

The Fuzzy Interface between Surface Chemistry, Heterogeneous Catalysis, and Organometallic Chemistry

Henry F. Schaefer III

Materials and Molecular Research Division, Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720

Received January 24, 1977

It should be acknowledged at the outset that any paper written in early 1977 with the above title will inevitably be somewhat speculative in nature. Some would argue that this is especially true of a theoretical review, such as the present. This realistic appraisal is offered here to obviate the necessity of making the same point on several occasions later in the text.

The leading paragraph may come as a bit of a surprise to some readers, since each of the three areas of surface chemistry,¹ catalysis,² and organometallic chemistry³ is well established and currently flourishing. However, for some time chemists have suspected an underlying relationship between the three, and this relationship or "fuzzy interface" is the subject of the present account. It seems clear, and has often been mentioned in the literature⁴ and even in undergraduate texts,⁵ that the transition-metal-organic-fragment chemical bond is the key to linking the three disciplines. Unfortunately, however, few scientists have been willing to comment beyond this broad generality. Two striking exceptions to this noncommittal posture should be cited here. Based on his experimental studies, Muetterties⁶ has advanced a detailed thesis that discrete metal cluster complexes [e.g., $(C_5H_5)_3Mn_3(NO)_4$] may be considered "models of the surface structure of a metal where there has been extensive chemisorption of molecules, radicals or atoms". Second is the theoretical work of Goddard,^{7,8} who is engaged in an ambitious study of the methanation of CO on nickel surfaces modeled by finite clusters Ni_n .

I have felt for some time^{9,10} that these three fields have suffered from a lack of sufficient thermochemical and structural information.¹¹ After all, one of the tremendous strengths of organic chemistry is the existence of well-established and reliable values for the bond energies and bond lengths of C-C single, double, and triple bonds. Building blocks of this nature allow the facile correlation of vast amounts of chemical data. In contrast, if one asks for comparable information on transition metal to carbon bonds, one is likely to come away empty-handed. Therefore one of the aims of both theorists and experimentalists should be a more fundamental understanding of bonding in organometallic systems. In fact, there is a substantial experimental effort now in progress along these lines, particularly by chemists using gas-phase transition-metal atoms for

chemical synthesis. Among the most important contributors have been Skell,¹² Timms,¹³ Ozin,¹⁴ and Klabunde.¹⁵ A particularly important recent paper is that of Ozin and co-workers,¹⁶ who have synthesized and taken the infrared spectra of the $Cu(C_2H_4)$, $Cu(C_2H_4)_2$, and $Cu(C_2H_4)_3$ species. Such studies are extremely important, since they hold out the possibility of a detailed understanding of the nature of the unadorned metal-organic-fragment entities. Thus far these experiments have not yielded either precise structures or bond energies, although these are expected to be forthcoming. In the meantime, the setting is ripe for theoretical studies of the type described below.

Before moving on, let us review very briefly the goals of the three disciplines in question, in what might be considered the "region of overlap". In surface chemistry¹ one traditionally attempts to study infinite, perfectly ordered structures, e.g., the (111) surface of platinum. One of the most exciting recent developments is the emergence of low-energy electron diffraction (LEED) as a technique capable of determining the structures of chemisorbed polyatomic molecules.¹⁷ The first example, acetylene on Pt(111), was reported in 1976 by Somorjai and co-workers.¹⁸ More generally

(1) G. A. Somorjai, "Principles of Surface Chemistry", Prentice-Hall, Englewood Cliffs, N.J., 1972.

(2) J. R. Anderson, "Structure of Metallic Catalysts", Academic Press, London, 1975.

(3) R. F. Heck, "Organotransition Metal Chemistry", Academic Press, New York, N.Y., 1974.

(4) For early references, see G. C. Bond, "Catalysis by Metals", Academic Press, New York, N.Y., 1962.

(5) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 2nd ed, Interscience, New York, N.Y., 1966, p 789; the third edition of this text includes a much more detailed discussion of homogeneous catalysis.

(6) E. L. Muetterties, *Bull. Soc. Chim. Belg.*, 84, 959 (1975); 85, 451 (1976); these two papers are primarily expository in nature. For some of the most significant experimental discoveries of the Muetterties group, see ref 30.

(7) Goddard's research, most of which is yet unpublished, has been given a popular description in *Chem. Eng. News*, 54 (9), 14 (1976). See also W. A. Goddard, S. P. Walch, A. K. Rappe, T. H. Upton, and C. F. Melius, *J. Vac. Sci. Technol.*, 14, 416 (1977).

(8) S. P. Walch and W. A. Goddard, *J. Am. Chem. Soc.*, 98, 7908 (1976); A. K. Rappe and W. A. Goddard, "Generalized Valence Bond Studies of the Electronic States of $NiCH_2$ and $NiCH_3$ ", to be published.

(9) W. C. Swope and H. F. Schaefer, *J. Am. Chem. Soc.*, 98, 7962 (1976).

(10) This idea was especially stressed by the present author and W. A. Goddard in their invited papers at the W. F. Libby Symposium on the Relation between Science and Technology in Heterogeneous Catalysis, University of California, Los Angeles, Calif., March 18-19, 1976. Proceedings to be published.

(11) Existing metal-organic-fragment data have been gathered and carefully analyzed by Muetterties.⁶

(12) E. M. Van Dam, W. H. Brent, M. P. Silvon, and P. S. Skell, *J. Am. Chem. Soc.*, 97, 465 (1975).

(13) P. L. Timms, *Angew. Chem., Int. Ed. Engl.*, 14, 273 (1975).

(14) G. A. Ozin and A. Vander Voet, *Acc. Chem. Res.*, 6, 313 (1973); G. A. Ozin, *ibid.*, 10, 21 (1977).

(15) K. J. Klabunde, *Acc. Chem. Res.*, 8, 393 (1975).

(16) H. Huber, D. McIntosh, and G. A. Ozin, *J. Organomet. Chem.*, 112, C50 (1976).

