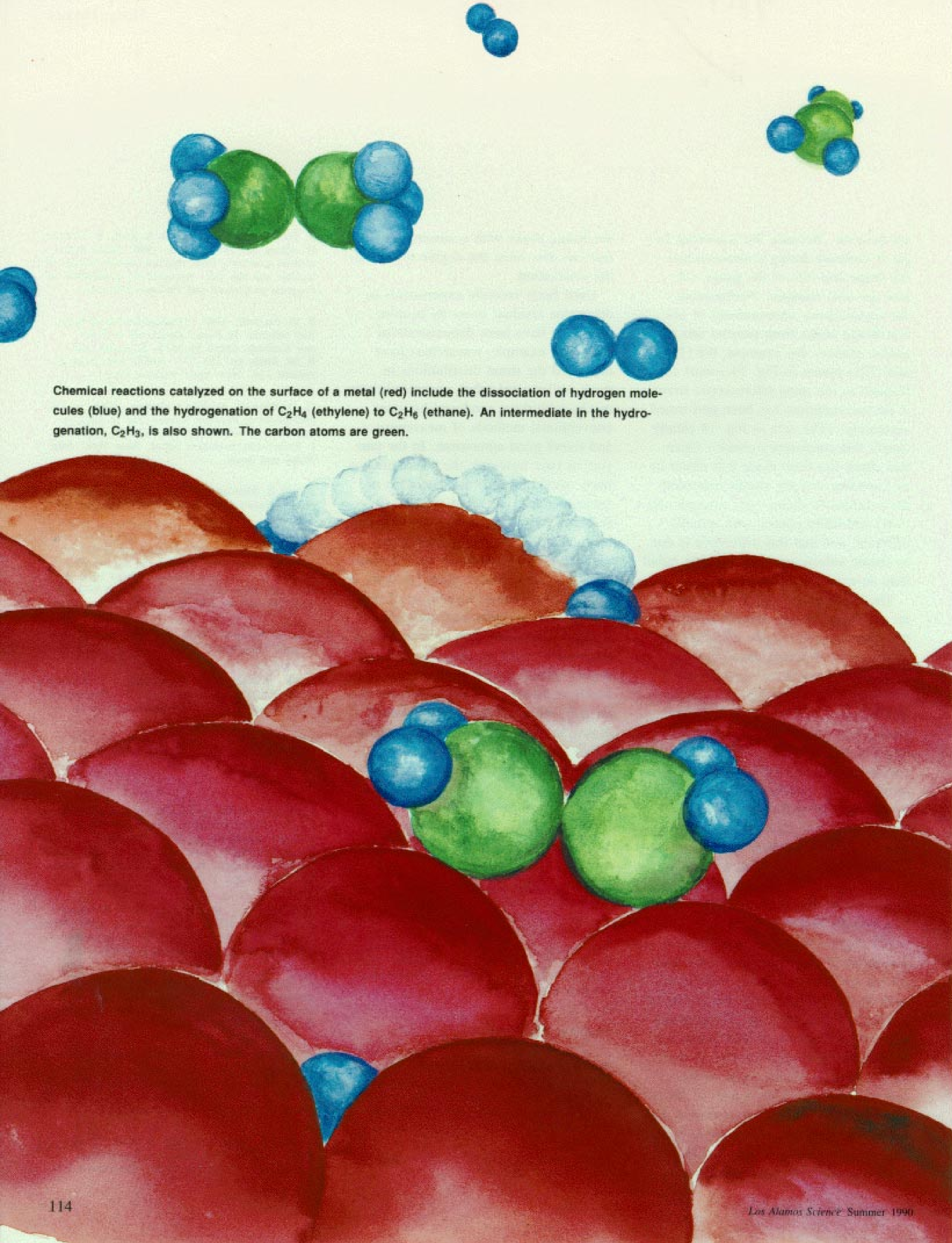


Chemical reactions catalyzed on the surface of a metal (red) include the dissociation of hydrogen molecules (blue) and the hydrogenation of C_2H_4 (ethylene) to C_2H_6 (ethane). An intermediate in the hydrogenation, C_2H_3, is also shown. The carbon atoms are green.

NEUTRONS & CATALYSIS

by Juergen Eckert and Phillip J. Vergamini

Catalysis—the ability of some substances to alter the rate of chemical reactions without being consumed-was recognized more than 150 years ago and has been applied on an industrial scale since the beginning of this century. Modern industrial chemistry, especially petroleum processing and the manufacture of chemicals, could not function without catalysts. It has been estimated, for example, that catalysts are involved at some point in the production of 60 to 70 percent of all industrial chemicals. Yet the store of knowledge about how catalysts work is surprisingly small. The search for a catalyst for a particular reaction, or for ways to improve existing catalysts, is still. as it always has been, largely empirical.

