(33) W. P. Kraemer and G. H. F. Diercksen, *Theor. Chem. Acta*, **23**, 398 (1972).
(34) A. R. Gregory and M. N. Paddon-Rolo, *J. Am. Chem. Soc.*, **98** 7521 (1976).
(35) D. J. McGinty, *J. Chem. Phys.*, **58**, 4733 (1973).
(36) P. Schuster in "Electron-Solvent and Anion Solvent Interactions, L. Keuan and B. C. Webster, Eds., American Elsevier, New York, 1976, Chapter 8, p 274.
(37) A. W. Castleman, Jr., P. Holland, and R. G. Keesee, *J. Chem. Phys.*, **68**, 1760 (1978).
(38) A. W. Castleman, Jr., "Studies of Ion Clusters: Relationship to Understanding Nucleation and Solvation Phenomena", *NATO Adv. Study Inst., Kinet. Ion Mol. React.* (1979).
(39) H. L. Friedman and C. V. Krishnan in "Water", Vol. 3, F. Franks, Ed., Plenum Press, New York, 1973, Chapter 1, p 56.
(40) B. Jönsson, G. Karlström, H. Wennerström, and B. Roos, *Chem. Phys. Lett.*, **41**, 317 (1976).
(41) K. F. Wissbum, D. M. Franch, and A. Patterson, *J. Phys. Chem.*, **58**, 693 (1954).
(42) F. J. W. Roughton, *J. Am. Chem. Soc.*, **63**, 2930 (1941).

# Bonding Capabilities of Transition Metal Clusters. 2.[1] Relationship to Bulk Metals

**Joseph W. Lauher**

*Contribution from the Department of Chemistry, State University of New York at Stony Brook, Stony Brook, New York 11794.*

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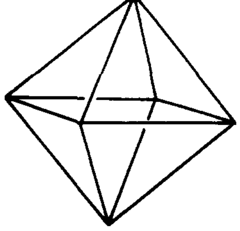
**Abstract:** The bonding capabilities of individual metal atoms of a cluster or of an infinite lattice have been estimated, based upon extended Hückel calculations. Each atom can be assigned a characteristic number of cluster valence molecular orbitals (CVMOs), which is dependent upon the site geometry. The CVMOs can contain metal electrons or can be used as ligand acceptor orbitals. The number of CVMOs located on an atom at a given site is inversely dependent upon the number of nearest neighbors.

A popular assumption as of late is that discrete organometallic transition metal cluster compounds are good models for chemisorption on to bulk metal surfaces and that catalysis by small metal particles involves species similar to known stoichiometric compounds.[2-5] Unfortunately, to date there has been little theoretical justification for any direct connection. This is due primarily to the fact that for bulk metals the observables of most concern to theoreticians are the diverse bulk electronic and magnetic properties, while for cluster compounds, which are almost always diamagnetic, the primary observables are structure and stoichiometry. Theoretical studies have generally been directed toward an understanding of one of these problems or the other; seldom have their direct relationships been explored. In this work we will explore such relationships and will offer a unified method for determining the bonding capabilities of an individual atom of a cluster or an individual atom of a bulk metal surface.

**Clusters.** It has been known for some time that structure and stoichiometry are closely related in group 8 organometallic cluster compounds.[5,6] A given cluster tends to have its stoichiometry determined not by the identity of the metal or the ligands, but by the geometry of the cluster. For example, if six metal atoms are arranged in an octahedral geometry they will in general form stable chemical compounds only if the sum of the cluster valence electrons (CVEs) is equal to 86 electrons.



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One such cluster is the anion $[Fe_6(CO)_{16}C]^{2-}$, which has 48 Fe electrons, 32 electrons from the CO ligands, 4 from the intersitial carbide, and a dinegative charge; the sum is 86 electrons.[7] Other diverse examples[6] include $[Co_6(CO)_{16}]$, $[Ni_6(CO)_{12}{}^{2-}]$, $[Ru_6(CO)_{17}C]$, $[Rh_6(CO)_{16}]$, and $[Ni_2Co_4(CO)_{14}]^{2-}$.

