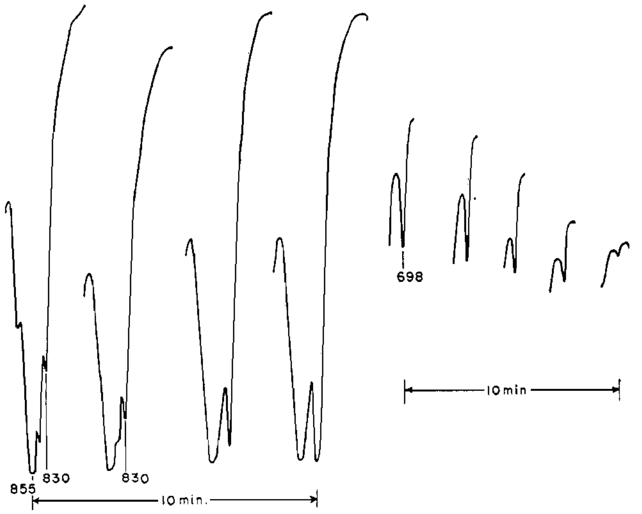
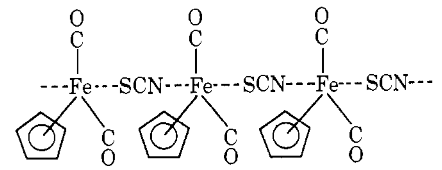


Figure 4.—Changes in the infrared spectrum in the CS stretching region showing thiocyanato-S to thiocyanato-N linkage isomerization of $C_5H_5Fe(CO)_2(SCN)$ in a Nujol mull at 35°.

voked to rationalize second-order dependence on $C_5H_5Fe(CO)_2Cl$ concentration of the rate of radiochloride exchange therein.[35] However, an alternative path, involving a single SCN bridge such as



is equally compatible with our observations in this study.

The incidence of thiocyanato-S derivatives of π-cyclopentadienylmetal carbonyls is in agreement with the earlier suggestion[4] that sulfur bonding should become more prevalent relative to nitrogen bonding as the oxidation state of the metal increases. The compounds $C_5H_5Fe(CO)_2(CNS)$ and $C_5H_5Cr(NO)_2(NCS)$ support this point most convincingly. In the latter, the formal oxidation state of chromium is 0; in the former, the formal oxidation state of iron is +2. In accord with this difference, the iron system yields both the S- and the N-bonded linkage isomer, whereas chromium affords only the N-bonded form.

Infrared and Nmr Spectra of Halogeno and Thiocyanato Complexes.—A comparison of the carbonyl stretching frequencies for a number of $C_5H_5M(CO)_xX$ complexes (Table I) reveals that they increase as a function of X in the order $I < Br \sim SCN < Cl < NCS$. This sequence parallels a decrease in polarizability of the anions which diminishes the electron density at the metal, thus reducing the extent of $M{=}CO$ π bonding. Clearly, if both thiocyanato linkage isomers are known, the above criterion permits unambiguous differentiation between them. In contrast, however, there is no rational trend among the nmr chemical shifts of the cyclopentadienyl protons in the complexes studied.

Acknowledgment.—This work was supported by a grant from the National Science Foundation (GP-5466). T. E. S. wishes to acknowledge the cooperation of Chemical Abstracts Service in this study. Thanks are also due to the Climax Molybdenum Co. for a generous gift of tungsten hexacarbonyl.

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Electronic Structure and Bonding in $V(CO)_6^-$, $Cr(CO)_6$, and $Mn(CO)_6^+$ [1a]

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The nature of the bonding of the isoelectronic series $V(CO)_6^-$, $Cr(CO)_6$, and $Mn(CO)_6^+$ is investigated by means of semiempirical molecular orbital (MO) calculations. As a preliminary to the calculations on the transition metal complexes, MO calculations are performed on the free ligand CO, and good agreement is found with SCF calculations. The ease of oxidation of $V(CO)_6^-$ to $V(CO)_6$ is explained, and the first nine ionization potentials of $Cr(CO)_6$ are calculated with an average accuracy of 5%. Changes in the charge density in the carbon–oxygen internuclear region are examined along the isoelectronic series, and these changes are correlated with infrared stretching frequencies. All such changes occur in the π-bonding orbitals, the C–O σ framework being invariant. The unusual *decrease* observed in metal–carbon stretching frequency upon increasing the metal oxidation state is explained on the basis of decreased interaction between the metal $3d_\pi$ orbital and the ligand antibonding 2π orbital. On the basis of net atomic charges, a number of reactions between hexacarbonyls and nucleophiles are rationalized, and several kinetic predictions are made.

Introduction

In recent years molecular orbital theory has gained tremendous popularity as a means of interpreting properties of transition metal complexes. This is due in part to an increasing interest in compounds whose properties defy a crystal field interpretation, but it is also the result of the formulation of a number of procedures which allow actual calculation of molecular

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(1) (a) Abstracted in part from the Ph.D. thesis of K. G. Caulton, University of Wisconsin, Jan 1968. (b) National Science Foundation Graduate Fellow.

orbitals.[2-7] The method to be used here has been used to calculate the crystal field splitting, Δ, for a number of transition metal chloride[8] and fluoride[9] complexes. In addition, the calculated degree of ligand orbital participation in the t_{2g} "crystal field" molecular orbital (MO) is in agreement with electron spin resonance and nuclear magnetic resonance data.[9] Finally, chlorine quadrupole coupling constants can be satisfactorily calculated with these wave functions.[8] There has been relatively little detailed examination of the computed wave functions and charge densities themselves in spite of the fact that these contain chemically valuable information. With this in mind and with an eye toward extending the computational procedure to polyatomic ligands, octahedral carbonyl complexes were chosen for this study.

One of the outstanding properties of carbon monoxide as a ligand is its ability to stabilize low oxidation states of transition metals. This has been rationalized[10] in terms of a transfer of electrons from the metal to the C–O antibonding 2π orbital (so-called "back-bonding"). On the basis of this hypothesis, the observed reduction of the C–O stretching frequency from the value for free CO is explained, since population of an antibonding orbital weakens the C–O bond. The increase in the C–O stretching frequency along the isoelectronic series $V(CO)_6^-$, $Cr(CO)_6$, $Mn(CO)_6^+$ has been rationalized in terms of decreased back-bonding with increasing metal oxidation state.[11] Although this hypothesis has led to useful results, it is based on the assumption of no alteration in the σ-bond strength between carbon and oxygen; the validity of this assumption has never been demonstrated. Indeed, a recent MO calculation dealing with CO as a ligand neglected the carbon and oxygen σ orbitals.[12] It was anticipated that the present work would provide a test of this assumption and at the same time provide a quantitative estimate of the importance of back-bonding.

An extremely attractive feature of the Hartree–Fock molecular orbital scheme is the fact that the calculated orbital energies are approximately equal in magnitude to the molecular ionization potentials.[13] Previous MO calculations have been unable to make such a comparison between theory and experiment because only isolated anions were studied, the corresponding cations being neglected. The recently developed technique of photoelectron spectroscopy[14] allows the determination of all single-electron ionization potentials less than an instrumentally determined upper limit (presently 21 eV). In the case of $Cr(CO)_6$ there are nine observed ionization potentials to be compared with the calculated orbital energies.

Computational Procedure

Details of the procedure for calculating matrix elements of the self-consistent field (SCF) Hamiltonian operator have been given elsewhere.[7] All energy and overlap integrals are calculated nonempirically and the resultant molecular orbitals (MO'S) are therefore uniquely determined by the choice of basis atomic orbitals (AO's). It is to be emphasized that no atomic spectral data are used, the atomic orbital energy of orbital ϕ_j being calculated by the relation

$$E(\phi_j) = \left(\phi_j \left| -\frac{\nabla^2}{2} - \frac{Z}{r} \right| \phi_j\right) + \sum_{i \neq j} n_i g(ij) + (n_j - 1) g(jj) \quad (1)$$

Here, the sum on i goes over all orbitals on the atom in question and the n_i are Mulliken[15] "gross atomic orbital populations," representing the number of electrons in atomic orbital ϕ_j. The $g(i,j)$ are average two-electron interaction integrals whose form has been tabulated.[16]

In order to make the calculation independent of the initial choice of electron configuration (the n_i), an iterative procedure is adopted. In the past, one has demanded that the gross atomic charges assumed as input into the SCF energy matrix (F matrix) equal the charge calculated from the resulting solution of the secular equation. Since the charge is calculated directly from the configuration, it seems to be more reasonable and more in keeping with SCF calculations to demand that the *population* of each atomic orbital on all centers be self-consistent. Thus, if n_i^{I} and n_i^{O} are the input and output populations of atomic orbital ϕ_i, one requires $\Sigma_i \left|n_i^{\mathrm{I}} - n_i^{\mathrm{O}}\right|$ be less than some small number δ; here, the sum on i goes over all atomic orbitals on all atoms in the molecule. In practice, δ was chosen in the range 0.01–0.04.