In the last few years, however, sophisticated new analytical and computational techniques have helped stimulate a renaissance in catalysis research. Powerful economic forces have motivated the study of catalysis as well: the need for new sources of energy and

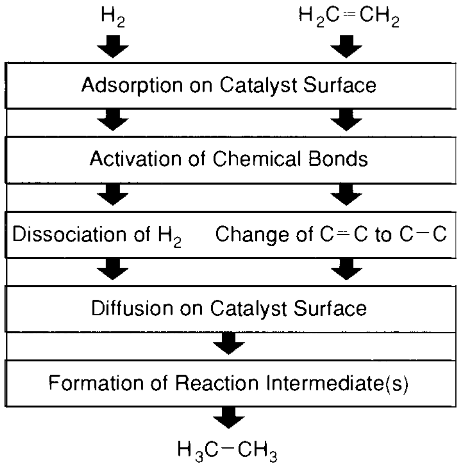
chemicals, changes in the availability of’ raw materials, potential restrictions on the availability of noble-metal catalysts, and the desire for new products have pointed up the need for a clearer understanding of catalytic processes.

Much of the research into catalysis is directed toward metals. because they catalyze many important reactions. Metals may be catalytically active in the form of finely divided particles, organometallic compounds in solution, or ions bound to large biologically active molecules, such as enzymes. The catalysis may be *heterogeneous* in the sense of involving more than one phase (solid metal and gaseous reactants, for example) or it may be *homogeneous* in the sense of involving only one phase (such as a solution). Whatever the form, when the metal binds to a reactant molecule, it almost always alters the chemical bonding in the reactant, If that alteration is favorable to some particular reaction, then the metal is a catalyst for that reaction.

To understand catalytic activity, or to tailor a catalyst to do a specific job, we need to know the individual steps in the catalytic process in great detail, For example, consider the hydrogenation of ethylene to ethane,

$$H_2C{=}CH_2 + H_2 \rightarrow H_3C{-}CH_3,$$

which can serve as a prototype of reactions used in producing synthetic fuels. The production of synthetic fuel from coal, for example, involves various series of reactions, including the stepwise hydrogenation of carbon to form acetylene (HCCH), ethylene, and ethane, as well as the stepwise hydrogenation of carbon chains with more than two carbon atoms. The hydrogenation of ethylene shown above is a particularly useful reaction to study because it can be carried out at moderate temperatures in the presence of a metal catalyst. The various steps to the reaction are represented schematically in Fig. 1, and a full understanding of the hydrogenation process requires knowing many details about each step. Knowledge of the spatial relationships of the adsorbed species and the metal atoms at the catalyst surface may enable us to identify reactive sites on the surface. Determination of the changes in bond angles and distances of the reactant molecules when they are adsorbed should make it possible to understand theoretically the changes in electronic structure that occur when the reactants are activated. Because the adsorbed species must diffuse on the surface to react and form new molecules, we need to know how this occurs. (We might wonder, for example, whether the adsorbed hydrogen diffuses only over the surface of the metal or also into its interior.) Finally, identification of reaction intermediates is crucial to understanding the entire process.



HYDROGENATION OF ETHYLENE

Fig. 1. The catalytic hydrogenation of ethylene to ethane involves various steps, all of which need to be examined in detail if we are to fully understand the reaction. Neutron scattering experiments can help provide some of the necessary detail.

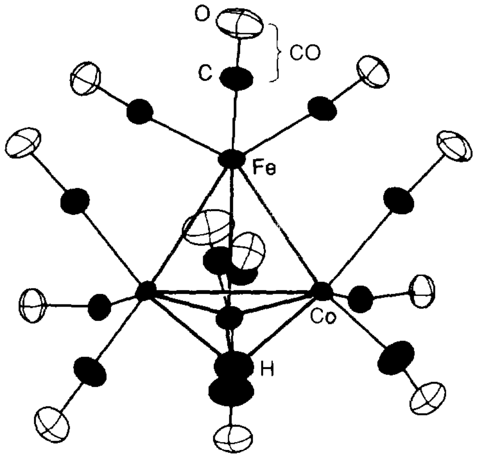
Unfortunately, these details of structure and dynamics cannot easily be determined in a “real-world” situation—that is, during an actual catalytic reaction. Catalytic processes usually proceed under conditions that preclude the direct application of many powerful analytical techniques-or at least make such application very difficult. Considerable effort has therefore been devoted to the study of so-called *model systems*, which are designed to reproduce the critical relationships as accurately as possible. One useful model system is a single crystal of a metal for which the surface arrangement of atoms is known. Others that have been widely used are synthetic molecules consisting of a metal atom (or a cluster of metal atoms) surrounded by stabilizing ligands, usually carbonyl groups (CO) or other more complex organic groups. When a reactant molecule such as ethylene or benzene binds to such a synthetic molecule, we can assume that, to some degree, the configuration of the resulting complex resembles that of the same reactant adsorbed on a metal surface. The complex can be studied with several spectroscopic techniques, and its crystalline form can be characterized by x-ray’ and neutron diffraction, which reveal details of its architecture with great accuracy.

