dibromomethane. Only isomer II is detectable in dibromomethane near room temperature, and higher temperatures increase the concentration of the higher energy form I. Further quantitative studies of this interesting phenomenon are contemplated; these compounds may provide an important insight into the dynamics of seven-coordination in solution.

Acknowledgment.—We thank the National Research Council of Canada for financial support.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF ALBERTA, EDMONTON, ALBERTA, CANADA

An Approach to the Separation of Inductive and Mesomeric Effects in Complexes of the Types $LMn(CO)_5$ and $LMo(CO)_5$

BY W. A. G. GRAHAM

Received July 17, 1967

It is assumed that inductive effects operating through the ligand–metal σ bond and ligand–metal π bonding are both important in determining the carbonyl stretching force constants in $LMn(CO)_5$ and $LMo(CO)_5$ molecules. It is suggested that the force constants of all carbonyl groups will change by the same amount owing to the change in inductive effect in going from one ligand to another; while the differences in π bonding between two ligands will affect the *trans* force constant twice as much as the *cis*. On this basis, scales of relative σ and π donor or acceptor character for a large number of ligands have been derived. The meaning of the σ and π parameters assigned to the ligands is discussed.

Introduction

In the interpretation of the infrared spectra and bonding of metal carbonyl derivatives, much stress has been placed on metal–ligand[1] π interaction.[2] The influence of inductive effects operating through the metal–ligand σ bond has not been explicitly considered, perhaps because it has not been possible to differentiate the σ effect from the π interaction. In surveying the current literature on metal carbonyls, however, it is difficult to avoid the conclusion that inductive effects have been relegated to a place of secondary importance.

By way of contrast, in discussions of the *trans* effect in square-planar platinum(II) complexes, both σ- and π-bonding effects are considered. Thus, it has been stated that a ligand of high *trans* effect can exert its influence by either electron release in the σ bonds or electron withdrawal in the π-coordinate bonds, the former enhancing SN1 and the latter SN2 substitution of the *trans* ligand.[3] From infrared studies of compounds of the type *trans*-$[PtLX(P(C_2H_5)_3)_2]$, Chatt and his coworkers[3] concluded that the lowering of the Pt–X stretching frequency by L was a measure of the inductive electron release by L. This approach has recently been applied to silicon–platinum derivatives of the type *trans*-$[PtX(SiCH_3(C_6H_5)_2)(P(CH_3)_2C_6H_5)_2]$, for which unusually low values of ν(Pt–X) are taken to mean that silicon has the greatest *trans* effect of inductive origin ever observed.[4]

Other spectroscopic techniques have been used to study the bonding in platinum(II) complexes. In hydrides of the type *trans*-$[PtHL(PR_3)_2]$, the *trans* effect of L has been related to both ν(Pt–H) and the chemical shift of H.[5] A particularly elegant approach was that of Parshall,[6] who attempted to discriminate between the σ-donor and π-acceptor aspects of the ligand–platinum bond by an adaptation of the ^{19}F nmr technique developed in organic chemistry by Taft and his school. In short, not only are σ and π effects both considered to be important, but there has been progress in assessing the extent to which each contributes for specific ligands.

Our attention was drawn to the role of inductive effects in metal carbonyl chemistry by the remarkable linearity of the carbonyl stretching frequencies in compounds such as $X_nR_{3-n}GeCo(CO)_4$[7] and $X_nR_{3-n}SnMn(CO)_5$[8] ($X = Cl, Br, I$; $R = CH_3, C_6H_5$) when plotted against the sum of the electronegativities of the halogens on germanium or tin. The trend to higher carbonyl frequencies with increased halogen substitution was explained[7] in terms of enhanced metal to ligand π bonding, the result of a contraction of germanium or tin d orbitals brought about by the increasing electronegativity of the substituents. Further consideration has led us to think that the ligand–metal σ bond might also be appreciably altered by the more electronegative substituents on the ligand and that such alterations could well affect the carbonyl stretching frequencies. Thus, taken as a whole, a Cl_3Sn group should be a

---

[1] We reserve the term "ligand" for the group which is not a carbonyl and designate it by the symbol L.

[2] For example, *cf.* F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, Interscience Publishers, Inc., New York, N. Y., 1966, p 728 ff.

[3] D. M. Adams, J. Chatt, J. Gerratt, and A. D. Westland, *J. Chem. Soc.*, 734 (1964).

[4] J. Chatt, C. Eaborn, and S. Ibekwe, *Chem. Commun.*, 700 (1966).

[5] J. Chatt, *Proc. Chem. Soc.*, 318 (1962); R. V. Lindsey, Jr., G. W. Parshall, and U. G. Stolberg, *J. Am. Chem. Soc.*, **87**, 658 (1965).

[6] G. W. Parshall, *ibid.*, **86**, 5367 (1964); **88**, 704 (1966).

[7] D. J. Patmore and W. A. G. Graham, *Inorg. Chem.*, **6**, 981 (1967); similar results in equally extensive series of tin–cobalt derivatives will be described in a forthcoming publication.

[8] J. A. J. Thompson and W. A. G. Graham, *ibid.*, **6**, 1875 (1967).

stronger σ-withdrawing[9] ligand than $(CH_3)_3Sn$.[10] The greater σ withdrawal from the transition metal should contract its d orbitals, thereby reducing metal to carbon monoxide π bonding and increasing ν(CO), the carbonyl stretching frequency.

The purpose of this paper is to describe an approximate method of distinguishing between π-withdrawal and σ-withdrawal effects by ligands in certain substituted metal carbonyls. Our method makes use of approximate carbonyl stretching force constants as calculated by the procedure of Cotton and Kraihanzel[12] and developed in later papers by Cotton.[13,14] We acknowledge our indebtedness to these authors, recognizing that the present paper represents in many ways an extension of the concepts advanced by them.

