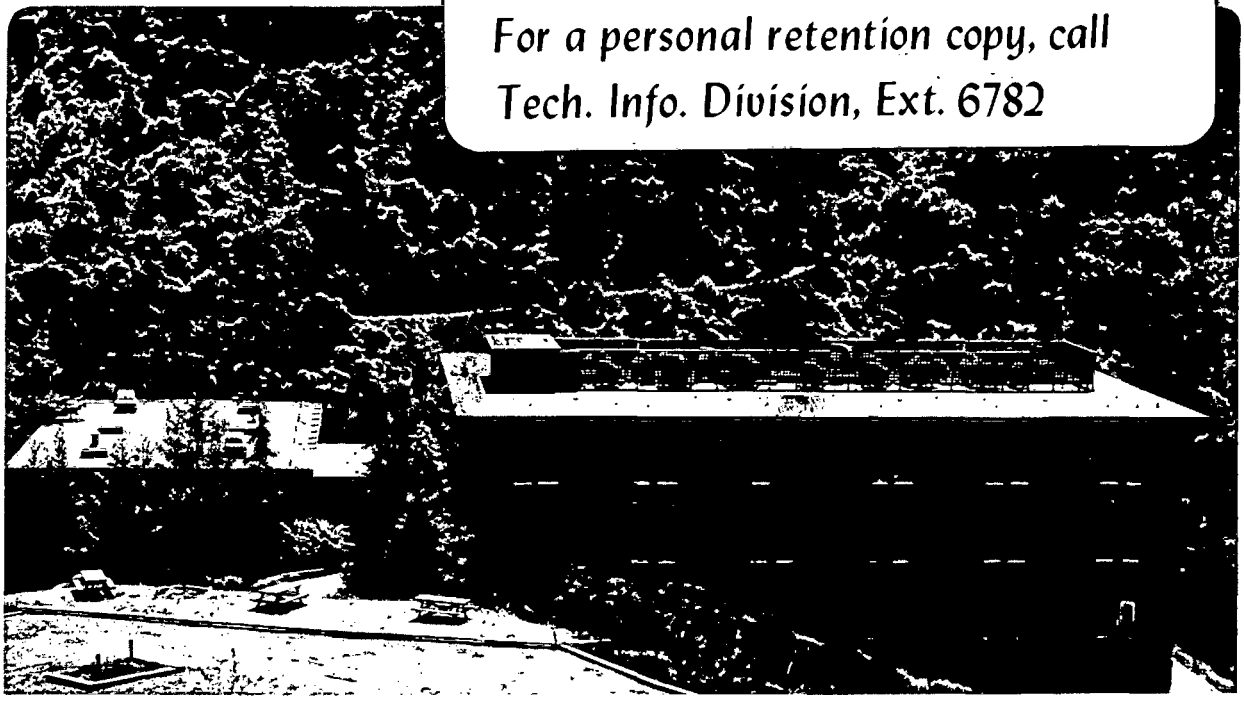

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An XPS Study of the σ- and π-Allyl Groups

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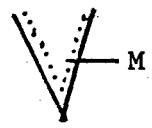
The allyl group is a commonly encountered ligand in organometallic reactions[1] and catalytic processes.[2] The ligand is of particular interest because it can engage in either η^1 or η^3 bonding to a transition metal; that is, it can be either σ-bonded, $CH_2{=}CH{-}CH_2{-}M$, or π-bonded,



In this gas phase XPS investigation we have studied the nature of the bonding of the σ-allyl and π-allyl groups to manganese by comparing the core binding energies of $(\sigma\text{-}C_3H_5)Mn(CO)_5$ and $(\pi\text{-}C_3H_5)Mn(CO)_4$ with those of $CH_3Mn(CO)_5$, $(n\text{-}C_3H_7)Mn(CO)_5$, $Mn_2(CO)_{10}$, and $(\eta^5\text{-}C_5H_5)\text{-}Mn(CO)_3$. In a previous study of a wide variety of $LMn(CO)_5$ compounds, we observed that the manganese, carbonyl carbon and oxygen core binding energies are linearly correlated with one another.[3] Although the electronegativities and polarizabilities of the L group studied varied over a considerable range, the electronegativities of the L groups were not correlated in any obvious way with the corresponding polarizabilities. If the binding energy shifts were significantly affected by changes in both atomic charge and relaxation energy, one would expect the relative proportions of these changes to be different for the manganese, carbonyl carbon, and oxygen atoms, and therefore that the binding energy shifts would not be linearly related. Hence we believe that those results indicate that the binding energy shifts in such closely related compounds are mainly due to changes in atomic charges and that changes in electronic relaxation energy are relatively small. This conclusion is supported by

the general observation that calculated relaxation energies for an atom are similar when the bonding environments of the atom are similar.[4] Therefore in this study we shall generally interpret core binding energy shifts in terms of changes in atomic charge.