(17) J. C. Buchholz and G. A. Somorjai, *Acc. Chem. Res.*, 9, 333 (1976).

Fritz Schaefer was born in 1944 in Grand Rapids, Mich., where his father grew up two doors away from President Gerald R. Ford. He received his undergraduate degree from Massachusetts Institute of Technology in 1966 and his Ph.D. from Stanford University in 1969. Since that time he has been a member of the faculty at the University of California, Berkeley. Professor Schaefer's research interests in theoretical chemistry revolve around the problem of electron correlation in molecules, and his nonscientific interests include Bible study, tennis when in Australia, and hiking in Northern California's Lassen National Park. He is a John S. Guggenheim Memorial Fellow for the academic year 1976-1977, and has spent part of that period at the Research School of Chemistry of the Australian National University, Canberra, where this manuscript was prepared.

the study of how chemical reactions occur on perfect surfaces is often considered a first step¹⁹ in the understanding of heterogeneous catalysis. This analogy becomes more realistic when irregularities are added to the surface, for example, steps, kinks, edges, and ledges.¹⁹ An extremely important recent realization is that stepped surfaces are vastly more effective than perfect surfaces as catalysts for gas-phase chemical reactions, e.g., the most carefully studied example being the $H_2 + D_2$ exchange reaction.²⁰

Heterogeneous catalysis, as carried out industrially, is extremely complicated in molecular terms. Perhaps best known is the Fischer-Tropsch synthesis,²¹ in which H_2 and CO are passed over metallic catalysts at 200 to 300 °C to produce hydrocarbons ranging from C_1 to C_{40} . The four metals which show significant activity in the Fischer-Tropsch synthesis are iron, cobalt, nickel, and ruthenium, and these require varying degrees of promotion and supporting.⁴ Although the structure of metallic catalysts is the subject of a certain amount of controversy,² it appears that even small metal clusters can display catalytic behavior. Most strikingly Hamilton and Logel²² at Kodak have shown that the Au_2 dimer and Ag_4 tetramer facilitate the photographic process. Work by Boudart,²³ Anderson,² Sinfelt,²⁴ and others²⁵ suggests that typical industrial metallic catalysts consist of finely divided, irregular particles of 100 or more metal atoms. This is clearly quite different from an ideal metal surface.²⁶

Perhaps best known to the readers of this journal are the homogeneous (i.e., in solution) catalysts of organometallic chemistry.²⁷ These have been known for some time, the most widely recognized being Wilkinson's catalyst,²⁸ $RhCl(PPh_3)_3$ or tris(triphenylphosphine)chlororhodium(I). Wilkinson's catalyst represented the first rapid and practical system for the homogeneous reduction of olefins and acetylenes under ordinary conditions. The two most frequently cited^{5,6} disadvantages of homogeneous (vs. heterogeneous) catalysis are the practical problem of separation of products from reactants and catalyst and the apparent inability to reduce nitrogen and carbon monoxide. The latter disparity with the Fischer-Tropsch synthesis is particularly obvious. However, two important recent advances should be noted. First, Chatt and co-workers²⁹ have succeeded in the reduction of N_2 to NH_3 under mild conditions, for example, when *cis*- $[W(N_2)_2-$

$(PMe_2PH)_4]$ is treated with sulfuric acid in methanol solution. Chatt's process is particularly intriguing since it appears to go against Muettterties' thesis⁶ that mononuclear metal complexes should not be particularly effective as catalysts. In another extremely important communication,³⁰ the homogeneous reduction of CO to CH_4 has been reported by the discrete clusters $Os_3(CO)_{12}$ and $Ir_4(CO)_{12}$. Although the reaction rates observed by Muettterties and co-workers were relatively low, selectivity (not present in the Fischer-Tropsch process) was a distinctive feature, with no hydrocarbons besides methane being detected. These and other recent discoveries (e.g., concerning the role³¹⁻³³ of metal-carbene complexes in olefin metathesis, discussed briefly below) suggest for the future an increasingly important role for homogeneous catalysis.

Some discussion should be devoted to the choice of theoretical methods adopted here. Seemingly since time began, theoreticians have been forced to choose between Scylla and Charybdis. Namely, does one use simple, sometimes unreliable, methods to study molecules that have actually been prepared in the laboratory, or does one accept more rigorous quantum mechanical methods and settle on smaller systems which hopefully serve as models for the chemical system in question? As the reader will shortly discover, we have adopted the latter philosophy, using *ab initio* molecular electronic structure theory.³⁴ This path has the well-documented comfort of showing that, as larger basis sets and more extensive configuration interaction are employed, one eventually reaches prediction of genuine chemical accuracy.³⁵ However the choice is a difficult one, and it should be noted here that the simpler methods have been applied, often successfully, to numerous problems in surface chemistry, catalysis, and organometallic chemistry. The reader is referred in this context to the work of Hoffmann,³⁶ Baetzold,³⁷ Schrieffer,³⁸ Blyholder,³⁹ Anderson,⁴⁰ and Johnson.⁴¹

Chemisorption Studies

It seems clear that a key to unlocking the relationships between these three seemingly diverse fields is: how many metal atoms are involved in the catalytic process? Obviously the answer will be different for different processes, so it makes some sense to begin with

(18) L. L. Kesmodel, P. C. Stair, R. C. Baetzold, and G. A. Somorjai, *Phys. Rev. Lett.*, **36**, 1316 (1976).

(19) G. A. Somorjai, *Acc. Chem. Res.*, **9**, 248 (1976).

(20) S. L. Bernasek and G. A. Somorjai, *J. Chem. Phys.*, **62**, 3149 (1975).

(21) S. J. Thomson and G. Webb, "Heterogeneous Catalysis", Oliver and Boyd, Edinburgh, 1968.

(22) J. F. Hamilton and P. C. Logel, *Photogr. Sci. Eng.*, **18**, 507 (1974).

