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THE SEPARATION OF SIGMA AND PI BONDING
PARAMETERS FOR LIGANDS IN COMPOUNDS OF THE
TYPE $LMn(CO)_5$ AND $LMo(CO)_5$

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DISCLAIMER

The Separation of Sigma and Pi Bonding

Parameters for Ligands in Compounds of the

Type LMn(CO)$_5$ and LMo(CO)$_5$

<u>Sir</u>:

The nature of the bonding between low-oxidation state transition

metal atoms and ligands such as phosphines, olefins, carbon monoxide, etc.

remains controversial.[2] In the case of phosphines, for example, the metal-

phosphorus bonds have been characterized as principally σ bonds[3-5] or as

synergic combinations of σ and π bonds.[6-9] In compounds such as $L_xM(CO)_y$,

the effects of changing the group L on the C-O stretching force constants

have been explained entirely in terms of π bonding,[10,11] entirely in terms

of σ bonding,[12,13] or in terms of both σ and π bonding.[14-17] Graham[17] has

attempted to establish the relative σ and π acceptor abilities of various

ligands in the compounds LM(CO)$_5$, where M = Mn and Mo, by an ingenious

analysis of the C-O force constants of the cis and trans CO groups. He

assumed a commonly accepted model, that is, that replacement of L by a

more σ-withdrawing group causes the positive charge on the metal atom to

increase and consequently causes the metal dπ orbitals to contract and the

backbonding to the CO groups to decrease. The effect on backbonding of

this change in the metal atom charge was assumed to be isotropic; that is,

the cis CO groups were assumed to be affected the same as the trans CO

group. The model also involved the assumption that replacement of L by a

more π-withdrawing ligand causes a shift of electron density from the π*

CO orbitals through the metal dπ orbitals to the new ligand. The trans

CO group shares two dπ orbitals with L, whereas each cis CO group shares

only one dπ orbital with L. Hence it was assumed that the effect of the change in the π-acceptor character of L on the trans CO group is twice as great as that on the cis CO group. On the basis of this model, Graham postulated that the changes in the σ- and π-acceptor abilities of a ligand, $\Delta\sigma$ and $\Delta\pi$, are related to the C-O force constant changes, Δk_{cis} and Δk_{trans}, by the following equations

$$\Delta k_{cis} = \Delta\sigma + \Delta\pi \qquad (1)$$

$$\Delta k_{trans} = \Delta\sigma + 2\Delta\pi \qquad (2)$$

The σ and π parameters calculated from force constant data using these relations can be rationalized with ordinary chemical experience only to a limited extent. Some of the trends and relative values are quite unreasonable. For example, the π value for $(CH_3)_3Sn$ is much greater than that for Cl_3Sn, whereas both theoretical considerations and structural data suggest that the Cl_3Sn group is a better π-acceptor than the $(CH_3)_3Sn$ group.[18] The π value for CF_3 is considerably lower than that for H, implying that CF_3 is a π-_donor_, whereas structural[19] and spectroscopic[20] data suggest that it may be a π-_acceptor_. The σ values for CO and PF_3 are similar to those for basic amines such as cyclohexylamine and piperidine, whereas the former compounds are generally classified as very weak bases. These and other irrational features of the σ and π values should not be taken as evidence against the idea of the separability of σ- and π-acceptor abilities of ligands; we believe that the irrational features are due to a poor choice of equations relating σ and π to k_{cis} and k_{trans} (equations 1 and 2). Let us reconsider the derivation of these relations.

First, consider the effects of increasing the σ-withdrawing strength of L. The backbonding to all the CO groups should tend to decrease, for the reason that we have already discussed. However, in the case of the trans CO group, this tendency is opposed by a rehybridization of the metal's bonding orbitals. When L is made more electronegative, the hybrid metal orbital directed toward L should increase in p character and decrease in s character. Because the p orbital involved is shared only with the trans CO group, the hybrid orbital directed toward the trans CO group should decrease in p character and increase in s character. Consequently, to achieve maximum orbital overlap, the σ donor orbital of the trans CO is expected to increase in s character, and the orbitals involved in the C-O σ bond are expected to decrease in s character.[3,21,22] The resulting weakening of the C-O σ bond tends to cancel the strengthening of the C-O π bond associated with the decrease in backbonding. Consequently back-bonding to the trans CO group is determined mainly by the π-acceptor or π-donor ability of L.