The more closely the properties of the model system approximate the properties of the real-world system, of course, the better. As a result, model systems are often structurally modified to refine their properties and bring them closer in line with the more complex system of interest. However. such modifications can complicate the structural characterization of the model system. For example, as the model system becomes larger and more complex. the chances increase that some portions of the molecule will be disordered or less easily defined. The necessity of modeling the disorder can decrease the precision of the results for the metal-hydrogen interaction, which is the feature of most interest. In effect, the results become slightly fuzzy and less precise.

Besides being useful in the study of catalysis, metal complexes are highly suitable for theoretical studies of chemical bonding between the bound molecule (ligand) and the metal atoms. They are therefore of fundamental interest to researchers studying chemical bonds from first principles. Finally, metal-cluster complexes can stabilize certain molecules that are unstable in pure form. For example, cyclobutadiene can be stabilized by binding to iron carbonyl, $Fe(CO)_3$; and ethylidyne, CH_3-C (a highly reactive intermediate formed in the hydrogenation of ethylene), can be isolated by reacting with cobalt carbonyl to form the metal-cluster complex $CH_3C–Co_3(CO)9$.

The kind of information available through the study of model compounds is illustrated by the case of the cluster compound $HFeCo_3(CO)_{12}$. Diffraction studies show that the single hydrogen atom is located at a site of threefold symmetry, that is, just outside the triangle formed by the three cobalt atoms (Fig. 2). The vibrational spectrum of hydrogen in this compound is very similar to that of hydrogen atoms chemisorbed on a nickel or a platinum surface. Since the vibrational spectrum of a molecule or atom strongly reflects the way in which it is bound to other atoms, the similarity here allows the inference that hydrogen chemisorbed on a catalyst surface is located at a site of threefold symmetry. We can further infer that the catalytically active surface is the so-called (111) plane of the metal, because that is the only crystal plane having threefold symmetry. This information could not have been easily obtained in any direct way.

How does one then study the model systems? There are many experimental techniques, each especially suited for a particular aspect of the problem, and neutron scattering is one of these. However, even the most intense neutron sources produce fluxes far below those commonly available from sources of photons (x rays, ultraviolet, visible light, and infrared), and so neutron scattering is not one of the principal tools of surface science. Nevertheless, when the systems include hydrogen or molecules containing hydrogen—as do the more important types of compounds involved in industrial catalytic processes—neutron scattering is extremely useful.



A CLUSTER COMPOUND

Fig. 2. The $HFeCo3(CO)_{12}$complex, which contains a single hydrogen atom (blue) located against an equilateral triangle of cobalt atoms (red), can serve as a model system for hydrogen atoms chemisorbed on a metal surface. In particular, comparison of vibrational spectra can help establish whether or not the hydrogen on the metal surface is also located at sites with threefold symmetry. (Adapted from a figure in an article by R. G. Teller, R. D. Wilson, R. K. McMullan, T. F. Koetzle, and R. Bau. *Journal of the American Chemical Society* 100: 3071, 1978.)

The singular utility of neutron scattering is in locating the all-important hydrogen atoms and highlighting the vibrational and rotational motions associated with them. This strength is a result of the fact that neutrons scatter as strongly from hydrogen as from most other elements (see "Neutron Scattering—A Primer" by Roger Pynn). Although it is nearly impossible to "see" hydrogen atoms in the presence of heavy metals using x rays, x-ray diffraction can sometimes *implicitly* locate hydrogen atoms bound to or interacting with metal atoms. If a site in a metal complex is usually filled, an apparent vacancy at that site, together with other physical and chemical evidence, can lead to the inference that hydrogen occupies the position. Neutron scattering, however, is needed to confirm the actual presence of hydrogen. Thus, the structures of compounds of interest are typically determined by first applying x-ray diffraction to locate the heavier atoms and then neutron diffraction to obtain precise metal-hydrogen distances and bond angles.

Historically, single-crystal neutron diffraction has been more difficult than x-ray diffraction. Neutrons can travel large distances through material without being scattered, so neutron diffraction requires a much larger crystal. This problem has been partly alleviated by the availability of more intense sources of neutrons. Furthermore, the time-of-flight wavelength measurements possible at pulsed-accelerator-based neutron sources makes all neutrons in each pulse usable. Area detectors make it possible to collect large volumes of data at one time and make feasible full structural determination from polycrystalline material.

For the observation of molecular vibrations, optical techniques (infrared absorption and Raman scattering) are far more common and much easier to use than neutron scattering. Once again, however. the difference in the nature of the interaction between the scatterer and the probe makes neutron-scattering vibrational spectroscopy advantageous in certain cases. First, absorption of photons in optical spectroscopy depends on the symmetry properties of the vibrational mode being excited in the sample, whereas no such symmetry-based selection rules apply to *inelastic* neutron scattering. (We use inelastic to refer to the fact that the neutron loses or gains energy during the scattering process. The change in energy corresponds to a change in the vibrational energy of the scattering molecule.) Hence, in principle (though not necessarily in fact), all vibrations of a molecule can be observed by inelastic neutron scattering.