These same authors have shown that 4-20 palladium atoms are required for the catalysis of electroless nickel deposition: *J. Catal.*, **29**, 253 (1973).

(23) M. Boudart, *CHEMTECH*, **4**, 748 (1974); J. E. Benson, H. S. Hwang, and M. Boudart, *J. Catal.*, **30**, 146 (1973).

(24) J. H. Sinfelt, Y. L. Lam, J. A. Cusumano, and A. E. Barnett, *J. Catal.*, **42**, 227 (1976).

(25) See, for example, P. E. Selwood, "Chemisorption and Magnetization", Academic Press, New York, N.Y., 1975.

(26) An interesting review of the relation between surface chemistry and catalysis has been given by J. T. Yates, *Chem. Eng. News*, **52** (34), 19 (1974).

(27) M. M. T. Khan and A. E. Martell, "Homogeneous Catalysis by Metal Complexes", Academic Press, New York, N.Y., 1974.

(28) J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc. A*, 1711 (1966).

(29) J. Chatt, A. J. Pearman, and R. L. Richards, *Nature (London)*, **253**, 39 (1975).

(30) M. G. Thomas, B. F. Beier, and E. L. Muettterties, *J. Am. Chem. Soc.*, **98**, 1296 (1976); G. C. Demitras and E. L. Muettterties, *ibid.*, **99**, 2796 (1977).

(31) C. P. Casey and T. J. Burkhardt, *J. Am. Chem. Soc.*, **96**, 7808 (1974).

(32) J. McGinnis, T. J. Katz, and S. Hurwitz, *J. Am. Chem. Soc.*, **98**, 605 (1976).

(33) N. Calderon, E. A. Olfstead, and W. A. Judy, *Angew. Chem., Int. Ed. Engl.*, **15**, 401 (1976).

(34) H. F. Schaefer, "The Electronic Structure of Atoms and Molecules: A Survey of Rigorous Quantum Mechanical Results", Addison-Wesley, Reading, Mass., 1972.

(35) See, for example, the papers in "Modern Theoretical Chemistry", Vol. 3 and 4, H. F. Schaefer, Ed., Plenum Press, New York, N.Y., 1977.

(36) A. B. Anderson and R. Hoffmann, *J. Chem. Phys.*, **61**, 4545 (1974); R. H. Summerville and R. Hoffmann, *J. Am. Chem. Soc.*, **98**, 7240 (1976).

(37) R. C. Baetzold, *J. Chem. Phys.*, **55**, 4363 (1971); M. G. Mason and R. C. Baetzold, *ibid.*, **64**, 271 (1976).

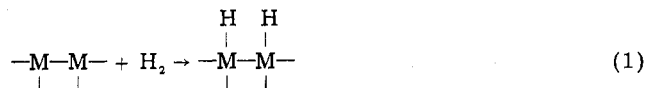
(38) J. R. Schrieffer, *J. Vac. Sci. Technol.*, **13**, 335 (1976). This paper is perhaps unique in that it provides a balanced presentation of finite cluster methods and band theoretical or solid-state techniques. For another discussion of the latter, see R. Gomer, *Acc. Chem. Res.*, **8**, 420 (1975).

(39) G. Blyholder, *Surf. Sci.*, **42**, 249 (1974); *J. Chem. Phys.*, **62**, 3193 (1975).

(40) A. B. Anderson, *J. Chem. Phys.*, **64**, 4046 (1976); **65**, 1729 (1976).

(41) K. H. Johnson and R. P. Messmer, *J. Vac. Sci. Technol.*, **11**, 236 (1974).

the simplest case—chemisorption. Probably the very best studied (from a molecular viewpoint) catalytic process is the dissociative chemisorption of molecular hydrogen on metal surfaces.⁴² We can schematically represent this as in eq 1. Whereas 103 kcal/mol is



normally required to dissociate H₂, dissociative chemisorption occurs on many metal surfaces with little or no activation energy.

One of the challenges which led us to the ab initio study of chemisorption was the statement in Clark's book:⁴³ "How many surface atoms of the adsorbent participate in the bonding of a single adsorbed particle is a question that has not been answered unequivocally for any real system and probably will not be in the near future". If one analyzes this statement, it seems clear that experimental studies designed to answer such questions will be extremely difficult. In principle, of course, one could build up, for example, a nickel surface by preparing the gaseous species Ni, Ni₂, Ni₃, Ni₄, and spectroscopically determining for each the binding energy and structural features of an adsorbed hydrogen atom. However, the problems inherent in such a scheme are apparent,⁴⁴ and the issue of the numbers of metal atoms involved in the chemisorbed bond seems rather the sort of conceptual question best answered by theory. After 3 years' work⁴⁵⁻⁴⁸ on this problem we may now state that, for one real system, this question has been answered in a reasonably comprehensive manner.

The choice of system for our chemisorption studies may be traced to a paper⁴⁹ by Bagus and me on diatomic manganese hydride, MnH. The electronic ground state of MnH is known experimentally to be of ⁷Σ⁺ symmetry, with electron configuration 6σ²7σ1δ²3π²8σ. The orbital energies obtained in this near-Hartree-Fock (i.e., using a very large basis set) study were -0.398 (6σ), -0.624 (7σ), -0.656 (1δ), -0.649 (3π), and -0.269 (8σ) hartree. It was initially surprising that the doubly occupied 6σ orbital lies much higher than the singly occupied 7σ orbital. However, inspection of the wave function shows that the 7σ, 1δ, and 3π orbitals are essentially pure (although somewhat distorted) manganese 3d orbitals. That is, the 3d⁵6s configuration of the atom is carried over directly to the diatomic hydride. The bonding may be thought to occur in the 6σ orbital, which is primarily a linear combination of Mn 4s, Mn 4p, and H 1s basis functions. The half-occupied 8σ orbital may be thought of as a 4s-4p hybrid non-

bonding orbital. This simple picture has been supported by more recent ab initio calculations by Richards⁵⁰ and by Kunz.⁵¹