Recently we reported a simple, reliable MO method for determining the bonding capabilities or stoichiometries of small metal clusters.[1] As aggregates of metal atoms are built up one atom at a time, the atomic orbitals combine to form molecular orbitals, which evolve at the infinite limit into the band structure of bulk metal. At the intermediate cluster stage we have found that the MOs can be conveniently divided into two classes on the basis of energy. The high-lying antibonding orbitals (HLAOs) are destabilized by metal–metal antibonding interactions and are too high in energy to contain electrons or to serve as ligand acceptor orbitals. The cluster valence molecular orbitals (CVMOs) are lower in energy, are suitable for containing metal electrons, and can serve as acceptor orbitals for ligand bonding.

The preference shown for 86 CVEs by the octahedral clusters is due to the presence of exactly 43 CVMOs. To determine the number of CVMOs of a given cluster we have used extended Hückel calculations[8] as a guide and have determined empirically that a reliable upper energy limit for the CVMOs is the level of the p orbitals of a single metal atom. Thus any orbital significantly destabilized with respect to the p level of a single atom is classified as a HLAO.

**Bulk Metals.** Transition metals have diverse physical properties and have thus been of interest to theoreticians for many years. Generally the bonding with metals is treated by various band theories, discussions of which can be found in standard texts.[9,10] Inherent in such theories is a delocalization of states, which sometimes makes information regarding discrete atomic sites difficult to abstract. Actually it is also difficult to determine the properties of individual atoms by most physical measurements as well.

To make comparisons with the discrete cluster compounds, we need to know the number of states or orbitals contributed by each metal atom to the energy band and which are available for electron occupancy. This information is most readily available for the group 8, ferromagnetic metals, Fe, Co, Ni, and their alloys. From the spontaneous magnetic moments of

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**Table I.** Bonding Capabilities of Selected Transition Metal Clusters[a]

| cluster | $N$ | $9N$ | HLAO | CVMO | CVE | CVMO/$N$ |
|---|---|---|---|---|---|---|
| **1** octahedron | 6 | 54 | 11 | 43 | 86 | 7.17 |
| **2** octahedron | 19 | 171 | 47 | 124 | 248 | 6.53 |
| **3** cube octahedron | 13 | 117 | 32 | 85 | 170 | 6.54 |
| **4** $D_{2h}$ | 20 | 180 | 52 | 128 | 256 | 6.40 |
| **5** square pyramid | 14 | 126 | 31 | 95 | 190 | 6.79 |
| **6** tetrahedron | 20 | 180 | 53 | 127 | 254 | 6.35 |

[a] $N$ is the number of atoms; $9N$ is the number of atomic orbitals; HLAO is the number of high-lying antibonding orbitals; CVMO is the number of cluster valence molecular orbitals; CVE is the number of cluster valence electrons.

these metals one can determine the number of unpaired electrons per metal atom and thus the number of occupied orbitals. Plots of measured spontaneous magnetic moments vs. atomic number for these metals and alloys are known as Slater–Pauling curves.[11-13] These curves reveal that there is a smooth variation of the spontaneous magnetic moment and thus the number of unpaired electrons, which rises to a maxima for an alloy consisting roughly of 75% iron and 25% cobalt and which falls to zero for nickel-copper alloys. These curves show that for all of these metals there is a roughly constant number of orbitals per metal atom available for occupancy. This number is approximately 5.3 orbitals per metal atom.[9] For pure cubic-close packed nickel and cobalt the value is 5.28 orbitals per atom. Body-centered iron, which is before the maximum of the Slater–Pauling curve, has 5.06 occupied orbitals per atom. The upper energy bound for these orbitals is of course the Fermi energy of the metal.