The factors determining the intensity of a given excitation are a second, and perhaps more important, difference between neutron-scattering and optical vibrational spectroscopy. Large-amplitude vibrations by nuclei with high neutron-scattering cross sections (such as hydrogen) typically give rise to intense inelastic neutron-scattering bands; whole-body Vibrations of molecules are typical examples. Such motions, however, usually involve only small changes (if any) in the polarizability or the dipole moment of the molecule, which are the factors that govern intensities in Raman scattering and infrared absorption. Thus, optical and neutron-scattering methods are remarkably complementary.

The utility of inelastic neutron scattering can be greatly enhanced by replacing certain atoms, whose vibrations are to be highlighted, with isotopes of different neutron-scattering cross sections. Such isotopic substitution is particularly valuable for studying hydrogen, because the neutron-scattering cross sections appropriate to inelastic neutron scattering for hydrogen and deuterium differ by more than an order of magnitude. For example, to distinguish the motions of the methyl group in toluene ($C_6H_5CH_3$, a benzene derivative in which one of the ring hydrogens is replaced by a methyl group), the remaining ring hydrogens can be replaced by deuterium atoms. Then, as far as neutron scattering is concerned, the deuterium atoms are much less "visible" than the three hydrogen atoms on the methyl group. (In optical spectroscopy, isotopic substitution alters the frequency of vibration but leaves the intensity of absorbed or scattered photons virtually unchanged.) Another application of isotopic substitution in neutron scattering involves the differential spectra of isotopic species, examples of which will be described in the following sections.

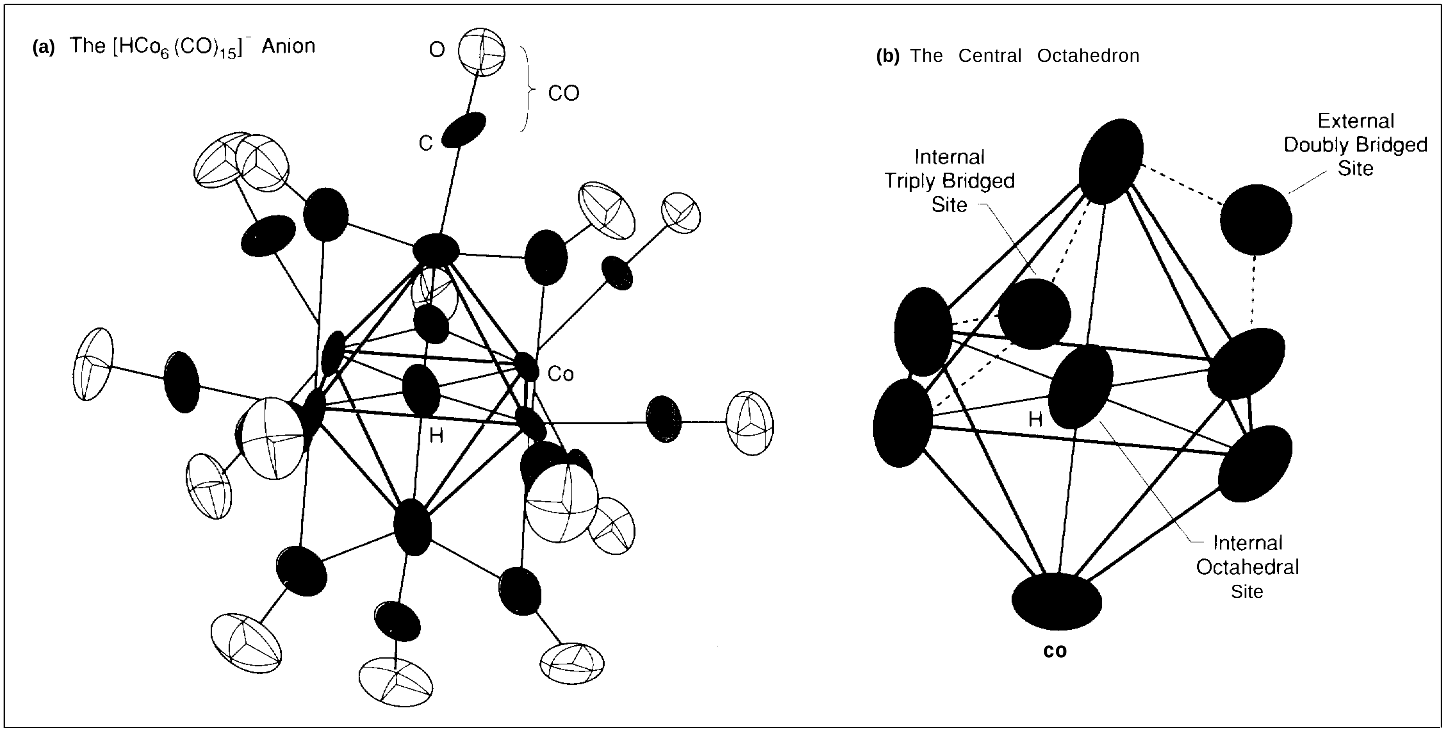
We have chosen to describe three examples of neutron-scattering studies on metal complexes, each of which may serve as a model system for a particular step in the hydrogenation reaction shown in Fig. 1. The first example is a hydride ligand in an octahedral cluster of metal atoms, a model system that may help us understand the motion of hydrogen atoms between the surface and the region just below the surface (once the H_2 molecule has dissociated on the surface). The other two examples—an ethylene-diosmium complex and a set of molecular-hydrogen complexes—may be regarded as models for the bond activation that precedes the actual reaction on the surface. The complexes that bind molecular hydrogen are particularly important in this context because they represent a "capture" of the long-sought intermediate in perhaps the most fundamental reaction, the dissociation of hydrogen molecules. As we shall show below, elastic and inelastic neutron-scattering studies of these compounds have provided remarkably detailed information on the nature of the chemical bond between the dihydrogen, or molecular hydrogen, ligand and the metal center, including evidence for back-donation of electron density from the metal to the antibonding orbital of the hydrogen molecule.

