

know that an unidentified cationic species, probably containing at least one SN linkage, is formed in high yield. (If less than 0.5 mol of this species forms per mole of S_4N_4 , its uv molar extinction coefficient exceeds $54,000 M^{-1}$ —a value which is unusually high.) Clearly

the reaction of S_4N_4 with sulfuric acid cannot be said to be understood until this important species is identified.

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Intramolecular Environmental Effects on the Bonding of Cyanide and Carbonyl

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The bonding characteristics of carbon monoxide and cyanide ion in transition metal complexes are examined *via* molecular orbital calculations on the isoelectronic series of complexes $Mn(CO)_6^+$, $Mn(CO)_5CN$, $Mn(CN)_5CO^{4-}$, and $Mn(CN)_6^{5-}$. Within the series, it is found that trends in carbonyl bonding can be attributed essentially to variations in π -acceptor ability. On the other hand, the bonding of cyanide appears to be a function of both σ -donor and π -acceptor abilities which vary according to the total intramolecular environment. Contrary to mixed systems of π donors and π acceptors, such as $Mn(CO)_5Cl$, the present complexes do not exhibit electron distributions which would predict significant trans influence. As the ligands are varied in the series, the metal atom acts primarily as a transmitter of electron density among the changing ligand systems.

I. Introduction

In our recent studies on the bonding in hexacarbonyl² and pentacarbonyl halide³ complexes, we were intrigued by the observation that the trends in bonding characteristics of the CO group could be described by the changes in the antibonding π -orbital occupations only. Based upon the reasonable assumption that all 1s electrons were in the core, our calculations showed that the orbital occupations $(1\sigma)^2(2\sigma)^2(1\pi)^4(3\sigma)^1$,^{3,5} remained essentially constant. Thus, except for the loss of 0.65 electron per ligand *via* σ bonding, the only noticeable changes were in the occupations of the 2π orbitals. A similar observation held for the nitrosyl groups in a series of metal pentacyanonitrosyl complexes.⁴ If this situation is general, it would permit calculational simplifications, such as a decrease in the size of the basis set. In addition, qualitative bonding discussions of π acceptors in which only changes in π occupation were considered would be on a firm footing. However, certain factors suggested that it would be unwise to generalize the observed constancy of σ -orbital occupation. For example, it appears that variation in σ -bond strength is required to interpret the trends in CN force constants in systems not involving metal complexes.⁵ Furthermore, our experience with the halogen energy levels in the manganese pentacarbonyl halides³ indicated that the halogen σ - and π -donating ability was drastically different than what one might expect from their bonding in hexahalide complexes. This latter experience led us to compare the σ -donor- π -ac-

ceptor abilities of cyanide and carbonyl relative to one another within the four complexes $Mn(CO)_6^+$, $Mn(CN)_6^{5-}$, $Mn(CO)_5CN$, and $Mn(CN)_5CO^{4-}$.

There were several reasons for our choices of the complexes to be studied. The systems are isoelectronic and closed shell. Of the four complexes, only $Mn(CN)_5CO^{4-}$ has yet to be prepared so that useful experimental information such as infrared stretching frequencies are available. In the first two complexes, the ligands compete only with themselves for the metal d_{π} electrons while in the latter two a single CN ligand is in the presence of five CO ligands and *vice versa*. These extremes permit examination of relative σ -donor and π -acceptor abilities as a function of the total ligand environment. Finally, since the complexes include a cation, anions, and a neutral molecule, one might expect to observe substantial changes in metal orbital occupations and relative positions of the eigenvalues.

II. Procedure

The computations used here are identical with those used in our previous work on the pentacarbonyl halides.³ As was the case in the pentacarbonyl halide calculations, the unique ligand, B, in MA_5B systems was presumed to be located along the positive z axis. The computational approximations are rotationally invariant and this choice is for convenience only. The internuclear distances were chosen as follows.

For all the complexes, the intraligand distances for CO and CN^- were set at 1.128 \AA ⁶ and 1.160 \AA ,⁷ re-

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(2) K. G. Caulton and R. F. Fenske, *Inorg. Chem.*, **7**, 479 (1968).

(3) R. F. Fenske and R. L. DeKock, *ibid.*, **9**, 1053 (1970).

(4) R. L. DeKock and R. F. Fenske, to be submitted for publication.

(5) K. F. Purcell, *J. Amer. Chem. Soc.*, **89**, 247 (1967).

