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

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Abstract

Motivated by the observation that the bonding in diatomic BeH is remarkably similar to that of transition metal hydrides, we have completed a theoretical study of chemisorption on the (0001) surface of metallic beryllium. Finite clusters as large as Be_{36} have been used to model the metal surface, and firm conclusions drawn concerning the chemisorptive bond energies at four principle surface sites. An important result is that the chemisorptive bond energy of Be_n-H is essentially the same as the dissociation energy of diatomic BeH. Since the same relationship has been demonstrated experimentally for the chemisorption of hydrogen on nickel surfaces, it may provide a key to the molecular understanding of surface chemistry and catalysis. These studies suggest that the transition metal-organic fragment bond provides a framework for probing the grey area between surface chemistry, catalysis, and organometallic chemistry. To test this hypothesis we have been engaged in a theoretical study of molecular models for catalysis. The specific systems considered to date include $Mn-C_2H_2$, $Mn-C_2H_4$, and $Mn-CH_2$, but it is hoped that the conclusions drawn will be of more general validity.

Introduction

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 chemistry[3] 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 literature[4] 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, Muetterties[6] 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, he 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 coworkers[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 chemistry[1] 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 coworkers[18]. More generally the study
of how chemical reactions occur on perfect surfaces is often considered a
first step[19] 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 extremly 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 Logel[22] 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 others[25] 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 coworkers[29] 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 sulphuric acid in methanol solution. Chatt's process is particularly intriguing since it appears to go against Muetterties thesis[6] 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 Muetterties and coworkers 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 role[31-33] 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 success-
fully, to numerous problems in surface chemistry, catalysis, and organo-
metallic chemistry. The reader is referred in this context to the work
of Hoffman[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 the simplest case - chemi-
sorption. 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

$$-M-M- \quad + \quad H_2 \quad \longrightarrow \quad \begin{array}{cc} H & H \\ | & | \\ -M-M- \\ | & | \end{array} \qquad (1)$$
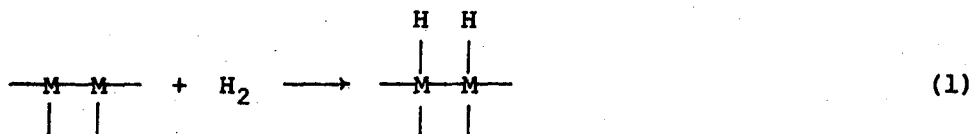
Whereas 103 kcal/mole are normally required to dissociate H_2, dissociative
chemisorption occurs on many metal surfaces with little or no activation
energy.

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, Ni_2, Ni_3, Ni_4, ... 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 three years work[45-48] 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 paper[49] by Bagus and the author on diatomic manganese hydride, MnH. The

electronic ground state of MnH is known experimentally to be of $^7\Sigma^+$ symmetry,

with electron configuration

$$\text{------} \quad 6\sigma^2 \; 7\sigma \; 1\delta^2 \; 3\pi^2 \; 8\sigma \tag{2}$$

The orbital energies obtained in this near Hartree-Fock (i.e. using a very

large basis set) study were $-0.398(6\sigma)$, $-0.624(7\sigma)$, $-0.656(1\delta)$, $-0.649(3\pi)$,

and $-0.269(8\sigma)$ hartrees. 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 $3d^5 \; ^6S$ 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 nonbonding orbital. This simple picture has been supported by

more recent *ab initio* calculations by Richards[50] 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 consider-

ably below the 4s orbital. For vanadium, the 3d and 4s orbital energies[52]

are -0.510 and -0.231 hartrees, while for Ni the analogous results are
-0.707 and -0.276 hartrees. 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 M^{+2} ion has
its 3d orbitals exposed for interactions of various kinds. Furthermore,
in metal carbonyl complexes the CO ligands effect (essentially via the
Dewar-Chatt-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 $1s^2 2s^2$ and the
$1s^2 2s 2p$ ^3P 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 separated[52]
than those of Ca. Other evidence can be brought to bear to strengthen the

Be - transition metal analogy. For example, ferrocene $Fe(C_5H_5)_2$ was

initially thought to require metal 3d orbitals as the key to its existence.

