EVOLUTION OF SIZE EFFECTS IN CHEMICAL DYNAMICS
Part 2

ADVANCES IN CHEMICAL PHYSICS
VOLUME LXX

Edited by
I. PRIGOGINE
University of Brussels
Brussels, Belgium
and
University of Texas
Austin, Texas

and

STUART A. RICE
Department of Chemistry
and
The James Franck Institute
The University of Chicago
Chicago, Illinois

AN INTERSCIENCE® PUBLICATION
JOHN WILEY & SONS
NEW YORK • CHICHESTER • BRISBANE • TORONTO • SINGAPORE
EVOLUTION OF SIZE EFFECTS IN CHEMICAL DYNAMICS
Part 2

ADVANCES IN CHEMICAL PHYSICS
VOLUME LXX
EDITORIAL BOARD

C. J. BALLAHUSEN, Københavns Universitets Fysik-Kemiske Institut, Kemisk Laboratorium IV, Copenhagen, Denmark
BRUCE BERNE, Department of Chemistry, Columbia University, New York, New York, U.S.A.
RICHARD B. BERNSTEIN, Department of Chemistry, University of California, Los Angeles, California, U.S.A.
G. CARERI, Istituto di Fisica "Guglielmo Marconi," Università dell'Istituto, Piazza delle Scienze, Rome, Italy
MORREL COHEN, Exxon Research and Engineering Company, Clinton Township, Annandale, New Jersey, U.S.A.
KARL F. FREED, The James Franck Institute, The University of Chicago, Chicago, Illinois, U.S.A.
ROBERT GOMER, The James Franck Institute, The University of Chicago, Chicago, Illinois, U.S.A.
RAYMOND E. KAPRAL, University of Toronto, Toronto, Ontario, Canada
WILLIAM KLEMPERER, Department of Chemistry, Harvard University, Cambridge, Massachusetts, U.S.A.
YU L. KLIMONTOVITCH, Moscow State University, Moscow, U.S.S.R.
V. KRINSKI, Institute of Biological Physics, U.S.S.R. Academy of Science, Puschino, Moscow Region, U.S.S.R.
M. MANDEL, Chemie-Complex der Rijks-Universiteit, Leiden, The Netherlands
RUDY MARCUS, Department of Chemistry, California Institute of Technology, Pasadena, California, U.S.A.
PETER MAZUR, Institut Lorentz voor Theoretische Natuurkunde, Leiden, The Netherlands
GREGOIRE NICOLIS, Pool de Physique, Faculté des Sciences, Université Libre de Bruxelles, Brussels, Belgium
A. PACAULT, Centre de Recherches Paul Pascal, Domaine Universitaire, Talance, France
YVES POMEAU, Commissariat à l'Energie Atomique, Centre d'Etudes Nucléaires de Saclay, Division de la Physique, Gif-sur-Yvette, France
A. RAHMAN, Argonne National Laboratory, Argonne, Illinois, U.S.A.
P. SCHUSTER, Institut für Theoretische Chemie und Strahlenchemie, Universität Wien, Vienna, Austria
I. SHAVITT, Department of Chemistry, Ohio State University, Columbus, Ohio, U.S.A.
KAZUHISA TOMITA, Department of Physics, Faculty of Science, Kyoto University, Kyoto, Japan
EVOLUTION OF SIZE EFFECTS IN CHEMICAL DYNAMICS

Part 2

ADVANCES IN CHEMICAL PHYSICS
VOLUME LXX

Edited by
I. PRIGOGINE
University of Brussels
Brussels, Belgium
and
University of Texas
Austin, Texas

and

STUART A. RICE
Department of Chemistry
and
The James Franck Institute
The University of Chicago
Chicago, Illinois

AN INTERSCIENCE® PUBLICATION
JOHN WILEY & SONS
NEW YORK • CHICHESTER • BRISBANE • TORONTO • SINGAPORE
CONTRIBUTORS TO VOLUME LXX PART 2

THOMAS L. BECK, Department of Chemistry and James Franck Institute, University of Chicago, Chicago, Illinois

R. STEPHEN BERRY, Department of Chemistry and James Franck Institute, University of Chicago, Chicago, Illinois

J. Chesnoy, Laboratoire d'Optique Quantique du C.N.R.S., Ecole Polytechnique, Palaiseau, France

DONALD M. COX, Corporate Research Laboratory, Exxon Research and Engineering Company, Annandale, New Jersey

LAWRENCE F. DAHL, Department of Chemistry, University of Wisconsin-Madison, Madison, Wisconsin

HEIDI L. DAVIS, Department of Chemistry and James Franck Institute, University of Chicago, Chicago, Illinois

M. F. DE FERAUDY, Laboratoire de Physique des Solides, Université de Paris Sud, Orsay, France

J. D. DOLL, Chemistry Division Los Alamos National Laboratory, Los Alamos, New Mexico

J. FARGES, Laboratoire de Physique des Solides, Université de Paris Sud, Orsay, France

DAVID L. FREEMAN, Department of Chemistry, University of Rhode Island, Kingston, Rhode Island

G. M. GALE, Laboratoire d'Optique Quantique du C.N.R.S., Ecole Polytechnique, Palaiseau, France

JULIUS JELLINEK, Chemistry Division, Argonne National Laboratory, Argonne, Illinois

WILLIAM L. JORGENSEN, Department of Chemistry, Purdue University, West Lafayette, Indiana

ANDREW KALDOR, Corporate Research Laboratory, Exxon Research and Engineering Company, Annandale, New Jersey

KARL C. C. KHARAS, Department of Chemistry, University of Wisconsin-Madison, Madison, Wisconsin
R. Naaman, Department of Isotope Research, Weizmann Institute of Science, Rehovot, Israel

Abraham Nitzan, School of Chemistry, Sackler Faculty of Sciences, Tel Aviv University, Tel Aviv, Israel

David W. Oxtoby, James Franck Institute and Department of Chemistry, University of Chicago, Chicago, Illinois

B. Raoult, Laboratoire de Physique des Solides, Université de Paris Sud, Orsay, France

Mark G. SCEATS, Department of Physical Chemistry, University of Sydney, Sydney, New South Wales, Australia

G. Torchet, Laboratoire de Physique des Solides, Université de Paris Sud, Orsay, France

Mitchell R. Zakin, Corporate Research Laboratory, Exxon Research and Engineering Company, Annandale, New Jersey
INTRODUCTION

Few of us can any longer keep up with the flood of scientific literature, even in specialized subfields. Any attempt to do more and be broadly educated with respect to a large domain of science has the appearance of tilting at windmills. Yet the synthesis of ideas drawn from different subjects into new, powerful, general concepts is as valuable as ever, and the desire to remain educated persists in all scientists. This series, Advances in Chemical Physics, is devoted to helping the reader obtain general information about a wide variety of topics in chemical physics, which field we interpret very broadly. Our intent is to have experts present comprehensive analyses of subjects of interest and to encourage the expression of individual points of view. We hope that this approach to the presentation of an overview of a subject will both stimulate new research and serve as a personalized learning text for beginners in a field.