(6) G. Herzberg, "Spectra of Diatomic Molecules," Van Nostrand, Princeton, N. J., 1950.

(7) A. Tullberg and N.-G. Vannerberg, *Acta Chem. Scand.*, **21**, 1462 (1967).

spectively. It is well established⁸ that these ligand distances show only slight variations within a variety of complexes. Furthermore, by keeping the distances constant, the interpretation of the results is greatly simplified since any computed trends in orbital occupations would not be a consequence of minor variations in carbon-oxygen or carbon-nitrogen distances. For the same reason, all manganese to carbonyl carbon distances were kept at 1.840 Å, corresponding to the mean equatorial Mn-C distance⁹ found in $\text{HMn}(\text{CO})_5$, and the manganese to cyanide carbon distances were set at 1.98 Å, identical with that observed⁷ in $\text{K}_3\text{Mn}(\text{CN})_5 \cdot \text{NO} \cdot 2\text{H}_2\text{O}$.

The basis functions chosen for the calculation of the simplified Fock and overlap matrices are Slater-type atomic orbitals. For the final calculations on each complex, Richardson's $\text{Mn}^+ 3d$ functions¹⁰ were used since the +1 oxidation state corresponds most closely to the manganese charge as computed by the Mulliken population analysis¹¹ of the molecular orbitals involving the 3d orbitals. The 4s, 4p, and 4d functions were contracted from the atomic orbital forms as previously described.² For the carbonyl ligands, the atomic orbitals of Clementi¹² for the neutral carbon and oxygen atoms were employed. The 2p functions were used in the double- ζ form, while the 1s and 2s functions were curve fit to single- ζ form by maintaining orthogonality and maximizing the overlaps with the available double- ζ functions. The 1s functions were used to evaluate the diagonal terms in the Fock matrix only; *i.e.*, they were considered to be localized on their respective atoms insofar as the Fock matrix was concerned. For the cyanide ligands, the final atomic charges indicated that neutral carbon and -1 nitrogen functions were apropos for $\text{Mn}(\text{CN})_5^{5-}$ and $\text{Mn}(\text{CN})_5\text{CO}^{4-}$. In $\text{Mn}(\text{CO})_5\text{CN}$, the calculated nitrogen charge using the N^- functions¹³ was found to be -0.58. This was sufficiently borderline that a comparative calculation with nitrogen functions corresponding to the neutral atom was also carried out. The resultant charge on the nitrogen was -0.31, a result to be expected when one uses a more contracted set of basis functions. Since a substantial negative charge remained even with the neutral atom functions and intercomparisons can be made more directly between the distributions within the complexes if the same functions are used throughout, all results reported here are on the basis of the N^- functions. Use of the nitrogen zero functions in $\text{Mn}(\text{CO})_5\text{CN}$ would change some of the absolute values but not the general trends and effects to be discussed.

III. The Isolated Ligands

While the calculations were carried out using an

(8) (a) F. A. Cotton and R. M. Wing, *Inorg. Chem.*, **4**, 314 (1965). (b) D. Britton in "Perspectives in Structural Chemistry," Vol. 1, J. D. Dunitz and J. A. Ibers, Ed., Wiley, New York, N. Y., 1967, p 109.

(9) S. J. La Placa, W. C. Hamilton, and J. A. Ibers, *Inorg. Chem.*, **3**, 1491 (1964).

(10) J. W. Richardson, W. C. Nieuwpoort, R. R. Powell, and W. F. Edgell, *J. Chem. Phys.*, **36**, 1057 (1962).

(11) R. F. Fenske and D. D. Radtke, *Inorg. Chem.*, **7**, 479 (1968).

(12) E. Clementi, *J. Chem. Phys.*, **40**, 1944 (1964).

(13) E. Clementi in "Tables of Atomic Functions," a supplement to E. Clementi, *IBM J. Res. Develop.*, **9**, 2 (1965).

atomic orbital basis set, it will be useful to discuss certain results from the viewpoint of changes within the ligand molecular orbitals. Our programming permits reexpression of all matrices and eigenvectors in either set of basis functions. Therefore, it is convenient to examine the characteristics of the free ligands prior to bonding. In order to make more valid comparisons between the isolated and bonded ligands, calculations of the free ligands were carried out under the same approximations used for the complexes. The resultant eigenvalues and overlap populations are given in Table I. Since the 1s atomic orbitals were placed on

