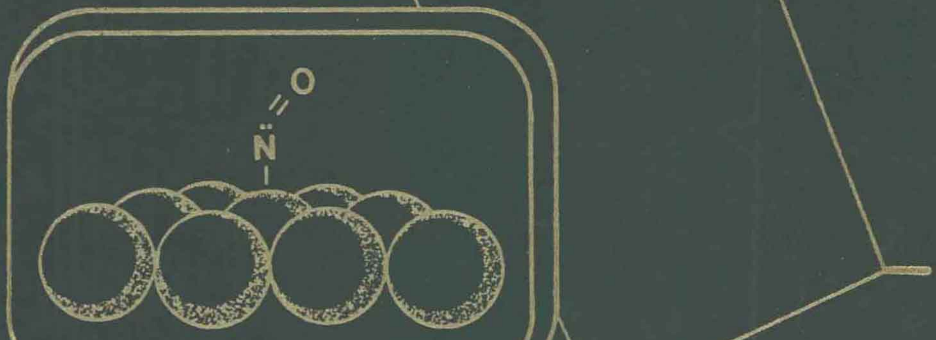
The Surface Scientist's Guide to Organometallic Chemistry



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The Surface Scientist's Guide to Organometallic Chemistry

About the Authors

MARK R. ALBERT is a research associate at Princeton University. He has been involved in the fields of organometallic chemistry and surface science since he was an undergraduate at the University of Maryland. There he studied organometallic chemistry and undertook honors research in the area of electron probe microanalysis of asbestos fibers. At the University of Maryland he was awarded the Noxell Corporation Scholarship Award. After graduation from Maryland, he spent a summer at the Eastman Kodak Corporation where he synthesized and studied transition metal complexes. In his graduate work at the University of Pennsylvania, he continued his study of organometallic chemistry and learned a variety of synthetic methods that he applied to an ultraviolet and X-ray photoelectron spectroscopy study of alkyne hexacarbonyl cobalt complexes. He also worked closely with the surface science group in the Department of Physics and studied the chemisorption of hydrocarbons on single-crystal surfaces, also with photoemission. This research gave him the opportunity to work at the Synchrotron Radiation Center at the University of Wisconsin. After receiving his Ph.D., he worked for the Dow Corning Corporation in the area of electron spectroscopy for chemical analysis and Auger spectroscopy and then went to the Surface Science Center at the University of Pittsburgh, where he coauthored this book. His research at the University of Pittsburgh involved the study of small-molecule chemisorption on supported metals using transmission infrared spectroscopy. He is presently at Princeton University, where he is studying chemisorption phenomena with high-resolution electron energy loss spectroscopy (HREELS).

JOHN T. YATES, JR., received his B.S. degree from Juniata College and his Ph.D. in physical chemistry from the Massachusetts Institute of Technology. Following a three-year term as Assistant Professor at Antioch College, he joined the National Bureau of Standards, first as a National Research Council Postdoctoral Research Fellow and then, from 1965 until 1982, as a member of its scientific staff. His research in the fields of surface chemistry and physics, including both the structure and spectroscopy of surface species, the dynamics of surface processes, and the development of new methods for research in surface chemistry, has put him in the forefront of an exciting and rapidly growing field of science. He is the author of more than 200 publications. Yates was Senior Visiting Scholar at the University of East Anglia, Norwich, in 1970–71, and Sherman Fairchild Distinguished Scholar at California Institute of Technology in 1977–78. He received the Silver Medal of the U.S. Department of Commerce in 1973, the Stratton Award for Distinguished Research at the National Bureau of Standards in 1978, and the Gold Medal—the highest award of the U.S. Department of Commerce—in 1981. In 1986, he received the Kendall Award in Colloid or Surface Chemistry from the American Chemical Society.

Yates joined the University of Pittsburgh in 1982 as the first R. K. Mellon Professor of Chemistry and as the first Director of the University of Pittsburgh Surface Science Center. Here, working with students and postdoctoral staff, his influence actively extends over a wide range of research projects in surface science. He is also active in undergraduate and graduate teaching. In addition, he maintains close relationships with many surface science research programs in academic, government, and industrial research laboratories throughout the world and serves on the editorial boards of five journals and two book series in surface science and catalysis.