**Calculations.** Using the same methods and parameters used previously[1] we have performed extended Hückel calculations[8] on a variety of cubic-close packed Rh clusters of up to 20 metal atoms (Table I). For each cluster the geometry was idealized with Rh–Rh distances of 2.69 Å corresponding to the distance found in Rh metal.[14] Rhodium was chosen as the representative element since it is the centermost group 8 metal and since it is known to form many cluster compounds of high nuclearity. The parameters used in our calculations are arbitrary, but their magnitudes are not very important since the number of CVMOs is determined mainly by symmetry and nodal patterns. Thus any method which produces MOs which are qualitatively correct will predict the same number of CVMOs.

**Octahedral Clusters.** An octahedron of six metal atoms, **1**, has 43 CVMOs, which is 7.17 CVMOs per metal atom. The next largest octahedron, **2**, with 19 metal atoms, has 124 CVMOs or 6.53 per metal atom; however, the atoms are not all equivalent. There are 6 apex A atoms, 12 edge B atoms, and 1 interior C atom. Each site contributes a different number of CVMOs to the cluster. By using the calculated atomic orbital coefficients of each CVMO it is possible to determine the number of CVMOs located on each individual atom. The results of these calculations are presented in Table II, which also gives a breakdown of s, p, and d contributions.

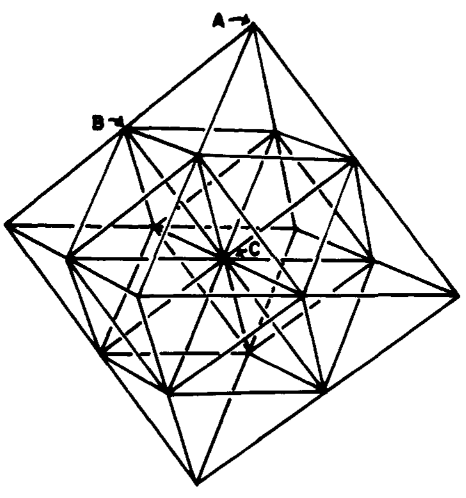

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**Table II.** Analysis of Site Bonding Capabilities[a]

| cluster | $N$ | site | $N_s$ | $N_{nb}$ | CVMO | $s$ | $p$ | $d$ |
|---|---|---|---|---|---|---|---|---|
| **1** octahedron | 6 | A | 6 | 4 | 7.17 | 0.71 | 1.56 | 4.90 |
| **2** octahedron | 19 | A | 6 | 4 | 7.13 | 0.71 | 1.52 | 4.90 |
| | | B | 12 | 6 | 6.29 | 0.55 | 0.89 | 4.86 |
| | | C | 1 | 12 | 5.71 | 0.44 | 0.54 | 4.74 |
| **3** cube octahedron | 13 | D | 12 | 5 | 6.61 | 0.65 | 1.08 | 4.88 |
| | | C | 1 | 12 | 5.67 | 0.42 | 0.51 | 4.74 |
| **4** $D_{2h}$ | 20 | D | 8 | 5 | 6.64 | 0.65 | 1.11 | 4.88 |
| | | D | 2 | 5 | 6.57 | 0.65 | 1.04 | 4.88 |
| | | F | 4 | 6 | 6.40 | 0.60 | 0.94 | 4.86 |
| | | E | 4 | 7 | 6.23 | 0.55 | 0.83 | 4.85 |
| | | C | 2 | 12 | 5.60 | 0.41 | 0.45 | 4.75 |
| **5** square pyramid | 14 | I | 4 | 3 | 7.43 | 0.75 | 1.75 | 4.93 |
| | | A | 1 | 4 | 7.17 | 0.71 | 1.53 | 4.93 |
| | | H | 4 | 5 | 6.63 | 0.62 | 1.12 | 4.89 |
| | | B | 4 | 6 | 6.32 | 0.54 | 0.92 | 4.86 |
| | | G | 1 | 8 | 6.27 | 0.54 | 0.94 | 4.79 |
| **6** tetrahedron | 20 | J | 4 | 3 | 7.09 | 0.76 | 1.42 | 4.91 |
| | | L | 12 | 6 | 6.23 | 0.57 | 0.80 | 4.86 |
| | | K | 4 | 9 | 5.98 | 0.48 | 0.71 | 4.79 |

[a] $N$ is number of atoms; site is label of site; $N_s$ is number of such sites; $N_{nb}$ is number of nearest neighbors of an atom at the site; CVMO is number of CVMOs at the site; $s$, $p$, and $d$ are the relative contributions from s, p, and d orbitals.