However the preparation of the comparable beryllium sandwich compound,

berylocene[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 LEED[57] and Auger 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 Be_4) be constructed from

the crystal structure parameters $a_0 = 2.2866\overset{o}{A}$ and $c_0 = 3.5833\overset{o}{A}$. These parameters

imply that neighboring atoms on the same layer are separated by $2.2866\overset{o}{A}$, while

nearest neighbors in adjacent layers are separated by $2.2255\overset{o}{A}$. The finite

cluster models investigated ranged from a single Be atom, for which chemi-

sorption is modeled by diatomic BeH, to a 36 atom cluster. Figure 1 illustrates

the Be_{22} 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 a

much larger basis of near Hartree-Fock quality. Both sets were used to

study chemisorption based on models as large as Be_{10}. 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/

mole. 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 Be_4 cluster, the smallest beryllium cluster to

be significantly bound. For Be_4 rather sophisticated theoretical methods

have been applied, including d functions[59] in the basis and explicitly

evaluating the correlation energy using the theory of self-consistent

electron pairs[60]. Be_4 is predicted to have tetrahedral structure, r(Be-Be) =

2.1 Å, and a dissociation energy of $\sim$ 40 kcal/mole. Again fortunately,

neither of these conclusions is qualitatively affected by electron correlation.

Chemisorption of atomic hydrogen was considered[45-48] for four different

sites on the (0001) surface and our results are summarized in Table I. Both

the open and eclipsed sites are three-fold 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 Be_{36} model in

which a third layer (of 14 atoms) has been added to the Be_{22} of Figure 1.

It is found that the directly overhead chemisorptive bond energy is unchanged,

but that the other sites have their bond energies reduced. Our conclusion

is that for an accuracy of 1 kcal/mole 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 Be_{13} 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

($\sim$ 4eV) and large dissociation energies ($\sim$ 6 kcal/nearest neighbor bond).

Table I represents a striking confirmation of Horiuti and Toya's

differentiation[42] between r and s sites. The 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 ($\sim$ -50 kcal). When the H atom lies on the metal surface, however,

the energy is still $\sim$4 kcal below that of the separated Be_n + H. Further,

when the hydrogen lies 0.9 Å below the surface, the interaction remains

slightly attractive, by $\sim$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 cm^{-1} (open), 1230 cm^{-1} (eclipsed), 1360 cm^{-1} (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 known[43] 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 we 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 questions. 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

A.   Be-C_2H_2 and Be-C_2H_4.

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 (excepting, of course for van der Waals

attractions, etc.). The same is true of the first-row transition metals

$4s^2 3d^n$ 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 $1s^2 2s2p$ ^3P state.

This state is spatially three-fold 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 $^3B_2$ state of Be-C_2H_2

and Be-C_2H_4 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-C_2H_2 and Be-C_2H_4 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.

B. $Mn-C_2H_2$ and $Mn-C_2H_4$

   The first lesson learned from these two systems[64] was that transition

metals are extremely demanding in terms of basis set requirements. Beginning

with a double zeta (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 $4s4p_y3d^5$ 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/mole in

the latter case. These states correspond to Mn electron configuration $4s3d^6$, or more specifically

$$4s \; 3d_{x2-y2} \; 3d_{z^2} \; 3d_{xy} \; 3d_{xz} \; 3d_{yz}^2 \qquad\qquad (3)$$
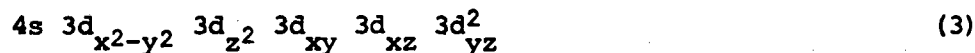
where the doubly-occupied $3d_{yz}$ should form a π bond with the unoccupied π^* (b_2) orbital of the unsaturated hydrocarbon. This result seems certainly to imply that the model adopted is <u>not</u> representative of surface chemistry, catalysis, or organometallic chemistry. For example, one would certainly expect the ethylene ligand in $H(CO)_4Mn(C_2H_4)$ 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 case[18] 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.

C. <u>Mn-CH$_2$</u>

This system appears to be a good model for probing the fuzzy interface, and the results obtained[65] are quite fascinating. Transition metal carbenes have been known since the preparation by Fischer and Maasböl[66] in 1964 of

$$(CO)_5 W = C \overset{\displaystyle OCH_3}{\underset{\displaystyle CH_3}{<}} \qquad\qquad (4)$$

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 Schrock[67] and coworkers of $Ta(C_5H_5)_2 \; CH_3CH_2$, the first such transition metal complex incorporating nonsubstituted methylene (CH$_2$) as a ligand.