The basis set for the hexacarbonyls consisted of one 2s and three 2p AO's on carbon and on oxygen and five 3d, one 4s, three 4p, and five 4d orbitals on the metal. These 62 orbitals yield energy and overlap matrices of order 62, but symmetry allows this to be reduced to a set of matrix equations coupled only through the Mulliken populations, n_i, which appear in the Fock operator. The symmetry labels and orders of these equations are $a_{1g}(5)$, $e_g(6)$, $t_{2g}(4)$, $t_{1g}(2)$, $t_{2u}(2)$, and $t_{1u}(7)$. The atomic coordinate systems and symmetry-adapted AO's used are those of Gray and Beach.[17] The inclusion of 62 orbitals and 66 electrons makes this the largest calculation of its type yet attempted. Although intuition might suggest the expedient of omitting

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certain ligand orbitals, a desire to test the effect of the formation of a metal–carbon bond on the σ bonding between carbon and oxygen made such a simplification inappropriate. An atomic orbital basis was used in all calculations, but the MO's for the hexacarbonyls were later transformed to a basis of metal AO's and free-ligand *molecular* orbitals (see Appendix). Such a transformation simplifies an interpretation of bond formation between the metal and the molecular entity CO.

In an initial calculation on $Cr(CO)_6$, all Cr–C, Cr–O, C–C, C–O, and O–O interactions were calculated. In view of the fact that matrix elements involving *trans* carbon and oxygen atoms and those involving *cis* and *trans* oxygen atoms were less than 0.005 eV, they were set equal to zero in all calculations. Other interactions between ligand atoms were included, however.

In order to facilitate comparison of the intraligand bond in the hexacarbonyls to the bond in free CO, the calculations used a basis set consisting of the same carbon and oxygen AO's used in the calculation on free CO reported in the Appendix. Only in this way will changes in overlap populations reflect the result of bonding, for it is known that a change of basis can alter overlap populations. The metal 3d radial wave functions used were those of V^-, Cr^0, and Mn^+.[18] It has been argued[8] that the atomic SCF 4s, 4p, and 4d functions are far too diffuse to participate significantly in bonding. That is, molecule formation will strongly alter the free-atom "outer orbitals," making these inappropriate for an LCAO expansion. These functions were therefore constructed in a fashion which in some sense optimizes both their σ- and π-bonding ability in the molecular species.[8,10,19]

In view of the known[20] insensitivity of the C–O bond length to changes in bond order when the latter is in the range 2–3 and the inability of diffraction to fix light-atom interatomic distances accurately in the presence of a heavy atom, the free C–O distance[21] (1.1289 Å) was used for all three compounds. This has the added feature of allowing changes in overlap population to be attributed entirely to bonding. The chromium–carbon distance in $Cr(CO)_6$ is 1.92 Å.[22] While the metal to carbon distance is not known in the charged hexacarbonyls, data on closely related species are available. The Mn–C distance was chosen to be 1.84 Å, which is the mean distance to equatorial carbonyl carbons in $HMn(CO)_5$.[23] The V–C distance was taken as 1.98 Å, which is somewhat longer than the 1.91 ± 0.03 Å found in $C_5H_5V(CO)_4$, where the cyclopentadienyl group leads to a shortening of the V–C bond.[24]

The MO's for the complex are uniquely determined by the internuclear distances and radial wave functions of the AO's. When the calculation was carried out, however, the gross atomic populations in the 4s, 4p, and 4d orbitals were all small but *negative*. Although this situation was not anticipated by Mulliken, this physically absurd result has been observed before.[4] These negative populations were traced to negative coefficients of 4s, 4p, and 4d AO's in the MO's $1a_{1g}$, $1e_g$, $1t_{2g}$, $1t_{1u}$. Since these orbitals are bonding with respect to all AO's, all coefficients should be positive. The cause of this problem can be seen from the following argument. The coefficients a and b in the MO

$$\psi = a\phi + b\chi$$

are fixed by the equation

$$a(F_{aa} - \epsilon) + b(F_{ab} - \epsilon G) = 0$$

where the F's are Fock matrix elements, ϵ is the molecular orbital energy, and G is the overlap integral (ϕ,χ). The relative signs of a and b are fixed by

$$\frac{a}{b} = \frac{\epsilon G - F_{ab}}{F_{aa} - \epsilon}$$

and since $|\epsilon| > |F_{aa}|$ for a bonding orbital, one must have $|\epsilon G| < |F_{ab}|$ if a and b are to have the same sign. Thus, the off-diagonal F matrix elements between metal 4s, 4p, and 4d functions and ligand functions are erroneously small in the above approach. This problem was traced to the simplification of not taking the average of the following two formally equivalent methods of evaluating F_{ab} for metal–ligand interactions

$$F_{ab} = (\chi^a,\psi^b)\epsilon_b - \left(\chi^a\middle|\frac{Z_a}{r_a}\middle|\psi^b\right) + \sum_{\upsilon \neq a,b}\left(\chi^a\middle|\frac{q_\upsilon}{r_\upsilon}\middle|\psi^b\right) + \sum_j n_j[(\phi_j{}^a\phi_j{}^a|\chi^a\psi^b) - {}^1\!/_2(\phi_j{}^a\chi^a|\psi^b\phi_j{}^a)] \quad (2)$$

$$F_{ba} = (\psi^b,\chi^a)\epsilon_a - \left(\psi^b\middle|\frac{Z_b}{r_b}\middle|\chi^a\right) + \sum_{\upsilon \neq a,b}\left(\psi^b\middle|\frac{q_\upsilon}{r_\upsilon}\middle|\chi^a\right) + \sum n_j[(\phi_j{}^b\phi_j{}^b|\psi^b\chi^a) - {}^1\!/_2(\phi_j{}^b\psi^b|\chi^a\phi_j{}^b)] \quad (3)$$

where q_υ is the gross charge[15] on the atom. Here, the superscripts a and b designate the nucleus upon which the AO is centered. To assure the Hermitian character of the energy matrix, one must take the average of these two expressions. When the two AO's involved are metal and ligand, however, there is a distinct advantage to choosing the form involving the overlap integral multiplied by the *metal* orbital energy.[7] In this way, the sum over two-center two-electron integrals goes over only ligand valence orbitals, which is considerably simpler than the alternative formulation. Although it has been shown that this is numerically accurate for ligand interactions with metal 3d orbitals,[25]

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[18] J. W. Richardson, W. C. Nieuwpoort, R. R. Powell, and W. F. Edgell, *J. Chem. Phys.*, **36**, 1057 (1962). Although a 3d function for V^- is not tabulated here, the linear variation of the orbital exponents mentioned by these workers was used to derive a 3d function for V^- from those of Cr and Mn^+.

[19] A complete tabulation of the metal AO's and MO eigenvectors and eigenvalues for all three hexacarbonyls has been deposited as Document No. 9928 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the document number and by remitting $1.25 for photoprints, or $1.25 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

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such is not the case for the more diffuse 4s, 4p, and 4d functions. The work of Basch and Gray[26] offers a formulation of the off-diagonal F matrix element which does not demand choosing between two formally equivalent procedures (eq 2 and 3). A reorganization of terms in the simplified Fock operator yields

$$(\phi^a|F|\chi^b) = (\phi^a,\chi^b)[\epsilon_a + \epsilon_b] - \left(\phi^a\left|-\frac{\nabla^2}{2}\right|\chi^b\right) + \sum_{v\neq a,b}\left(\phi^a\left|\frac{q_v}{r_v}\right|\chi^b\right) \qquad (4)$$

This result is formally equivalent to eq 2 and 3 but avoids the dilemma of choosing *either* the ϵ_a *or* the ϵ_b form and also replaces all difficult two-electron integrals by a kinetic energy term. As expected, metal–ligand terms involving 3d orbitals are very similar when calculated by either eq 2 or 4. Terms involving 4s, 4p, and 4d orbitals are substantially larger by eq 4, however, indicating that eq 2 alone underestimates such terms. As a further comparison of the two methods for evaluating F_{ab}, R. De Kock of these laboratories has performed (unpublished) parallel calculations on BF (isoelectronic with CO) using both methods for calculating F_{ab}. Gross orbital populations differ by less than 0.04 electron for the two calculations, and the five occupied orbital energies differ by 0.5, 0.5, 0.2, and 0.1 eV. The off-diagonal F matrix elements themselves differ by as little as 0.003 eV for $(\pi_B|F|\pi_F)$ and as much as 1.3 eV for $(s_F|F|p_B)$. In general, these observations agree with the above conclusion that the greater deviations involve strongly interacting diffuse functions. In view of the fact that the method of calculating off-diagonal interactions within a ligand does not affect the results, the kinetic energy formulation (eq 4) was used only for metal–ligand terms.