Results and Discussion

Since the Cotton–Kraihanzel (CK) approximate force constant method was devised in 1962,[12] it has been applied to a large number of metal carbonyl derivatives. In this paper, we consider only pentacarbonyl derivatives of manganese (such as $Cl_3SnMn(CO)_5$) and molybdenum (such as $(C_6H_5)_3PMo(CO)_5$); as election of CK force constants calculated from the best available infrared data will be given subsequently. In these octahedral $LM(CO)_5$ molecules, k_1 is the stretching force constant of the carbonyl group *trans* to L, while k_2 is the stretching force constant for carbonyl groups *cis* to L.

We now set down some assumptions which make possible an ordering of ligands in terms of σ- and π-withdrawing properties. Suppose that we wish to compare the metal–ligand bonding in two compounds $LM(CO)_5$ and $L'M(CO)_5$ involving different ligands.

(1) When force constants for the two compounds are compared, the differences ($\Delta k_1 = k_1' - k_1$ and $\Delta k_2 = k_2' - k_2$) will be due to the combined effect of the difference in the σ-inductive properties of the ligands ($\sigma' - \sigma = \Delta\sigma$) and the difference in their π-acceptor properties ($\pi' - \pi = \Delta\pi$).

(2) *The inductive property of a given ligand is assumed to operate equally on all five carbonyl groups.* Viewed as a process of inducing a charge on M, it should operate in isotropic fashion. Thus, for the σ-inductive portion only of the over-all change in force constants, one can write $\Delta k_1 = \Delta\sigma$ and $\Delta k_2 = \Delta\sigma$.

This assumption may seem inconsistent with the explanation usually given for the inductive *trans* effect in platinum(II) complexes.[15] In that case, the inductive effect is viewed as an electrostatic mutual polarization process which weakens the bond to the *trans* ligand *without affecting* the *cis* ligands. Irrespective of the merits of this polarization theory for platinum(II) complexes, the $LM(CO)_5$ compounds are members of quite a different class; they are less polar, making an electrostatic theory less appropriate, and they are octahedral, a situation in which the classical *trans* effect is less well established. Moreover, we are examining quite different properties in the two classes of compounds. Carbonyl stretching frequencies are usually considered to be determined mainly by π bonding with the metal.[16] This depends on the energy of the metal d_π orbitals, which is in turn largely dependent on the net charge on the metal. To a first approximation, changes in the L–M σ bond influence carbonyl frequencies *indirectly* by altering the net charge on the metal atom; within the same approximation, the three d_π orbitals will be equally affected, as required under the above assumption.

Although a rigorous justification of this assumption has never been offered, it appears to be a reasonable one. Cotton has earlier suggested that both k_1 and k_2 should have the same dependence on the inductive factor.[14,17]

(3) *The change in the π-acceptor property ($\Delta\pi$) in going from L to L' will affect Δk_1 more than Δk_2 by a factor of 2.* Thus, for the π-inductive portion of the over-all change in force constants, $\Delta k_1 = 2\Delta\pi$ and $\Delta k_2 = \Delta\pi$.

This assumption is made for exactly the same reason that, in dealing with carbonyl stretching interaction constants, the CK treatment[12] took $k_{trans} = 2k_{cis}$. The carbonyl group *trans* to L in $LM(CO)_5$ (to which k_1 refers) interacts with two π orbitals of L *via* two d_π orbitals of M, whether the π orbitals of L are of p or d type. Reference to Figure 1 and Table I will make clear the possible π interactions.

On the other hand, the antibonding orbitals of carbonyl groups *cis* to L can interact with L only through a single d_π orbital of M.[18] Thus it is reasonable that the *cis* carbonyls will feel a given change in the π-acceptor capability of the ligand only half so strongly.

(4) For the *over-all* changes in force constants that result from changing ligands, we have: $\Delta k_1 = \Delta\sigma + 2\Delta\pi$ and $\Delta k_2 = \Delta\sigma + \Delta\pi$. These simple equations can be solved in terms of experimental Δk's to yield $\Delta\sigma$ and $\Delta\pi$, the difference in the σ- and π-bonding parameters of the two ligands. By choosing one compound as reference and determining all of the Δ values relative to it, a scale of relative σ and π parameters can be set up.

---

(9) Or, synonymously, a poorer σ donor.

(10) One might conveniently think of this in terms of Bent's rule,[11] whereby halogen substituents would permit a higher proportion of s character in the hybrid tin σ orbital directed to the transition metal; the tin would then be a more electronegative ligand as far as the transition metal is concerned.

(11) H. A. Bent, *Chem. Rev.*, **61**, 290 (1961).

(12) F. A. Cotton and C. S. Kraihanzel, *J. Am. Chem. Soc.*, **84**, 4432 (1962).

(13) C. S. Kraihanzel and F. A. Cotton, *Inorg. Chem.*, **2**, 533 (1963).

(14) F. A. Cotton, *ibid.*, **3**, 702 (1964).

(15) F. Basolo and R. G. Pearson, *Progr. Inorg. Chem.*, **4**, 417 (1962).

(16) The σ bond in which carbon monoxide donates a lone pair to the metal also influences ν(CO), as mentioned by G. R. Dobson, *Inorg. Chem.*, **4**, 1673 (1965). The contribution of this effect to the net frequency change when free CO becomes bonded to a metal is unknown at present. Changing the inductive character of L could influence ν(CO) by altering the M–CO σ bond, representing a transmission solely through σ bonds. This σ transmission may well be approximately isotropic, in line with the assumption. In any case, one suspects that this transmission mechanism will make a relatively small contribution in view of the rapid diminution of the σ inductive effect with distance that is found in organic chemistry: J. N. Murrell, S. F. A. Kettle, and J. M. Tedder, "Valence Theory," John Wiley and Sons, Inc., New York, N. Y., 1965, p 296.

(17) In a paper which appeared after the submission of this work, F. A. Cotton and R. M. Wing, *J. Organometal Chem.* (Amsterdam), **9**, 511 (1967), have restated this view in terms very similar to our own: "A purely inductive effect would be isotropic."