TABLE I
FREE LIGAND EIGENVALUES AND OVERLAP POPULATIONS

Orbital	Carbon monoxide		Cyanide ion	
	Energy, eV	OP ^a	Energy, eV	OP ^a
2π	+0.37	0.000	+15.90	0.000
5σ	-13.81	-0.256	+3.06	-0.555
1π	-20.99	+0.917	-8.21	+1.140
4σ	-22.46	+0.192	-9.13	+0.303
3σ	-42.10	+0.746	-25.81	+0.822

^a Mulliken overlap populations (OP) on a per molecular orbital basis. The 1π occupation is taken to be four electrons to account for the orbital degeneracy.

core in the calculations, the molecular orbital labeling begins with 3σ. For both CO and CN^- , the energy level ordering and occupations are $(3\sigma)^2(4\sigma)^2(1\pi)^4(5\sigma)^2$. Because of their importance in the bonding within the complexes, the eigenvalues of the unoccupied 2π orbitals are also presented.

The differences in the eigenvalues of the two ligands reflect the changes which occur in going from CO to CN^- . The effects can be rationalized by envisioning the removal of a proton from the oxygen nucleus in CO to form the nitrogen atom in CN^- . Each of the energy levels is destabilized by roughly 13-17 eV. The *relative* energy separations are not as severe, however. Of course, in a physical situation, the levels of the cyanide ion would be stabilized by the charge on the cation which has not been included in the calculations. Since we are interested in interpreting the interaction effects which occur when these free ligands are bonded to the Mn^+ species, the greater stability (lower eigenvalues) of the CO compared to CN^- will become important.

Examination of the overlap populations reveals that the formal triple bond, $\text{A}\equiv\text{B}$, is principally a result of the 3σ and 1π orbitals. The 4σ orbital is mainly localized on the more electronegative atom in each case, whereas the 5σ orbitals consist predominantly of carbon atomic orbitals. However, it is important to note that in both ligands the 5σ orbital is *antibonding*, as illustrated by the negative overlap populations, and that the cyanide 5σ is decidedly more antibonding in character than its carbonyl counterpart. Removal of electron density from these orbitals should result in σ-bond strengthening. Conversely, occupation of the 2π orbitals *via* interaction with the metal 3d_π orbitals will effect a weakening of the π bonding.

IV. Results and Discussion

Eigenvalues.—Figures 1 and 2 present schematic representations of the diagonal matrix elements and those eigenvalues which will be pertinent to the discussion to follow.¹⁴ For clarity, the diagrams have been

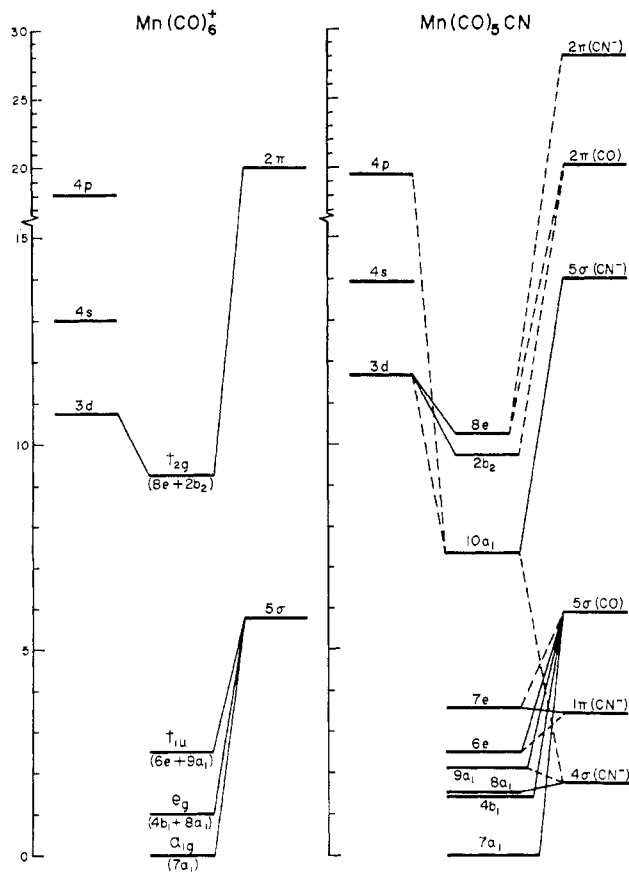


Figure 1.—Occupied energy levels of Mn(CO)₆⁺ (a) and Mn(CO)₅CN (b).