ILYA PRIGOGINE

STUART A. RICE
CONTENTS

LIGAND-STABILIZED METAL CLUSTERS: STRUCTURE, BONDING, FLUXIONALITY, AND THE METALLIC STATE 1
by Karl C. C. Kharas and Lawrence F. Dahl

STRUCTURAL MODELS FOR CLUSTERS PRODUCED IN A FREE JET EXPANSION 45
by J. Farges, M. F. de Feraudy, B. Raoult, and G. Torchet

SOLID–LIQUID PHASE BEHAVIOR IN MICROCLUSTERS 75
by R. Stephen Berry, Thomas L. Beck, Heidi L Davis, and Julius Jellinek

THE QUANTUM MECHANICS OF CLUSTERS 139
by David L. Freeman and J. D. Doll

SMALL CLUSTERS—REACTIONS OF VAN DER WAALS MOLECULES 181
by R. Naaman

MOLECULAR SURFACE CHEMISTRY: REACTIONS OF GAS-PHASE METAL CLUSTERS 211
by Andrew Kaldor, Donald M. Cox, and Mitchell R. Zakin

NUCLEATION OF CRYSTALS FROM THE MELT 263
by David W. Oxtoby

VIBRATIONAL RELAXATION IN CONDENSED PHASES 297
by J. Chesnoy and G. M. Gale

SIZE EFFECTS IN ENCOUNTER AND REACTION DYNAMICS 357
by Mark G. Sceats

ENERGY PROFILES FOR ORGANIC REACTIONS IN SOLUTION 469
by William L. Jorgensen

ACTIVATED RATE PROCESSES IN CONDENSED PHASES: THE KRAMERS THEORY REVISITED 489
by Abraham Nitzan
CONTENTS

AUTHOR INDEX 557
SUBJECT INDEX 583
LIGAND-STABILIZED METAL CLUSTERS:
STRUCTURE, BONDING, FLUXIONALITY,
AND THE METALLIC STATE

KARL C. C. KHARAS AND LAWRENCE F. DAHL

Department of Chemistry,
University of Wisconsin-Madison,
Madison, Wisconsin 53706

CONTENTS

I. Brief Survey of Metal Cluster Compounds

II. Structure and Bonding in Metal Clusters
   A. The Isolobal Analogy
   B. Lauher's Rule
   C. Edge-Localized Versus Delocalized Bonding
   D. The Polyhedral Skeletal Electron-Pair Model
   E. Tensor Surface Harmonic Theory
   F. The Topological Electron-Counting Model
   G. The Graph-Theory-Derived Model
   H. Electron-Counting Procedures for Large Clusters
   I. Applications of Electron-Counting Methods
   J. Importance of d–d Metal Interactions

III. Stereochemical Nonrigidity of Metal Atoms in Clusters
   A. Metal Cluster Motion in a Fixed Ligand Cage
   B. Metal-Core Rearrangements in Several Tetrametal Clusters
   C. Intertriangular Metal Rotations About Pseudo Threefold Axes
   D. Metal Fragment Migration Over Cluster Surfaces
   E. Metal Cluster “Breathing” Fluxionality
   F. Fluxionality in Gold Clusters
   G. Icosahedral Interconversions
   H. Octahedral Interconversions
   I. Importance of Connectivity and Electron-Counting Rules

IV. Clusters, Surfaces, and the Metallic State
   A. Structural Chemistry of Large Metal Carbonyl Clusters
   B. Large Metal Phosphine Clusters
   C. Transition of Metal Clusters Toward the Metallic State
      1. Unusual Magnetic Behavior
      2. A New, Cluster-Based Electronic Conductor
   D. Nonexistence of Binary Palladium Carbonyl Clusters

V. Concluding Remarks

References
I. BRIEF SURVEY OF METAL CLUSTER COMPOUNDS

For nearly 30 years, the field of metal clusters has provided chemists a vast arena in which to work. Early results were often surprising. Crystallographic analysis revealed that compounds, such as Os₃(CO)₁₂ and Rh₆(CO)₁₆, were often incorrectly formulated by traditional techniques. It was quickly evident that a large number of ligand-stabilized metal clusters could be synthesized, and extensive exploratory research opened a rich, interesting field. Discovery of unprecedented structural features was the norm and remains common. The fact that each platonic solid (namely, the tetrahedron, octahedron, cube, icosahedron, and pentagonal dodecahedron) is now represented in transition metal cluster chemistry illustrates the structural variety present in this class of compounds. A short preview of particular metal clusters whose geometries approximately conform to these Platonic solids provides an introduction to some of the structural phenomena considered elsewhere in this chapter.

A review now nearly 10 years old discusses the rich chemistry of four-atom tetrahedral clusters (Fig. 1a). The first evidence for the existence of a tetrahedral metal carbonyl cluster was obtained from a two-dimensional X-ray diffraction study of Co₄(CO)₁₂. Recently a few 10-atom ν₂-tetrahedral metal clusters (Fig. 1b) have been synthesized. The ν₂-tetrahedral notation denotes that each of the six tetrahedral edges has three metal atoms with two metal-metal connections. These 10-atom metal clusters may be readily envisioned as arising from the capping of a metal octahedron on four nonadjacent faces by the other four metal atoms. Examples include two palladium clusters, the [Os₁₀C(CO)₂₄]²⁻ dianion and several closely related, electronically equivalent anions, the mixed-metal [Cu₆Fe₄(CO)₁₆]²⁻ dianion, and the mixed-metal Hg₆Rh₄(PMe₃)₁₂ cluster. As discussed in Section IV, one of these compounds, H₂Os₁₀C(CO)₂₄, exhibits anomalous paramagnetic behavior at low temperatures, which may reflect nascent metallic properties.