Preface

WITHIN THE FIELD OF SURFACE SCIENCE, concepts from the fields of organometallic and coordination chemistry are becoming increasingly relevant as a means of understanding chemisorption systems. This situation has occurred because the two fields work with the same metals and the same ligands that bond to these metals, and very often they pursue similar research issues. But the two fields employ a different language and ways of gaining experimental information. These differences are detrimental to surface science research because many insights into ligand structure and bonding that are common to organometallic chemistry are hidden from the surface science community. This book was written, therefore, as a means of communicating to the surface science community the aspects of organometallic and coordination chemistry that are relevant to the research issues currently being pursued by surface scientists.

The many ligands commonly used by the coordination chemist are all good candidates for study on surfaces, and it would not be surprising for each ligand to enhance the understanding of surface processes to the extent already accomplished by CO chemisorption research. The application of theoretical calculations useful within coordination chemistry research to surface science research seems to be a natural extension of the experimental organometallic chemistry research that has already contributed to the understanding of chemisorption systems. However, this book is only a beginning in surface science's full exploitation of organometallic and coordination chemistry. It emphasizes issues concerning characterization, bonding, and preparation of ligand bonding modes. Issues related to heterogeneous catalytic chemistry are not directly addressed. Most likely, organometallic and coordination chemistry will provide a similar degree of insight into these issues, where ligand–ligand interactions become important.

But the exploitation of coordination chemistry by surface scientists does not come without its challenges. No indexes or computer searches can painlessly extract from the coordination chemistry literature analogies or new research ideas that will interest the surface scientist. This book can only be a beginning in this regard. The only real solution to this problem is through diligence in the study of the coordination chemistry literature and by following the new developments in coordination chemistry as closely as new surface science developments are followed. Some of the journals and monograph series worth following include *Journal of the American Chemical Society, Chemical Reviews, Journal of Coordination Chemistry, Inorganic Chemistry, Organometallics, Journal of Organometallic Chemistry, JCS Dal-*

ton Transactions, Coordination Chemistry Reviews, Advances in Organometallic Chemistry, Progress in Inorganic Chemistry, Advances in Inorganic Chemistry, and Radiochemistry. Most of the coordination chemistry references in this book are from one of these journals.

At this stage there appears to be no limit to the number of new ideas that surface science can draw from coordination chemistry research. However, coordination chemistry is an active, ongoing field of research that will continue to contribute to the further understanding of surface chemisorption systems. This kind of interaction is dependent only upon the communication that exists between surface scientists and coordination chemists. This book is only the beginning of this challenging and inevitably beneficial interaction.

Acknowledgments

We wish to acknowledge support of this work by the 3M Science Research Laboratory and the Corporate Research Laboratory. A special note of thanks is given to Kurt Kolasinski, who drew all of the molecular structures in this book; the excellent quality of his work has improved the clarity of this review enormously. We especially acknowledge the encouragement and support of Allen Siedle of the 3M Corporation during the writing of this book. Another special note of thanks is given to Michael Bozack, who provided extensive editing of the text and improved the book's readability. Thanks are also offered to Rex E. Shepherd, E. Ward Plummer, Miles J. Dresser, Larry G. Sneddon, John E. Crowell, and Valerie Shalin, who read and offered helpful comments about the manuscript prior to publication. Appreciation is also expressed to Neil R. Avery who provided several of his publications prior to their publication. Many thanks are also offered to Phyllis Roy, Mary Ann Stevwing, Cathy Veneskey, and Nancy Caldiera for their excellent typing of the many drafts of the manuscript.

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Dedication

THE FIRST DRAFT OF THIS BOOK was about half-finished when the world of organometallic and inorganic chemistry was saddened by the death of Earl Muetterties in Berkeley. Because of his significant contributions to organometallic chemistry and surface science, we dedicate this book to his memory.