simplified in several respects. First of all, the 3σ, 4σ, and 1π carbonyl and cyanide diagonal terms and the resultant MO's to which they are the primary contributors have not been included, except in the case of the 4σ and 1π elements of the cyanide ligand in Mn(CO)₅CN. They were, of course, included in the calculations. Second, the metal 4d basis functions, whose diagonal matrix elements are approximately 9–10 eV above the 4p, are not presented. The 4d contributions to the occupied orbitals are so negligible that their per cent participation will be ignored. Third, the resultant virtual molecular orbitals are not included in the figures. Finally, so that intercomparison of complexes with different charges can be made, the eigenvalues are presented relative to the 1a₂ energy level in C_{4v} symmetry whose eigenvalue was arbitrarily set at zero. The eigenfunction associated with this level is made up of a

(14) Materials supplementary to this article including all overlap matrices, eigenvectors, and eigenvalues have been deposited as Document No. NAPS-01170 with the ASIS National Auxiliary Publication Service, c/o CCM Information Corp., 909 3rd Ave., New York, N. Y. 10022. A copy may be secured by citing the document number and by remitting \$2.00 for microfiche or \$5.00 for photocopies. Advance payment is required. Make checks or money orders payable to: CCMIC-NAPS.

linear combination of ligand 1π orbitals in the XY plane that are nonbonding with respect to the metal orbitals. In O_h symmetry this combination is one of the three functions which form a basis for the t_{1g} irreducible representation. Since the basis functions for this set

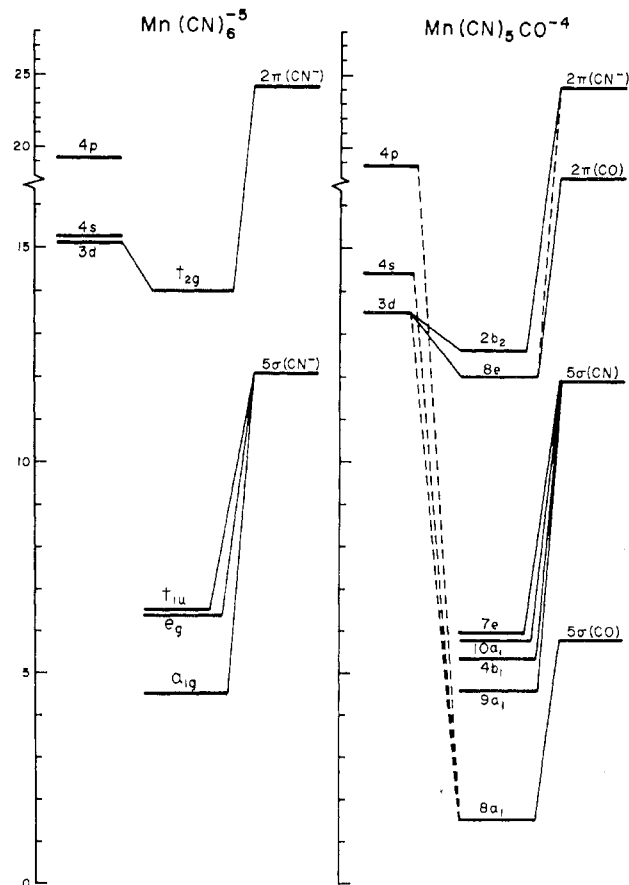


Figure 2.—Occupied energy levels of Mn(CN)₆⁵⁻ (a) and Mn(CN)₅CO⁴⁻ (b).

are carbonyl functions in the Mn(CO)₆⁺ and Mn(CO)₅CN complexes and are cyanide functions in the other two complexes, caution must be used in comparing Figure 1 with Figure 2. Nevertheless, one immediately notices the qualitative similarity between the diagrams for Mn(CO)₆⁺ and Mn(CN)₆⁵⁻. In both, the 5σ levels are below and the 2π levels are well above the metal 3d diagonal terms. The π interaction stabilizes the t_{2g} molecular orbitals relative to the 3d starting energies, in accord with long-standing qualitative assumptions¹⁵ concerning the effect of the virtual ligand 2π orbitals on the t_{2g} orbitals.¹⁶

Despite the general similarities in Figures 1a and 2a, it is possible to note several differences. At self-consistent charge, the separation of the 5σ level from the metal diagonal terms is smaller in the hexacyanide than for the hexacarbonyl. This suggests that the participation of the metal orbitals in the resultant σ-bonding MO's should be greater for the hexacyanide, and this is, indeed, the case. However, it must be kept in mind

(15) L. E. Orgel, "An Introduction to Transition Metal Chemistry," 2nd ed, Methuen, London, 1966, p 138.