Octahedral metal clusters (Fig. 1c) have been known since the crystallographic characterization of Rh₆(CO)₁₆, nearly 25 years ago. Examples exist in iron, ruthenium, osmium, cobalt, rhodium, iodide, and nickel carbonyl chemistry, and several mixed-metal octahedral clusters are also known. Particularly interesting are three hexacobalt octahedral clusters, Co₆(CO)₁₆, [Co₆(CO)₁₅]²⁻, and [Co₆(CO)₁₄]⁴⁻, in which a pair of electrons substitutes for each carbonyl ligand. All of these octahedral metal clusters possess one pair of valence electrons in excess of that required for the formation of electron-pair bonds between adjacent metal atoms. Intriguing features of structure and bonding in organometallic clusters are considered in Section II. Large 44-atom ν₃-octahedral clusters have been synthesized recently. These [Ni₃₈Pt₆(CO)₄₈H₆₋ₙ]ⁿ⁻ anions (n = 4, 5) possess a hexaplatinum octahedron surrounded by an octahedral array of 38 nickel surface atoms. A ν₂-
Figure 1. Examples of cluster cores whose shapes approximately conform to those of the five platonic solids. (a) Tetrahedron; Co$_4$(CO)$_{12}$ containing a bonding Co$_4$ tetrahedron. (b) v$_2$ tetrahedron (a 10-atom tetrahedron with each edge formed by three atoms linked by two metal–metal bonds): [Os$_{10}$C(CO)$_{24}$]$^{2-}$ dianion containing an interstitial C atom within the bonding Os$_{10}$ v$_2$ tetrahedron. (c) Octahedron: Rh$_6$(CO)$_{15}$. (d) Cube; Ni$_8$(PR)$_6$(CO)$_8$ (in which the bonding Ni$_8$ cube is hexacapped by PR ligands) and Se$_6$(CoPPh$_3$)$_6$ (in which the bonding Se$_6$ cube is hexacapped by CoPPh$_3$ fragments). (e) Noncentered icosahedron; [Ni$_{10}$(AsMe)$_2$(CO)$_{14}$]$^{2-}$ containing a bonding noncentered closo-1,12-Ni$_{10}$As$_2$ icosahedron. (f) Centered icosahedron; [Au$_{13}$(PM$_2$Ph)$_{10}$Cl$_2$]$^{3+}$ containing a bonding Au-centered Au$_{13}$ icosahedron. (g) Pentagonal dodecahedron. (h) Ni$_{34}$Se$_{22}$(PPh$_3$)$_{10}$ containing a bonding Ni$_{20}$ dodecahedron formed by the 20 surface nickel atoms not ligated by phosphine groups.
octahedral metal cluster, which would possess 19 metal atoms, has not yet been reported. Octahedral metal halide clusters\(^\text{18}\) possess significantly different electronic structures than organometallic clusters and, for the most part, will not be considered in this chapter.

The \(\text{Ni}_8(\text{CO})_8(\mu_4-\text{PPh})_6\) cluster (Fig. 1d) provided the first example of a bonding cube as a basic structural unit. Its \(\text{Ni}_8\text{P}_6\) core possesses an octametal cube capped on its six square faces by an octahedral array of bridging phosphorus atoms.\(^\text{19}\) Its monoanion\(^\text{19}\) (which corresponds to an electron in a hexacapped box) and several closely related complexes have been prepared subsequently.\(^\text{20}\) There are also clusters, such as the \(\text{Se}_8\text{Co}_6(\text{PPh}_3)_6\) species,\(^\text{21}\) which may be viewed as the inverse of \(\text{Ni}_8(\text{CO})_8(\mu_4-\text{PPh})_6\) [that is, a nonmetal \(\text{Se}_8\) cube (Fig. 1d) hexacapped by a metal octahedron] rather than as an octahedral cobalt cluster with its eight faces capped by selenium atoms. Determining which atoms are cluster atoms and which are capping atoms has electronic implications. In Section II it is shown from electronic considerations that it is advantageous to view \(\text{Se}_8\text{Co}_6(\text{PPh}_3)_6\) and related molecules as chalcogen clusters instead of as metal clusters. Finally, the \([\text{Rh}_{15}(\text{CO})_{30}]^{3-}\) trianion consists of a central metal atom surrounded by interpenetrating cubic and octahedral arrays of metal atoms.\(^\text{22}\)

The icosahedron, possessing 12 vertices, is another platonic solid that encloses a cavity large enough to accommodate a metal atom. Both non-centered 12-atom icosahedral clusters (Fig. 1e) and centered 13-atom clusters (Fig. 1f) are known. Examples of the latter include the \([\text{Rh}_{12}\text{Sb}(\text{CO})_{27}]^{3-}\) trianion,\(^\text{23}\) which has a Sb-centered \(\text{Rh}_{12}\text{Sb}\) icosahedral core, and the \([\text{Au}_{13}(\text{PMe}_2\text{Ph})_{10}\text{Cl}_2]^{3+}\) trication,\(^\text{24}\) which has an Au-centered \(\text{Au}_{13}\) icosahedral core. Examples of the former are the \([\text{Ni}_6(\text{AsPh})_3(\text{CO})_{15}]^{2-}\) and \([\text{Ni}_{10}(\text{AsMe})_2(\text{CO})_{18}]^{2-}\) dianions,\(^\text{25}\) which possess noncentered \(\text{Ni}_9\text{X}_3\) and \(\text{Ni}_{10}\text{X}_2\) icosahedral cores (\(\text{X} = \text{As}\)), respectively. Related anions with phosphinidene (\(\text{X} = \text{P}\)) and stibinidene (\(\text{X} = \text{Sb}\)) fragments have also been discovered.\(^\text{26}\) The cores of icosahedral clusters can be fluxional.\(^\text{23b}\) Some aspects of stereochemical nonrigidity of cluster cores are examined in Section III.