Although the outer metal orbital populations were now computed to be positive, these orbitals still had small negative coefficients in some occupied bonding orbitals. This was again traced to the underestimation of a metal–ligand off-diagonal energy term. In particular, the effect of carbon electron density, $\psi^C\psi^C$, on functions centered at an adjacent metal (χ^M) and oxygen (ϕ^O) was approximated as a nuclear attraction integral multiplied by the Mulliken "gross charge" on carbon $q_C = \Sigma_j n^C{}_j - Z_C$

$$(\chi^M\phi^O|\psi^C\psi^C) - {}^1/_2(\chi^M\psi^C|\psi^C\phi^O) \approx q_C\left(\chi^M\left|\frac{1}{r_C}\right|\phi^O\right) \qquad (5)$$

While this is a good approximation when the "overlap density" $\chi^M\phi^O$ does not penetrate the density $\psi^C\psi^C$, it is particularly unsuitable in the situation considered here, where the metal–oxygen density is probably a *maximum* near carbon. Rigor demands the evaluation of these three-center two-electron integrals, but programs for this purpose are not available. As a result, the deficiency of the nuclear attraction integral approximation was corrected by using a fictitious charge Q_C, *in eq 5 only*, of the form $Q_C = q_C RF$. Calculations were carried out varying RF and it was found that RF = 0.6 was required to make all outer AO coefficients positive in bonding MO's. The introduction of this integral approximation altered orbital energies on the order of only 0.1 eV.

Results and Discussion

The calculated molecular electronic configuration is $(1e_g)^4(1a_{1g})^2(1t_{1u})^6(2e_g)^4(2a_{1g})^2(2t_{1u})^6(1t_{2g})^6(3e_g)^4(3a_{1g})^2(3t_{1u})^6(1t_{2u})^6(1t_{1g})^6(4t_{1u})^6(2t_{2g})^6$, which gives a $^1A_{1g}$ ground state in agreement with the observed diamagnetism of all three compounds.[27] The highest occupied MO, $2t_{2g}$, is the counterpart of the t_{2g} orbital of ligand field theory. In contrast to the assumptions of ligand field theory, however, there is strong mixing of metal and ligand orbitals.[19] Table I shows the large reduction of the 3d coefficient in the $2t_{2g}$ MO from the "ionic" value of 1 coupled with large coefficients of the ligand orbitals. By way of comparison, the $3d_\pi$ coefficient in the $2t_{2g}$ MO of $CrCl_6{}^{3-}$ is 0.957.[8]

Table I

Effect of the 2π Orbital of CO on the $2t_{2g}$ Molecular Orbitals of the Isoelectronic Hexacarbonyls

	$F(2\pi)-F(3d\pi)^a$	$C(2\pi)^b$	$C(3d\pi)^b$	$\delta\pi^a$	$\epsilon(2t_{2g})^a$
$V(CO)_6{}^-$	1.88	0.632	0.574	−3.18	−1.33
$Cr(CO)_6$	4.42	0.576	0.649	−2.12	−8.19
$Mn(CO)_6{}^+$	5.53	0.478	0.753	−1.22	−14.20

[a] All energies in electron volts. [b] Coefficients of the $2t_{2g}$ MO in a basis of ligand molecular orbitals: $\psi(2t_{2g}) = C(1\pi)\phi(1\pi) + C(2\pi)\varphi(2\pi) + C(3d_\pi)\phi(3d_\pi) + C(4d_\pi)\phi(4d_\pi)$.

Figure 1 shows qualitative molecular orbital diagrams for the interaction of metal and ligand π orbitals of t_{2g} symmetry. Figure 1a shows the situation for π-donor ligands such as halogens, oxides, and amines. The diagonal F matrix elements of $3d_\pi$ and ligand π orbitals are represented at the far right and left of Figure 1a, with the resultant molecular orbital energies appearing in the center. A π-donor ligand contributes only occupied AO's which are more stable than $F(3d_\pi)$ to the molecular basis set. This arrangement of F matrix elements dictates that $\delta\pi \equiv \epsilon(2t_{2g}) - F(3d_\pi)$ be positive. In other words, π-donor ligands destabilize the lower of the two predominantly 3d levels. As shown in Figure 1b, π-acceptor ligands have, in addition to a low-lying π orbital, an *empty* orbital of π symmetry (also called π^*) which is less stable than $F(3d_\pi)$. When the distance $F(2\pi)-F(3d_\pi)$ is small, the amount of interaction ("back-bonding") between 2π and $3d_\pi$ is large and the net effect of 2π on $2t_{2g}$ is a stabilization, with $\delta\pi$ negative. As $F(3d_\pi)$ becomes more negative (as when the metal becomes more electronegative), $\delta\pi$ approaches zero and may ultimately become slightly positive when $F(2\pi) - F(3d_\pi)$ is so large that 2π is effectively noninteracting. Thus, the degree to which a ligand exhibits π-acceptor char-

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TABLE II

MULLIKEN GROSS AO POPULATIONS IN THREE HEXACARBONYL COMPLEXES

	3d	4s	4p	4d	$2s^C$	$2p\sigma^C$	$2p\pi^C$	$2s^O$	$2p\sigma^O$	$2p\pi^O$
$V(CO)_6^-$	4.58	0.56	1.76	−0.16	1.17	0.96	1.62	1.63	1.58	2.91
$Cr(CO)_6$	5.05	0.52	1.58	−0.13	1.16	0.98	1.66	1.62	1.59	2.82
$Mn(CO)_6^+$	5.67	0.42	1.40	−0.03	1.21	0.99	1.63	1.61	1.59	2.73
CO	. . .	. . .	. . .	. . .	1.57	1.24	1.33	1.61	1.60	2.67

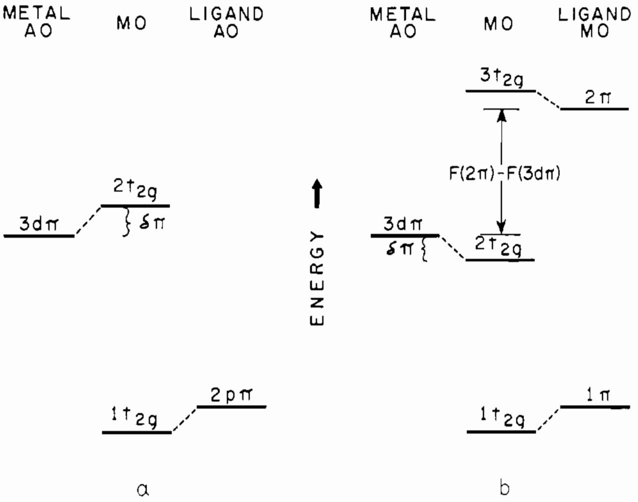

Figure 1.—(a) t_{2g} molecular orbital energies for an octahedral complex with π-donor lignads. (b) t_{2g} molecular orbital energies for an octahedral complex with π-acceptor ligands.

acteristics is dependent upon the metal to which it bonds. The capacity of the molecular environment to determine the bonding function of a ligand is exemplified by the isoelectronic hexacarbonyls studied here.