(16) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, Interscience, New York, N. Y., 1966, p 707.

that these ligand and metal atomic orbitals participate in other low-lying energy levels not indicated by the diagram. As will be shown, the electron distributions in the 5σ orbitals are surprisingly similar.

One also observes that the stabilization of the t_{2g} molecular orbital relative to the $3d_{\pi}$ metal diagonal term is 0.35 eV greater for the hexacarbonyl complex than for the hexacyanide species, even though the relative $3d_{\pi}$ to 2π separations are about the same. This does suggest that, as has been traditionally held,¹⁷ carbonyl is a better π acceptor than cyanide. The interesting observation is that the difference in stabilization is not greater.

It is in the mixed complexes, however, that the more striking differences between the two ligands are observed. Figure 1 permits comparison of $Mn(CO)_6^+$ and $Mn(CO)_5CN$. We can consider the latter compound in terms of the changes that can be expected upon removal of a proton from the oxygen nucleus along the positive z axis of $Mn(CO)_6^+$, thus converting this ligand from CO to CN^- . If we keep in mind the differences in absolute values of the eigenvalues for CO and CN^- , Table I, what occurs in the hypothetical proton extraction is quite understandable. Relative to their CO counterparts, the 4σ , 1π , and 5σ levels of CN^- are substantially destabilized. Indeed, the 5σ cyanide level in the mixed complex is actually above the diagonal matrix element for the metal $3d$ orbitals. This is in sharp contrast to its position in $Mn(CN)_6^{5-}$.

Several features of the energy levels in $Mn(CO)_5CN$ are of interest. The $8e$ and $2b_2$ eigenvalues,¹⁸ which constituted the degenerate π t_{2g} energy levels in $Mn(CO)_6^+$, are separated in energy by approximately 0.5 eV. Since we would expect the π interaction of cyanide to be less than that of carbonyl, it is not surprising that the $8e$ level is higher in energy than the $2b_2$. The stabilization of the $2b_2$ energy, relative to the $3d$, is greater for the linear combination of the four 2π carbonyl groups in the XY plane than the stabilization due to the three 2π carbonyls and one 2π cyanide combination which constitutes one of the basis functions for the degenerate e representation.

Most noticeable of the energy levels in $Mn(CO)_5CN$ is the position of the $10a_1$ eigenvalue. Because of the substantial destabilization of the 5σ cyanide orbital relative to the 5σ of the carbonyl ligands, the final molecular orbital lies intermediate to the "metal" $8e$ and $2b_2$ orbitals and the σ -bonding "carbonyl" orbitals. The eigenvector for the $10a_1$ molecular orbital indicates that the MO is principally cyanide in character, 57% 5σ and 10% 4σ . However there is, as expected, substantial metal orbital interaction. In C_{4v} symmetry, the $3d_{z^2}$, $4s$, and $4p_z$ metal functions all belong to the a_1 representation. Of these, the $3d_{z^2}$ (8%) and $4p_z$ (15%) participations are greater than the $4s$ (2%). In fact, the 2π orbitals of the four carbonyls in the XY plane that are perpendicular to the XY plane have a partici-

pation (5%) which is at least as significant as that of the metal $4s$. This direct interaction of the cyanide σ with the four π orbitals in the XY plane is similar to that previously discussed in our work on the pentacarbonyl halides.⁸

As far as we have been able to ascertain, the photoelectron ionization energies of the valence levels of $Mn(CO)_5CN$ have yet to be obtained. This presents us with an opportunity to predict their approximate values. The scale factor for the eigenvalues in Figure 1b was 21.1 eV so if this value is subtracted from those presented in the figure the ionization energy estimates are as follows: $8e$, 10.9 eV; $2b_2$, 11.4 eV; $10a_1$, 13.8 eV. Because of the problems of correlating the eigenvalues associated principally with the 5σ carbonyl levels which we have previously discussed,⁸ we hesitate to assign the next grouping of ionization energies as given by Figure 1b. Rather, in accord with the considerations presented with respect to the pentacarbonyl halides,⁸ we estimate the $7e$ to $4b_1$ grouping of levels to begin at roughly 14.8 eV. These same considerations suggest that the ionization energy of the $10a_1$ level might be somewhat less than 13.8 eV, but it is difficult to estimate, so we will leave the prediction as is. A substantial change in absorption intensity might be expected for the $10a_1$ energy level compared to the $8e$ and $2b_2$ since there is a substantial delocalization of the $10a_1$ orbital while the others are principally metal d orbital in character.