We would like to point out that the pentagonal dodecahedron (Fig. 1g), possessing 20 vertices, occurs in metal cluster chemistry. In \(\text{Ni}_{34}\text{Se}_{22}(\text{PPh}_3)_{10}\) (Fig. 1h)\(^\text{21}\) the 20 nickel atoms in the outer layer that are not ligated by triphenyl phosphine ligands appear to be arranged in a dodecahedral framework. This giant-sized molecular cluster also possesses an icosahedral \(\text{Ni}_{10}\text{Se}_2\) array, although these atoms are not within bonding distances of one another.

\section*{II. STRUCTURE AND BONDING IN METAL CLUSTERS}

Theoretical work over the last 15 years has done much to advance our understanding of structure and bonding in metal clusters. The isolobal analogy\(^\text{27}\)
provides the means for appreciating similarities between organic chemistry and the chemistry of small metal clusters. The polyhedral skeletal electron-pair (PSEP) model\textsuperscript{28-30} originally applied to boron clusters by Wade\textsuperscript{28a,e} and Williams\textsuperscript{28d} and further developed by Mingos,\textsuperscript{28b,c,29,30} Lauher's rule,\textsuperscript{31} the topological electron-counting (TEC) model developed by Teo,\textsuperscript{32} and the graph-theory-derived (GTD) model put forth by King\textsuperscript{33} each provide methods for rationalizing the stereochemistry of moderately large clusters in terms of the number of valence electrons a cluster possesses. Applications of graph theory to molecular orbital theory and the realization that solid-state considerations are relevant to the structural chemistry of clusters both indicate ways metal clusters are different from boron clusters. Each of these electronic models will be briefly considered in turn.

A. The Isolobal Analogy

The isolobal analogy\textsuperscript{27} takes note of the essential electronic equivalence of seemingly different molecular fragments which possess analogous frontier orbitals (of similar symmetry properties) containing the same number of valence electrons. The fact that the hydrogen atom, methyl radical, and Mn(CO)\textsubscript{5} radical are isolobal gives rise to the probable existence of all six compounds resulting from combinations of any two of these isolobal fragments. Conceptually and experimentally,\textsuperscript{34a} two 17-electron square pyramidal Mn(CO)\textsubscript{5} radicals (each containing one electron in an octahedral-like orbital) are linked together by a direct electron-pair metal–metal bond to give Mn\textsubscript{2}(CO)\textsubscript{10}.\textsuperscript{34} The resulting formation of a normal electron-pair covalent bond between the manganese atoms complies with the noble-gas configuration required by the 18-electron rule.\textsuperscript{34b,35} Similarly, the octahedral Mn(CO)\textsubscript{5}H and Mn(CO)\textsubscript{5}CH\textsubscript{3} molecules also obey the 18-electron rule and are also analogous to H\textsubscript{2} or ethane (Fig. 2). The 16-electron Fe(CO)\textsubscript{4} fragment (with one electron in each of two frontier orbitals), which is isolobal with both the triplet methylene CH\textsubscript{2} fragment and the 16-electron Co(\eta^{5}-C\textsubscript{5}Me\textsubscript{5})(CO) fragment, undergoes a cycloaddition across the formal Co—Co double bond of the 32-electron ethylene-like Co\textsubscript{2}(\eta^{5}\textsubscript{5}-C\textsubscript{5}Me\textsubscript{5})\textsubscript{2}(CO)\textsubscript{2} dimer to give the 48-electron cyclopropane-like FeCo\textsubscript{2}(\eta^{5}\textsubscript{5}-C\textsubscript{5}Me\textsubscript{5})\textsubscript{2}(CO)\textsubscript{6} cluster.\textsuperscript{36} Since the 15-electron Co(CO)\textsubscript{5} fragment is isolobal with both the CR fragment (R = H, CH\textsubscript{3}) and the main group V atoms, such as As (with one electron in each of three frontier orbitals), the existence of the entire homologous series of As\textsubscript{n}[Co(CO)\textsubscript{5}]\textsubscript{4-n} complexes\textsuperscript{37} (n = 0-4) containing tetrahedral-like As\textsubscript{n}Co\textsubscript{4-n} cores as well as the electronically analogous Co\textsubscript{3}(CO)\textsubscript{6}CCH\textsubscript{3} possessing a tetrahedral-like Co\textsubscript{3}C core\textsuperscript{38} is not surprising. In fact, the latter similarity in bonding properties (electronic equivalence) among the As, CCH\textsubscript{3}, and 15-electron Co(CO)\textsubscript{5} groups was pointed out\textsuperscript{37} prior to the elegant development by Hoffmann, Mingos, and coworkers\textsuperscript{27} of the isolobal connection interrelating organic and organometallic chemistry.
(a) \[ 
\begin{align*}
H & \text{CH}_3 \quad \text{Mn(CO)}_5 \\
H - H & \quad H - \text{CH}_3 \quad H - \text{Mn(CO)}_5 \\
\text{H}_3\text{C} & - \text{CH}_3 \quad \text{H}_3\text{C} - \text{Mn(CO)}_5 \\
\text{OCO}_5\text{Mn} & - \text{Mn(CO)}_5
\end{align*} \]

(b) \[ 
\begin{align*}
\text{H}_2\text{C} & \overset{\sigma}{} \text{Fe(CO)}_4 \overset{\sigma}{} \text{MCP}^*(\text{CO}) \\
\text{H} & \text{C} = \text{C} \quad \text{C} & \text{M} = \text{M} - \text{Cp}^* \quad \text{O} & \text{C} \quad \text{O} & \text{C}
\end{align*} \]

Figure 2. Use of isolobal model (where \(\sigma\) denotes an isolobal relationship) to account for the existence of a wide variety of organometallic complexes (including metal clusters) by relating (a) their structures and (b) their reactivity patterns with those of corresponding organic molecules. The isolobal model can also be used (c) to rationalize the electronic equivalence between organometallic and main group element species. Inorganic, organic, and organometallic groups are defined as isolobal if the number and symmetry properties (including relative energies) of their frontier orbitals and the number of valence electrons occupying these orbitals are similar.