Second, consider the effects of changing L on the π-bonding in the complex. The argument that the change in backbonding to the trans CO group should be about twice as great as that to a cis CO group does not take account of the fact that the two lobes of a metal dπ orbital which overlap with a π orbital on L also overlap with the π* orbitals of cis CO groups. That is, even a relatively weak π-acceptor orbital on L can share some electron density with a π* orbital on a cis CO group, as crudely shown by the following MO representation.

Similarly, a π-donor L can cause a shift of electron density from a cis CO to the metal dπ orbital.

The effect of these three-center interactions is to cancel part of the π-withdrawing or π-donating character of L with respect to the cis CO groups; that is, electron withdrawal from the π^* orbital of a cis CO to a π-acceptor L is reduced, and shift of electron density to the π^* orbital of a cis CO from a π-donor L is reduced. Consequently backbonding to the cis CO groups is determined principally by the σ-acceptor ability of L.

If the cancellations were complete, we could equate Δk_{trans} to π and Δk_{cis} to σ. Indeed, this procedure yields σ and π parameters which are

more reasonable than those of Graham. However by trial we have found that the following relations give parameters (designated σ' and π' to distinguish them from Graham's σ and π) which are even in closer accord with chemical intuition.

$$\Delta k_{cis} = \Delta\sigma' + \Delta\pi'/2$$

$$\Delta k_{trans} = \Delta\sigma'/3 + 2\Delta\pi'$$

The calculated values of σ' and π' are given in Tables I and II. Notice that the previously mentioned irrational features of the σ and π values have disappeared. It is significant that the π' values for CF_3, $(CH_3)_3Sn$ and H are practically identical, whereas the σ' values are quite different and have relative magnitudes consistent with the electronegativities of these groups. This result may be interpreted as evidence that the different behavior of these three groups in coordination compounds must be ascribed to differences in the σ bonding of the groups. The properties[19,20] which have been ascribed to metal-CF_3 π bonding may simply be due to rehybridization of the carbon orbitals, i.e. increased s character in the bond to the metal and increased p character in the bond to the fluorine atoms. The π' value for CH_3 is comparable to that for the halogens, indicating that this group can act as a π-donor, as shown by the resonance structures
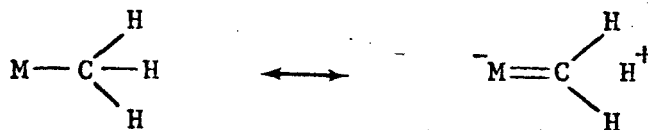
It is satisfying that, in Table II, the lowest σ' values are those of organic phosphines, phosphites, and amines, all of which are recognized as strong

σ donors. The highest σ' and π' values are those of PF₃ and CO, acknowledge
to be very weak σ-donors and very strong π-acceptors.

The use of cis and trans C-O stretching force constants to quantify
the σ and π bonding characteristics of ligands seems to be a valid method.
Probably other physical measurements (or combinations of these measurements)
such as NMR,[8,23] Mössbauer spectroscopy,[24] UPS,[25-28] and XPS,[29,30] and
C-O stretching infrared band intensities,[16] can be used for the same
purpose.

References and Notes

(1)   This work was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, U. S. Department of Energy, and the National Science Foundation, Grant CHE78-03222.

(2)   For a review of concepts in this field, see A. Pidcock, Chapters 2-5 in "Transition Metal Complexes of Phosphorus, Arsenic and Antimony Ligands," C. A. McAuliffe, ed., Halstead Press, John Wiley, New York, 1973.

(3)   R. Mason and D. W. Meek, Angew. Chem. Int. Ed. Engl., 17, 183 (1978).

(4)   A. Pidcock, R. E. Richards, and L. M. Venanzi, J. Chem. Soc. (A), 1707 (1966).

(5)   L. M. Venanzi, Chem. Britain, 4, 162 (1968).

(6)   J. Chatt and R. G. Wilkins, J. Chem. Soc., 273 (1952).

(7)   J. Chatt, L. A. Duncanson, and L. M. Venanzi, J. Chem. Soc., 4456 (1955).

(8)   S. O. Grim and D. A. Wheatland, Inorg. Chem., 8, 1716 (1969).

(9)   F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 3rd ed., Interscience, 1972, pp. 719-721.

(10)   W. D. Horrocks, Jr. and R. C. Taylor, Inorg. Chem., 2, 723 (1963).

(11)   F. A. Cotton, Inorg. Chem., 3, 702 (1964).

(12)   R. J. Angelici and M. D. Malone, Inorg. Chem., 6, 1731 (1967).

(13)   M. Bigorgne, J. Inorg. Nucl. Chem., 26, 107 (1964).