The Hydride Ligand

The first example we want to discuss in detail is the interstitial hydride ligand—a single hydrogen atom bound to a metal atom or atoms. Hydride ligands are usually formed on metal surfaces when molecular hydrogen dissociates and are referred to as terminal, doubly bridging, triply bridging, and so forth. depending on whether they are bonded to one, two, three, or more metal atoms.

In large cluster complexes with many metal atoms, hydride ligands may also occupy interior, or interstitial, sites. Among the large metal-cluster compounds of this type that have been synthesized, two—the octahedral clusters of cobalt and ruthenium—stand out for their remarkable simplicity. Both these compounds have a cluster of six metal atoms that form the octahedral site, a single hydride ligand, and several carbonyl groups outside the metal cluster that serve to stabilize the molecule.

This kind of hydride coordination looks very much like that observed in bulk metals, where interstitial sites of octahedral or tetrahedral symmetry may be occupied by hydrogen. A hydrogen atom in a metal is of course surrounded by many more metal atoms than the six of a cluster compound. There are six atoms as *nearest* neighbors in an octahedral site, but further shells of metal atoms occur at ever increasing distances. However, if the hydrogen atom is located just below the surface of the metal, that is, between the first two layers of metal atoms, the number of more distant neighbors is minimized in one direction. The interstitial hydrogen in the cluster may therefore be a better model for "subsurface" hydrogen than for hydrogen within the bulk of the metal. Such a system may help answer a question raised earlier in the discussion of hydrogenation-that is, where the hydrogen is likely to move,



AN OCTAHEDRAL CLUSTER

Fig. 3. (a) The location of the hydride ligand in the anion $[HC0_6(CO)_{15}]^-$ has been determined with considerable certainty by neutron diffraction from a single crystal containing the cation $[(Ph_3P)_2N]^+$. The hydride ligand (blue) is located at the center of an octahedron of cobalt atoms (red); the cobalt atoms, in turn, are surrounded by twelve carbonyl ligands (green and yellow). The shapes at each atomic position are thermal ellipsoids, which indicate the extent and direction of the thermal motion of the atoms about their equilibrium positions. (The surface of each ellipsoid defines the volume in which the atom is contained 50 percent of the time.) (b) There are a number of alternative sites close to the central octahedron of cobalt atoms that may, in some compounds, serve as the location of the hydride ligand (two possibilities are shown in light blue). The alternative sites are either external or internal to the octahedron of cobalt atoms, and the hydrogen atom can be doubly or triply bridged to those atoms. However, such sites have considerably less symmetry than the central octahedral site, and the vibrational spectra of hydrogen when located at such a site would be quite different from the single excitation that is actually observed in the spectrum of $[HC0_6(CO)_{15}]$. (Adapted from a figure in an article by D. W. Hart, R. G. Teller, C.-Y. Wei, R. Bau, G. Longoni, S. Campanella, P, Chini, and T. F, Koetzle, ***Journal of the American Chemical Society*** **103: 1458, 1981.)**

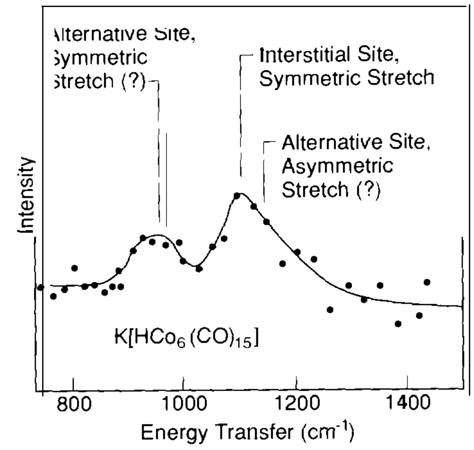
after dissociation, relative to the metal catalyst's surface.

The first step, however, in understanding the microscopic properties of hydrogen in a metal cluster is to attempt to locate it by diffraction studies. The only reliable way to do this is by use of neutron beams, for the reasons discussed earlier. Because hydrogen is a minor component of the rather large metal-cluster molecules, single crystals must be used for the diffraction studies. Also, cluster compounds are most commonly ionic species, and a suitable *counter ion* -a large, oppositely charged ion—must be added to produce sufficiently large single crystals. In the present case, the complex of interest is $[HC_06(CO)_{15}]^-$, and the counter ion used to produce the single crystal is $[(Ph_3P)_2N]^+$, in which Ph is the phenyl group, C_6H_5.