We note that the removal of the proton in going from CO to CN^- has resulted in substantial mixing of 1π and 4σ cyanide orbitals in the energy levels which had been mainly 5σ carbonyl in character. Thus, the $7e$ and $6e$ molecular orbitals are a mixture of 5σ carbonyl and 1π cyanide wave functions. Similarly the $9a_1$ and $8a_1$ MO's are blends of the 5σ orbitals of the carbonyls and the 4σ of the cyanide. The clear separability of orbital character is lost when one combines ligands with disparate energies. This already suggests that caution must be observed in qualitative discussions which employ a separated orbital approach.

Examination of Figures 2a and 2b illustrates the alternate situation of π -acceptor competition, a carbonyl group in the cyanide environment. As expected, the stabilization of the carbonyl levels relative to the cyanides has precisely the reverse effects on the energy levels from those in the previous compounds. The carbonyl 5σ is further removed from the $3d$ orbital energies so that the MO in which it primarily participates is substantially more stable. It is the influence of the 2π carbonyl level which becomes most important. For space reasons, the upper ranges of the figures are on a different scale than the lower portion so the figure does not adequately suggest the appreciable stabilization (6.4 eV) of the 2π carbonyl level from that of the 2π cyanides. Naturally, this results in the reverse splitting of the t_{2g} levels from what occurred in $Mn(CO)_5CN$. Thus, the $8e$ energy level is approximately 0.5 eV lower in energy than the $2b_2$.

Orbital Occupations.—On the basis of the previous

(17) F. A. Cotton and G. Wilkinson, ref 16, p 754.

(18) The designation of the e and b_2 levels is in accord with the size of the basis set and the use of the aufbau principle.

discussion, it is clear that in mixed systems, such as $\text{Mn}(\text{CO})_5\text{CN}$ and $\text{Mn}(\text{CN})_5\text{CO}^{4-}$, carbonyl is a better π acceptor than cyanide. For further insights, it is useful to examine the orbital occupations of the metal AO's and the ligand MO's as obtained from Mulliken population analyses.¹⁹ These are given Table in II. In

TABLE II
ORBITAL OCCUPATIONS

Orbital	Mn-				
	$\text{Mn}(\text{CO})_6^+$	$\text{Mn}(\text{CO})_5\text{CN}$	$(\text{CN})_5\text{CO}^{4-}$	$\text{Mn}(\text{CN})_6^{5-}$	
1CO	5σ	1.34	1.35
	$2\pi_x$	0.19	0.20
	$2\pi_y$	0.19	0.22
5CO	5σ	1.34	...	1.39	...
	$2\pi_x$	0.19	...	0.39	...
	$2\pi_y$	0.19	...	0.39	...
6CO	5σ	1.34	1.35
	$2\pi_x$	0.19	0.23
	$2\pi_y$	0.19	0.23
1CN	5σ	1.30	1.31
	$2\pi_x$	0.10	0.14
	$2\pi_y$	0.11	0.14
5CN	5σ	...	1.19	...	1.31
	$2\pi_x$...	0.05	...	0.14
	$2\pi_y$...	0.05	...	0.14
6CN	5σ	1.29	1.31
	$2\pi_x$	0.10	0.14
	$2\pi_y$	0.10	0.14
Metal	d_{z^2}	0.81	0.83	0.72	0.68
	$d_{x^2-y^2}$	0.81	0.79	0.73	0.68
	d_{xy}	1.37	1.30	1.62	1.51
	d_{xz}	1.37	1.41	1.38	1.51
	d_{yz}	1.37	1.41	1.38	1.51
	d total	5.72	5.73	5.83	5.90
	4s	0.34	0.36	0.45	0.48
4p _x	0.46	0.49	0.51	0.56	
4p _y	0.46	0.46	0.54	0.56	
4p _z	0.46	0.46	0.54	0.56	
Metal total	7.42	7.45	7.88	8.06	

this table, the designation 1CO indicates any one of the four carbonyl groups in the XY plane. The $2\pi_y$ orbital represents that antibonding combination of carbon and oxygen 2p functions that are perpendicular to the XY plane, while $2\pi_x$ is a similar set in the XY plane. As explained in our previous work,³ the orbital occupations of these two orbitals need not be the same because of the possibility of "direct donation" from ligand σ orbitals along the master z axis to the $2\pi_y$ orbitals. Position 5 indicates the ligand along the positive z axis and in the mixed complexes is the site of the substituted ligand while position 6 is the ligand trans to the substituted ligand.