His perception of the possible relationship between organometallic chemistry and chemisorption and catalysis on surfaces has been a driving force among many surface chemists. This book would not now exist if Earl Muetterties had not set his theory of the metal cluster–surface analogy down on paper. Already numerous works based on the cluster–surface analogy exist, and the many more to follow will undoubtedly uncover new insights into chemisorption and surface reactivity.

Earl Muetterties worked for his students and for the field of surface chemistry in ways that his friends and colleagues will always remember. We received a personal letter from him, mailed 14 days before his death, containing recent preprints from his group. One of us (M.A.), who did most of the writing and thinking about this book, had hoped that Earl Muetterties's friendly and perceptive criticism might have played a role in making this a better book. The other one of us (J.Y.) had hoped that, through Earl Muetterties's work, the field of surface science would undergo a distinctive revolution from a physics-dominated, technique-oriented subject to a more chemically oriented field, filled with molecular orbitals, interesting structures, interesting chemical concepts, and new classes of surface reactions.

It remains for all of us to carry on in the tradition and direction first charted by Earl Muetterties. We hope that this book in some small way may be a tribute to Earl Muetterties, his work, and his students.

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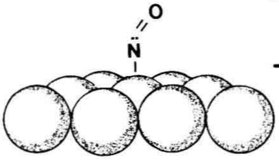

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Introduction

THE INCREASED UNDERSTANDING OF THE INTERACTION of gases with transition metal surfaces has been accompanied by a growing awareness that many gas–surface interactions have analogues in the literature of organometallic and coordination chemistry. This analogy, also known as the cluster–surface analogy, was first proposed by Muetterties (*1, 2*), and he and others have since developed this idea in more recent works (*3–6*). Opposing opinions have also been expressed (*7*). Since Muetterties's pioneering efforts, a number of workers studying various chemisorption systems have attempted to interpret data in light of analogous transition metal–ligand interactions. These include studies comparing photoemission spectra (*8–12*) and, more commonly, works comparing the frequencies of ligand vibrations with those of the corresponding surface-bound species (*13–19*). The general conclusion of these studies has been that, qualitatively, the nature of the gas–surface interaction is similar to the metal–ligand interaction. In addition to the direct experimental studies, Muetterties (*3, 6*) also hypothesized that similarities in reactivity should be expected in both metal clusters and surfaces, and he found many correlations between surface-bound molecules and ligands in clusters.

In spite of this growing relevance of coordination chemistry to chemisorption, there is as yet no means to easily extract information from the coordination chemistry literature that may be relevant to surface studies. The voluminous literature of coordination chemistry is composed largely of information that is not pertinent to the study of chemisorption systems. This extra information includes methods of preparing coordination compounds, the characterization of large complexes that have a variety of coordinated ligands, and the reactions of these complexes. Although these areas of research are quite challenging, the resulting body of information only obscures the issues that are important to surface science research. These

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relevant issues include the nature of the bonding interaction of a given ligand with a metal center, the number of possible ways that a given ligand may bond to a metal center or cluster, and how the bonding mode of a given ligand can be characterized spectroscopically. Coordination chemists have studied these areas in detail, but isolating this information in the literature can at times be a very tedious task.

This book is intended to be a means of simplifying this process by reviewing the numerous ligands commonly used in coordination chemistry and discussing the aspects of each that might aid in the understanding of how that ligand may bond to a surface. A less extensive review of organometallic ligands has already appeared (*20*). In addition, the nature of coordination sites in transition metal complexes and clusters is explored in the hope that the insights gained from understanding these coordination sites will add to the understanding of bonding sites on surfaces. Also, it is hoped that this book will generate new ideas for chemisorption studies that may not have been considered previously. Those interested in gaining an exposure to the basics of surface science research should refer to one of the many works on the subject (*3, 21*).