The only previous XPS study of the allyl group of which we are aware involved solid complexes containing the $(\pi\text{-}C_3H_5)Mo(CO)_2$ moiety.[5] Peaks due to the C_3H_5 group were not deconvoluted, and study of the bonding of the allyl group was not the main thrust of the study.

A typical carbon 1s spectrum, that of $(\pi\text{-}C_3H_5)Mn(CO)_4$ (Figure 1), shows, from left to right, shake-up, carbonyl carbon, and allyl carbon bands. Although there are two stereochemically distinct types of carbon atom in the π-allyl ligand, resolution was inadequate to justify deconvolution of the allyl carbon 1s band into two lines. Similarly, neither the σ-allyl nor n-propyl carbon 1s bands were deconvolutable.

The binding energy data are given in Table I, where we have listed the manganese compounds in order of decreasing Mn $2p_{3/2}$ binding energy. Almost without exception, the ordering of the carbonyl C 1s and O 1s binding energies is the same as that of the corresponding Mn $2p_{3/2}$ binding energies. That is, the charge on a carbonyl group is essentially a measure of the charge on the manganese atom to which it is attached.

The binding energies of $Mn_2(CO)_{10}$ may be taken as characteristic of an $Mn(CO)_5$ group attached to a ligand with no charge. Because the

manganese and carbonyl groups of the methyl, n-propyl, and σ-allyl compounds have higher binding energies than those of $Mn_2(CO)_{10}$ (corresponding to positively charged $Mn(CO)_5$ groups in the former compounds), we conclude that the organic ligands have net negative charges. Indeed, if we interpret the manganese and carbonyl data of Table 1 with the potential equation

$$\Delta E_B(A) = \left\langle \frac{1}{r} \right\rangle \Delta Q_A + \Delta \sum_{B \neq A} (Q_B/R_{AB})$$

(assuming zero relaxation energies), we estimate net charges of -0.14, -0.07, and -0.07 for the methyl, propyl, and σ-allyl groups, respectively.[6,7,8] The organic ligand C 1s binding energies of the n-propyl and σ-allyl compounds are considerably higher than that of the methyl compound partly because of a more negative charge on the methyl group, and partly because the measured binding energies of the former compounds are the weighted averages for three carbon atoms and, to some extent, the negative charges of those groups are spread over all the atoms of the groups.

It is remarkable that the manganese and carbonyl binding energies of the n-propyl and σ-allyl compounds are essentially identical, whereas the C 1s binding energy for the σ-allyl group is 0.47 eV lower than that for the n-propyl group. We believe this difference can be accounted for in terms of an unusually large relaxation energy associated with the ionization of the terminal carbon atom of the σ-allyl group. Core ion-

ization of the terminal carbon would yield a species which can be well represented by the following equivalent-cores formula, in which a full unit of formal negative charge has been withdrawn from the $Mn(CO)_5$ group:

$$H_2N\text{-}CH{=}CH_2 \quad Mn(CO)_5^{+}$$

No such extraordinary relaxation would be expected for the terminal carbon atom of the n-propyl group. In that case, a reasonable equivalent-cores formula of the core-ionized species has the positive formal charge on the terminal atom:

$$H_3\overset{+}{N}\text{-}CH_2\text{-}CH_2\text{-}Mn(CO)_5$$

This explanation is supported by calculations of the C 1s relaxation energies using the transition state concept and CNDO/2 wavefunctions.[9] The terminal carbon of the σ-allyl group is calculated to have a relaxation energy 0.75 eV greater than that of the terminal carbon of the n-propyl group, whereas the carbon atoms attached to the Mn atom are calculated to have relaxation energies differing by only 0.02 eV.

The relatively high binding energies of the carbon atoms in the hydrocarbons propene and ethane (see Table I) are consistent with negative charges on the σ-bonded organic ligands in the $Mn(CO)_5$ complexes, but in these cases the assumption regarding relaxation energy is less valid.