A neutron-diffraction study of a single crystal of $[(Ph_3P)_2N]$[HCo6(CO)15],, carried out on the high-flux-beam reactor at Brookhaven National Laboratory, showed quite convincingly that the hydrogen is located approximately at the center of a somewhat irregular octahedron of cobalt atoms (Fig. 3) even though other locations. such as threefold coordination inside or outside one of the triangular faces of the octahedron, are possible. The vibrational spectrum of hydrogen in a regular octahedral site would show a single excitation, a triply degenerate hydrogen-metal stretching mode. If, however, the hydrogen were to also move significantly off center, additional peaks would appear in the vibrational spectrum. It is in just such cases that vibrational spectra are of great value in obtaining structural information. An inelastic neutron-scattering study of the cesium salt of the same cobalt cluster showed primarily a single excitation at a frequency of 1056 reciprocal centimeters (cm^{-1}), confirming the central location of the hydride ligand in the octahedral site.

Prompted by the results of some infrared spectroscopic studies that showed interesting changes in the spectra of the $[HCo_6(CO)_{15}]^-$ cluster as the crystalline environment was altered, we recently investigated the vibrational spectrum of the cluster combined with the very much smaller counter ion K+. The data, shown in Fig. 4, were obtained by the differential technique on the Filter Difference Spectrometer at the Manuel Lujan, Jr. Neutron Scattering Center (LANSCE) at Los Alamos. Two samples were measured, one with hydrogen and one with deuterium as the ligand. Because the scattering cross section for deuterium is much smaller than that for hydrogen, the vibrational spectrum of the deuterated compound serves essentially as a "blank" to be subtracted from that of the protonated compound. The resulting differential spectrum is free of all the many vibrational modes of this large molecule that do not involve motion of the hydrogen and thus highlights the vibrational modes that do involve hydrogen.

The features shown in the differential spectrum can be immediately identified with hydrogen vibrations and suggest that all the hydrogen atoms are by no means located at the center of the octahedron of cobalt atoms. The broad band in the region between 1050 and 1100 cm^{-1} may certainly be assigned to the stretching vibration of hydrogen at the interstitial site, but the band at 950 cm^{-1} must then be indicative of hydrogen at a different site—one bridging either two or three cobalt atoms. In either case, a second vibrational line at higher frequency would be expected. The data are not conclusive in this respect, but if the band at 950 cm^{-1} is the symmetric stretching vibration for the doubly or triply bridged hydrogen, then the high-frequency shoulder just above 1100 cm^{-1} has about the expected frequency for the asymmetric stretch of triply bridged hydrogen.



VIBRATIONAL SPECTRUM OF THE OCTAHEDRAL CLUSTER

Fig. 4. The differential spectrum shown here for the $[HCo_6(CO)_{15}]^-$ cluster (Fig. 3)—only crystallized with the much smaller counter ion K^+—includes only those vibrations that involve the hydride ligand. The broad peak just below 1100 cm^{-1} has been identified as the symmetric stretching vibration of hydrogen located at the center of the interstitial octahedral site; this peak appears in various spectra regardless of which counter ion is present. The second peak at about 950 cm^{-1} is *not* present in the spectra of crystals containing Cs^+ as a counter ion and may be the stretching vibration of doubly or triply bridged hydrogen located at an alternative site (such as those shown in light blue in Fig. 3b). If the latter assignment is correct, the high-frequency shoulder just above 1100 cm^{-1} would correspond to the asymmetric stretching vibration of hydrogen at a triply bridged site. These data were obtained by using the Filter Difference Spectrometer at LANSCE.

The spectrum thus appears to reveal an instance of the *fluxionality* of the hydride ligands in cluster compounds. Fluxionality-commonly detected in nuclear-magnetic-resonance studies—refers to the movement of hydrogen from one site to another. Because the movement occurs on a time scale that is many orders of magnitude greater than the time scale of a typical vibration, the hydrogen can be "caught" vibrating rapidly at more than one site. However, if the binding energy is much larger at one site than at others, such fluxionality is unlikely.

In any case, the remarkable result of our studies is that the position of the hydride ligand in these metal clusters apparently depends on the nature of the counter ion used to crystallize the compound. This fact suggests that the binding strengths for hydrogen at the various sites differ by only small amounts and may, in fact, be affected by the charge balance between the complex ion and its counter ion. Such a conjecture is needed to explain the observed change in fluxionality of the hydrogen atom in the cluster. Moreover, the conjecture is in agreement with nuclear-magnetic-resonance observations of the $[HCo_6(CO)_{15}]^-$ ion in solution, which show that the hydrogen can easily leave the octahedron and exchange with protons of the solvent molecules.