Carbonyl Bonding.—The extremes in electron occupancy of the carbonyl orbitals are represented by $\text{Mn}(\text{CO})_6^+$ and $\text{Mn}(\text{CN})_5\text{CO}^{4-}$. As expected from the energy level considerations, there is a dramatic alteration in the occupancy of the 2π orbitals, *i.e.*, a total difference of 0.40 electron. On the other hand, the increase in 5σ occupancy of the carbonyl group in the pentacyanocarbonyl complex over the hexacarbonyl is only

0.05 electron. Especially when one recalls that the antibonding character of the 5σ orbital is less pronounced than the 2π , it is without a doubt that the bonding properties within the carbonyl groups of the series are primarily functions of the 2π occupancy.

It is worthwhile to compare orbital occupancies of the cis and trans groups in $\text{Mn}(\text{CO})_5\text{CN}$ and $\text{Mn}(\text{CN})_5\text{CO}^{4-}$. In contrast to our results³ on $\text{Mn}(\text{CO})_5\text{X}$, where $\text{X} = \text{H}$ or halide, the present complexes do not show significant trans influence.²⁰ It is interesting to note that the 5σ occupancy of the cyanide in $\text{Mn}(\text{CO})_5\text{CN}$ is the same as that of the hydrogen 1s in $\text{Mn}(\text{CO})_5\text{H}$, and the metal orbital occupancies are essentially identical as well, yet the hydride, even when calculated with all metal to carbonyl groups at the same internuclear distance, displayed a substantial trans influence while the cyanide complex did not. In the halide complexes, the 2π occupancy of the trans carbonyl group was approximately 0.12 electron greater than that for a cis carbonyl group. There is only 0.04 electron difference in the pentacarbonyl cyanide complex. Analogously, the strong π -acceptor ability of the carbonyl group causes only minor differences in the trans and cis cyanide occupations in $\text{Mn}(\text{CN})_5\text{CO}^{4-}$. Thus, it appears that the trans influence in $\text{M}(\text{CO})_5\text{L}$ or $\text{M}(\text{CN})_5\text{L}$ complexes will be more readily observable in those cases where L is either a π -electron donor or has no π -interaction capabilities, whereas its existence will be less clear-cut when the L group has some degree of π -acceptor ability.

Cyanide Bonding.—While the characteristics of carbonyl bonding in the series could be rationalized primarily on the basis of the π interactions, this is not the case for the cyanide group. The two complexes of interest are $\text{Mn}(\text{CN})_6^{5-}$ and $\text{Mn}(\text{CO})_5\text{CN}$ since they display the extremes in orbital occupation. The decrease in total 2π occupancy is 0.18 electron so there should be a substantial strengthening of the carbon to nitrogen bond in the cyanide in $\text{Mn}(\text{CO})_5\text{CN}$ compared to its $\text{Mn}(\text{CN})_6^{5-}$ counterpart. However, there is also an important change in the 5σ populations. The decrease in 5σ from 1.31 to 1.19 electrons indicates a strengthening of both the metal to carbon and carbon to nitrogen bonds. The 1.19 value suggests greater covalent bonding to the metal and since the electron transfer occurs from an orbital which is antibonding with respect to the carbon-nitrogen bond, it will be strengthened as well. It is not surprising, therefore, that the CN stretching frequency in $\text{Mn}(\text{CO})_5\text{CN}$ is substantially greater than that in $\text{Mn}(\text{CN})_6^{5-}$, as indicated by the values presented in Table III. The difference in the cyanide

(19) Analogous trends were obtained using Lowdin distributions, but only the results from the Mulliken method will be presented.