The calculations presented here exhibit all features discussed qualitatively above. The first column of Table I shows that $F(3d_\pi)$ becomes more removed from the 2π ligand molecular orbital of free CO as the metal oxidation state increases. It is to be emphasized that the constraint of self-consistency fixes $F(3d_\pi)$ and $F(2\pi)$ nonempirically so that the trend observed here is independent of arbitrary assumptions. The $2t_{2g}$ orbital covalency, as measured by $C(3d_\pi)$, decreases from vanadium to manganese with a concomitant decrease in ligand 2π participation in $2t_{2g}$. *Back-bonding therefore decreases with increasing metal oxidation state.* Another symptom of this effect is $\delta\pi$, the amount of stabilization of $\epsilon(2t_{2g})$ by interaction with 2π. $\delta\pi$ is negative for all three hexacarbonyls but decreases in magnitude from vanadium to manganese. By way of comparison, $\delta\pi$ for $CrCl_6^{3-}$ is +1.18 eV, showing the destabilizing effect of a π-donor ligand.[8]

The electronic configurations which result from a Mulliken population analysis also show the effect of decreased back-bonding with increasing metal oxidation state. These gross atomic populations are given for each participating AO in Table II. The most significant trend shown is the increase in the population of the 3d AO from vanadium to manganese. This reflects a decreased ability of the CO 2π orbital to remove electrons (back-bond) from the metal as the oxidation state of the latter increases. This effect is examined in more detail later. The fact that the oxygen 2s and $2p_\sigma$ populations are unchanged from the free-ligand values reflects the fact that there is no σ bonding between metal and oxygen. Although these populations could also be affected by net changes in the σ bond between carbon and oxygen, it may be correctly concluded that such changes do not occur. This, too, will be discussed in detail. Covalency of the stable, predominantly ligand σ-bonding orbitals brings about a transfer of electrons to the metal and causes the observed decrease in carbon 2s and $2p_\sigma$ populations from the free-ligand values. This same effect is observed for complexes of the halogens.[8] On the other hand, the $2p_\pi$ AO's on both carbon and oxygen show an increased population over the free-ligand values since back-bonding has the effect of populating a previously unoccupied ligand orbital (2π). In spite of the fact that this is an antibonding orbital, it will increase gross AO populations. The marked decrease in the occupation of $2p_\pi$ on oxygen from vanadium to manganese is therefore symptomatic of decreased back-bonding.

For the purpose of examining the bonding between a metal and a diatomic ligand, CO, it is most convenient to have the $M(CO)_6$ MO's in a basis of metal AO's and free-ligand *molecular* orbitals. Provided one includes the empty antibonding MO's of the free ligand, the results are in all respects equivalent in content to the results in an AO basis.[19] The MO's for $Cr(CO)_6$ are shown in Table III in terms of the free-ligand MO's described in the Appendix. This free CO calculation shows that 3σ is strongly bonding between the carbon and oxygen nuclei and that the energy of this orbital, −37 eV, is far below that of any other MO. As a result, 3σ does not mix with the other metal and ligand orbitals in the hexacarbonyls. The set of six carbon monoxide ligands contributes six orbitals of type 3σ, and these are recovered almost unchanged in $1a_{1g}$, $1e_g$, and $1t_{1u}$. The orbital energies of these hexacarbonyl MO's are also unaffected by bonding to Cr. Thus, these orbitals are metal–ligand nonbonding, being in some ways similar to the "core" fluoride 1s AO's neglected in earlier work on transition metal hexafluorides.[7,9]

Although the ligand 3σ MO is recovered unchanged in $Cr(CO)_6$, 4σ and 5σ show strikingly different behavior. The orbitals $2a_{1g}$, $3a_{1g}$, $2e_g$, $3e_g$, and $4t_{1u}$ all show strong mixing of 4σ with 5σ in the hexacarbonyl wave functions, and as a result the orbital energies of these MO's deviate from those of free CO. The mixing of 4σ and 5σ is such that the less stable orbital of a given symmetry (the orbital which bonds more effectively to the metal) increases its p_σ character. While over-all molecular stability demands an increase in carbon p_σ

TABLE III

EIGENVECTORS AND ENERGIES OF OCCUPIED MO'S OF $Cr(CO)_6$ IN A BASIS OF FREE CO MO'S

	3σ	4σ	5σ	6σ	4s	ϵ, eV		
$1a_{1g}$	1.0284	0.0356	0.0009	−0.0093	0.0068	−37.22		
$2a_{1g}$	−0.0481	0.5490	0.3156	−0.0131	0.2063	−18.51		
$3a_{1g}$	−0.0457	−0.6232	0.6627	−0.0010	0.2042	−15.23		
	3σ	4σ	5σ	6σ	$3d\sigma$	$4d\sigma$	ϵ, eV	
$1e_g$	0.9677	−0.0067	−0.0157	0.0197	0.0269	0.0512	−37.33	
$2e_g$	−0.0617	0.6995	0.3611	0.0116	0.4179	−0.0356	−19.01	
$3e_g$	−0.0616	−0.6957	0.5800	−0.0648	0.2680	0.1390	−16.14	
	1π	2π	$3d\pi$	$4d\pi$	ϵ, eV			
$1t_{2g}$	0.9829	0.2004	0.1915	−0.2161	−16.24			
$2t_{2g}$	−0.3636	0.5763	0.6493	−0.1201	−8.19			
	3σ	4σ	5σ	6σ	1π	2π	4p	ϵ, eV
$1t_{1u}$	0.9987	0.0219	0.0012	0.0051	−0.0061	−0.0067	0.0006	−37.21
$2t_{1u}$	0.1388	−0.9033	−0.1478	−0.0068	−0.0210	0.0007	−0.1659	−17.69
$3t_{1u}$	0.0319	−0.2015	0.2420	−0.0027	0.9138	0.0334	0.0637	−14.97
$4t_{1u}$	0.0675	−0.3102	0.7273	0.0039	−0.4334	0.0209	0.2599	−14.02
	1π	2π	ϵ, eV					
$1t_{2u}$	0.9984	0.0249	−14.95					
$1t_{1g}$	0.9963	0.0062	−14.90					

character in the metal–carbon bond, it is a striking feature of the 4σ–5σ mixing that it does not weaken the carbon–oxygen bond. This point is examined below in detail.

(a) **Absorption Spectra.**—Ever since crystal field theory yielded to a molecular orbital viewpoint, it has been the goal of MO calculations for transition metal complexes to compute Δ, the crystal field splitting between the t_{2g} and e_g components of the 3d orbital. The quantity Δ has been taken as the difference between the orbital energies of these antibonding t_{2g} and e_g MO's regardless of whether or not these orbitals are occupied.

There is no theoretical basis for expecting to be able to approximate excitation energies as the differences between ground-state orbital energies. However, a variety of semiempirical calculations[8,9] seem to indicate that if a certain choice of metal and ligand basis functions appropriately reproduce Δ as the $t_{2g} - e_g$ separation, then calculations carried out using the same-size basis set for similar complexes will faithfully represent trends in Δ for these complexes. The choice of basis set will strongly influence the success of the calculation, however. For example it has been demonstrated[7,28–31] that the inclusion of 2s ligand orbitals strongly alters the molecular orbital energies of unoccupied MO's, regardless of geometry or the particular computational scheme used. In an attempt to counteract this, use of the 4d metal orbital has been suggested to buffer the observed instability of the unoccupied MO's.[7] More recently, others have employed unoccupied AO's in related applications. In an attempt to calculate the spectrum of ethylene and the total energy for the reactive transition state $Cl\cdots CH_3\cdots Cl^-$, other workers have included 3s and 3p orbitals on carbon, 2s and 2p orbitals on hydrogen, and 3d orbitals on chlorine.[32] They show that the highest occupied orbital energy is unaffected by the augmented basis set, while the first two vacant MO's are stabilized by as much as 18 eV. On the basis of closer agreement between experimental excitation energies and differences in occupied and unoccupied orbital energies for the ground-state calculation, they conclude that "inclusion of outer AO's improves especially the excited states of normal molecules. . . ."[32]

The reason for this substantial effect of unoccupied "virtual" AO's on empty MO's was explained long ago using only the mathematical characteristics of the secular equation. A theorem, due to MacDonald,[33] shows in all generality that increasing the size of the matrix equation $|F - EG| = 0$ by one row and one column stabilizes all eigenvalues which were more negative than the newly introduced diagonal element and destabilizes all eigenvalues which were above this new term in the lower order equation. That is, all eigenvalues are "repelled," by the introduction of a new basis function, from the newly introduced diagonal term. This is why the ligand 2s orbital cited above destabilizes all upper orbital energies and, conversely, why outer orbitals on carbon and hydrogen decrease predicted excitation energies in ethylene. In view of the fact that *any* outer orbital will decrease these excitation energies, care must obviously be exercised in choosing *which* function is actually used. It is worth remarking that the instability of unoccupied MO energies is also encountered in rigorous SCF calculations as the basis set is augmented by outer orbitals. While Ransil's minimum basis calculation[21] for CO gives $\epsilon(2\pi) = 7.096$ eV, an extended basis calculation,[34] including $3d_\pi$ orbitals, yields $\epsilon(2\pi) = 4.147$ eV.