### B. Lauher's Rule

Each of the metal clusters considered in Section A obeys the Lauher rule,\(^{31}\) which is based on extended Hückel calculations. That is, the number of occupied orbitals in each polyhedral cluster is equal to \(9v - e\), where \(v\) is the number of metal vertices and \(e\) the number of edges. Completely bonding triangular and tetrahedral clusters have, respectively, \(27 - 3 = 24\) and \(36 - \)
6 = 30 occupied orbitals and, hence, are often called 48- and 60-electron systems. Lauher's rule, where each edge represents a localized electron-pair bond, and the 18-electron rule are complementary; the former considers the entire cluster, while the latter considers each metal atom. Often if a cluster obeys the 18-electron rule, it also obeys Lauher's rule. While clusters that possess the "correct" electron count are usually stable, they may be susceptible to redox processes that result in distortions of their idealized geometries. In this connection an extensive part of our systematic research on transition metal cluster chemistry has focused on the geometric effects caused by changes of electronic configurations in a variety of metal cluster systems, many of which function as electron-transfer reagents (by gain and/or loss of valence electrons) without breakdown of their central cluster frameworks. These structural-bonding analyses, which have been pedagogically called experimental quantum mechanics, not only have been utilized in correlating and predicting alterations in metal-core geometries with changes in electronic configurations, but also have proven highly useful in rationalizing the observed variations in physicochemical properties of related metal clusters.

C. Edge-Localized Versus Delocalized Bonding

Two closely related six-atom clusters demonstrate how subtly nature confronts chemists who seek to understand questions of structure and bonding in metal cluster compounds. The neutral Os₆(CO)₁₈ cluster is a capped trigonal bipyramid or, equivalently, a bicapped tetrahedron (regarded as three fused tetrahedra). It obeys Lauher’s rule and possesses 84 valence electrons. Reduction of this compound by two electrons results in the formation of the 86-electron [Os₆(CO)₁₈]²⁻ octahedral cluster, which does not conform to Lauher's rule. The PSEP, TEC, and GTD models account for this combination of shape and number of valence electrons. Reduction of this compound by two electrons results in the formation of the 86-electron [Os₆(CO)₁₈]²⁻ octahedral cluster, which does not conform to Lauher's rule. The PSEP, TEC, and GTD models account for this combination of shape and number of valence electrons. The conversion of a bicapped tetrahedron into an octahedron involves breaking one “bonding edge” and making one new “bonding edge.” Although the change in polyhedral geometry results from the addition of two valence electrons, both the bicapped tetrahedral and the octahedral Os₆ cores possess the same number of metal–metal bonding contacts (namely, 12). This illustrates that metal–metal bonding edges (contacts) in a polyhedral metal cluster do not necessarily correspond to edge-localized bonding involving two-center electron-pair bonds. In this connection, the bicapped tetrahedral Os₆ core of Os₆(CO)₁₆ has been viewed from the GTD method as an edge-localized polyhedron with an electron-pair metal–metal bond along each of the 12 edges. In contrast, the octahedral Os₆ core of the closo [Os₆(CO)₁₈]²⁻ dianion is considered to possess globally delocalized metal–metal bonding, which combines surface bonding with a multicentered two-electron bond within the central octahedral cavity. (Fig. 3).
Figure 3. Polyhedral core rearrangement of the Os₆ core of Os₆(CO)₁₈ upon reduction to its \([\text{Os}_6(\text{CO})_{18}]^{2-}\) dianion.

D. The Polyhedral Skeletal Electron-Pair Model

The PSEP model, originally derived for boron hydride compounds, and its extensions have been immensely successful in rationalizing the electron count of a large number of cluster geometries. For main group atoms, three of the four valence orbitals are viewed as internal orbitals which are involved in cluster bonding, while the fourth external orbital is ligand bonding or contains a lone pair. Transition metals, with nine valence \(nd\), \((n + 1)s\), and \((n + 1)p\) orbitals, are likewise presumed to use three (hybrid) internal valence orbitals for cluster bonding; the other six external valence orbitals contain ligand-bonding or nonbonding electron pairs. The three internal cluster orbitals per metal atom combine to form \(3n\) bonding and antibonding skeletal orbitals, where \(n\) is the number of cluster atoms. For closo geometries \(n + 1\) skeletal bonding orbitals are filled, for nido, \(n + 2\) are filled, and for arachno \(n + 3\) are filled.* An 86-electron octahedron, such as the closo Rh₆(CO)₁₆, would have, formally at least, 36 occupied Rh–CO bonding and Rh nonbonding orbitals.

* A deltahedron is a polyhedron whose faces are all triangular. For a given number of vertices, a closo polyhedron is the most highly symmetric deltahedron. For example, an icosahedron, rather than a tetracapped cuneane, is the closo polyhedron for 12-vertex polyhedra. A nido (netlike) polyhedron is a closo polyhedron with one vertex removed, while an arachno (web-like) polyhedron is a closo polyhedron with two vertices, not necessarily adjacent, removed.
seven occupied skeletal bonding orbitals, and 11 unoccupied skeletal antibonding orbitals. In order to convert the total electron count number for a given cluster polyhedron into the apparent skeletal electron count, 12n electrons (where n denotes the number of metal vertices) are subtracted from the total electron count. Thus the 86-electron Rh₆(CO)₁₆ cluster possesses 86 − 12(6) = 14 skeletal electrons, or seven skeletal electron pairs occupying the seven skeletal bonding orbitals. This relationship assumes that only three of the nine valence orbitals at each metal vertex are internal orbitals and six are external orbitals. The total electron count does not depend on the distribution of the ligands (such as carbonyl groups) about the metal cluster core and likewise is invariant as to whether a two-electron donating carbonyl ligand is terminal or bridging.