(20) We wish to express our thanks to Professor L. Venanzi and coworkers for calling our attention to the term trans influence which they have used to characterize ground-state properties as distinguished from trans effect which is defined in terms of kinetics of reactions and hence involves energy differences of the ground state and the activated complex. When applied to the MA₂B system, the term trans influence signifies the effects of the B ligand on that ligand A which is trans compared to those which are cis. In particular, bond lengths should reflect possible trans influence. Insofar as vibrational force constants can be assumed to be related to ground-state electronic distributions, differences in force constants (and hence stretching frequencies) of the cis and trans ligands could also be used as indicative of trans influence. Cf. A. Pidcock, R. E. Richards, and L. M. Venanzi, *J. Chem. Soc. A*, 1707 (1966).

TABLE III

EXPERIMENTAL INFRARED STRETCHING FREQUENCIES (CM⁻¹)

Mn(CO) ₆ ⁺ ^a	Mn(CN) ₆ ⁵⁻ ^b	Mn(CO) ₅ CN ^c
2101	1930	2145 (CN)
		2075 sh
		2055
		1985-1930 broad unresolved band

^a R. J. H. Clark, *J. Organometal. Chem.*, **6**, 167 (1966). ^b K. Schwochau and W. Herr, *Z. Anorg. Allg. Chem.*, **319**, 148 (1962).
^c B. Chiswell and L. M. Venanzi, *J. Chem. Soc. A*, 417 (1966).

stretching frequencies for the two species is so substantial that, while it would be preferable to have sufficient experimental information to determine force constants, the stronger carbon to nitrogen bond in Mn(CO)₅CN is clearly indicated. While the stretching frequencies assigned to the carbonyl groups of the latter compound are somewhat less than the t_{1u} stretch in Mn(CO)₆⁺, the mixing of the various a₁ modes coupled with the broad, unresolved bands in Mn(CO)₅CN prohibit any comment on possible alteration of carbon to oxygen bond strengths.

A comparison of 5σ and 2π occupations in the three complexes containing cyanide is informative. In going from Mn(CN)₆⁵⁻ to Mn(CN)₅CO⁴⁻, the major changes in orbital occupations are in the 2π orbitals with little variation in the 5σ populations. Thus, when the principal ligand "environment" is due to the cyanide groups, alterations within the carbon-nitrogen bonds are primarily due to changes in π bonding. However, when the "environment" is mainly that of the carbonyl group and the cyanide is the minor component, the bonding characteristics are dependent on changes in both the σ- and π-electron distributions. It is clear that in a discussion of trends within compounds it is important to realize that *the observations will be dependent upon the total intramolecular environment.*

Metal Orbital Occupations.—An interesting sidelight on the foregoing discussions is that they were essentially independent of changes taking place in metal orbital populations. This is all the more intriguing when one recalls that the series represents a change of six protons in going from Mn(CO)₆⁺ to Mn(CN)₆⁵⁻.

As Table II displays, substantial alterations do occur

within a particular orbital. Thus, the presence of the carbonyl group in Mn(CN)₅CO⁴⁻ causes a decrease of 0.13 electron in both the d_{zz} and d_{yz} populations compared to Mn(CN)₆⁵⁻. However, there is a compensatory increase in the d_{xy} and the σ-bonding d_{z²} and d_{x²-y²} occupations so that the change in total d-orbital participation is only 0.07 electron. Across the series from Mn(CO)₆⁺ to Mn(CN)₆⁵⁻, the removal of the protons does result in a slow increase in metal d-orbital occupancy from 5.72 to 5.90 electrons. A somewhat more pronounced trend is apparent in the 4s and 4p orbital occupations which reflects the increased participation of these orbitals as the removal of protons destabilizes the 5σ levels of the ligands and brings them closer to the metal 4s and 4p energies. However, it should be kept in mind that these latter metal orbitals are quite diffuse and have a substantial electron density in the vicinity of the carbon atoms of the ligands so whether these changes constitute an actual alteration in electron density is somewhat uncertain. Even if one accepts the changes from 7.42 to 8.06 electrons as real, this represents only a change of 0.64 electron during the total change of 6.00 protons. Thus, we suggest that the primary activity of the metal in the series is to act as a transmitter of electron density from one ligand system to the other through both its σ and π framework.

V. Summary

The results of our investigation indicate that while consideration of trends in the bonding properties of the carbonyl group in octahedral metal complexes can be interpreted primarily on the basis of alterations in the degree of π-antibonding orbital participation, a similar conclusion is invalid for the bonding of cyanide. Rather, cyanide displays considerable changes in both its σ- and π-orbital contributions and its bonding characteristics are dependent upon the total molecular environment.

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