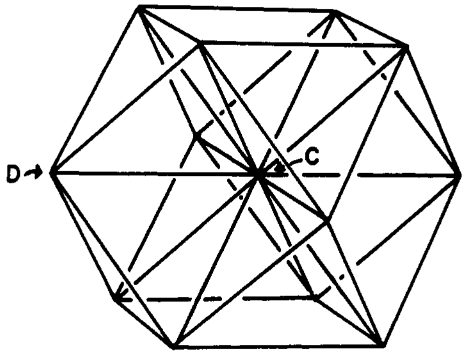
It can be seen that the number of CVMOs per site varies considerably. The vertex A atoms have only 4 nearest neighbors and 7.13 CVMOs, while the center C atom has all 12 nearest neighbors of a cubic-close packed lattice and only 5.71 CVMOs. The edge sites B have 6 nearest neighbors and are intermediate with 6.29 CVMOs. The compositions of the orbitals also vary with the biggest differences due to changes in the p orbital contributions. There is a 1.52 p orbital contribution at site A, but only a 0.54 contribution at site C.

If we apply these results to cluster chemistry they can be interpreted as follows. The six-atom octahedron with 43 CVMOs forms stoichiometric cluster compounds with 86 CVEs. Thus the 19-atom octahedral cluster with 124 CVMOs requires 248 CVEs for stability. The anion $[Rh_{19}(CO)_{36}]^{5-}$ is a hypothetical example. The relative number of CVMOs per site (A and B) will help to determine the number of terminal and bridging CO ligands bound to each surface atom, although ligand–ligand repulsions will also be important.

The interior atom C presents somewhat of a problem. Our calculations suggest that atom C contributes 5.71 CVMOs to the cluster, which must be satisfied if the cluster is to be stable. Rhodium has only nine d electrons so there must be some mechanism for stabilizing this central atom. The simplest possibility is a buildup of negative charge on the site C contributed by the surface atoms which are in turn stabilized by ligands. Large localized charges are not reasonable, however, and other mechanisms may be used. One mechanism is a distortion of the geometry of the cluster, which brings the next nearest neighbors of the central atom closer than they would be in a perfect close-packed lattice. The new metal–metal interactions will decrease the number of CVMOs located on the central metal atom and thus reduce the required charge buildup. Such distortions have been found in certain large cluster compounds such as the anions $[Rh_{15}(CO)_{27}]^{3-}$ and $[Rh_{14}(CO)_{25}]^{4-}$ reported by Martinengo et al.[15]

Another mechanism for the stabilization of interior atoms is the presence of interstitial atoms such as hydrides, carbides, or other heteroatoms. An interstitial atom is essentially an internal ligand and can donate electrons to an interior metal atom in the same manner that a normal exterior ligand donates its pair of electrons to a surface atom. Many of the large clusters with internal metal atoms do have interstitial atoms, including the hydride,[16] $[Rh_{13}(CO)_{24}H_3]^{2-}$, the carbide,[17] $[Rh_{15}(CO)_{27}C_2]^-$, and the sulfide,[18] $[Rh_{17}(CO)_{32}S_2]^{3-}$. Thus a more probable formulation for our hypothetical 19-atom octahedral cluster might be as a hydride such as $[Rh_{19}(CO)_{36}H_3]^{2-}$ or as one of the many possible carbides which could be formulated. We believe that one of these two phenomena, distortion of the framework to bring next nearest neighbors closer or the presence of interstitial ligands, will be found for most large clusters with interior atoms.