(18) It is assumed that M–L interaction *via* a δ bond between d_{xy} orbitals of M and L is negligible, since this would permit the π_x^* or π_y^* orbitals of the *cis* CO groups to interact with L. We thank Dr. S. F. A. Kettle for pointing this out.

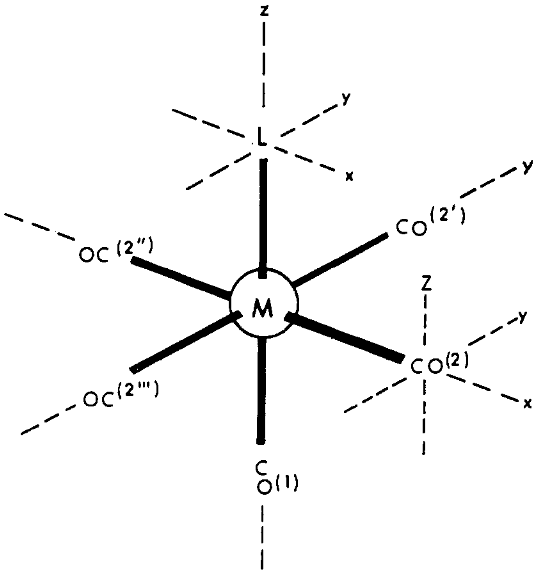


Figure 1.—Coordinates used to label orbitals in Table I.

TABLE I

LIGAND–CO π INTERACTIONS IN LM(CO)$_5$ COMPOUNDS[a]

Ligand	Metal	CO$^{(1)}$	CO$^{(2)}$	CO$^{(2')}$	CO$^{(2'')}$	CO$^{(2''')}$
d_{xz} or p_x	d_{xz}	$\pi_x{}^*$	$\pi_z{}^*$	. . .	$\pi_z{}^*$	. . .
d_{yz} or p_y	d_{yz}	$\pi_y{}^*$	. . .	$\pi_z{}^*$	. . .	$\pi_z{}^*$

[a] Labeling of axes and CO groups is shown in Figure 1. π^* represents the antibonding orbital of a CO group.

For compounds LMn(CO)$_5$, we have chosen CH$_3$Mn(CO)$_5$ as the reference compound; for the series LMo(CO)$_5$, we have chosen C$_6$H$_{11}$NH$_2$Mo(CO)$_5$ as reference.

Before discussing the σ and π parameters in each of these series, some comment on the CK force constants is necessary. Our concern is not with the *absolute* accuracy of the CK values, but with the validity of trends in related series of compounds. Cotton has stated[14] that *differences* in force constants in series of the same structural type should have "rigorous significance." Jones[19] has concluded that the approximate force constants "are in the right ball park and certainly trends among similar compounds (such as M(CO)$_5$L and M(CO)$_5$L') are meaningful." Although Cotton suggested[13,14] that the probable uncertainty in CK force constants was at least ±0.1 mdyn/Å, we have carried out all calculations here to the second decimal. We defend this policy on several grounds. First, and this applies particularly to the pentacarbonylmanganese derivatives of Table II, the spectra were obtained under the most favorable conditions in cyclohexane solution and band positions are known to within ± 1 cm^{-1}. Additive errors of 1 cm^{-1} in each of the three bands used in the CK calculation change the values of k_1 and k_2 by only about 0.02 unit in a typical case.[20] Thus, the *experimental* precision in determining the force constants is high, and the concomitant experimentally imposed uncertainties are ± 0.08 for π and ± 0.12 for the σ parameter.

Second, it is precisely those compounds with similar force constants that are most closely related, and hence those for which small differences are most likely to have significance.

Third, much more exact force constant calculations have been carried through by Kaesz and his coworkers for several pentacarbonylmanganese derivatives.[21] When these values are used (plotted as filled triangles in Figure 2 for L = H, CH$_3$, Cl, Br, I), essentially similar trends are noted.

Finally, rounding the force constants to 0.1 mdyn/Å would obscure some interesting and reasonable fine structure of Figure 2. The major trend in the σ and π parameters nonetheless survives an uncertainty of 0.1 mdyn/Å in the force constants.

Pentacarbonylmanganese Derivatives, LMn(CO)$_5$.—In Table II we give force constants and derived σ and π parameters for 31 compounds of the type LMn(CO)$_5$. The compounds are ordered in terms of decreasing π parameter in Table II and represented in graphic form in Figure 2. A broad range of ligand types is encompassed, from halides and organic groups to metals and metalloids.

It is apparent that algebraically increasing values of the π parameter are associated with increasing π-electron withdrawal by L, negative values implying that L is a π donor relative to the standard. Thus, the Cl$_3$Sn ligand ($\pi = 0.31$) is a π acceptor, while chlorine ($\pi = -0.57$) is a π donor, both conclusions in harmony with those reached for platinum(II) complexes by other means.[6] Considering next the σ parameter (the abscissa of Figure 2), it is evident that ligands tending to raise force constants (*i.e.*, the strong σ-withdrawing groups) are characterized by large positive values (*e.g.*, for Br, $\sigma = 1.03$), while the more electropositive ligands, for which one would expect little σ withdrawal, have large negative values (*e.g.*, (CH$_3$)$_3$Sn, $\sigma = -0.84$).

Another general feature of Figure 2 is that most of the compounds tend to lie in the upper left or lower right quadrants; that is, ligands of the strong π-acceptor type tend to be σ donors, while strongly σ-withdrawing ligands tend to be π donors. This is perhaps a consequence of the synergic character of the metal–ligand bond, in which the drift of π electrons is assumed to be in the opposite direction to that of σ-electron density.[22] Ligands in metal carbonyl chemistry are normally regarded as σ donors and π acceptors. Relative to the standard, (CH$_3$)$_3$Sn would fall into this category; but the halogens appear to be σ acceptors and π donors. Since HMn(CO)$_5$ or CH$_3$Mn(CO)$_5$ is unlikely to involve appreciable π character in the L–Mn bond, it may be that the sense of each of the components of the bond is the opposite in the upper left region of Figure 2 (I) to what it is at the lower right (II). The idea that

---

[19] L. H. Jones, *Inorg. Chem.*, **6**, 1269 (1967).