Actually, the above picture is not too surprising if one realizes that for the transition metals V through Ni the atomic 3d orbitals lie considerably below the 4s orbital. For vanadium, the 3d and 4s orbital energies⁵² are -0.510 and -0.231 hartree, while for Ni the analogous results are -0.707 and -0.276 hartree. It would be incorrect, of course, to immediately assume that 3d orbitals do not play an important role in the bonding of transition-metal compounds. In many situations (e.g., in solution) the metal is able to shed its 4s electrons, and the resulting M²⁺ ion has its 3d orbitals exposed for interactions of various kinds. Furthermore, in metal carbonyl complexes the CO ligands effect (essentially via the Dewar-Chat-Duncanson bonding scheme^{53,54}) a reduction of the metal 4s population. However, this is less likely to be the case for transition-metal surfaces and metal particles. Here the adsorbates are typically insufficient in quantity (per metal atom) and electron-withdrawing ability to depopulate the 4s (and 4p) orbitals. For example, the presence of 4s-4p bands in bulk transition metals is certainly well established.⁵⁵ For these reasons, our research was initially motivated by the hypothesis that bonding in catalytic systems involves the 4s and 4p orbitals of the (first row) transition metals in question.

If the d orbitals of transition metals do not always play the most important role, then one naturally raises the question: are there simpler metals which might show the same qualitative behavior? If, as model theoretical studies suggest, the key feature of the bonding is the presence (in the isolated metal atom) of a doubly occupied 4s orbital and a companion nearly degenerate (but unoccupied in the atom) 4p orbital, the answer is certainly yes. In this case the simplest example of a metal atom of this general type is the Be atom, with electron configuration 1s²2s² and the 1s²2s2p³P state lying only 63 kcal higher. The Mg and Ca atoms also suggest themselves as models, but in the calcium case the proximity of the 4s, 4p, and 3d orbitals could conceivably cause complications. Note, of course, that the 3d and 4s orbitals of V-Ni are much more widely separated⁵² than those of Ca. Other evidence can be brought to bear to strengthen the Be-transition-metal analogy. For example, ferrocene (Fe(C₅H₅)₂) was initially thought to require metal 3d orbitals as the key to its existence. However the preparation of the comparable beryllium sandwich compound, beryllocene,⁵⁶ has invalidated this initial line of reasoning.

Although its suitability as a model system was of primary importance to us, it is well to point out that there have been a number of experimental studies of beryllium surfaces, using both LEED⁵⁷ and Auger

(42) J. Horiuti and T. Toya in "Solid State Surface Science", Vol. 1, M. Green, Ed., Marcel Dekker, New York, N.Y., 1969.

(43) A. Clark, "The Chemisorptive Bond", Academic Press, New York, N.Y., 1974.

(44) Actually, some interesting experimental research along these lines has been reported. See K. A. Gingerich, D. L. Cocke, and F. Miller, *J. Chem. Phys.*, **64**, 4027 (1976).

(45) C. W. Bauschlicher, D. H. Liskow, C. F. Bender, and H. F. Schaefer, *J. Chem. Phys.*, **62**, 4815 (1975).

(46) C. W. Bauschlicher, C. F. Bender, H. F. Schaefer, and P. S. Bagus, *Chem. Phys.*, **15**, 227 (1976).

(47) C. W. Bauschlicher, Ph.D. Thesis, University of California, Berkeley, August, 1976; available as Lawrence Berkeley Laboratory Report LBL-5474.

(48) H. F. Schaefer, *Annu. Rev. Phys. Chem.*, **27**, 261 (1976).

(49) P. S. Bagus and H. F. Schaefer, *J. Chem. Phys.*, **58**, 1844 (1973); see also R. W. Hand, W. J. Hunt, and H. F. Schaefer, *J. Am. Chem. Soc.*, **95**, 4517 (1973).

(50) P. R. Scott and W. G. Richards, *J. Phys. B*, **7**, 500, L347, 1679 (1974).

(51) A. B. Kunz, M. P. Guse, and R. J. Blint, *J. Phys. B*, **8**, L358 (1975); *Chem. Phys. Lett.*, **36**, 191 (1975); **37**, 512 (1975).

(52) E. Clementi and C. Roetti, *At. Data Nucl. Data Tables*, **14**, 177 (1974).

(53) M. J. S. Dewar, *Bull. Soc. Chim. Fr.*, **18C**, 79 (1951).

(54) J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 2939 (1953).

(55) T. L. Loucks, "Augmented Plane Wave Method", W. A. Benjamin, New York, N.Y., 1967.

(56) A. Haaland, *Acta Chem. Scand.*, **22**, 3030 (1968).

(57) J. M. Baker and J. M. Blakely, *J. Vac. Sci. Technol.*, **8**, 56 (1971); R. S. Zimmer and W. D. Robertson, *Surf. Sci.*, **43**, 61 (1974).

Table I
Models of Chemisorption of Atomic Hydrogen by the (0001) Surface of Beryllium Metal

Open site			Eclipsed site			Bond midpoint site			Directly overhead site		
Model	r_e	D_e	Model	r_e	D_e	Model	r_e	D_e	Model	r_e	D_e
Be(3,0)	1.25	19.1	Be ₂ (3,1)	1.24	28.7	Be ₃ (4,0)	1.26	70.1	Be ₁ (1,0)	1.42	46.4
Be ₃ (4,1)	1.02	23.2	Be ₃ (4,1)	1.15	30.1	Be ₃ (4,1)	1.14	32.4	Be ₇ (7,0)	1.43	71.3
Be ₆ (6,0)	1.18	47.3	Be ₇ (6,1)	1.11	40.8	Be ₁₀ (10,0)	1.17	45.3	Be ₁₀ (7,3)	1.43	27.3
Be ₆ (3,3)	1.11	55.3	Be ₁₃ (10,3) ^b	0.90	57.2	Be ₁₃ (10,3)	1.05	44.8	Be ₁₃ (10,3)	1.41	31.1
Be ₉ (6,3)	1.13	50.2				Be ₂₂ (14,8)	1.04	53.4	Be ₂₂ (14,8)	1.39	31.4
Be ₁₃ (10,3)	0.99	39.0	Be ₂₂ (14,8)	0.97	51.9						
Be ₂₂ (14,8)	0.94	55.1									

^a The cluster notation Be₁₀(7,3) denotes a model with seven atoms for the surface layer and three atoms for the second layer. Bond distances r_e are in Å and chemisorptive bond energies D_e in kcal mol⁻¹. ^b Two distinct Be₁₃(10,3) clusters were studied.