**Interior Atoms.** The interior atom of the octahedron has 5.71 CVMOs. It is useful to compare this number with the results found for other clusters with interior atoms. The simplest case is the 13-atom cube octahedron **3**, which has a single metal atom surrounded by its 12 cubic-close packed nearest neighbors. The resulting cluster has 85 CVMOs, 5.67 of them contributed by the central atom and 6.61 from each of the 12 exterior atoms. Also considered is the 20-atom cluster **4** which has $D_{2h}$ symmetry and has two interior atoms surrounded by 18 exterior atoms. The entire cluster has 127 CVMOs which includes 5.60 from each interior atom.



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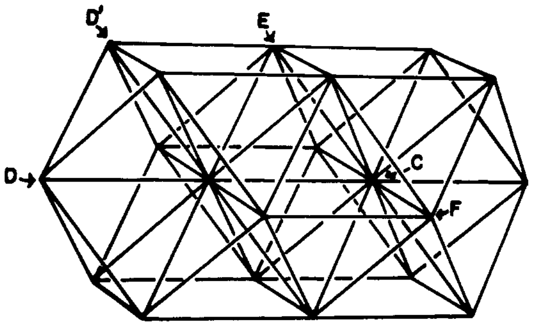

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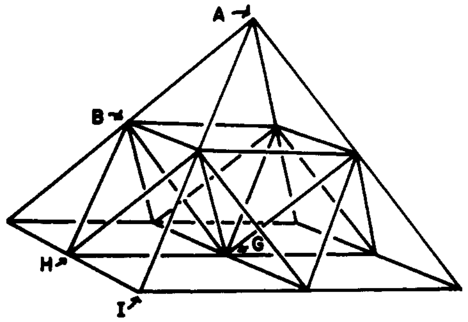
The values found for the interior atoms of the three clusters **2–4** are thus in good agreement and average 5.7 orbitals per site. Since interior atoms have a close geometric similarity to an individual atom of a bulk metal there should be a bonding relationship as well. The CVMOs were defined as those orbitals available for electron occupancy or for acting as ligand acceptor orbitals. For the ferromagnetic bulk metals the number of orbitals per metal atom available for electron occupancy is known to be about 5.3 orbitals per atom. These 5.3 orbitals are the major component of the 5.7 CVMOs centered upon the interior atom of a cluster.

The 0.4-orbital discrepancy is not large and may be rationalized in differing ways. One interpretation is that the number of orbitals for the two cases should actually be the same, but that the extended Hückel method is not capable of such accuracy. We believe that the phenomenon is real, however, and that it is simply explained by stating that the highest of the CVMO orbitals can serve as acceptor orbitals, but that they are too high in energy for electron occupancy. In discrete chemical compounds such low-lying unfilled orbitals would lead to instability and thus all such empty CVMOs must be satisfied; there must be an energy gap between the occupied and empty orbitals. In a bulk metal it is of course certain that there are low-lying orbitals and that there is indeed a continuum between the occupied and empty states. From a chemical viewpoint the presence of low-lying acceptor orbitals on the interior atoms of bulk metal can help to explain various chemical phenomena such as the ready formation of many carbides and hydrides and such processes as surface reorganization.

A detailed examination of the CVMOs of interior atoms (Table II) reveals a contribution of 0.54 p orbitals per site. Since most band calculations of bulk metals reveal little if any p character, it would seem probable that the 0.4 discrepancy is due mainly to the p-orbital contribution to the CVMOs and that the low-lying empty orbitals of an atom in a metal lattice would be of p character.

**Surface Atoms.** Most detailed chemisorption studies are of interactions of small molecules with fundamental crystallographic habit planes. For face-centered cubic metals the most studied surfaces are the (100) and (111) habit planes. The base of the 14-atom square pyramid, **5**, is representative of a (100) plane. The central atom G has the environment of an atom located on a (100) plane. This atom has 8 nearest neighbors and 6.21 CVMOs (Table II). The faces of the 20-atom tetrahedron, **6**, represent (111) surfaces. The central atom, K, has 9 nearest neighbors and 5.98 CVMOS. The (111) atom K has more nearest neighbors than the (100) atom G and thus fewer CVMOs.