[20] Unpublished calculations by R. S. Gay in which the partial derivatives of k_1 and k_2 with respect to the A$_1^{(2)}$, E, and A$_1^{(1)}$ band positions were numerically evaluated for typical values of the latter bands (2080, 1960, and 1945 cm^{-1}, respectively).

[21] H. D. Kaesz, R. Bau, D. Hendrickson, and J. M. Smith, *J. Am. Chem. Soc.*, **89**, 2844 (1967); P. S. Braterman, R. W. Harrill, and H. D. Kaesz, *ibid.*, **89**, 2851 (1967). We thank Professor Kaesz for making these papers available in advance of publication.

[22] This has been stressed for the M–CO bond by L. E. Orgel, "An Introduction to Transition Metal Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1960, p 137. See also ref 2.

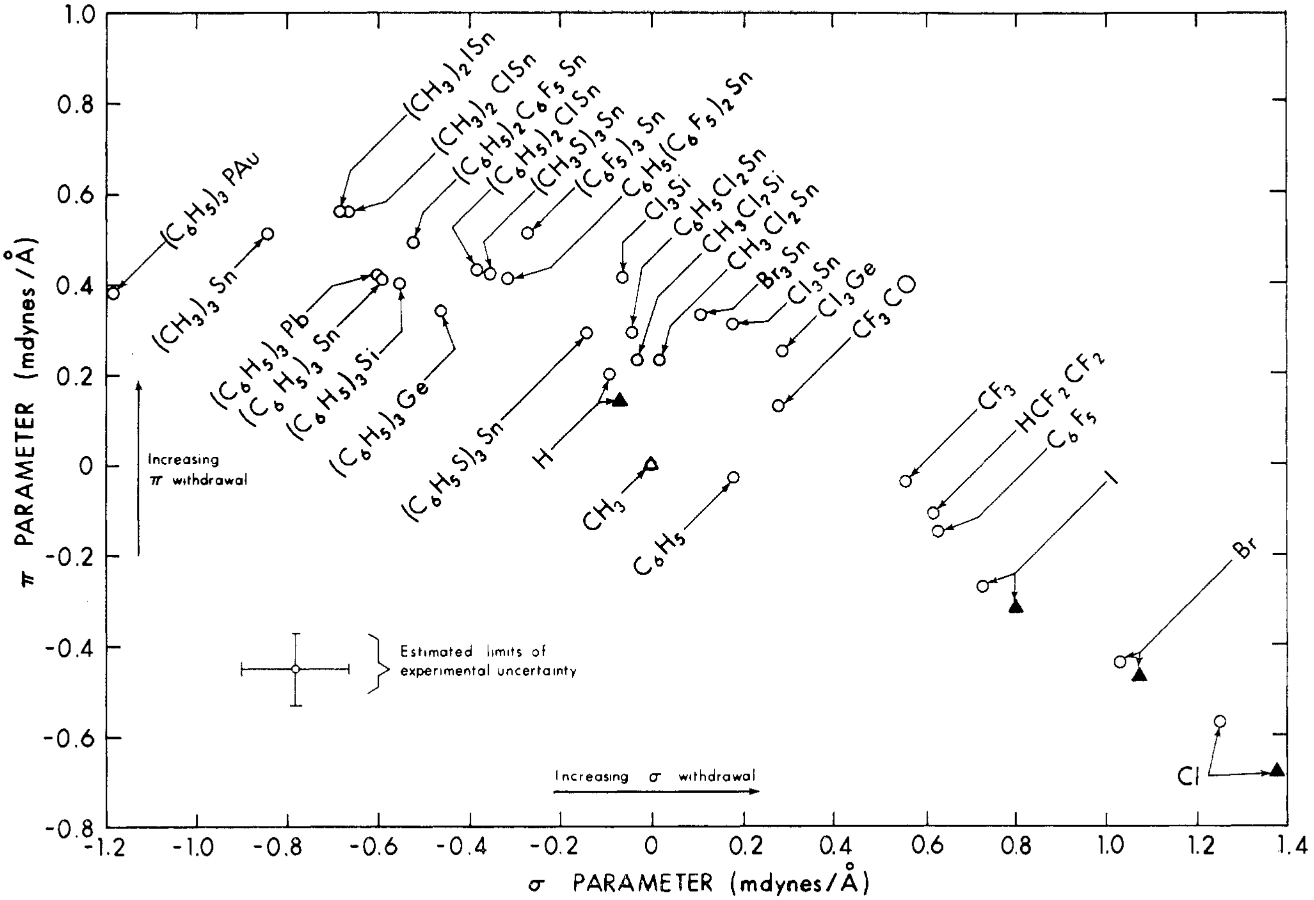
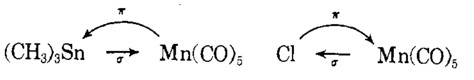


Figure 2.—Relative σ and π parameters for pentacarbonylmanganese derivatives. Points are labeled by L in $LMn(CO)_5$. Open circles based on Cotton–Kraihanzel force constants; filled triangles based on more refined force constants of Kaesz, *et al.* (ref 21). Limits shown for experimental uncertainty are those estimated for cumulative 1-cm^{-1} inaccuracies in each of the three bands used in the CK force constant calculation.



I II

$(C_6H_5)_3Si$ is among the stronger σ donors (σ = −0.55) is consistent with Chatt's conclusion, noted in the Introduction, that the $(C_6H_5)_2CH_3Si$ ligand in platinum(II) complexes has the greatest *trans* effect of inductive origin yet observed,[4] that is to say, greater than H and CH_3.

An interesting progression is observed in the series of methylchlorotin derivatives shown below.