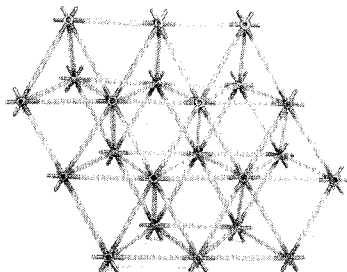


Figure 1. Be₂₂ finite cluster model adopted for chemisorption studies.

electron spectroscopy.⁵⁸ A particularly important experimental result is that the (0001) surface, considered exclusively in our studies, is not reconstructed. That is, the positions of the surface atoms are qualitatively the same as those of the bulk metal. This finding provides some justification for our assumption that all finite Be_n clusters (except Be₄) be constructed from the crystal-structure parameters $a_0 = 2.2866$ Å and $c_0 = 3.5833$ Å. These parameters imply that neighboring atoms on the same layer are separated by 2.2866 Å, while nearest neighbors in adjacent layers are separated by 2.2255 Å. The finite cluster models investigated ranged from a single Be atom, for which chemisorption is modeled by diatomic BeH, to a 36 atom cluster. Figure 1 illustrates the Be₂₂ model adopted.

In any theoretical study of molecular electronic structure, the selection of basis set is critical. In our work two basis sets have been employed. The first is a minimum basis set of Slater-type orbitals, and the second is a much larger basis of near-Hartree-Fock quality. Both sets were used to study chemisorption based on models as large as Be₁₀. Fortunately the minimum basis yields predictions in good qualitative agreement with the much more reliable near-Hartree-Fock set. Another theoretical concern is with the importance of electron correlation, which is neglected in the restricted Hartree-Fock or self-consistent-field (SCF) approximation. We seem to have been extremely lucky in the Be_n-H systems in that electron correlation appears to have little effect on the chemisorption predictions. This was anticipated by the fact that the Hartree-Fock dissociation energy (50.3 kcal) of diatomic BeH agrees remarkably well with experiment (49.8 kcal). Even more remarkable is our minimum basis SCF dissociation energy, 46.4 kcal/mol. It can hardly

be overemphasized that this agreement with experiment is fortuitous, and we most definitely do *not* recommend that minimum basis SCF theory be used in general studies of chemisorption. For systems such as Ni_n-O this approach would certainly lead to meaningless predictions.

Some of the Be_n clusters considered are of intrinsic interest. This is especially true of the Be₄ cluster, the smallest beryllium cluster to be significantly bound. For Be₄ rather sophisticated theoretical methods have been applied, including d functions⁵⁹ in the basis and explicitly evaluating the correlation energy using the theory of self-consistent electron pairs.⁶⁰ Be₄ is predicted to have tetrahedral structure, $r(\text{Be-Be}) = 2.1$ Å, and a dissociation energy of ~40 kcal/mol. Again, fortunately, neither of these conclusions is qualitatively affected by electron correlation.

Chemisorption of atomic hydrogen was considered⁴⁵⁻⁴⁸ for four different sites on the (0001) surface, and our results are summarized in Table I. Both the *open* and *eclipsed* sites are threefold sites, the difference being that for the latter there is a Be atom directly below, in the second layer. The terms *bond midpoint* and *directly overhead* should be self-explanatory. As expected the convergence in chemisorbed properties is initially oscillatory, and, in fact, these oscillations continue on an abated scale for the larger models. Several calculations have been carried out for a Be₃₆ model in which a third layer (of 14 atoms) has been added to the Be₂₂ of Figure 1. It is found that the directly overhead chemisorptive bond energy is unchanged, but that the other sites have their bond energies somewhat reduced. Our conclusion is that for an accuracy of 1 kcal/mol in all chemisorption sites it is quite possible that a 200-atom cluster would be required. On the other hand it is also clear that a qualitatively correct picture emerges from the Be₁₃ models. This result can be generalized to the statement that a reasonable description of chemisorption requires the surface atoms closest to the approaching atom or molecule, plus the nearest neighbors of the same surface atoms. From a different perspective, we have found that suitable cluster models Be_n have relatively low ionization potentials (~4 eV) and large dissociation energies (~6 kcal/nearest neighbor bond).

Table I represents a striking confirmation of Horiuti and Toya's differentiation⁴² between r and s sites. The

(58) D. M. Zehner, N. Barbulesco, and L. H. Jenkins, *Surf. Sci.*, **34**, 385 (1973); R. G. Musket and R. J. Fortner, *Phys. Rev. Lett.*, **26**, 80 (1971); M. Suleman and E. B. Pattison, *J. Phys. F*, **1**, L24 (1971); **3**, 497 (1973).

(59) R. B. Brewington, C. F. Bender, and H. F. Schaefer, *J. Chem. Phys.*, **64**, 905 (1976).

(60) C. E. Dykstra, H. F. Schaefer, and W. Meyer, *J. Chem. Phys.*, **65**, 2740 (1976); **65**, 5141 (1976).