While boron hydrides usually have closo, nido, or arachno structures, transition metal clusters frequently exhibit more condensed structures, such as capped square pyramids or face-fused bioctahedra. Extensions of the original PSEP model treat many of these situations. The oldest extension, a capping rule,²⁹ᵃ states that a metal fragment capping a face of a cluster results in an electron count of 12 greater than that of the uncapped cluster. Consider the monocapped octahedral 98-electron Os₇(CO)₁₂ cluster.³¹ Three unoccupied metal frontier orbitals (a₁ + e under C₃ᵥ symmetry) of the capping 12-electron [Os(CO)₃]²⁺ fragment are presumed to interact with three symmetry-equivalent filled nonbonding external cluster orbitals of the 86-electron octahedral [Os₆(CO)₁₈]²⁻ dianion. Since the bonding (a₁ + e) combinations of these orbitals are filled and the corresponding (a₂ + e) antibonding orbitals are empty, the fragment needs only the 12 electrons for its ligand-bonding and nonbonding orbitals. The PSEP model thereby predicts a 98-electron count for the monocapped octahedral Os₇(CO)₁₂ cluster, as observed.

A further extension is the fusion rule,²⁹ᵇ which treats condensed clusters formally composed of polyhedra that intersect at a vertex, an edge, or a face. According to this rule,²⁹ᵇ the sum of the electron counts for the constituent polyhedra minus the electron count for the intersecting set of atoms equals the electron count for the condensed cluster. For example, the fusion rule predicts that an edge-fused bioctahedron, such as the [Ru₁₀C₂(CO)₂₄]²⁻ dianion ⁴² (Fig. 4a) which contains a four-electron donating interstitial carbon atom at each octahedral site, should possess 2 × 86 − 34 = 138 electrons, in accordance with the observed electron count. Each metal octahedron requires 86 electrons, while the common metal–metal edge [in being analogous to a singly bound dimer like the 34-electron Mn₂(CO)₁₀] debits 34 electrons from the total number of valence electrons the cluster possesses. Later in this section we provide more examples of clusters that obey the capping and fusion rules. It will become apparent that these rules apply to compounds even when the
Figure 4. Examples of widely different metal clusters whose polyhedral cores generally conform to electron-counting models (a) 138-electron [Ru$_{10}$C$_2$(CO)$_{24}$]$^{2-}$ dianion which has an edge-fused biocahedral Ru$_{10}$ core containing an interstitial carbon atom at each octahedral site. (b) 198-electron Hg$_6$Co$_6$(CO)$_{18}$ containing a hexa (Co-capped) tricapped trigonal prismatic Co$_6$Hg$_6$ core (alternatively described as a rectangular Co$_6$ prism with Hg atoms at the midpoints of the nine edges). (c) 220-electron [(Re$_7$AgC(CO)$_{21}$)$_2$Br]$^{5-}$ anion containing two Re, Ag-bicapped octahedral Re$_7$Ag cores linked by normal covalent Ag—Br—Ag bonds. (d) 144-electron (BrCu)$_6$[P$_3$Co(triphos)$_2$]$_2$ [where triphos denotes MeC(CH,PPh$_3$)$_2$] containing a Co, Co-bicapped cuboctahedral Cu$_8$P$_6$Co$_2$ core (alternatively depicted as two CoP$_3$ units each face fused to a planar Cu$_6$ hexagon). The predicted electron count is 134. (e) Two geometrical isomers of the 66-electron ($\eta^5$-C$_5$H$_5$)$_2$Mo$_4$Fe$_2$(CO)$_6$(\(\mu_3\)-S)$_2$ containing an Mo$_3$Mo-edge-fused bitetrahedral Mo$_2$Fe$_2$S$_2$ core. (f) 64-electron Co$_4$(CO)$_{10}$($\mu_2$-Te)$_2$ containing a cyclobutanelike Co$_4$ core. An alternate description of an octahedral-like Co$_4$Te$_2$ core leads to an observed 68-electron count due to the inclusion of the unshared electron pair on each Te when it is regarded as a core atom. (g) 66-electron Co$_4$(CO)$_{11}$($\mu_4$-Te)$_2$ containing a cis-butane-like Co$_4$ core. An alternate description of a nido-pentagonal bipyramidal Co$_4$Te$_2$ core gives rise to an observed electron count of 70. (h) 66-electron Fe$_4$(CO)$_{11}$($\mu_2$-PR)$_2$ containing an octahedral-like Fe$_4$P$_2$ core. (i) 90-electron [Fe$_6$(PEt$_3$)$_6$($\mu_3$-S)$_6$]$^{2+}$ dication containing an octahedral Fe$_6$ core. (j) 143-electron Co$_9$($\mu_4$-Se)$_3$(PPh$_3$)$_6$($\mu_2$-Se)$_6$ containing an octacapped hcp truncated v$_2$-trigonal bipyramidal Co$_9$Se$_3$ core. The predicted electron count is 144.
cluster fragments that are capped or fused do not themselves obey the Wade-Mingos rules.

While the capping and fusion rules significantly increase the power of the PSEP model for clusters whose atoms have relatively high metal–metal connectivity, the newest extensions apply the model to lower connectivity clusters. For transition metals, $15n$ electrons (where $n$ is the number of vertices) are expected for clusters whose metal atoms are connected to three other metal atoms (that is, three-connected clusters). Examples include tetrahedra, cubes, and cuneanes. In the four-connected clusters, such as octahedra, square antiprisms, and cuboctahedra, the electron count can range from $14n$ to $14n + 4$, depending on the nature of the polyhedron.

E. Tensor Surface Harmonic Theory

These last two extensions of the PSEP model were derived by use of the tensor surface harmonic (TSH) formalism outlined below. The TSH approach to cluster bonding allows one to develop vivid images of bonding and antibonding molecular orbitals, thereby clarifying why electron-counting rules work. Metal cluster atoms are assumed to lie on the surface of a sphere. The symmetry properties of spherical harmonics can therefore be used to classify orbitals according to their global (cluster-wide) angular momentum. Atomic orbitals possessing cylindrical symmetry along the vector containing the
spherical center and the atomic center are considered σ orbitals. These combine by LCAO methods to produce one molecular orbital with zero nodes, three with one node, five with two nodes, and so on until \( n \) σ orbitals are formed. Thus there are one \( s^\sigma \), three \( p^\sigma \), five \( d^\sigma \), and so on. In fact, these molecular orbitals can be generated by using the value of the relevant spherical harmonic at each atomic position as the coefficient for the σ orbital at that position. The π and δ molecular orbitals have, respectively, one or two nodal planes intersecting the vector containing the atomic center and the spherical center. The lowest quantum number for the π orbitals is \( L = 1 \), while for the δ orbitals it is \( L = 2 \). A parity operation involving rotation of each atomic orbital by 90° about its radial vector transforms each \( L^\sigma \) orbital to an \( L^\pi \) orbital. A similar rotation transforms each \( D^\delta \) orbital to the \( D^\delta \) orbital. The TSH formalism also provides an economic method of generating approximate energies for the cluster molecular orbitals. The TSH method has been applied to derive PSEP counting rules for deltahedra, four-connected, and four-connected clusters.