Such complexes have taken on additional significance with the finding[31-33] that they are critical intermediates in the olefin metathesis reaction

$$CHR=CHR + CHR'=CHR' \longrightarrow 2 \; CHR=CHR' \qquad (5)$$

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) ground state. Some of our theoretical results are summarized in Figure 4, where it is seen that the $^8B_1$ state of $MnCH_2$ is representative of the s^2d^n-triplet combination, while the $^8A_1$ state should be a prototype for the sd^n-triplet combination. Not shown in Figure 4, the $^6B_2$ state, representative of the sd^{n+1}-singlet species, is also strongly bound. The fourth combination, s^2d^n-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 $\sim$50 kcal. Thus it seems clear that CH_2 is a much more strongly bound ligand than, e.g. CO, N_2, C_2H_2, or C_2H_4. This conclusion is supported by Goddard's findings[8] for $NiCH_2$ and by recent experimental work on the diazo compound $Mn_2(CO)_{10}CH_2N_2$. Upon electron impact ionization, Herrmann[68] finds the primary chain of events to be

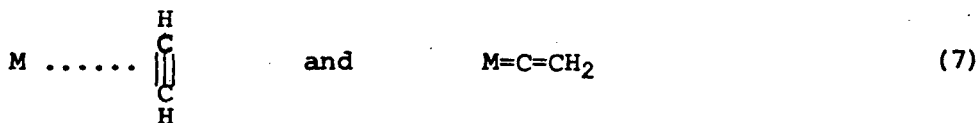$$Mn_2CH_2N_2^+ \longrightarrow MnCH_2N_2^+ \longrightarrow MnCH_2^+ \qquad (6)$$
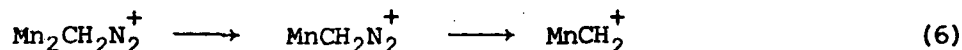
That is, the CH_2 fragment is the last to be expelled from the Mn atom. Only

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 AH_2 orbital binding energy diagram[69] are a) the $1b_1$ orbital is flat,

i.e. its binding energy is independent of angle, and b) the $3a_1$ energy

decreases monotonically with decreasing bond angle. Thus with one electron

in the $3a_1$ orbital, the CH_2 bond angle[70] is 134°, but with $3a_1$ doubly-occupied

it becomes 102.4°. If the Mulliken populations of CH_2 within $MnCH_2$ are

extracted, the same analysis is remarkably valid. The $^8B_1$ and $^6B_2$ states,

with $3a_1$ populations somewhat less than two, have bond angles somewhat larger

than the 102.4° found for singlet methylene. And the $^8A_1$ state, with only

0.79 electrons in the $3a_1$ 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 C_2H_2 suggests that the two isomers

$$ M \ldots\ldots \overset{\overset{\displaystyle H}{\overset{\displaystyle |}{C}}}{\underset{\underset{\displaystyle H}{\underset{\displaystyle |}{C}}}{\|\|}} \qquad \text{and} \qquad M=C=CH_2 \qquad\qquad (7) $$

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 study[73] of the $CCH_2 \rightarrow C_2H_2$ 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 concluding, 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 $Cr(CO)_5CH_2$ and $Mn_4-C_2H_4$. 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.

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Table I Models of the chemisorption of atomic hydrogen by the (0001) surface of beryllium metal. The cluster notation $Be_{10}(7,3)$ 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 mole^{-1}.

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	$Be_4(3,1)$	1.24	28.7	$Be_4(4,0)$	1.26	70.1	$Be_1(1,0)$	1.42	46.4
$Be_5(4,1)$	1.02	23.2	$Be_5(4,1)$	1.15	30.1	$Be_5(4,1)$	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	$Be_{13}(10,3)$[a]	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		0.94	58.3	$Be_{22}(14,8)$	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									