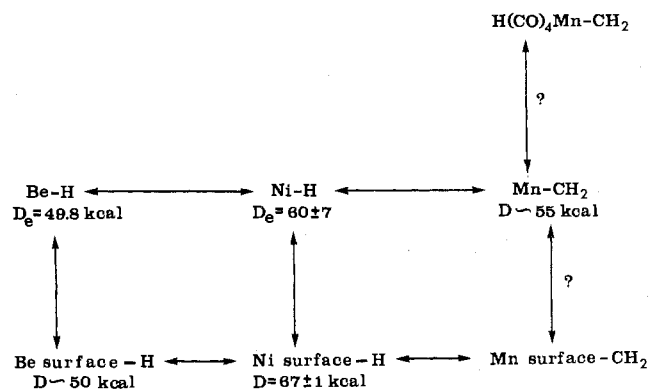


Figure 2. From gaseous molecules to surface chemistry and organometallic complexes.

r site is unique, corresponding to our directly overhead site, and the open, eclipsed, and bond midpoint sites would all be labeled "s" in the Horiuti-Toya scheme. It is apparent that the three s sites are comparable in chemisorptive bond energy, clearly implying a considerable degree of surface mobility for hydrogen atoms. It is noteworthy, however, that the energetic ordering s more favorable than r is the opposite of that anticipated by these pioneers of surface chemistry.

Two other topics may be mentioned here. The first concerns the diffusion of hydrogen into a perfect (0001) beryllium surface. At the most obvious site for diffusion (the open site), the total energy goes monotonically up as the surface-hydrogen distance is decreased from the chemisorptive equilibrium (~ -50 kcal). When the H atom lies on the metal surface, however, the energy is still ~ 4 kcal below that of the separated $\text{Be}_n + \text{H}$. Further, when the hydrogen lies 0.9 \AA below the surface, the interaction remains slightly attractive, by ~ 2 kcal. Thus, although diffusion into the bulk is much less favorable energetically than chemisorption, it would be possible were a beam of H atoms directed at the (0001) Be surface. This topic is certainly worthy of detailed dynamical studies, since diffusion of hydrogen into alkali metals is observed experimentally.⁶¹ It is pertinent, of course, that the alkali metals have larger nearest-neighbor bond distances than do the alkaline earths.

Finally the vibrational frequencies for the four chemisorption sites have been predicted, and these are 1220 (open), 1230 (eclipsed), 1360 (bond midpoint), and 2060 cm^{-1} (directly overhead). Again we see the clear-cut distinction between r and s sites. Perhaps even more important, the ordering of frequencies (terminal $>$ bridging) is consistent with that found for organotransition-metal complexes.⁶²

The Fuzzy Interface

A key finding of the above studies is that the chemisorptive bond energy of hydrogen on (0001) Be is essentially indistinguishable from the dissociation energy of diatomic BeH. Furthermore, this result does not seem entirely coincidental since the same relationship has been found experimentally for nickel, where the chemisorptive bond energy is known⁴³ to an unusual degree of reliability. These findings suggest an analogy of the type sketched in Figure 2. This is

obviously a drastic oversimplification, in particular in the use of only a single metal atom for surface chemistry. However, Figure 2 does provide the simplest possible interface between the three areas and a testing ground for molecular theories of catalysis. In the remainder of this Account I will discuss model studies in this vein and ask the degree to which these models reflect experimental reality.

Our analogy is not likely to be popular with experimentalists in any of the fields in question. Organometallic chemists generally do not like their metal atoms to have only a single ligand attached—at least three additional CO ligands need be present. Students of catalysis know that an irregular 100 atom particle is not the same as a single metal atom, and although surface chemists do not necessarily insist on 6×10^{23} metal atoms, a regular array of a dozen or so would certainly be considered mandatory. Nevertheless we shall insist on looking at the unadorned M-OF species (M = transition metal; OF = organic fragment), since this is all the three fields really have in common.⁶³ The M-OF entity is the common denominator of surface chemistry, catalysis, and organometallic chemistry.

Mononuclear Metal Models

Be-C₂H₂ and Be-C₂H₄. Pursuing the analogy between beryllium and the transition metals, these were the first M-OF systems chosen. They nicely illustrate the fact that the interaction between the doubly occupied $2s^2$ orbital and a closed-shell OF species is essentially repulsive (except, of course, for van der Waals attractions, etc.). The same is true of the first-row transition metals $4s^23d^n$ when the $4s$ orbital is doubly occupied. Thus the first prerequisite for chemical bonding is the modification of this doubly occupied valence s orbital.

For Be, this may be done by forming metal clusters (which have roughly $2s2p$ hybridization) or in the atomic case by exciting to the $1s^22s2p^3P$ state. This state is spatially threefold degenerate ($^3P_x, ^3P_y, ^3P_z$), and each of the three components interacts differently with an approaching acetylene or ethylene molecule. Figure 3 analyzes this situation in terms of the beryllium and acetylene orbitals. As it turns out,⁹ the π -bonded 3B_2 states of Be-C₂H₂ and Be-C₂H₄ are predicted to be substantially bound, by 19 and 25 kcal, respectively. The 3B_1 potential curves are very flat, while the 3A_1 states of Be-C₂H₂ and Be-C₂H₄ are repulsive. The simplest explanation of the bonding in the 3B_2 states follows Dewar,⁵³ Chatt, and Duncanson,⁵⁴ but using the metal p orbitals rather than d orbitals as intended by DCS. In particular, Figure 3 shows that the $2p_y$ HOMO of Be is of the same symmetry (b_2) as the acetylene (or ethylene, not illustrated in the figure) LUMO π^* orbital. Since the other π^* orbital is of a_2 symmetry (not matched by any of the $2p$ components), the $2p_y$ orbital must be occupied to lead to this classic "back-bonding" and hence to a strongly attractive potential-energy curve. These results suggested that the analogous $4s4p3d^n$ transition-metal complexes might be comparably bound.

Mn-C₂H₂ and Mn-C₂H₄. The first lesson learned from these two systems⁶⁴ was that transition metals are

(61) A. B. Kunz, D. J. Mickish, and P. W. Deutsch, *Solid State Commun.*, **13**, 35 (1973).

(62) H. D. Kaesz, *Chem. Brit.*, **9**, 344 (1973).