The results of a $Cr(CO)_6$ calculation with and without the 4d metal orbital are shown in Table IV. The a_{1g} and t_{1u} MO's show small random stabilization and destabilization since these are affected only indirectly by the self-consistency procedure. For the t_{2g} MO's, however, the 4d orbital always stabilizes the orbital

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TABLE IV
EFFECT OF A 4d ATOMIC ORBITAL ON THE ORBITAL ENERGIES FOR $Cr(CO)_6$

n	$D^a(na_{1g})$	$D(ne_g)$	$D(nt_{2g})$	$D(nt_{1u})$
1	0.06	−0.04	−0.99	0.07
2	−0.15	−0.46	−0.72	−0.08
3	−0.08	−0.68	−0.55	0.00
4	−0.13			−0.06
5	−0.20	+56		0.04
6		+116		−0.01
7				−0.16

[a] $D(n\Gamma) = \epsilon(n\Gamma)_{\text{with 4d}} - \epsilon(n\Gamma)_{\text{without 4d}}$ in electron volts.

energies. This agrees with MacDonald's theorem, since the 4d diagonal term is 5 eV above the highest t_{2g} orbital energy in the calculation without the 4d AO. In the e_g secular equation, F_{4d} lies between $\epsilon(3e_g)$ and $\epsilon(4e_g)$ so that the 4d AO stabilizes the three lowest MO's and destabilizes the two highest MO's. Pragmatically speaking, *outer orbitals definitely make the lowest unoccupied orbitals less sensitive to small changes in the calculational procedure.* For example, without the 4d AO, the e_g secular equation is of order 5, with three of the resulting MO's totally occupied. The $4e_g$ orbital energy changes 0.26 eV when ligand–ligand interaction is removed in the presence of a 4d AO, but this becomes 5.5 eV in the absence of this outer metal AO. The highest orbitals of a given symmetry are therefore much less stable to neglect of ligand–ligand interaction in the smaller secular equation. This shows the buffering as well as the stabilizing capacity of outer orbitals.

In an attempt to calculate the d-to-d spectrum of $Cr(CO)_6$, two calculations were carried out, one with the 4d AO and another without this "outer orbital." The separation $\epsilon(4e_g) - \epsilon(2t_{2g})$ is calculated to be 31.9 eV without the 4d AO in the basis set and 11.6 eV with the 4d orbital, compared to the experimental Δ value of 4.23 eV.[17] The 4d AO shows the usual effect of decreasing the $t_{2g} - e_g$ separation, but, in spite of its huge effect, it is not able to reproduce the experimental Δ. The effect of the form of the 4d radial function on the $\epsilon(4e_g) - \epsilon(2t_{2g})$ separation was investigated. Extensive variation in the 4d orbital exponent showed that it is not possible to cause the difference in orbital energies to agree with the observed Δ value. In spite of the failure to reproduce Δ from a calculation of the ground-state electronic structure, these results exhibit several interesting characteristics. Gross orbital populations are quite insensitive to the form of the 4d AO. Even more significant, a large change in the 4d orbital exponent changes the orbital energy of the *unoccupied* $4e_g$ MO 5.8 eV, whereas the orbital energy of the *occupied* $2t_{2g}$ MO changes only 0.4 eV. This shows that outer orbitals are not dictating ground-state properties and that they are important only as they affect the unoccupied MO's.

In view of the fact that stable ligand MO's "repel" upper MO's, the inability of the 4d AO to suppress the $4e_g$ MO in $Cr(CO)_6$ sufficiently, whereas it was adequate in the MX_6 species, is attributed to the doubling of the number of ligand AO's in the carbonyls compared to the halide complexes. In order to establish the validity of this idea, calculations were carried out in which various ligand MO's were omitted from the basis set. Removal of the free CO 3σ molecular orbital from the basis decreases $\epsilon(4e_g) - \epsilon(2t_{2g})$ by 0.73 eV, 86% of the change resulting from a 0.63-eV drop in $\epsilon(4e_g)$. The proposed reason for the inability of any 4d AO to reproduce is therefore correct.

Thus, the theoretically correct procedure of including all ligand valence AO's does not allow Δ to be identified as $\epsilon(4e_g) - \epsilon(2t_{2g})$ in $M(CO)_6$ systems. It is worth noting that this conclusion is not a defect of the simplified SCF scheme employed here, since the $4e_g - 2t_{2g}$ separation far exceeds the experimental Δ in a Wolfsberg–Helmholz calculation on $Cr(CO)_6$.[35] There is a very fundamental reason why Δ cannot be successfully calculated as the difference between unoccupied and occupied orbital energies, however, since the Hartree–Fock scheme is designed to calculate *ground-state* properties. With this in mind, the emphasis throughout this work will be to show the validity of the calculated ground-state molecular properties. If a better reproduction of absorption spectra is the desired goal of a calculation, configuration interaction and variation of the ligand radial AO's would be required.

(b) **Relative Ease of Oxidation of the Three Hexacarbonyls.**—Table I shows that $\epsilon(2t_{2g})$ rapidly becomes more stable along the series $V(CO)_6^-$, $Cr(CO)_6$, and $Mn(CO)_6^+$. The greater part of this effect is caused by the stabilization of all orbital energies as a result of the increasing positive charge on the hexacarbonyl, and it would be greatly diminished by the field of the cation and anion in $V(CO)_6^-$ and $Mn(CO)_6^+X^-$, respectively. It is known, however, that of the three hexacarbonyls only $V(CO)_6^-$ can be readily oxidized[36] to give a paramagnetic d^5 species. In order to examine these MO results for evidence of this effect, one must first correct for the neglect of the counterions in the calculations on charged species. In order to do this, one needs an occupied orbital which is not substantially affected by the change in bonding with changing central metal, but only by the total molecular charge. The metal–ligand nonbonding $1t_{2u}$ orbital is an appropriate internal standard, with the difference $\epsilon(2t_{2g}) - \epsilon(1t_{2u})$ being indicative of the actual stabilization of $2t_{2g}$ by the ligand 2π orbital. Since orbital energy is proportional to ionization (or oxidation) potential, a larger difference $\epsilon(2t_{2g}) - \epsilon(1t_{2u})$ implies easier oxidation. For $V(CO)_6^-$, $Cr(CO)_6$, and $Mn(CO)_6^+$, this difference has the values 8.17, 6.76, and 6.48 eV, respectively. The trend observed for $\epsilon(2t_{2g})$ itself is therefore maintained, but greatly decreased in magnitude: the hexacarbonyl of vanadium(−1) is most easily oxidized. Note that this is in spite of the fact that the ligand 2π orbital stabilizes $2t_{2g}$ most ef-

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fectively in $V(CO)_6^-$, an effect which tends to increase the oxidation potential of this compound. The effect of changing metal nuclear charge therefore predominates over the influence of back-bonding in determining the ease of oxidation.

(c) **Ionization Potentials of $Cr(CO)_6$.**—Koopmans' theorem[37] states that the energy required to ionize an electron from the ith molecular orbital with the geometry fixed at that of the neutral molecule (vertical IP) is $-\epsilon_i$ providing the other MO's are not appreciably affected by the ionization process. It is important to emphasize that, while there is no sound theoretical basis for calculating spectra as a difference in orbital energies, Koopmans' theorem does give physical meaning to the orbital energies of occupied MO's. Calculation of spectra and that of ionization potentials are unrelated problems. On the basis of a large number of examples, one can say that Koopmans' theorem allows calculation of ionization potentials to within 10% of the observed vertical ionization potential.[38,39] The appearance potential of a singly positive ion in a mass spectrometer is an upper limit to the adiabatic (0–0 vibrational transition) ionization potential. For the $2t_{2g}$ electrons, the vertical and adiabatic IP's should not differ greatly, and it is valid to compare the appearance potential of $Cr(CO)_6$ to $-\epsilon(2t_{2g})$. The calculated 8.19 eV compares very favorably to the observed values of 8.15 ± 0.17[40] and 8.18 ± 0.07 eV.[41]