In the case of $(\pi\text{-}C_3H_5)Mn(CO)_4$, there are only four carbonyl groups withdrawing electron density from the manganese atom; thus the manganese atom and carbonyl groups have greater electron densities than they have in the $LMn(CO)_5$ compounds. In spite of the more negative charge on the manganese atom in $(\pi\text{-}C_3H_5)Mn(CO)_4$, the $\pi\text{-}C_3H_5$ group has a considerably lower electron density than the $\sigma\text{-}C_3H_5$ group in $(\sigma\text{-}C_3H_5)Mn(CO)_5$. This result is undoubtedly due to the fact that the $\pi\text{-}C_3H_5$ group is formally a 3-electron donor, whereas the $\sigma\text{-}C_3H_5$ group is formally a 1-electron donor. The actual net charge on the $\pi\text{-}C_3H_5$ group is probably close to zero; it is clear from the data that back-bonding to a $\pi\text{-}C_3H_5$ group is much less than to a CO group. The data for $(\eta^5\text{-}C_5H_5)Mn(CO)_3$ show that, when one removes another CO group and goes to an aromatic 5-electron donor group, the manganese atom and carbonyl groups become even more negatively charged and the organic ligand carbon atoms have lower electron density. It is not surprising (in view of the strong π-acceptor character of the carbonyl groups) that the C 1s binding energy of the C_5H_5 group in $(\eta^5\text{-}C_5H_5)Mn(CO)_3$ is higher than that in $(\eta^5\text{-}C_5H_5)_2Mn$ (290.31 eV) or $(\eta^5\text{-}C_5H_5)_2Fe$ (290.03 eV).[10] Indeed, the C 1s binding energy of the C_5H_5 group in $(\eta^5\text{-}C_5H_5)Mn(CO)_3$ is higher than that of benzene (290.42 eV).[11] The relaxation energy associated with the C 1s ionization of $(\eta^5\text{-}C_5H_5)Mn(CO)_3$ is probably greater than that for benzene, and so it seems certain that the C_5H_5 group bears a positive charge in this complex.

Experimental

Spectra were obtained in the gas phase using a GCA/McPherson ESCA 36 spectrometer and Mg Kα x-rays. The Ne 1s, N 1s of N_2, and Ne 2s lines served as calibration standards.[12] The general procedures have been described previously.[13] Spectra were fit to Gaussian/Lorentzian lineshapes using the non-linear least-squares program CURVY.[14]

The compounds $CH_3Mn(CO)_5$, $(\sigma\text{-}C_3H_5)Mn(CO)_5$, $(\pi\text{-}C_3H_5)Mn(CO)_4$, and $(\eta^5\text{-}C_5H_5)Mn(CO)_3$ were synthesized according to literature procedures,[15-18] and the preparative procedure for $(n\text{-}C_3H_7)Mn(CO)_5$ was adapted from that of a similar compound.[19] The purity of each compound was verified by infrared and/or NMR spectroscopies, as well as melting point determinations where appropriate.

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orbital was used, and for oxygen, the value for an orbital with 20% s character was used. For manganese, the (1/r) value was taken to be that for carbon times the ratio of covalent radii of carbon and manganese, 23.0 (0.77/1.18) = 15.0. The covalent radius for manganese was obtained by subtracting the covalent radius of double-bonded carbon (0.67 Å) from the metal-carbon distance in $HMn(CO)_5$ (1.85 Å).

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Table I. Core Binding Energies (eV)

compound	Mn $2p_{3/2}$	carbonyl groups C 1s	carbonyl groups O 1s	C 1s (organic ligand)
$CH_3Mn(CO)_5$ [a]	647.30(5) [b]	293.62(7) [b]	539.91(7) [b]	289.5(1) [b]
$(n\text{-}C_3H_7)Mn(CO)_5$	647.13(2)	293.44(7)	539.89(4)	290.32(11)
$(\sigma\text{-}C_3H_5)Mn(CO)_5$ [a]	647.13(3)	293.47(4)	539.82(3)	289.85(3)
$Mn_2(CO)_{10}$ [a]	647.01(3)	293.28(3)	539.57(7)	
$(\pi\text{-}C_3H_5)Mn(CO)_4$	646.80(4)	293.03(4)	539.41(4)	290.44(6)
$(\eta^5\text{-}C_5H_5)Mn(CO)_3$	646.72(3)	292.30(7)	538.90(5)	290.85(3)
$CH_3CH{=}CH_2$				290.68(4)
C_2H_6 [c]				290.74

[a] Reference 3. [b] The uncertainty in the last digit, estimated as twice the standard deviation determined by the least-squares fit, is indicated parenthetically. [c] Perry, W. B.; Jolly, W. L. Inorg. Chem. 1974, 13, 1211.