(63) This statement is probably a bit too strong. For example, Muettterties (ref 6) might argue that it is the M_3 unit which is critical to the catalytic aspects of the three areas.

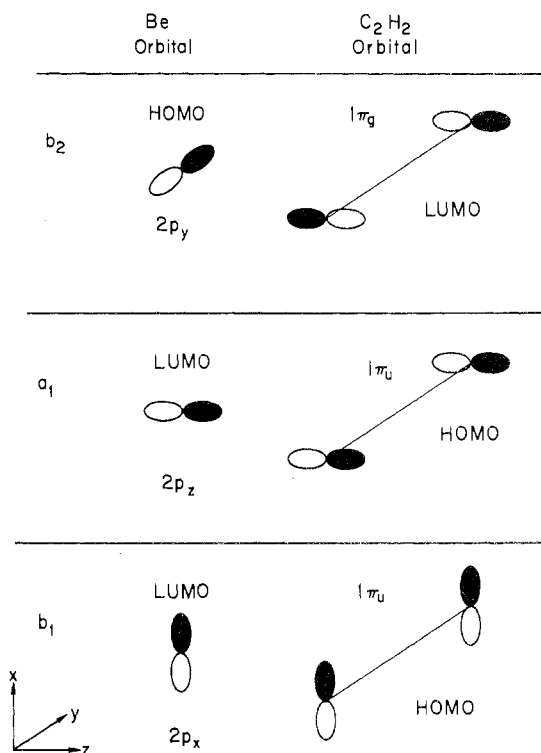


Figure 3. Symmetry matching of some of the highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO) of atomic beryllium with those of acetylene.

extremely demanding in terms of basis set requirements. Beginning with a double ζ (twice as large as the standard minimum basis) basis, two sets of p functions were added to describe the 4p orbital, which of course is unoccupied in the electronic ground state of the atom. In addition, however, it was found that a third, more diffuse, set of d functions was required to provide a consistent description of the s^2d^n and sd^{n+1} electronic states. Thus one finds that meaningful results for systems with even a single transition-metal atom require moderately large basis sets.

The electronic states arising from the interaction of Mn $4s4p, 3d^5$ with C_2H_2 and C_2H_4 are much less strongly bound than was the case for beryllium. This is essentially a "size" effect. That is, the amount of attraction is roughly constant, but the larger repulsive core of the Mn atom prevents the C_2H_2 or C_2H_4 from approaching the metal atom closely. For example, in 3B_2 Be- C_2H_2 the perpendicular distance from Be to the C=C bond midpoint is 1.8 Å, while for the analogous Mn species the equilibrium separation is 2.7 Å.

Our biggest surprise from the Mn- C_2H_2 and Mn- C_2H_4 systems was that the classic DCS electronic states are only very weakly bound, by less than 10 kcal/mol in the latter case. These states correspond to the Mn electron configuration $4s3d^6$, or more specifically, $4s3d_{x^2-y^2}23d_{z^2}23d_{xy}3d_{xz}3d_{yz}^2$, where the doubly occupied $3d_{yz}$ should form a π bond with the unoccupied π^* (b_2) orbital of the unsaturated hydrocarbon. This result seems certainly to imply that the model adopted is *not* representative of surface chemistry, catalysis, or organometallic chemistry. For example, one would certainly expect the ethylene ligand in

(64) W. C. Swope and H. F. Schaefer, "Model Studies of π -Bonded Organometallic Systems. Mn- C_2H_2 and Mn- C_2H_4 ", to be published in *Mol. Phys.*

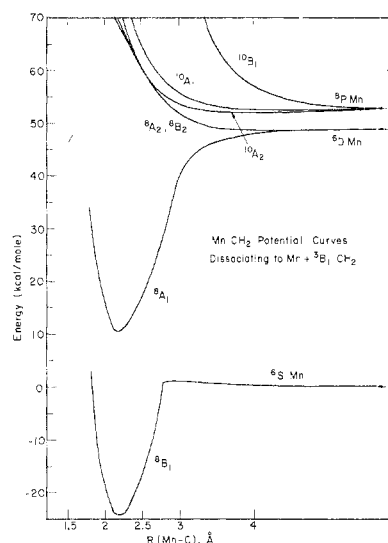
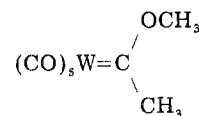


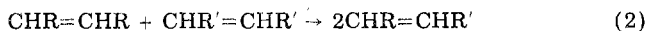
Figure 4. Mn- CH_2 potential energy curves arising from manganese atom plus triplet methylene. 3B_1 CH_2 is fixed at its equilibrium geometry here, namely $r(CH) = 1.08$ Å, $\theta(HCH) = 134^\circ$.

$H(CO)_4Mn(C_2H_4)$ to be bound by at least 20 kcal. In addition, estimates of the chemisorptive bond energies of acetylene on metal surfaces are in the 20–40-kcal range. We rather suspect that in this particular case the CO ligands of organometallic chemistry and the neighboring metal atoms of surface chemistry play a similar role in "promoting" the metal atom (or atoms in the case¹⁸ of multiple coordination) to a state more favorable for chemical bonding to the acetylene or olefin. The logical continuation of these studies would be an investigation of the interaction of C_2H_2 and C_2H_4 with Mn_2 or Mn_3 , the next simplest cluster models.

Mn- CH_2 . This system appears to be a good model for probing the fuzzy interface, and the results obtained⁶⁵ are quite fascinating. Transition-metal carbenes have been known since the preparation by Fischer and Maasböl⁶⁶ in 1964 of



and the presence of the alkoxy group OCH_3 is characteristic of Fischer-type carbenes. Our interest was spurred by the synthesis and characterization by Schrock⁶⁷ and co-workers of $Ta(C_5H_5)_2CH_2CH_3$, the first such transition-metal complex incorporating nonsubstituted methylene (CH_2) as a ligand. Such complexes have taken on additional significance with the finding³¹⁻³³ that they are critical intermediates in the olefin metathesis reaction, eq 2, one of the most



important examples of homogeneous catalysis.