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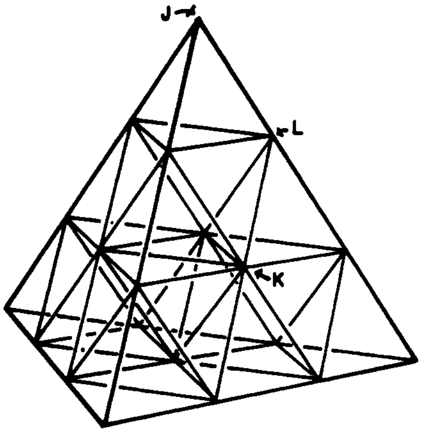

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If the 20-atom tetrahedron were made up of Ni atoms and a stable carbonyl cluster compound formed, the K atom with essentially six CVMOs would be expected to bind one CO ligand. The remaining five CVMOs would contain the ten Ni electrons. A very similar chemical process would take place on a (111) surface of a nickel crystal. If CO is chemisorbed each Ni atom has the bonding capacity to bind one CO ligand. An interior nickel atom has 5.28 occupied orbitals with a number of unpaired electrons. A surface Ni atom cannot have this electronic configuration if a ligand is bound. Ligand bonding will reduce the number of available orbitals to five and force a pairing of spins. At low coverage the CO could bridge two or even three Ni atoms without forcing such changes in electronic configuration since available orbitals from the two or three Ni atoms would be shared.

**Edge Atoms.** The exterior atoms of most of the known cluster compounds are not representative of fundamental crystallographic habit planes, but are similar to edge or vertex atoms of crystals. They would be characteristic of high-order stepped or channeled surfaces, which have atoms with fewer nearest neighbors. Table II lists the site analyses for the various edge and vertex atoms found in clusters **1–6.** Generally the number of CVMOs is inversely proportional to the number of nearest neighbors. The highest number of orbitals, 7.43, is found for site I of the square pyramid **5**, which has three nearest neighbors. The edge atom E of the $D_{2h}$ structure with seven nearest neighbors has 6.23 available orbitals and is thus similar in bonding capacity to a (100) atom.

The atoms with fewer than six nearest neighbors are representative of the atoms of the known small cluster compounds. These atoms have the bonding capacity and the geometry needed for multiple ligand bonding. In homogeneous catalysis most fundamental steps involve multiple ligand bonding.[19] The situation is likely to be the same in heterogeneous systems. Edge atoms and the atoms of high-order stepped or channeled surfaces have more orbitals available for ligand bonding. They should thus be the sites of greatest reactivity.

### Summary

The number of cluster valence molecular orbitals located on any given metal atom of a cluster or an infinite lattice is dependent upon the site geometry. In cluster-compound chemistry this number of available orbitals will determine compound stoichiometries and structures. In analysis of bulk metals this number of available orbitals can be used to determine electron configurations and the bonding capabilities of surface atoms. Discrete stoichiometric cluster compounds are good models for chemisorption onto bulk metals and we believe that the simple qualitative molecular orbital approach presented here can help establish their detailed relationship.