	L			
	$(CH_3)_3Sn$	$(CH_3)_2ClSn$	CH_3Cl_2Sn	Cl_3Sn
σ	−0.84	−0.66	0.02	0.18
π	0.51	0.56	0.23	0.31

First, the increase in the σ parameter with chlorine substitution is as expected. Although differences are smaller in the π parameter, it appears not to change significantly with the first chlorine but to *decrease* with further chlorine substitution. Since chlorine substitution should contract the tin d orbitals and increase its π-acceptor character, another factor must operate. This may well be back donation from chlorine to tin, which would reduce the π-acceptor ability of tin as far as the $Mn(CO)_5$ moiety is concerned. Such a possibility has been suggested elsewhere in another context.[23]

Another indication that more than one factor is involved is the near identity of $(CH_3)_2ClSn$ and $(CH_3)_2ISn$ as ligands. Not only are the CK force constants nearly the same, but the three observed carbonyl stretching fundamentals in the chloro derivative are all just 1 cm^{-1} higher than in the corresponding iodide.[24] The previous discussion would suggest that the lower inductive effect of iodine is offset by its reduced back donation to tin.

In a previous paper, the π bonding of ligands to $Mn(CO)_5$ was discussed on the basis of k_1 alone.[25] This resulted in a somewhat different ordering; in particular, the low k_1 value for $(C_6H_5)_3PAu$ (the lowest yet observed by a margin of about 0.3 mdyn/Å) led us to suggest that this ligand was serving as a π donor. According to the present analysis, however, $(C_6H_5)_3PAu$ has a reasonably high π-acceptor capability, and the low force constants are to be attributed to a very high σ-donor property. Although the halogen-like character of the $(C_6H_5)_3PAu$ ligand has been stressed,[26] our analysis suggests that they represent opposite extremes of bond type. The

---

[23] N. Flitcroft, D. A. Harbourne, I. Paul, P. M. Tucker, and F. G. A. Stone, *J. Chem. Soc., Sect. A*, 1130 (1966).

[24] We thank Professor H. C. Clark for infrared spectra of $(CH_3)_2ISnMn(CO)_5$ and $CH_3Cl_2SnMn(CO)_5$.

[25] W. Jetz, P. B. Simons, J. A. J. Thompson, and W. A. G. Graham, *Inorg. Chem.*, **5**, 2217 (1966).

[26] C. E. Coffey, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 1741 (1964); J. Lewis and R. S. Nyholm, *Sci. Progr.*, **82**, 569 (1964).

TABLE II

σ- AND π-BONDING PARAMETERS FOR PENTACARBONYLMANGANESE COMPLEXES[a]

L in LMn(CO)$_5$	Force constants, mdyn/Å					σ,	π,
	k_1	k_2	k_1	Δk_1	Δk_2	mdyn/Å	mdyn/Å
$(CH_3)_2ClSn^b$	16.57	16.72	0.23	0.46	−0.10	−0.66	0.56
$(CH_3)_2ISn^c$	16.55	16.70	0.23	0.44	−0.12	−0.68	0.56
$(CH_3)_3Sn^b$	16.29	16.49	0.24	0.18	−0.33	−0.84	0.51
$(C_6F_5)_3Sn^d$	16.86	17.06	0.22	0.75	0.24	−0.27	0.51
$(C_6H_5)_2C_6F_5Sn^d$	16.57	16.79	0.22	0.46	−0.03	−0.52	0.49
$(C_6H_5)_2ClSn^d$	16.59	16.87	0.21	0.48	0.05	−0.38	0.43
$(C_6H_5)_3Pb$	16.35	16.64	0.22	0.24	−0.18	−0.60	0.42
$(CH_3S)_3Sn^e$	16.60	16.89	0.21	0.49	0.07	−0.35	0.42
Cl_3Si^f	16.87	17.17	0.22	0.76	0.35	−0.06	0.41
$(C_6H_5)_3Sn^b$	16.34	16.64	0.23	0.23	−0.18	−0.59	0.41
$C_6H_5(C_6F_5)_2Sn^d$	16.62	16.92	0.22	0.51	0.10	−0.31	0.41
$(C_6H_5)_3Si^b$	16.36	16.67	0.24	0.25	−0.15	−0.55	0.40
$(C_6H_5)_3PAu^b$	15.69	16.02	0.25	−0.42	−0.80	−1.18	0.38
$(C_6H_5)_3Ge^b$	16.33	16.70	0.23	0.22	−0.12	−0.46	0.34
Br_3Sn^b	16.88	17.26	0.20	0.77	0.44	0.11	0.33
Cl_3Sn^b	16.91	17.31	0.20	0.80	0.49	0.18	0.31
$C_6H_5Cl_2Sn^d$	16.65	17.07	0.21	0.54	0.25	−0.04	0.29
$(C_6H_5S)_3Sn^e$	16.55	16.97	0.21	0.44	0.15	−0.14	0.29
Cl_3Ge^f	16.90	17.36	0.21	0.79	0.54	0.29	0.25
$CH_3Cl_2Sn^c$	16.59	17.07	0.21	0.48	0.25	0.02	0.23
$CH_3Cl_2Si^g$	16.54	17.02	0.22	0.43	0.20	−0.03	0.23
H^h	16.42	16.93	0.26	0.31	0.11	−0.09	0.20
CF_3CO^i	16.65	17.23	0.24	0.54	0.41	0.28	0.13
CH_3 (ref)^j	16.11	16.82	0.25	0	0	0	0
$C_6H_5{}^j$	16.23	16.97	0.24	0.12	0.15	0.18	−0.03
$CF_3{}^i$	16.59	17.34	0.24	0.48	0.52	0.56	−0.04
$HCF_2CF_2{}^j$	16.51	17.33	0.24	0.40	0.51	0.62	−0.11
$C_6F_5{}^j$	16.44	17.30	0.23	0.33	0.48	0.63	−0.15
I^k	16.30	17.28	0.21	0.19	0.46	0.73	−0.27
Br^k	16.26	17.41	0.22	0.15	0.59	1.03	−0.44
Cl^k	16.22	17.50	0.22	0.11	0.68	1.25	−0.57