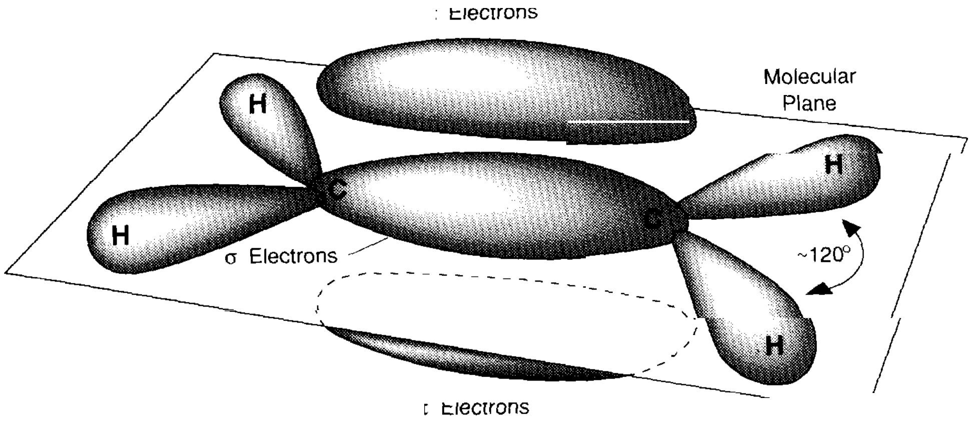
The factors that govern fluxionality of the hydride ligand in cluster compounds may, of course, differ considerably from those that determine the diffusion of hydrogen between the metal surface and, for example, the subsurface layer. If one wishes to hydrogenate, say, ethylene on a metal surface. it is important to know that the hydrogen atoms will stay on the surface long enough after dissociation to react with the ethylene rather than diffuse rapidly into the bulk metal. Despite the above caveats, the detailed structural picture, and in some cases the detailed dynamical picture of hydride motion, that can be obtained from model cluster systems is quite important for understanding the diffusion of hydrogen along a metal surface or between the surface and the bulk.

The Ethylene-Metal Complex

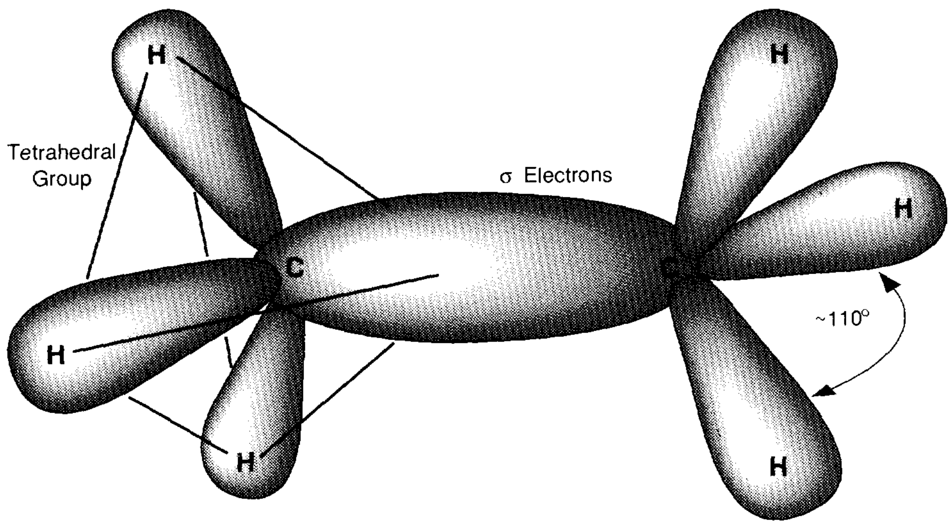
We now focus on another question in the hydrogenation reaction, namely the formation of a complex between ethylene and the metal and the resulting bond activation that is necessary for ethylene to take up hydrogen. Hydrogenation changes the ethylene molecule from an arrangement in which all the atoms are coplanar and the carbon-carbon bond is a short double bond that includes n-bonding electrons (Fig. 5) to an ethane molecule in which the atoms are grouped tetrahedrally and the carbon-carbon bond is the longer single bond based solely on σ electrons. Here again, we shall examine a model compound in which the precise. arrangement of the ethylene molecule and the metal atoms can be studied by neutron diffraction.

Ethylene molecules can interact with a metal surface in several ways. Perhaps the most common configuration is the so-called side-on π complex shown in Fig. 6a, in which the planar ethylene molecule is parallel to the surface of the metal and the π electrons in the carbon-carbon double bond interact directly with the electrons on a single metal atom. A second species, the di-σ-bonded complex (Fig. 6b), has also been observed: in this case the double bond