Although Muetterties (*6*) has limited his analogy of surface bonding to organometallic cluster compounds, this review will encompass the bonding of ligands to any metal center, be it in clusters or the much more common monometal center. The research just mentioned and the further comparisons of monometal complexes and chemisorbed species to be discussed later show that a ligand on a surface usually bonds in a manner similar to that on monometal centers, clusters, and surfaces. Therefore, it seems reasonable to extend the cluster–surface hypothesis to any ligand that bonds to a metal center in coordination complexes.

The issue of greatest concern regarding the analogy of organometallic complex bonding to surface chemisorption lies in the fact that although metal complexes and small clusters can be described by discrete orbitals, surfaces are usually described by band structure (*22, 23*). Some believe that this difference invalidates the analogy to be considered in this book. However, the final chapter of this book presents recent calculations that appear to effectively bridge this gap and provide a method for extending the experimental and theoretical understanding of metal–ligand structure and bonding developed in organometallic chemistry to surface chemisorption (*24, 25*).

This review is structured in the following way: Following this introduction, a short discussion of some fundamental concepts in coordination chemistry is presented to provide a basis in understanding for those who may be unfamiliar with the fundamentals of organometallic chemistry. Next, the various ligands used in coordination chemistry are discussed in terms of bonding modes, orbital overlaps, molecular orbital diagrams when available, and methods of characterizing each ligand's individual bonding modes.

Following this largest chapter, the molecular orbital structures of metal complex and cluster bonding sites are presented. The final chapter of this book discusses the theoretical treatment that can bridge the gap between orbital arguments and issues of surface band structure.

The characterization methods discussed in Chapter 3 are limited almost exclusively to vibrational spectroscopy* because it is the most common technique used in synthetic coordination chemistry and is the only technique readily available to both coordination chemistry and surface science. Techniques such as nuclear magnetic resonance (NMR) spectroscopy and X-ray crystallography, which are powerful characterization tools for the chemist, are not as yet generally applicable to surface science studies on single-crystal surfaces, even though some reports of NMR studies of chemisorbed species have appeared in the literature (*26–29*), as well as in a literature review (*30*). Low-energy electron diffraction (LEED) can approximate the high accuracy of X-ray crystallography, and many chemisorption systems have been studied in detail by using dynamical LEED calculations (*21, 31, 32*). However, as yet, there is little overlap between the surface and metal complex systems studied by the two techniques. This situation complicates comparisons of organometallic ligands and surface adsorbates through structural similarities. Surface extended absorption fine structure (SEXAFS) (*33*) is a more exact method of determining bond lengths of chemisorbed species. However, it is still a relatively new technique, and relatively few surface systems have been studied with SEXAFS.

Conversely, ultraviolet photoemission spectroscopy (UPS), a significant surface analysis tool, is of limited use to the coordination chemist because relatively few of the known transition metal complexes have the high symmetries required to resolve all the energy levels of a single ligand. Many complexes have a variety of ligands that usually result in complicated UPS spectra in which the peaks of the various ligands overlap. In addition, most organometallic complexes are not sufficiently volatile, or decompose with heating and thus could not be analyzed at high resolution in the gas phase. Electron spectroscopy for chemical analysis (ESCA) can be used to study both surface adsorbates and coordination complexes; however, few comparisons have been made between coordination compounds and surface species with ESCA (*34–36*). In addition, there are few ESCA studies of a given ligand in a series of electronic environments in metal complexes—studies that can correlate binding energies and peak splittings with

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**Several works have extensive compilations of characteristic vibrational data of organometallic compounds.* Infrared and Raman Spectra of Inorganic and Coordination Compounds, *Third Edition (John Wiley and Sons: New York), by K. Nakamoto, is one of the more complete works.* Physical Methods in Chemistry *(W. B. Saunders: Philadelphia), by R. S. Drago, also contains extensive compilations of vibrational data as well as a good discussion of the theoretical aspects of vibrational spectroscopy. Other good compilations include* Vibrational Spectra of Organometallic Compounds *(John Wiley and Sons: New York), by F. Maslowsky, and* Infrared Spectra of Inorganic Compounds *(Academic: New York), by R. A. Nyquist and R. O. Kagel.*