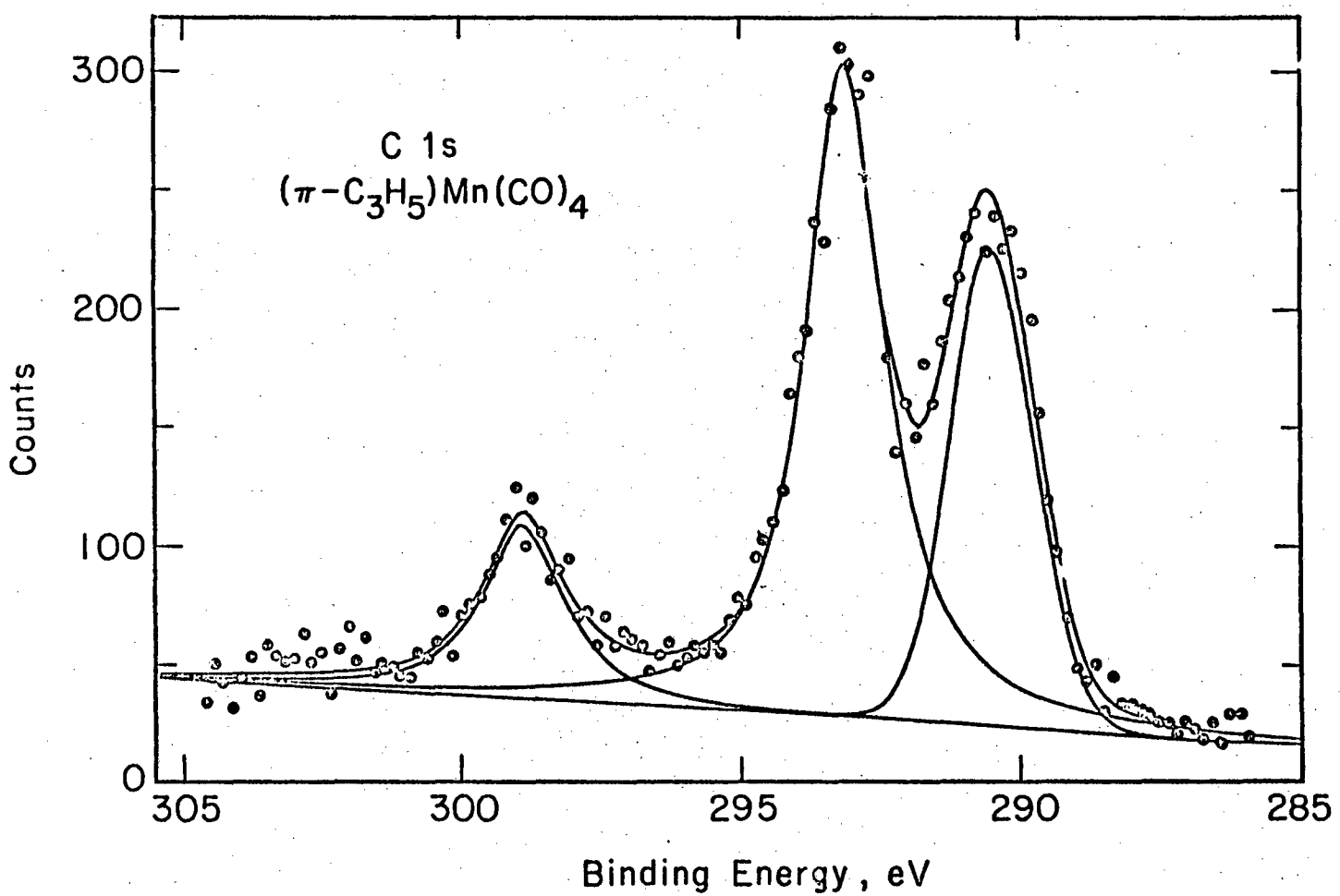

Figure 1. Carbon 1s spectrum of $(\pi\text{-}C_3H_5)Mn(CO)_4$, showing shake-up, carbonyl carbon, and allyl carbon bands.

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