Although mass spectral data yield only the ionization potential from the least stable MO, photoelectron spectroscopy[14] gives all ionization potentials below an instrumentally determined limit, presently 21 eV. In addition, it is possible to identify clearly the vertical IP, to which $-\epsilon$ should correspond. Table V compares the vertical photoelectron IP's with the calculated orbital energies.[42] The calculation of nine observed ionization potentials with an average accuracy of 5% is exceedingly satisfactory and constitutes supporting evidence for the accuracy of the calculated molecular orbitals. The pattern of spacings between IP's is well reproduced. Note the large gap between the "ligand field orbital" $2t_{2g}$ and the predominantly ligand $4t_{1u}$, as well as the smaller but still distinct gap between $1t_{2g}$ and $2t_{1u}$. It is becoming evident that the relative intensity of two bands in a photoelectron spectrum reflects orbital degeneracy provided the orbitals from which ionization occurs are very similar. Thus, the first two peaks for $Fe(CO)_5$, with configuration (CORE) $(e'')^4(e')^4$, are of equal intensity, while for $Ni(CO)_4$, (CORE) $(t_2)^6(e)^4$, the first IP has only two-thirds the intensity of the second IP.[47] Intensity relationships of this sort affirm several of the assignments proposed here. For example, the bands observed at 14.12 and 15.6 eV all originate in predominantly ligand 1π orbitals. The near degeneracy of $1t_{1g}$, $1t_{2u}$, and $3t_{1u}$ leads to the prediction that the 14.12-eV photoelectron peak should be 3 times as intense as the 15.6-eV band. The observed ratio is 2.5. Finally, it is of interest that the $4t_{1u}$ MO is *above* the ligand nonbonding $1t_{1g}$ and $1t_{2u}$ levels. Although intuition would place $4t_{1u}$ below the nonbonding $1t_{1g}$ and $1t_{2u}$ owing to a stabilizing interaction with metal 4p orbitals, the calculations indicate that this is not the case. Magnetic circular dichroism suggests the order $t_{1u} > t_{2u}$ for $IrCl_6^{2-}$ also.[43]

TABLE V

CALCULATED AND OBSERVED[42] IONIZATION POTENTIALS FOR $Cr(CO)_6$

Vertical ionization potential, eV		
Obsd	Calcd	Orbital symmetry
8.40	8.19	$2t_{2g}$
13.32	14.02	$4t_{1u}$
14.12	14.90, 14.95, 14.97	$1t_{1u}$, $1t_{2u}$, $3t_{1u}$
14.49	15.23	$3a_{1g}$
15.2	16.14	$3e_g$
15.6	16.24	$1t_{2g}$
17.48	17.69	$2t_{1u}$
18.7	18.51	$2a_{1g}$
19.3	19.01	$2e_g$

(d) **The C–O Bond.**—The most striking evidence for back-bonding in transition metal carbonyls is the reduction in the carbon–oxygen stretching frequency or force constant compared to free CO. For example, the C–O stretching force constant is 17.87 mdyn/Å in $Cr(CO)_6$ compared to 18.5 mdyn/Å in free CO.[44] Significant trends in the CO frequency are also found upon varying the transition metal. For example, the t_{1u} C–O stretching frequency for the hexacarbonyls of V(−1), Cr(0), and Mn(+1) are 1859, 1981, and 2101 cm^{-1} respectively.[45] Force constants are not available for this series of molecules, but the energetic isolation of the C–O stretching fundamental gives some assurance that force constants and frequencies will exhibit the same trend. The observed frequency variation has been interpreted in terms of increased C–O bond strength as a result of decreased back-bonding with increasing metal oxidation state. Implicit in this argument is the assumption that the σ bond between carbon and oxygen is unchanged upon bonding to a transition metal. Since these calculations include the σ-bonding orbitals on carbon and oxygen, one has the opportunity to test this assumption.

A rigorous comparison of the stretching force constants of the three hexacarbonyls should be based on a complete calculation of total energy surfaces, but this would require a massive amount of computation. Since the force constant should be related to the bond strength, the ability to correlate experimental frequencies with calculated indices of bond strength such as overlap populations and/or bond orders should lend support to the idea that these indices are capable of

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furnishing insight into the origin of stretching frequency trends in the hexacarbonyls. We have examined both overlap populations and bond orders in this regard. Since the trends and conclusions associated with each of these indices are completely analogous, only the correlations of frequencies with overlap populations will be presented here.

The interatomic overlap population, which represents the amount of charge transferred into the internuclear (bonding) region by covalent bonding between atoms A and B, is defined[15] as

$$P_{\mathrm{AB}} = \sum_{i} \sum_{j,k} 2N(i)C_{ij}(\mathrm{A})C_{ik}(\mathrm{B})G(j,k) \qquad (6)$$

where $C_{ij}(\mathrm{A})$ is the coefficient of the jth symmetry-adapted AO in the ith MO; $N(i)$ is the number of electrons in the ith MO (*e.g.*, 6 for a triply degenerate MO); $G(j,k)$ is the group overlap integral between the AO's k and j. The summation on i indicates all of the occupied MO's, and that over j and k concerns all of the AO's in the ith MO. The irreducible representations are indexed by Γ and in most cases it will be worthwhile to tabulate interatomic overlap populations for each representation separately. This is particularly true for the octahedral hexacarbonyls since it permits a clear distinction to be drawn between σ and π bonding in all representations except t_{1u}.

The computed interatomic overlap populations between carbon and oxygen are tabulated in Table VI. The constancy of the overlap populations for σ-bonding orbitals is striking and *fully confirms the assumption of invariant σ-bond strength along the isoelectronic series of hexacarbonyls.* The total σ-overlap population for six noninteracting CO molecules is 4.50. The values in Table VI are only slightly higher than this value, indicating that the σ-orbital framework of CO is not only constant within the series of hexacarbonyls, but it is approximately unchanged from free CO itself.

TABLE VI

INTERATOMIC OVERLAP POPULATIONS

$P_{\mathrm{CO}}{}^{\Gamma}$ BETWEEN CARBON AND OXYGEN

Γ	$V(CO)_6^-$	$Cr(CO)_6$	$Mn(CO)_6^+$
	σ Bonds		
a_{1g}	0.75	0.75	0.75
e_g	1.60	1.52	1.63
t_{1u}	2.33	2.33	2.33
Total	4.68	4.60	4.71
	π Bonds		
t_{2g}	0.22	0.48	0.65
t_{1g}	1.16	1.17	1.19
t_{2u}	1.17	1.18	1.19
t_{1u}	1.15	1.17	1.19
Total	3.69	4.00	4.23

The C–O σ bond is essentially unaffected by bonding to a transition metal because of the energetic isolation of the free CO 3σ molecular orbital. It is this orbital which is strongly bonding between carbon and oxygen (overlap population 0.72), 4σ and 5σ being very weakly bonding (overlap populations 0.08 and 0.03, respectively). Thus, although 4σ and 5σ mix strongly with metal AO's in the hexacarbonyls, the resultant decrease in C–O overlap population is very small. The 3σ free ligand MO is the strongly C–O σ-bonding orbital, and its very stable orbital energy makes it effectively nonbonding to the less stable metal AO's.

Looking now to the π-bonding orbitals between carbon and oxygen, one finds a distinct increase in the total π-overlap populations from $V(CO)_6^-$ to $Mn(CO)_6^+$ indicating an increase in C–O bond strength with increasing metal oxidation state. The change in C–O bond strength is therefore dominated by a change in the π orbitals, and the change in total π overlap population is in turn dominated by changes in the t_{2g} MO's. Since only the $3d_\pi$ metal AO's are of t_{2g} symmetry, it is the interaction between $3d_\pi$ and 1π and 2π (*i.e.*, back-bonding) which determines the variation in CO infrared frequencies.

(e) **The Metal–Carbon Bond.**—The t_{1u} metal–carbon stretching vibrational frequency decreases regularly with increasing metal oxidation state for the isoelectronic hexacarbonyls. The observed[45] frequencies are 460, 441, and 416 cm^{-1} for $V(CO)_6^-$, $Cr(CO)_6$, and $Mn(CO)_6^+$, respectively. Although a complete force field analysis is not available for these three species, an energy-factored vibrational analysis should be valid, and the observed frequencies should reflect the trend in stretching force constant. For example, Kaesz, *et al.*,[46] have shown that the Re–D stretching frequency at 1822 cm^{-1} perturbs the 2000-cm^{-1} C–O stretching frequency in $DRe(CO)_5$ only 5 cm^{-1}. Equally small perturbations in the hexacarbonyl metal–carbon stretching frequencies are expected as a result of interaction with other low-frequency t_{1u} fundamentals.

Table VII gives the interatomic overlap populations, $P_{\mathrm{MC}}{}^{\Gamma}$ of eq 6, for the three hexacarbonyls. No metal–oxygen overlap populations are included since they are all negative and less than 0.1 in magnitude. The intuitive idea that there is no bonding between metal and oxygen atoms is thus confirmed. Note that the metal 4p AO, which transforms as t_{1u}, is almost exclusively a σ-bonding orbital. This is also evident from the wave functions in the basis of free ligand MO's (Table III), since 1π undergoes very little mixing in the $3t_{1u}$ MO of the hexacarbonyls. The metal–carbon overlap populations clearly show a decrease with increasing metal oxidation state, in agreement with the observed stretching frequencies.