[a] Symbols are as explained in text. Reference compound is $CH_3Mn(CO)_5$. Spectra of all compounds were measured in cyclohexane. Force constants quoted by other workers have been recalculated for complete internal consistency and may therefore differ slightly from literature values. [b] W. Jetz, P. B. Simons, J. A. J. Thompson, and W. A. G. Graham, *Inorg. Chem.*, **5**, 2217 (1966). [c] H. C. Clark, personal communication; R. S. Gay, unpublished work. [d] J. A. J. Thompson and W. A. G. Graham, *Inorg. Chem.*, **6**, 1875 (1967). [e] J. A. J. Thompson and W. A. G. Graham, unpublished work. [f] W. Jetz and W. A. G. Graham, *J. Am. Chem. Soc.*, **89**, 2773 (1967). [g] W. Jetz and W. A. G. Graham, unpublished work. [h] D. K. Huggins and H. D. Kaesz, *J. Am. Chem. Soc.*, **86**, 2734 (1964). [i] Unpublished results of Mr. J. Hoyano in this laboratory. [j] Frequencies from J. B. Wilford and F. G. A. Stone, *Inorg. Chem.*, **4**, 389 (1965). [k] Frequencies from H. D. Kaesz, R. Bau, D. Hendrickson, and J. M. Smith, *J. Am. Chem. Soc.*, **89**, 2844 (1967).

similarity may lie in a high ligand–metal bond order and the difference in the sense of the σ and π components of the bonds, as discussed above.

One might have expected size effects to differentiate rather sharply a series of ligands such as $(C_6H_5)_3Si$, $(C_6H_5)_3Ge$, $(C_6H_5)_3Sn$, and $(C_6H_5)_3Pb$, but they are in fact rather closely grouped. Likewise the ligands Cl_3Si, Cl_3Ge, and Cl_3Sn are rather similar (as previously noted[27]), and the meaning of the relative orders within the series is not clear, if indeed it is significant. It might also have been expected that effects depending on the principal quantum numbers of the valence electrons of the ligand and the metal would change the pattern if pentacarbonyl*rhenium* derivatives were used, $CH_3Re(CO)_5$ being taken as the standard. However, when this is done for the approximately 15 $LRe(CO)_5$ derivatives for which reliable infrared spectra are available, an essentially similar σ–π graph results. There are some minor differences in detail relative to the $LMn(CO)_5$ graph, but the significance of these cannot be assessed at present.

The bonding of perfluoroalkyl ligands is a matter of considerable interest. It is considered[28] that the stability of these compounds is due to the combination of an inductive effect and a π withdrawal of electrons into the antibonding C–F orbitals (a $d_\pi \rightarrow \sigma^*$ bond). Observed bond shortenings[28b] and higher carbonyl stretching frequencies[28a] could be due to either or both effects, the problem being to distinguish their relative contributions. It has also been suggested that unusually low carbon–fluorine stretching frequencies in $CF_3Mn(CO)_5$ are the result of $d_\pi \rightarrow \sigma^*$ bonding.[29]

A surprising outcome of the approach adopted here is that the relative contribution of the $d_\pi \rightarrow \sigma^*$ bond in $CF_3Mn(CO)_5$ is essentially zero.[30] Emphasizing the synergic character of ligand–metal bonds, one could say that the polarity of the CF_3–Mn σ bond would tend to diminish the tendency for π bonding of the same

---

(27) W. Jetz and W. A. G. Graham, *J. Am. Chem. Soc.*, **89**, 2773 (1967).

(28) (a) F. G. A. Stone, *Endeavour*, **25**, 33 (1966); (b) M. R. Churchill and J. P. Fennessey, *Inorg. Chem.*, **6**, 1213 (1967).

(29) F. A. Cotton and J. A. McCleverty, *J. Organometal. Chem.* (Amsterdam), **4**, 490 (1965).

(30) It is difficult to know whether this result should be interpreted as casting doubt on π bonding by the CF_3 group, or whether $d_\pi \rightarrow \sigma^*$ bonding by CF_3 is sufficiently well accepted to raise questions about our approach. The matter requires further investigation.

polarity or sense. The perfluoroalkyls emerge as a unique group, showing the expected strong σ-withdrawing tendency without the disadvantage of being π donors as well. The stability of $R_fCo(CO)_4$ relative to the analogous halogen compounds (which apparently do not exist) may well be due to this factor.

The trifluoro*acetyl* derivative shows a smaller σ-withdrawing tendency and a slight π-acceptor character relative to CH_3 and CF_3. On the basis of lowered acyl carbonyl stretching frequencies, it was suggested some time ago that perfluoroacyl groups were π acceptors.[31]

Pentacarbonylmolybdenum Derivatives, $LMo(CO)_5$.—A similar treatment can be applied to pentacarbonylmolybdenum derivatives, and this has been done in Table III, with results shown graphically in Figure 3.