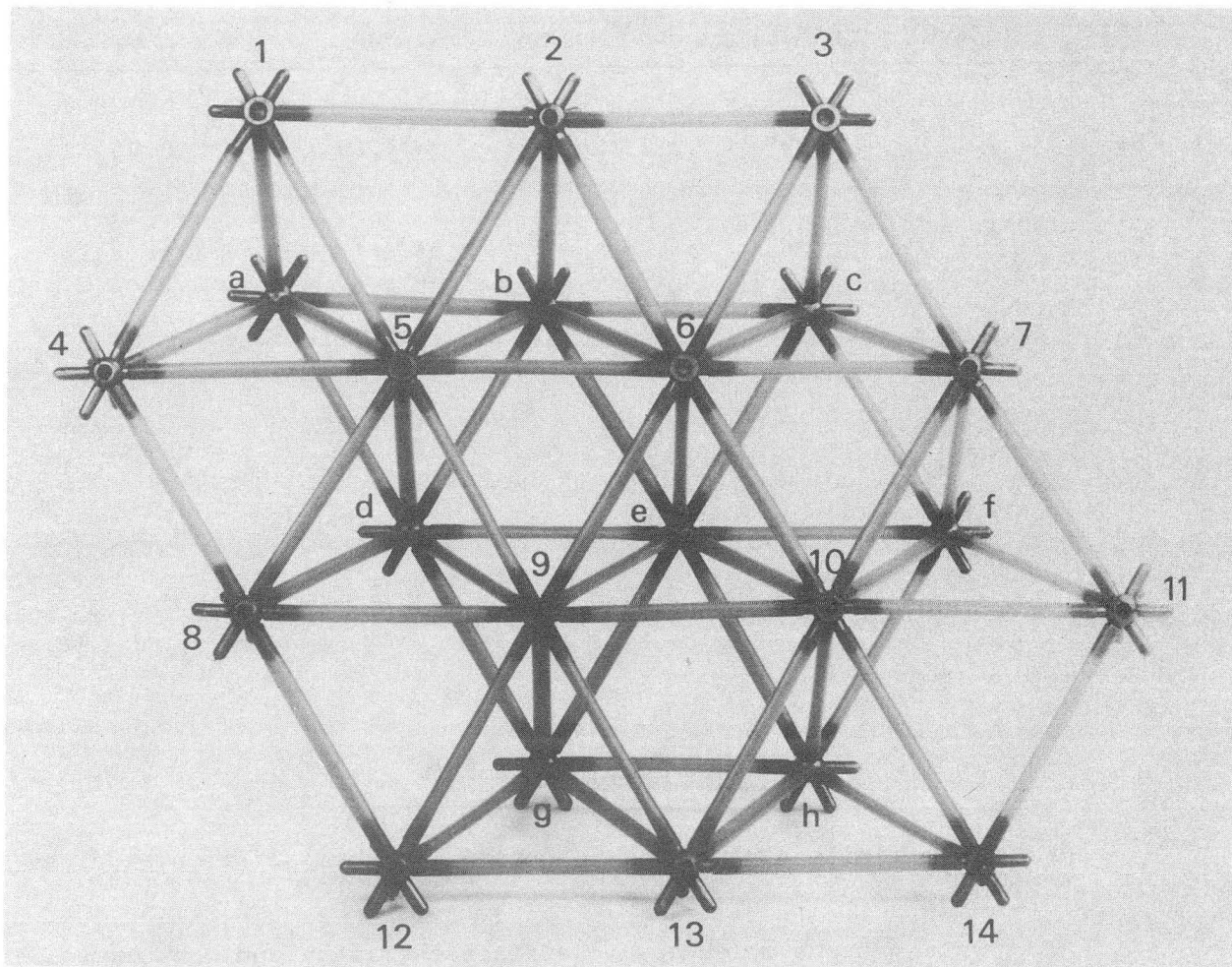[a] Two distinct $Be_{13}(10,3)$ clusters were studied.

Table II. Three strongly bound electronic states of Mn-CH_2.

State	r(Mn-C)	θ(HCH)	Bond Energy	CH$_2$ Orbital Populations	
				$3a_1$	$1b_1$
$^8B_1$	2.16 Å	109°	33 kcal	1.69	0.95
$^8A_1$	2.18 Å	142°	39 kcal	0.79	1.78
$^6B_2$	1.90 Å	108°	38 kcal	1.76	0.63

Figure Captions

1. Be_{22} finite cluster model adopted for chemisorption studies.

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

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.