TABLE VII

METAL–CARBON OVERLAP POPULATIONS[a]

	$V(CO)_6^-$	$Cr(CO)_6$	$Mn(CO)_6^+$
a_{1g}	0.72	0.71	0.62
e_g	1.54	1.34	1.12
t_{2g}	1.74	1.39	0.95
$t_{1u}(\sigma)$	2.19	2.16	2.04
$t_{1u}(\pi)$	−0.014	−0.016	−0.019

[a] 4d orbital contributions not included in e_g and t_{2g} totals.

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(46) P. S. Braterman, R. W. Harrill, and H. D. Kaesz, *J. Am. Chem. Soc.*, **89**, 2851 (1967).

The observed decreasing metal–ligand stretching frequency with increasing metal oxidation state is unusual and significant since it is contrary to the "normal" trend of increasing frequency with increasing metal oxidation state. For example, $MnCl_4^{2-}$ and $FeCl_4^-$ exhibit infrared-active stretching frequencies at 378 and 482 cm^{-1}.[47] VO_4^{3-}, CrO_4^{2-}, and MnO_4^- have stretching force constants of 5.11, 5.58, and 5.84 mdyn/Å, respectively.[48] In view of the fact that the observed trend has been successfully reproduced as opposite to that in chloride and oxide complexes, it is worthwhile to search for the origin of the trend. One of the largest contributions to the decreasing overlap populations is in the t_{2g} representation. In order to show clearly the interaction of the 1π, 2π, and $3d_\pi$ orbitals, the t_{2g} metal–carbon overlap populations are tabulated for the individual basis orbital pairs in Table VIII. The change in total overlap population, $P_{CO}^{t_{2g}}$, in Table VI is now seen to be dictated by a reduction in the 2π–$3d_\pi$ overlap population in the $2t_{2g}$ MO on passing from the vanadium to chromium compounds. This in turn is caused by a smaller interaction between the $3d_\pi$ and 2π basis orbitals as well as by the contraction of the metal AO with increasing metal nuclear charge. Note that the interaction between 2π and $3d_\pi$ in $2t_{2g}$ is strongly bonding in the metal–carbon region despite the fact that 2π is carbon–oxygen antibonding. This explains the inverse relation between the changes in metal–carbon and carbon–oxygen stretching constants along the series of isoelectronic hexacarbonyls: the 2π gross orbital population can decrease only through decreased $3d_\pi$–2π mixing in $2t_{2g}$, so that a decreasing 2π population (increasing ν_{CO}) accompanies decreasing $2t_{2g}$ orbital covalency (decreasing ν_{MC}).

Table VIII

Orbital Overlap Populations[a] within the t_{2g} Representation

	$n(1t_{2g};$ $1\pi, 3d\pi)$	$n(1t_{2g};$ $2\pi, 3d\pi)$	$n(2t_{2g};$ $1\pi, 3d\pi)$	$n(2t_{2g};$ $2\pi, 3d\pi)$
$V(CO)_6^-$	0.41	0.03	−0.50	1.69
$Cr(CO)_6$	0.34	0.04	−0.42	1.36
$Mn(CO)_6^+$	0.28	0.06	−0.39	1.02

[a] $n(i;\ rs) = 2N(i)C_{ir}C_{is}G(r,s)$.

The reason that the isoelectronic hexacarbonyls do not exhibit the "normal" trend of increasing metal–ligand stretching frequency with increasing metal oxidation state is also clear from the above discussion. Ligands which exhibit this "normal" trend are all π-donor ligands which have no counterpart of the empty 2π MO of carbon monoxide. As the metal $3d_\pi$ F matrix element becomes more negative (*i.e.*, as the metal oxidation state increases), the covalent interaction with the occupied ligand π orbital increases regularly, thereby increasing the metal–ligand bond strength. For complexes of π-acceptor ligands such as CO, however, this increased interaction with the 1π MO is available only at the expense of bonding interaction with the free-ligand antibonding orbital which has the effect of weakening the metal–ligand bond. The foregoing arguments are quite general, and therefore all isoelectronic complexes of π-acceptor ligands should exhibit this "unusual" trend in metal–ligand stretching frequencies.[49]

In concluding this discussion on metal–ligand bonding, it is instructive to compare the metal–ligand overlap populations in the t_{2g} MO's of $Cr(CO)_6$ and $CrCl_6^{3-}$. The overlap populations in $1t_{2g}$ are very similar while in $2t_{2g}$ they are 0.89 and −0.27 in the carbonyl and chloride, respectively; as expected, π bonding is substantially weaker in $CrCl_6^{3-}$, but the reason for this is interesting. The overlap population in $2t_{2g}$ is smaller in absolute value in the chloride owing to less orbital covalency as well as the fewer number of electrons; the *signs* are different since the $2t_{2g}$ MO is antibonding with respect to $F(3d_\pi)$ in the chloride while it is bonding in the carbonyl owing to the stabilizing influence of the ligand 2π orbital. This stabilization has been estimated quantitatively earlier.

(f) **Reactivity toward Nucleophiles.**—There is a substantial body of information scattered throughout the literature which indicates that the hexacarbonyls are susceptible to attack by nucleophiles. Such information is most abundant for the neutral chromium group hexacarbonyls, but this reflects on their availability rather than their reactivity. Cationic hexacarbonyls have been shown to react with nucleophiles in the few cases studied.[50,51]

There has been speculation[50,52] that these reactions take place by attack at the carbonyl carbon, but this is difficult to verify experimentally. However, since it is possible to estimate approximate "atomic charges" by means of the Mulliken population analysis, one can locate reactive molecular sites from the results of the calculations presented here. The situation is complicated somewhat by the earlier observation that isolated atomic metal 4s, 4p, and 4d AO's are so diffuse that they contribute to charge density at the ligands rather than at the metal.[7] However, the method used to derive the 4s, 4p, and 4d functions in the present work substantially contracts these orbitals. Plots of the radial functions used here show the charge density to lie primarily in the internuclear region rather than at the ligand atoms. Consequently, it is reasonable to assume that the calculated charges on the carbon and oxygen atoms reflect to some degree the charges in the vicinity of the carbon and oxygen nuclei. For the vanadium, chromium, and manganese compounds, carbon bears charges of +0.25, +0.20, and +0.18, respectively. Thus, carbon is predicted to be susceptible to nucleophilic attack in all three hexacarbonyls. The positive charge on carbon is in contrast to the carbon charge of −0.13 in free CO, indicating that the

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(47) D. M. Adams, J. Chatt, J. M. Davidson, and J. Geratt, *J. Chem. Soc.*, 2189 (1963).

(48) A. Müller and A. Fadini, *Spectrochim. Acta*, **22**, 1523 (1966).

(49) In addition to complexes of CN^-, the PF_3 analogs of the isoelectronic hexacarbonyls are likely candidates for showing this effect: T. Kruck, *Angew. Chem.*, **79**, 27 (1967).

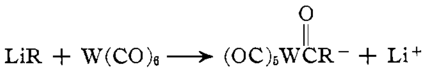
(50) T. Kruck and M. Noack, *Chem. Ber.*, **97**, 1693 (1964).

(51) E. L. Muetterties, *Inorg. Chem.*, **4**, 1841 (1965).

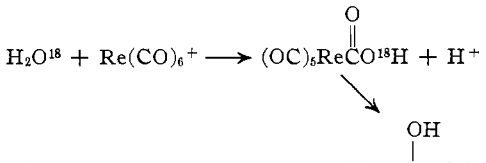
(52) W. Beck and H. S. Smedal, *Angew. Chem. Intern. Ed. Engl.*, **5**, 253 (1966).

carbon site becomes electrophilic by bond formation with a transition metal.

On the basis of the atomic charges calculated here, the following known reactions are predicted to obey a second-order rate law, mechanisms being suggested where appropriate.

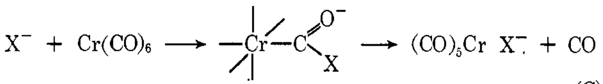

$$\mathrm{LiR + W(CO)_6 \longrightarrow (OC)_5W\overset{O}{\overset{\|}{C}}R^- + Li^+}$$

(A)[53,54]



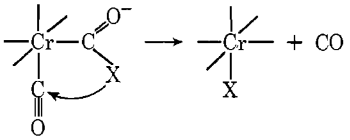
(B)[51]

In contrast to this reaction, $Mo(CO)_6$ shows no exchange with H_2O^{18} after 75 hr.[51] This is probably due to the low nucleophilicity of H_2O, as well as to the fact that the positive metal charge in $Re(CO)_6^+$ promotes the approach of a nucleophile. $Mn(CO)_6^+$ reacts with water, but the isolable products are $HMn(CO)_5$ and CO_2.[50] Although $(OC)_5MnCOOH$ is predicted to be an intermediate, it is evidently not stable relative to $HMn(CO)_5$. The different behavior of $Mn(CO)_6^+$ and $Re(CO)_6^+$ is in no way contradictory, since an MO calculation on a molecule can predict reactive sites, but is not expected to yield information on the most stable final reaction product.