Table III

σ- and π-Bonding Parameters for Pentacarbonylmolybdenum Complexes[a]

L in $LMo(CO)_5$	Force constants, mdyn/Å k_1	k_2	k_i	σ, mdyn/Å	π, mdyn/Å
PF_3[b]	16.59	16.54	0.28	−0.09	0.79
CO[c]	16.52	16.52	0.27	−0.06	0.74
PCl_3	16.43	16.46	0.25	−0.09	0.71
$P(OCH_3)_3$	15.90	16.06	0.31	−0.36	0.58
$P(OC_2H_5)_3$	15.82	16.01	0.31	−0.38	0.55
$P(n\text{-}C_4H_9)_3$	15.58	15.84	0.30	−0.48	0.48
$P(OC_6H_5)_3$	15.93	16.19	0.29	−0.13	0.48
$Sb(C_6H_5)_3$	15.69	16.00	0.29	−0.27	0.43
$P(C_6H_5)_3$	15.49	15.96	0.30	−0.15	0.27
$As(C_6H_5)_3$	15.51	15.98	0.30	−0.13	0.27
$S(C_2H_5)_2$	15.35	15.94	0.30	−0.05	0.15
Cyclohexylamine	15.10	15.84	0.32	0	0
Pyridine	15.14	15.88	0.32	0.04	0.00
Piperidine	15.10	15.87	0.33	0.00	−0.03
CH_3CN[d]	15.14	16.04	0.32	0.36	−0.16
$(i\text{-}C_3H_7)_2O$[e]	14.64	15.89	0.35	0.56	−0.51
CH_3HNCHO[f]	14.16	15.78	0.35	0.82	−0.88
$(CH_3)_2NCHO$[g]	13.93	15.67	0.36	0.83	−1.00

[a] Symbols are as explained in the text; reference compound is cyclohexylamine. Except where noted, the data are unpublished results of T. L. Brown and D. J. Darensbourg, based on measurements in hexane solution. [b] Calculated from frequencies measured in hexane solution by R. J. Clark and P. I. Hoberman, *Inorg. Chem.*, **4**, 1771 (1965). [c] F. A. Cotton and C. S. Kraihanzel, *J. Am. Chem. Soc.*, **84**, 4432 (1962); the frequencies here were "best average values" from gas-phase and solution measurements which were considered to be appropriate for comparison with other spectra in nonpolar solvents. [d] Recalculated in this work from frequencies reported for a hydrocarbon solution by G. R. Dobson, I. W. Stolz, and R. K. Sheline, *Advan. Inorg. Chem. Radiochem.*, **8**, 1 (1966). [e] Calculated from frequencies measured in *isopropyl ether* solution by I. W. Stolz, G. R. Dobson, and R. K. Sheline, *Inorg. Chem.*, **2**, 323 (1963). [f] Calculated from frequencies measured in *methylformamide* solution by I. W. Stolz, *et al.*, *ibid.*, **2**, 323 (1963). [g] Calculated from frequencies measured in *dimethylformamide* solution by I. W. Stolz, *et al.*, *ibid.*, **2**, 323 (1963).

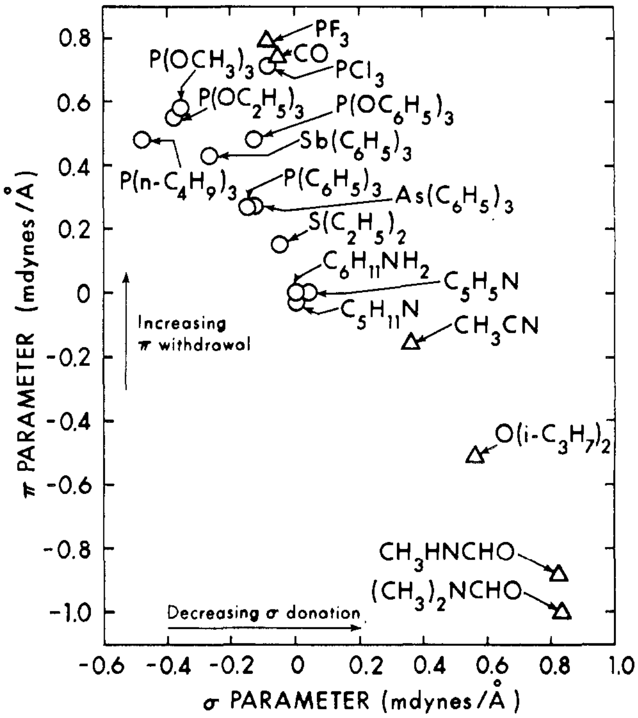


Figure 3.—Relative σ and π parameters for pentacarbonylmolybdenum derivatives. Points are labeled by L in $LMo(CO)_5$. Open circles based on data of T. L. Brown and D. J. Darensbourg. Open triangles based on other sources as noted in footnotes to Table III.

For most of the compounds, the force constant values were kindly made available by Professor T. L. Brown and Mr. D. J. Darensbourg of the University of Illinois and are based on their own unpublished measurements in hexane solution. The infrared data which are available in the literature for these compounds were frequently obtained in chloroform or other polar solvents and are not well suited for the kind of analysis we are undertaking here. For three complexes (L = isopropyl ether, methylformamide, and dimethylformamide) the only available spectra were obtained using excess ligand as the solvent; the low stability of these particular complexes makes it unlikely that spectra will ever be obtained in a hydrocarbon solvent. These results are nonetheless included because the ligands are of a unique type; it seems probable that solvent effects will not alter qualitatively the location of these ligands with respect to the others. Cyclohexylamine was taken as the reference ligand in this series, since, as already discussed, no π bonding should be possible in this case.[13]

Values of the π parameter correspond for the most part with generally accepted qualitative views. Phosphorus trifluoride and carbon monoxide are the best π acceptors, with phosphines and phosphites next. The most negative π values result for methylformamide and dimethylformamide, which have been characterized by Cotton as π donors on the basis of force constants alone.[32] Cotton, on the other hand, considered that acetonitrile functioned as a π acceptor.[14]

Examining next the σ scale of Figure 3, we anticipate that greater σ-donor character will tend to lower the

---

(31) E. Pitcher and F. G. A. Stone, *Spectrochim. Acta*, **18**, 585 (1962).