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, θ(HCH) = 134°.
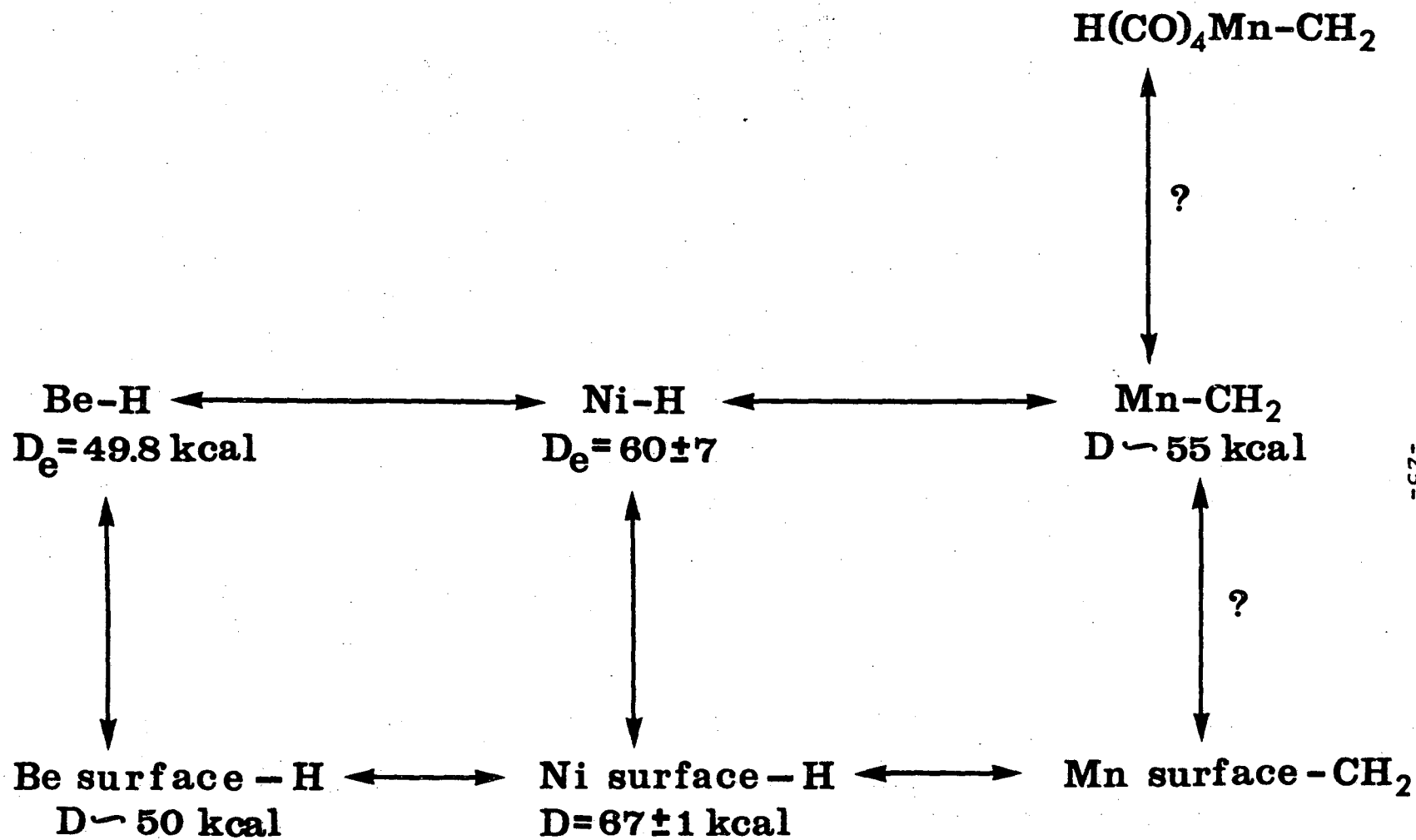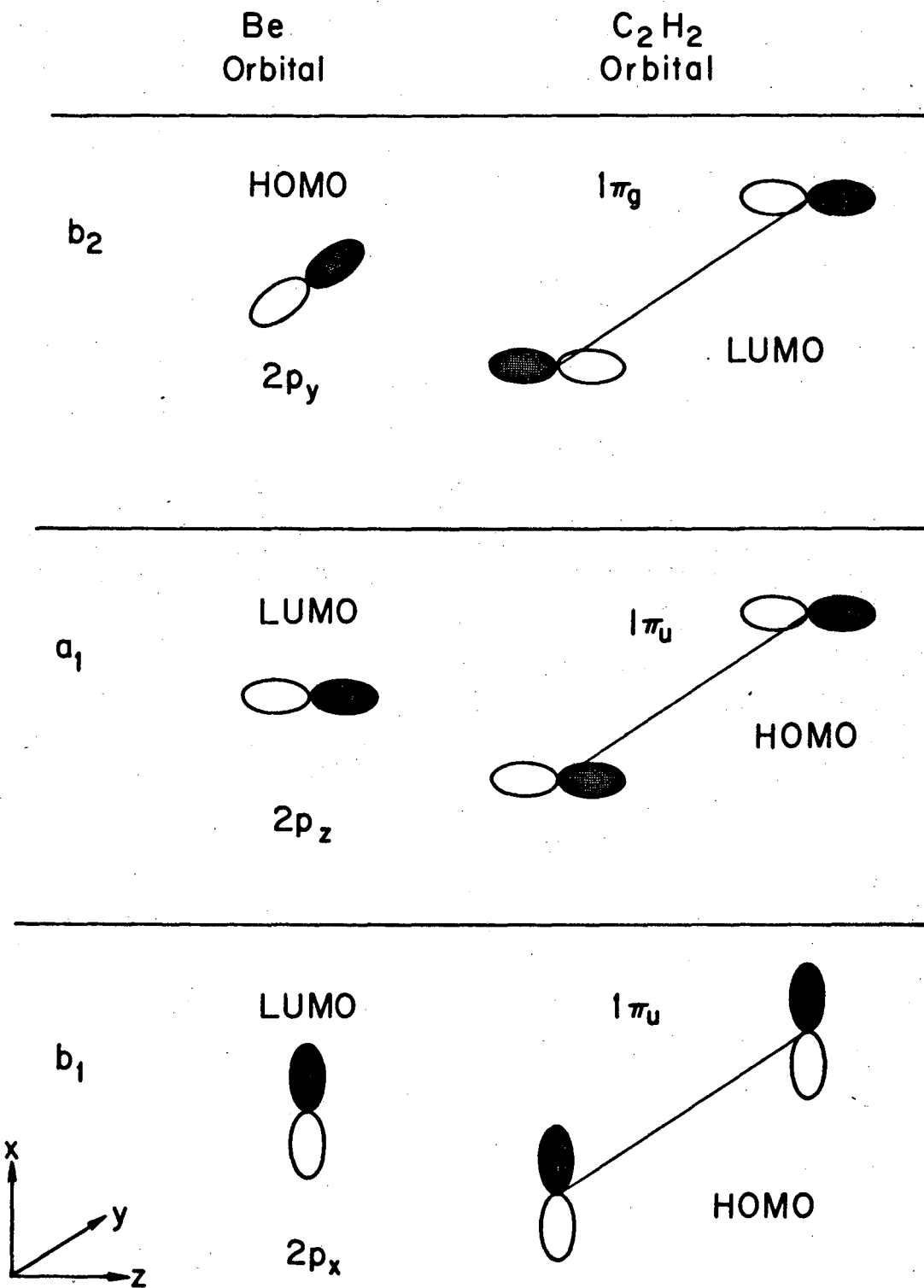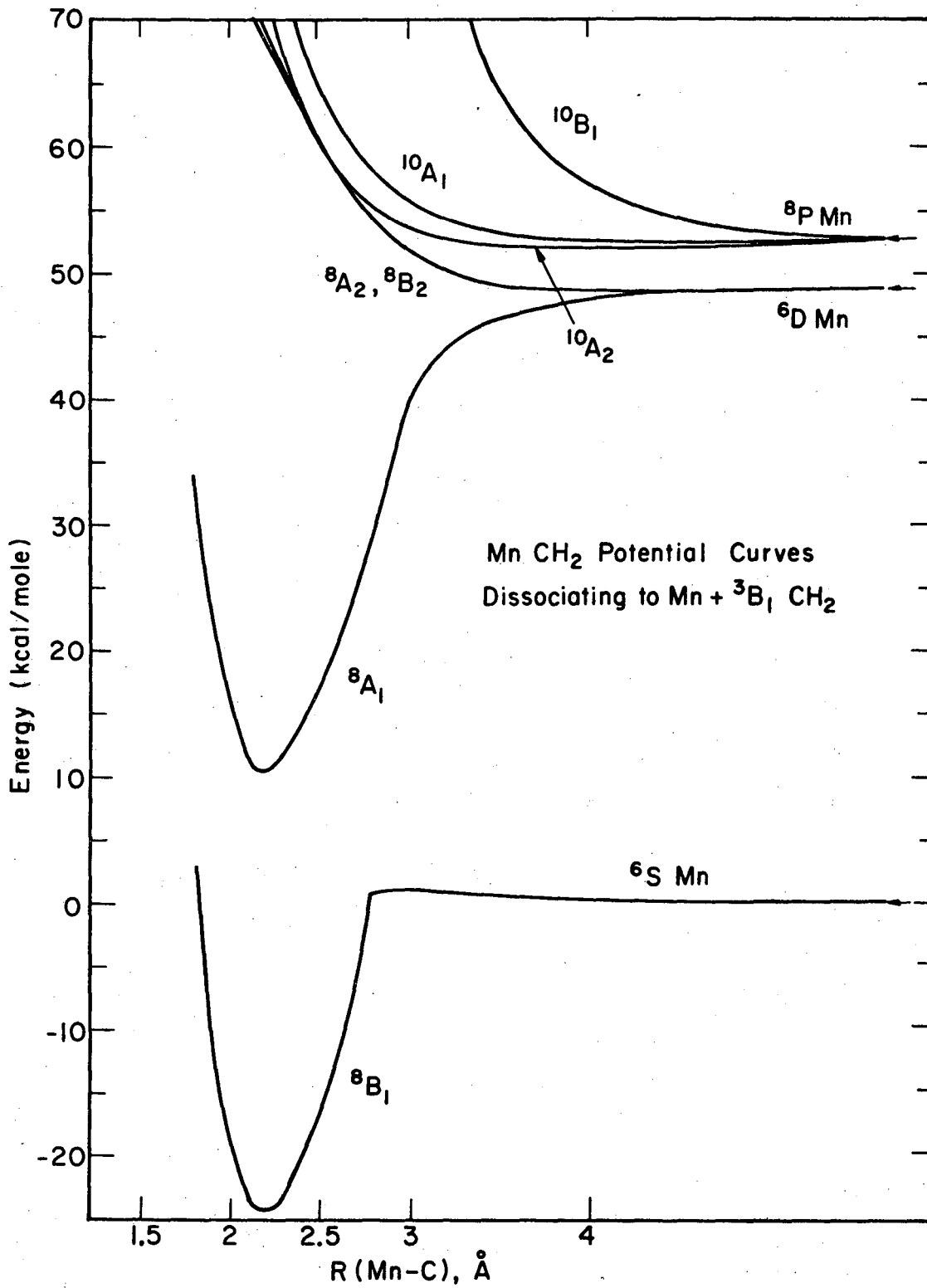
XBB 7512-8737A

Fig. 1

$$H(CO)_4Mn-CH_2$$

$$\updownarrow \ ?$$

$$\text{Be-H} \longleftrightarrow \text{Ni-H} \longleftrightarrow \text{Mn-CH}_2$$

Be–H
$D_e = 49.8$ kcal

Ni–H
$D_e = 60 \pm 7$

Mn–CH$_2$
$D \sim 55$ kcal

$$\updownarrow \qquad\qquad \updownarrow \qquad\qquad \updownarrow \ ?$$

Be surface – H
$D \sim 50$ kcal

Ni surface – H
$D = 67 \pm 1$ kcal

Mn surface – CH$_2$

Be surface – H $\longleftrightarrow$ Ni surface – H $\longleftrightarrow$ Mn surface – CH$_2$

Fig. 2

	Be Orbital	C_2H_2 Orbital

b_2 — HOMO — $2p_y$; $1\pi_g$ — LUMO

a_1 — LUMO — $2p_z$; $1\pi_u$ — HOMO

b_1 — LUMO — $2p_x$; $1\pi_u$ — HOMO

XBL763-5261

Fig. 3

Fig. 4