While TSH theory represents a significant advance toward the goal of easy visualization of bonding and antibonding interactions in clusters, the pictorial aspect lags behind the analytical aspect of this method. Yet the essential premise of TSH theory, that is, that cluster atoms are on the surface of a sphere, suggests that cartography can supply the means to new insights. In this regard, Mollweide projections have been utilized as a general, easily visualized means to present the σ-, π-, and δ-type metal-based orbital interactions in metal clusters possessing different point group symmetries.

F. The Topological Electron-Counting Model

The TEC model developed by Teo also has been successfully applied to rationalize the geometries of a large number of cluster compounds. The TEC model combines Lauher’s rule with Euler’s theorem* and adds an adjustable parameter \( X \). This parameter \( X \) is equal to the number of electron pairs present in excess of that predicted by the 18-electron rule. \( X \) has also been interpreted in terms of the number of “missing” antibonding orbitals. Given a value for \( X \), determined by the shape of the cluster, an equation predicts the electron count for a cluster. Theoretical justification of the parameter \( X \) is based largely upon the classical molecular orbital calculations performed by Hoffmann and Lipscomb via the extended Hückel method on the corresponding polyhedral boron hydride clusters \( [B_nH_{12}]^{-} \). The values of \( X \) derived phenomenologically agree with theoretical results in the literature. Approaches based on naked metal clusters to determine cluster

---

* Euler’s theorem states that the number of vertices \( v \), edges \( e \), and faces \( f \) of a simple convex polyhedron are related by the equation \( v + f = e + 2 \).
electron counts were made by Lauher and Ciani and Sirini. The fact that the isolable small-to-large transition metal clusters described herein are electronically stabilized by ligands (and thus are not small ensembles of bare-metal atoms) makes it difficult to justify electron-counting models for ligand-stabilized metal clusters from theoretical work based on naked metal clusters.

G. The Graph-Theory-Derived Model

Another interesting framework for considering metal cluster bonding questions is provided by the GTD model developed by King. It allows a simple bookkeeping of electrons and provides bonding orbitals even for large, complicated clusters. This model also suggests that bonding in various regions of metal cluster compounds can be classified as delocalized or localized. Delocalized polyhedral bonding, which involves bonding interactions both on the surface and at the center of the polyhedron, occurs when the number of available skeletal orbitals at the vertices is not equal to the connectivity at those vertices. Closo deltahedral clusters and closo cluster fragments at least the size of octahedra fit this criterion. Delocalized bonding in these types of clusters is viewed as analogous to delocalized bonding in aromatic hydrocarbons. The number and disposition of delocalized centers in the \( \text{Rh}_6(\text{CO})_{16}, [\text{Rh}_{12}(\text{CO})_{30}]^{2-}, [\text{Rh}_9(\text{CO})_{19}]^{3-}, \text{and } [\text{Rh}_{11}(\text{CO})_{23}]^{3-} \) anions make them topologically analogous to benzene, biphenyl, naphthalene, and the perinaphthenide anion, respectively (Fig. 5). This model proposes that edge-localized bonds, (that is, two-center, two-electron bonds along the polyhedral edges) occur when the number of skeletal orbitals equals the metal-metal connectivity, as in the three-connected tetrahedral \( \text{Rh}_4(\text{CO})_{12} \) cluster.

The GTD approach, which has been utilized to interrelate the topology of osmium carbonyl clusters containing 5 to 11 osmium atoms, provides a distinction between localized and delocalized bonding within the monocapped octahedral \( \text{Os}_7(\text{CO})_{21} \). This cluster, formally derived by the face fusion of a tetrahedral cluster to an octahedral cluster, is presumed to possess a composite of localized bonding around the tetrahedral chamber and delocalized bonding within the octahedron. According to this method of bonding analysis, each of the three capped atoms in \( \text{Os}_7(\text{CO})_{21} \) that are part of both polyhedra contribute four (instead of three) internal skeletal orbitals. The use of one nonbonding external filled orbital as the fourth internal orbital by each of the three osmium vertices in the capped octahedral face to form one of the edge-localized bonds to the capping osmium vertex (resulting in an edge-localized tetrahedral cavity) does not change the skeletal electron count involving the delocalized bonding within the octahedron. Hence the skeletal electron count [that is, \( 98 - 12(7) = 14 \)] of the capped octahedron is the same as that of the uncapped octahedron. Although the apparent electron counts predicted by the PSEP and GTD models are in agreement with the existence
Figure 5. Topological analogies between various formal fusions of electron-delocalized Rh₆ octahedra in rhodium carbonyl clusters and related fusions of benzene rings in corresponding planar polycyclic aromatic hydrocarbons. (a) Benzene analog; Rh₆(CO)₁₆. (b) Biphenyl analog; [Rh₁₂(CO)₃₀]²⁻ dianion containing two vertex-linked Rh₆ octahedra. (c) Naphthalene analog; [Rh₉(CO)₁₉]³⁻ trianion containing two face-fused Rh₆ octahedra. (d) Perinaphthenide analog; [Rh₁₁(CO)₂₃]³⁻ trianion containing three face-to-face fused Rh₆ octahedra with a common, hidden Rh-Rh edge.

of Os₇(CO)₂₄ as a monocapped octahedral cluster, electron-counting models per se do not provide a distinction between different geometries which are electronically equivalent. For example, the [Os₆(CO)₁₈]²⁻ and [H₂Os₆(CO)₁₈⁻] anions have an octahedral Os₆ geometry expected for an 86-electron (14-skeletal-electron) system, whereas the Os₆ core of the 86-electron H₂Os₆(CO)₁₈ conforms to a capped square pyramidal geometry with the hydrogen atoms occupying opposite edge-bridged sites in the basal square Os₄ plane. These contrasting geometries, which both conform to the same electron count, demonstrate that the cluster polyhedron depends not only upon the total electron count (that is, the number of skeletal electron pairs available) but also upon the number and type of ligands about the cluster core. The particular metal atoms in the core can also play a vital role in determining the stereochemistry, as exemplified by the electronically equivalent H₂Ru₆(CO)₁₈ and H₂Os₆(CO)₁₈ possessing different geometries.