(14)   R. Poilblanc and M. Bigorgne, Bull. Soc. Chim. France, 1301 (1962).

(15)   L. S. Meriwether and M. L. Fiene, J. Am. Chem. Soc., 81, 4200 (1959).

(16)   D. J. Darensbourg and T. L. Brown, Inorg. Chem., 7, 959 (1968).

(17)   W. A. G. Graham, Inorg. Chem., 7, 315 (1968).

(18)   J. F. Young, Adv. Inorg. Chem. Radiochem., 11, 91 (1968).

(19)   M. R. Churchill and J. P. Fennessey, Inorg. Chem., 6, 1213 (1967).

(20)   F. A. Cotton and J. A. McCleverty, J. Organometal. Chem., 4, 490 (1965).

(21) C. A. Coulson, "Valence," Oxford Univ. Press, New York, 1952, p. 199.

(22) H. A. Bent, Chem. Revs., 61, 275 (1961).

(23) G. W. Parshall, J. Am. Chem. Soc., 88, 704 (1966).

(24) G. J. Long, D. G. Alway, and K. W. Barnett, Inorg. Chem., 17, 486 (1978).

(25) S. Evans, J. C. Green, M. L. H. Green, A. F. Orchard, and D. W. Turner, Discuss. Faraday Soc., No. 47, 112 (1969).

(26) M. A. Weiner and M. Lattman, Inorg. Chem., 17, 1084 (1978).

(27) H. Daamen and A. Oskam, Inorg. Chim. Acta, 26, 81 (1978).

(28) H. Daamen, G. Boxhoorn, and A. Oskam, Inorg. Chim. Acta, 28, 263 (1978).

(29) W. L. Jolly, S. C. Avanzino and R. R. Rietz, Inorg. Chem., 16, 964 (1977).

(30) H. Binder and D. Sellmann, Z. Naturforsch., 33b, 173 (1978).

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Table I.

σ' and π' Parameters from $LMn(CO)_5$ Complexes

L	σ'	π'
$(C_6H_5)_3Sn$	0.08	0.37
Cl_3Si	0.24	0.35
Cl_3Sn	0.44	0.35
Br_3Sn	0.37	0.34
Cl_3Ge	0.51	0.33
$(CH_3)_2ClSn$	−0.32	0.27
$(CH_3)_2ISn$	−0.34	0.26
$C_6H_5(C_6F_5)_2Sn$	−0.04	0.26
$(C_6H_5)_2C_6F_5Sn$	−0.22	0.26
$(CH_3S)_3Sn$	−0.08	0.25
$(C_6H_5)_2ClSn$	−0.10	0.25
$C_6H_5Cl_2Sn$	0.17	0.25
CF_3CO	0.41	0.22
CH_3Cl_2Sn	0.20	0.22
$(C_6H_5S)_3Sn$	0.06	0.21
CH_3Cl_2Si	0.14	0.20
CF_3	0.60	0.17
$(C_6H_5)_3Pb$	−0.36	0.16
$(C_6H_5)_3Si$	−0.32	0.16
$(CH_3)_3Sn$	−0.56	0.16
$(C_6H_5)_3Sn$	−0.36	0.16
H	0.05	0.15
$(C_6H_5)_3Ge$	−0.26	0.14
HCF_2CF_2	0.62	0.13
C_6F_5	0.60	0.09
C_6H_5	0.18	0.04
I	0.62	0.02
CH_3 (ref)	0	0
Br	0.83	−0.03
Cl	0.98	−0.06

Table II.

σ' and π' Parameters from LMo(CO)$_5$ Complexes

L	σ'	π'
PF$_3$	0.49	0.69
CO	0.49	0.65
PCl$_3$	0.43	0.61
P(OCH$_3$)$_3$	0.03	0.40
P(OC$_6$H$_5$)$_3$	0.21	0.39
P(OC$_2$H$_5$)$_3$	−0.02	0.36
Sb(C$_6$H$_5$)$_3$	0.02	0.29
P(n−C$_4$H$_9$)$_3$	−0.18	0.26
As(C$_6$H$_5$)$_3$	0.06	0.20
P(C$_6$H$_5$)$_3$	0.03	0.19
S(C$_2$H$_5$)$_2$	0.06	0.12
pyridine	0.04	0.01
cyclohexylamine	0	0
piperidine	0.04	−0.01
CH$_3$CN	0.28	−0.01
(i−C$_3$H$_7$)$_2$O	0.25	−0.26
CH$_3$HNCHO	0.26	−0.50
(CH$_3$)$_2$NCHO	0.18	−0.61