(32) In his discussion of π donation by the formamides (ref 14, pp 707–708) Cotton touches on the fractional distribution of π-electron density from the ligand between $CO^{(1)}$ and $CO^{(2)}$ (the *trans* and *cis* carbonyls, respectively). We differ from Cotton, anticipating that $^2/_6$ of the π-electron density will go to $CO^{(1)}$ and $^1/_6$ to each of the four $CO^{(2)}$ groups, for the reasons discussed under assumption (3) above.

force constants and be indicated by negative σ values. It is at once evident from Figure 3 that there is little correlation between the basicities of the free ligands and their position on the σ scale. We suggest that what the σ parameter measures is the donor property of the ligand *as it exists in the complex, modified by synergic effects.* Thus the π-acceptor portion of the Mo–CO bond would enhance donation of the normally nonbasic lone pair on the carbon atom, while the π-donor component of the Mo–OCHNR$_2$ bond would diminish the tendency of this ligand to donate its lone pair. Figure 3 shows that, in general, as in the manganese derivatives, strong π-donor ligands tend to be poor σ donors, and conversely.

It seems unlikely that the σ component of bonds involving these neutral, lone-pair donating ligands could undergo any reversal of sense as postulated for the manganese derivatives.[33] For ligands at the lower right of Figure 3, this implies that both σ and π components are tending to move electron density toward molybdenum. This is consistent with the generally low stability of such complexes and their low solubility in nonpolar solvents.

Conclusions.—In a simplified approach to a very complicated bonding situation, we have been able to proceed from a few reasonable assumptions to develop crude scales of σ and π donor–acceptor ability. The general principle, which is that carbonyl groups *cis* and *trans* to L will respond differently to changes in the σ- and π-bonding properties of the ligand, should be capable of further refinement. One obvious need is for improved carbonyl stretching force constants, and it appears that this need is being met.[21]

In general, we might expect a relation between the Δk's to have the form $\Delta k_2 = \Delta\sigma + \Delta\pi$ and $\Delta k_1 = m\Delta\sigma + n\Delta\pi$. We have taken $m = 1$ and $n = 2$, but more sophisticated considerations may suggest other values, which would of course alter the scales. Small changes in m and n, however, should not seriously alter the general ordering of ligands proposed here.

Acknowledgment.—We are indebted to our coworkers for synthesis and infrared spectra of many of the compounds in Table II which prompted this paper. We thank especially Mr. R. S. Gay for helpful discussions and for executing the force constant calculations. We are greatly indebted to Professor T. L. Brown for making available his infrared data in advance of publication and for discussions. The work was supported by the National Research Council of Canada.

[33] This can be seen by considering resonance structures for the σ bond. In LMn(CO)$_5$, the canonical forms are

$$\underset{\text{III}}{\mathrm{L^-{:}Mn(CO)_5{}^+}} \longleftrightarrow \underset{\text{IV}}{\mathrm{L{-}Mn(CO)_5}} \longleftrightarrow \underset{\text{V}}{\mathrm{L^+{:}Mn(CO)_5{}^-}}$$

Form III will make a larger contribution at the expense of V as the electronegativity of L increases, ultimately reversing sense. For LMo(CO)$_5$, the only reasonable forms to describe the σ bond are L:Mo(CO)$_5$ $\longleftrightarrow$ L$^+$–Mo(CO)$_5{}^-$. A form L$^-$::Mo$^+$ (corresponding to sense reversal) would involve σ^* orbitals or σ orbitals from a higher quantum level, neither one an attractive possibility.

CONTRIBUTION FROM THE WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES,
UNIVERSITY COLLEGE, LONDON, ENGLAND

Cyclooctatetraene–Rhodium(I) Complexes

BY M. A. BENNETT[1] AND J. D. SAXBY

Received July 24, 1967

The known, dimeric complex of cyclooctatetraene (C_8H_8) with rhodium(I), $[C_8H_8RhCl]_2$, is conveniently prepared by displacing cyclooctene from its rhodium(I) complex, $(C_8H_{14})_2RhCl$, with cyclooctatetraene. The chlorine bridges of $[C_8H_8RhCl]_2$ are split by pyridine and triphenylphosphine giving monomeric complexes of formula C_8H_8RhCl(ligand) and by 2,4-pentanedione (acetylacetone, acacH) in the presence of base giving monomeric C_8H_8Rh(acac). Infrared and proton nmr spectroscopic data suggest that in these compounds the eight-membered ring has a tub conformation and is coordinated to the metal *via* the 1,5 double bonds, the 3,7 double bonds being free. In solution, the complex $[C_8H_8RhCl]_2$ decomposes to give a brown, insoluble, probably polymeric compound of formula $[C_8H_8Rh_2Cl_2]_n$. This reacts with pyridine and triphenylphosphine giving complexes of formula $C_8H_8Rh_2Cl_2$(ligand)$_2$ and with 2,4-pentanedione in the presence of base giving $C_8H_8Rh_2$(acac)$_2$. In these compounds, tub-shaped cyclooctatetraene probably bridges a pair of rhodium atoms *via* its 1,5 and 3,7 double bonds.

Introduction

Metal–cyclooctatetraene complexes are of particular interest owing to the variety of ways in which metal–ring bonding can take place.[2] Only three such complexes of rhodium(I) have so far been reported: $[C_8H_8RhCl]_2$,[3,4] $C_8H_8RhC_5H_5$,[5] and $C_8H_8Rh_2(C_5H_5)_2$.[6] Subsequent attempts to repeat the preparation of $[C_8H_8RhCl]_2$ from rhodium(III) chloride and cyclooctatetraene[3,4] have not been successful, and a reinvestigation

---

[1] Research School of Chemistry, Australian National University, Canberra, Australia.

[2] M. A. Bennett, *Advan. Organometal. Chem.*, **4**, 353 (1966).

[3] E. W. Abel, M. A. Bennett, and G. Wilkinson, *J. Chem. Soc.*, 3178 (1959).

[4] M. A. Bennett and G. Wilkinson, *ibid.*, 1418 (1961); the figure of 50° given in this paper should read 5°.

[5] A. Davison, W. McFarlane, L. Pratt, and G. Wilkinson, *ibid.*, 4821 (1962).

[6] K. S. Brenner, E. O. Fischer, H. P. Fritz, and C. G. Kreiter, *Chem. Ber.*, **96**, 2632 (1963).