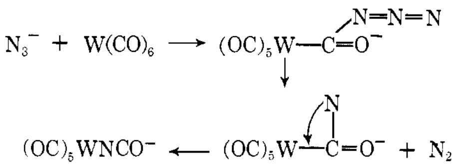


(C)[55]

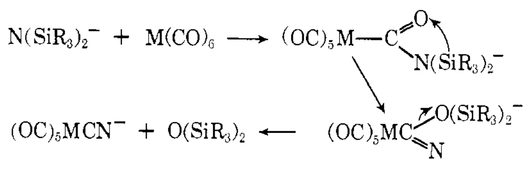
Here the intermediate, an acyl halide derivative of chromium hexacarbonyl, could react to form the pentacarbonyl halide by an internal displacement mechanism analogous to that suggested for the decarbonylation of $RCOMn(CO)_5$[56]



Isolation of an acyl halide derivative would provide convincing evidence for the mechanism proposed here. If actual isolation of the intermediate at low temperatures proves impossible, CO infrared or C^{13} nmr evidence for a reacting species would suffice.



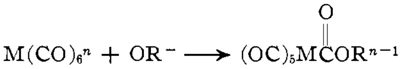
(D)[52]



(M = Cr, Mo, W) (E)[57]

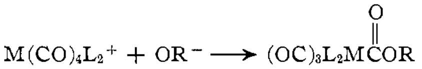
In addition to explaining the kinetics and mechanisms of the above reactions, the calculations also suggest the possibility of the reactions

$$\mathrm{Re(CO)_6^+ + X^- \longrightarrow Re(CO)_5X + CO} \qquad \text{(F)}$$


$$\mathrm{M(CO)_6^{\it n} + OR^- \longrightarrow (OC)_5M\overset{O}{\overset{\|}{C}}OR^{\it n-1}}$$

(G)

Although no information is available on the reaction of hexacarbonyls with alkoxide, reaction G shows that an acylmetal pentacarbonyl should be produced. Such behavior is exhibited by substituted carbonyl cations.[50]


$$\mathrm{M(CO)_4L_2^+ + OR^- \longrightarrow (OC)_3L_2M\overset{O}{\overset{\|}{C}}OR}$$

(M = Mn, Re; L_2 = $(P(C_6H_5)_3)_2$ or *o*-phenanthroline)

With the use of this analogy, a word of caution must be injected, however. The calculations presented here describe the charge density only in *octahedral* hexacarbonyl complexes, and extrapolation of these results to different stereochemistries or degrees of substitution is dangerous. Thus, carbon is expected to be more negative in $Ni(CO)_4$ and $Fe(CO)_5$ than in $Cr(CO)_6$ since there are more electrons to back-bond and fewer ligands to accept them. Likewise, in $XMn(CO)_5$ the CO group *trans* to X accepts more metal electrons than the other four.[11] As a result of this alteration in electron density, the reaction of $XMn(CO)_5$ with X^- or CO is an SN1 process.[58,59]

It is important to recognize that the prediction that nucleophiles will react with hexacarbonyls by a second-order rate law is a nontrivial result of these calculations which cannot be deduced from "chemical intuition" alone. Indeed, octahedral complexes are considered to have a strong preference for a dissociative (SN1) mechanism in substitution reactions.[60] For example, $Mo(CO)_6$ has been shown to react with neutral phosphines, L, to form $Mo(CO)_5L$ by an SN1 process.[61] However, it has been demonstrated recently that this is actually a dual-path reaction, with second-order kinetics in evidence at high phosphine concentrations.[62] It is of interest that the enthalpy of activation is only 21.7 kcal/mol for the SN2 pathway, while it is 31.7 kcal/mol for the SN1 mechanism; the enthalpy change clearly favors nucleophilic attack, presumably at carbon.

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Appendix

It is clear that if MO calculations based on a simplified Fock operator are successfully to explain and predict ground-state molecular properties of large molecules, then it is desirable that the method be capable of reasonable reproduction of the results of rigorous SCF calculations on small molecules. Such a comparative calculation has never been carried out with the computational scheme to be used here, and since diatomic ligands were under study, it seemed appropriate to calculate MO's for free CO. The SCF results which are available[21] provide a stringent test for the simplified MO scheme. The basis functions and internuclear distances used in the calculations reported here are identical with those used in the SCF work. This condition was imposed in order truly to test the method for calculating the Fock matrix elements and to avoid variations due to choice of atomic orbitals.

Results from the calculation on CO are given in Table IX along with the rigorous SCF values for comparison. Ransil's "Slater LCAO–MO" basis was used in the calculation.[21] The oxygen and carbon 1s atomic orbitals were assumed to be unperturbed by bond formation, and they are unmixed in MO's 1σ and 2σ, respectively. The table shows generally good agreement between orbital energies calculated by the rigorous and simplified SCF schemes. Also shown are the experimental ionization potentials, which should equal minus the orbital energies.[13] The simplified MO wave functions satisfactorily weight atomic orbitals with the correct relative size and phase. The coefficients themselves are represented fairly accurately in absolute value.

TABLE IX

CALCULATED EIGENVECTORS[c] AND ORBITAL ENERGIES FOR CO[a]

	$2s^C$	$2s^O$	$2p^C$	$2p^O$	ϵ, eV	Exptl IP[b]
3σ	0.302 (0.234)	0.711 (0.738)	0.213 (0.169)	0.068 (0.223)	−37.74 (−40.78)	. . .
4σ	0.441 (0.525)	−0.462 (−0.635)	−0.016 (0.067)	0.744 (0.635)	−18.22 (−19.92)	19.65
5σ	0.664 (0.739)	0.059 (0.036)	−0.664 (−0.566)	−0.364 (−0.438)	−13.02 (−13.08)	14.00
1π	. . .	. . .	0.488 (0.469)	0.757 (0.771)	−15.52 (−15.86)	16.91

[a] Rigorous SCF values in parentheses.[21] [b] Observed vertical ionization potentials.[14] [c] The local $+z$ axes on C and O point toward each other.

One error is evident upon comparison of the simplified and rigorous SCF functions: the coefficients of $2p^O$ and $2p^C$ are underestimated in 3σ and 4σ, respectively. Since these MO's are largely $2s^O$ and $2s^C$, respectively, this error is the result of a poor representation of the one-center off-diagonal F matrix elements $(2s^O|F|2p_\sigma{}^O)$ and $(2s^C|F|2p_\sigma{}^C)$. Since the kinetic energy and one-center nuclear attraction integrals are rigorously zero in these cases, only a two-center nuclear attraction or "crystal field" integral remains in the simplified SCF method

$$(2s^a|F|2p_\sigma{}^a) = q_b\left(2s^a\left|\frac{1}{r_b}\right|2p_\sigma{}^a\right)$$

Since CO is nearly nonpolar, q_b is very small and the resulting off-diagonal F matrix element is small. A small off-diagonal F matrix element leads to the inadequate mixing of $2s^a$ with $2p_\sigma{}^a$ observed in these calculations. It is possible to calculate the true values of these terms in a relatively simple fashion. Starting with the Hartree–Fock matrix equations $FC = SC\epsilon$, one may multiply by C^{-1} from the right to give $F = SC\epsilon C^{-1}$. Thus, knowing S, C, and ϵ, we may calculate F. In this way, one calculates the SCF one-center off-diagonal carbon and oxygen terms for Ransil's basis set to be −7.2 and −5.9 eV, compared to the values −0.6 and +0.5 eV which result from the simplified SCF procedure. All attempts to rectify this situation have been unsuccessful and the simplified SCF scheme has been used unchanged in spite of this defect. These one-center terms are set equal to zero in the Wolfsberg–Helmholz scheme, but their importance has been emphasized recently by Lipscomb, *et al.*,[6] who are also unable to evaluate them in a nonempirical fashion. Since the results on $M(AB)_6$ species to be presented here are ultimately expressed in terms of free-ligand *molecular* orbitals, this problem loses some of its gravity. In addition, the problem occurs only in 3σ and 4σ, which are energetically rather isolated from the transition metal diagonal F matrix elements; the importance of these ligand orbitals to metal–ligand bonding is therefore minimal.