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### References and Notes

(1) Part 1 in this series: J. W. Lauher, *J. Am. Chem. Soc*, **100**, 5305 (1978).
(2) E. L. Muetterties, T. N. Rhodin, E. Band, C. F. Brucker, and W. R. Pretzer, *Chem. Rev.*, in press.
(3) E. L. Muetterties, *Bull. Soc. Chim. Belg.*, **84**, 959 (1975); **85**, 451 (1976).
(4) J. H. Sinfelt, *Acc. Chem. Res.*, **10**, 15 (1977).
(5) P. Chini, G. Longoni, and V. G. Albano, *Adv. Organomet. Chem.*, **14**, 285 (1976).
(6) R. B. King, *Prog. Inorg. Chem.*, **15**, 287 (1972).
(7) M. R. Churchill, J. Wormald, J. Knight, and M. J. Mays, *J. Am. Chem. Soc.*, **93**, 3073 (1971).
(8) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963); R. Hoffmann and W. N. Lypscomb, *ibid.*, **36**, 2179, 3489 (1962); **37**, 2872 (1962).
(9) C. Kittel, "Introduction to Solid State Physics", 4th ed., Wiley, New York, 1976.
(10) N. F. Mott and H. Jones, "Theory of the Properties of Metals and Alloys", Oxford University Press, London, 1936; Dover Publications, New York (reprint), 1958.
(11) L. Pauling, "The Nature of the Chemical Bond", 3rd ed., Cornell University Press, Ithaca, N.Y., 1960, p 398.
(12) D. H. Martin, "Magnetism in Solids", Iliffe Books, London, 1967, p 30.
(13) S. H. Charap in "Magnetism and Metallurgy", Vol. 1, A. E. Berkowitz and E. Kneller, Eds., Academic Press, New York, 1969, p 37.
(14) J. Donohue, "The Structures of the Elements", Wiley, New York, 1974, p 215.
(15) S. Martinengo, G. Ciani, A. Sironi, and P. Chini, *J. Am. Chem. Soc.*, **100**, 7097 (1978).
(16) V. G. Albano, A. Ceriotti, P. Chini, G. Ciani, S. Martinego, and W. M. Anker, *J. Chem. Soc., Chem. Commun.*, 859 (1975).
(17) V. G. Albano, M. Sansoni, P. Chini, S. Martinego, and D. Strumolo, *J. Chem. Soc., Dalton Trans.*, 970 (1976).
(18) J. L. Vidal, R. A. Fiato, L. A. Cosby, and R. L. Pruett, *Inorg. Chem.*, **17**, 2574 (1978).
(19) C. A. Tolman, *Chem. Soc. Rev.*, **1**, 337 (1972).

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# A Study of the Bonding in Transition Metal Carbonyl Hydrides

**Hsiang-Wen Chen, William L. Jolly,* Jürgen Kopf, and Ting Ho Lee**

*Contribution from the Department of Chemistry, University of California, and the Materials and Molecular Research Division, Lawrence Berkeley Laboratory, Berkeley, California 94720.* *Received November 27, 1978*

**Abstract:** The metal $2p_{3/2}$, carbon 1s, and oxygen 1s binding energies of the gaseous molecules $Co_2(CO)_8$, $HCo(CO)_4$, $Fe(CO)_5$, $H_2Fe(CO)_4$, $Mn_2(CO)_{10}$, and $HMn(CO)_5$ have been measured by X-ray photoelectron spectroscopy. From qualitative considerations of the binding energy shifts on going from the transition-metal carbonyls to the corresponding carbonyl hydrides, it is concluded that the hydrogen atoms in the carbonyl hydrides are negatively charged. By application of the potential model, approximate hydrogen atom charges of −0.3, −0.8, and −0.75 are calculated for $H_2Fe(CO)_4$, $HMn(CO)_5$, and $HCo(CO)_4$, respectively.

### Introduction

It has been well established that chemical shifts in core electron binding energies are related to changes in atomic charges.[1,2] In general, an increase in core binding energy corresponds to an increase in the positive charge of the atom. However, it is recognized that changes in binding energy are not always entirely due to changes in atomic charge; sometimes they are at least partly caused by changes in the electronic relaxation energy associated with core ionization.[3,4] Fortunately, this relaxation energy is essentially the same in compounds which have similar molecular structures in the vicinity of the core-ionizing atom. For example, the calculated[5] C 1s relaxation energies for $CH_4$ (15.89 eV) and $CH_3F$ (15.92 eV) are quite similar, whereas that for CO (11.91 eV) is considerably different from both values. Hence core binding energies *for a series of carefully chosen molecules with similar*

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