Metal atom-carbene complexes can take on four fundamentally different forms, depending on whether the transition metal has an s^2d^n (e.g., Mn) or sd^{n+1} (e.g., Cr) ground state and whether the carbene in question has a triplet (e.g., CH_2) or singlet (e.g., vinylidene CCH_2)

(65) B. R. Brooks and H. F. Schaefer, *Mol. Phys.*, **34**, in press.

(66) E. O. Fischer, *Adv. Organometal. Chem.*, **14**, 1 (1976).

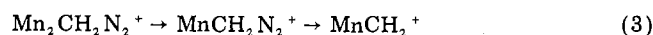
(67) R. R. Schrock, *J. Am. Chem. Soc.*, **97**, 6577 (1975); L. J. Gugenberger and R. R. Schrock, *J. Am. Chem. Soc.*, **97**, 6578 (1975).

Table II
Three Strongly Bound Electronic States of Mn-CH₂

State	r(Mn-C), Å	θ(HCH), deg	Bond energy, kcal	CH ₂ Orbital Populations	
				3a ₁	1b ₁
⁸ B ₁	2.16	109	33	1.69	0.95
⁸ A ₁	2.18	142	39	0.79	1.78
⁶ B ₂	1.90	108	38	1.76	0.63

ground state. Some of our theoretical results are summarized in Figure 4, where it is seen that the ⁸B₁ state of MnCH₂ is representative of the s²dⁿ-triplet combination, while the ⁸A₁ state should be a prototype for the sdⁿ⁺¹-triplet combination. Not shown in Figure 4, the ⁶B₂ state, representative of the sdⁿ⁺¹-singlet species, is also strongly bound. The fourth combination, s²dⁿ-singlet, is found to be repulsive as it corresponds to the interaction between two closed shells, discussed above.

When the methylene fragment geometry is allowed to relax, the predictions seen in Table II are obtained. Electron correlation will increase the predicted M=C bond energies, most likely to ~50 kcal. Thus it seems clear that CH₂ is a much more strongly bound ligand than, e.g., CO, N₂, C₂H₂, or C₂H₄. This conclusion is supported by Goddard's findings⁸ for NiCH₂ and by recent experimental work on the diazo compound Mn₂(CO)₁₀CH₂N₂. Upon electron-impact ionization, Herrmann⁶⁸ finds the primary chain of events to be that shown in eq 3. That is, the CH₂ fragment is the last



to be expelled from the Mn atom. Only two manganese carbenes have been geometrically characterized, and these crystal structures show Mn=C distances of 1.95 and 1.96 Å, in reasonable agreement with the predictions of Table II.

A simple modification of Walsh's rules provides a very nice explanation of the methylene bond angles in Table II. Recall that the key features of Walsh's AH₂ orbital binding energy diagram⁶⁹ are (a) the 1b₁ orbital is flat, i.e., its binding energy is independent of angle, and (b) the 3a₁ energy decreases monotonically with decreasing bond angle. Thus with one electron in the 3a₁ orbital, the CH₂ bond angle⁷⁰ is 134°, but with 3a₁

(68) W. A. Herrmann, M. L. Ziegler, K. Weidenhammer, H. Biersack, K. A. Mayer, and R. D. Minard, *Angew. Chem., Int. Ed. Engl.*, **15**, 164 (1976).

(69) A. D. Walsh, *J. Chem. Soc.*, 2260 (1953).

doubly occupied it becomes 102.4°. If the Mulliken populations of CH₂ within MnCH₂ are extracted, the same analysis is remarkably valid. The ⁸B₁ and ⁶B₂ states, with 3a₁ populations somewhat less than two, have bond angles somewhat larger than the 102.4° found for singlet methylene, and the ⁸A₁ state, with only 0.79 electron in the 3a₁ orbital, does indeed have a bond angle even greater than that (134°) of triplet methylene.

Finally, the fact that carbenes are so much more strongly bound to Mn than C₂H₂ suggests that the two isomers



might be comparable energetically. This suggestion is strengthened by recent structural determinations of transition-metal-vinylidene complexes.^{71,72} We have carried out a detailed study⁷³ of the CCH₂ → C₂H₂ potential surface and find the vinylidene isomer to lie ~40 kcal higher. Since this is roughly the difference between the metal-acetylene and metal-carbene bond energies, the two forms should be competitive, depending of course on the metal chosen and substituents involved.

In conclusion, it is well to note the limitations of ab initio theoretical work to date on transition-metal systems. An urgent goal of future studies should be the examination of more realistic systems such as Cr(CO)₅CH₂ and Mn₄-C₂H₄. Nevertheless, it is hoped that the present Account will provide a framework for future discussions of the many fascinating relationships between three increasingly important branches of science.

I am deeply indebted to my colleagues Charles W. Bauschlicher, Jr., Dean H. Liskow, Charles F. Bender, Paul S. Bagus, Clifford E. Dykstra, Wilfried Meyer, Robert B. Brewington, William C. Swope, and Bernard R. Brooks, who carried out much of the research summarized in this Account. The support of the U.S. Energy Research and Development Administration is gratefully acknowledged. Finally, I wish to thank Professor D. P. Craig and Dr. Leo Radom for their helpful comments on the manuscript.

(70) H. F. Schaefer, *Chem. Brit.*, **11**, 227 (1975).

(71) R. M. Kirchner and J. A. Ibers, *J. Organomet. Chem.*, **82**, 243 (1974); *Inorg. Chem.*, **13**, 1667 (1974).

(72) A. N. Nesmeyanov, G. G. Aleksandrov, A. B. Antonova, K. N. Anisimov, N. E. Kolobova, and Y. T. Struchkov, *J. Organomet. Chem.*, **110**, C36 (1976).

(73) C. E. Dykstra and H. F. Schaefer, "The Vinylidene-Acetylene Rearrangement. An SCEP Study of a Model Unimolecular Reaction", to be published.