As clusters become more condensed by capping and fusion operations, the
GTD model requires an increase in the number of skeletal orbitals in the internal atoms. According to the PSEP model, which was originally employed in boron cluster chemistry and only later applied to metal clusters, these orbitals are considered to be nonbonding. Thus, the GTD model implicitly emphasizes the importance of metal d orbitals in cluster bonding. In so doing, it emphasizes that capped and fused structures are highly unusual in boron hydride clusters due to the boron atoms possessing only four s and p valence AOs which thereby restrict the number of internal cluster orbitals to three.

H. Electron-Counting Procedures for Large Clusters

While the PSEP or TEC methods can often be applied to account for the shape and composition of large, highly condensed clusters, these procedures become cumbersome and do not necessarily give correct values. Within the last several years other electron-counting approaches, which are more convenient to apply to high-nuclearity transition metal clusters, have been presented. An electron-counting rule, which is an extension of the well-established Hume-Rothery rule for intermetallic compounds, was developed by Teo for close-packed high-nuclearity metal clusters containing at least one completely encapsulated "bulk" atom. This model involves the allocation of electrons to the surface and encapsulated metal atoms in accordance with the packing arrangement of the metal atoms. A simple equation with two (more or less) fixed parameters gives good, but not perfect agreement with the observed electron count for a large number of clusters with interstitial metal atoms.

More recently Teo and Sloane carried out a detailed mathematical investigation concerning the preferred numbers of nuclearity (so-called magic numbers) for close-packed spherical clusters, including various symmetrical polygons (in two dimensions) and polyhedra (in three dimensions). They also showed that their atom-counting results could be successfully applied to give correct electron counts for close-packed high-nuclearity metal clusters such as the \([\text{Pt}_{38}(\text{CO})_{44}]^{-}\) dianion. Mingos has also put forth electron-counting rules for high-nuclearity clusters with close-packed metal-atom arrangements. His formulated procedures of electron counting are dependent on whether the bonding interactions are predominantly radial between surface and interstitial atoms or whether tangential bonding interactions among surface atoms also make important contributions. When a large close-packed cluster is spherical, or perhaps equivalently when radial bonding dominates, each surface atom requires 12 electrons, while an encapsulated atom or group of atoms requires the same number of electrons as its molecular analog. Thus, a single interstitial metal atom requires 18 electrons, an encapsulated metal triangle 48 electrons, and an encapsulated metal octahedron 86 electrons. The contrast between these types of approaches is striking. The extended Hume-Rothery approach implicitly emphasizes an analogy...
between transition metal clusters and a class of metallic compounds, while the latter ones would indicate that these materials are large but otherwise normal, closed-shell molecules.

The preceding discussion indicates that our theoretical understanding of metal clusters is still limited in scope: schemes for electron counting in clusters are still being worked out. Precisely why ligands stabilize clusters is not completely clear. Whether metal atoms or clusters are net electron donors or acceptors to carbonyl ligands remains controversial. Little detailed understanding of bond strengths, the role of $d$ electrons in cluster bonding, the origin of fluxional processes in metal cores, and the relationship between cluster geometry and reactivity is available. About some of these we shall comment by the end of this chapter. First we wish to illuminate the application and shortcomings of counting rules, as currently formulated, mainly with examples that have not yet been discussed.

I. Applications of Electron-Counting Methods

Mixed-metal clusters involving transition and postransition metals frequently obey PSEP counting rules. For example, $\text{Hg}_6\text{Co}_6(\text{CO})_{18}$ (Fig. 4b) is a cluster of six $\text{CoHg}_3$ tetrahedra. Each tetrahedron is vertex-fused to three other tetrahedra through the Hg atoms. Since bonding metal tetrahedra require 60 electrons, the fusion rule predicts the observed electron count of $6 \times 60 - 9 \times 18 = 198$. The $\text{[Re}_7\text{AgC}(\text{CO})_{21}]_2\text{Br}^{-}$ anion (Fig. 4c), which consists of two Re, Ag-bicapped octahedra linked by a bridging bromine atom, conforms to electron-counting rules which predict $2(86 + 12 + 12) = 220$ valence electrons. The 144-electron $\text{Co}_{12}\text{P}_6\text{Co}_2$ cluster (BrC$_6$)$_2[\text{P}_3\text{Co}(\text{triphos})]_2$ (Fig. 4d) has a predicted electron count of $(110 + 12 + 12) = 134$ and is also the largest known metal cluster without an encapsulated atom.

Transition metal chalcogenide clusters present varied puzzles to counting schemes. Sometimes sulfur atoms may be considered as members of the cluster, while at other times they are best thought of as ligands. In $\text{FeCo}_2(\text{CO})_9(\mu_3-\text{S})$ the sulfur atom may be considered as a ligand of a completely bonding 48-electron FeCo$_2$ triangle or as part of a 50-electron fully bonded tetrahedron. (In general, the substitution of a metal cluster atom by a main group cluster atom reduces the predicted electron count by 10 since the main group atom does not have any $d$ valence electrons.) It is useful to consider both geometric isomers of $(\eta^5-\text{C}_5\text{H}_5)_2\text{Mo}_2\text{Fe}_2(\text{CO})_8\text{S}_2$ (Fig. 4e) as edge-sharing Mo$_2$Fe$_2$S$_2$ bitetrahedra, for which an electron count of $(2 \times 50 - 34) = 66$ is obtained. On the other hand, there are cases where the bridging chalcogen atoms are preferably viewed as ligands. The $\text{Co}_4(\text{CO})_{10}(\mu_4-\text{Te})_2$ species (Fig. 4f) could be considered either as a 68-electron Co$_4$Te$_2$ octahedron or as a 64-electron Co$_4$ rectangle. Only the