(a) Ethylene



(b) Ethane



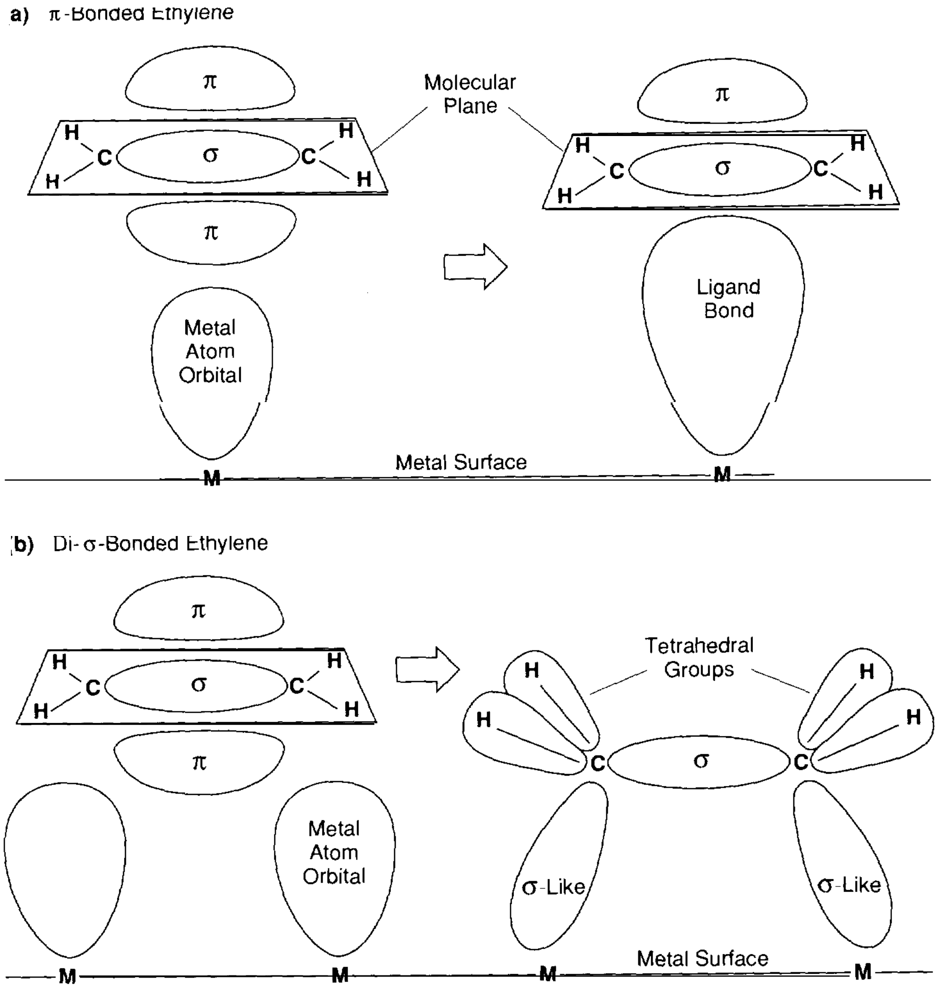
GEOMETRY OF ETHANE AND ETHYLENE

Fig. 5. (a) All the atoms of ethylene lie in a single plane, and almost all of its electron orbitals are concentrated close to that plane. The exception is the double bond between the two carbon atoms, which includes two π electrons in an orbital that juts above and below the plane, as well as two σ electrons in the central bonding orbital in the plane. (b) The atoms of ethane, on the other hand, are arranged in two overlapping tetrahedral groups that surround each carbon atom (one tetrahedron is outlined in red), and it has a single σ bond between the carbon atoms. This arrangement allows the two CH_3 groups to rotate with respect to one another.

between the carbon atoms is reduced to a single bond and a further σ bond is formed between each carbon atom and one of two adjacent metal atoms. Obviously, this last complex could be an intermediate species in the hydrogenation reaction,

The $Os_2(CO)_8(C_2H_4)$ complex (Fig. 7) does in fact have an ethylene ligand that shows the di-σ binding geometry. Further, the vibrational spectrum of this complex is very similar to that of ethylene chemisorbed on platinum at temperatures below 100 kelvins, and the complex can serve as a model for that system. X-ray diffraction studies of $Os_2(CO)_8(C_2H_4)$ show both that the carbon-carbon distance is longer than a normal ethylene double bond and that the four-membered ring formed by the two osmiums and two carbons is twisted and nonplanar. This last observation implies that the hydrogens have probably also twisted out of their plane with the carbons. However, as we already pointed out, it is very difficult to directly determine the positions of the hydrogen atoms with x rays. Spectroscopic evidence also suggests unusual structural features within the bridging ethylene ligand. This evidence may or may not be consistent with the x-ray observations but cannot be interpreted in an unambiguous way. Therefore, a knowledge of the detailed structure, particularly the positions of the hydrogen atoms, is necessary to resolve questions regarding the bonding in this compound.

Neutron-scattering measurements show that two hydrogens, an osmonium atom, and the other carbon atom are arranged approximately tetrahedrally around each ethylene carbon atom. This observation is consistent with the elongation of the carbon-carbon bond, as well as with the spectroscopic evidence and theoretical calculations that allow for simple σ bonding between each carbon atom and an osmium atom. In this example, then, the bonding of ethylene to a metal-cluster compound results in rearrangement of the bonding electrons in the smaller molecule.

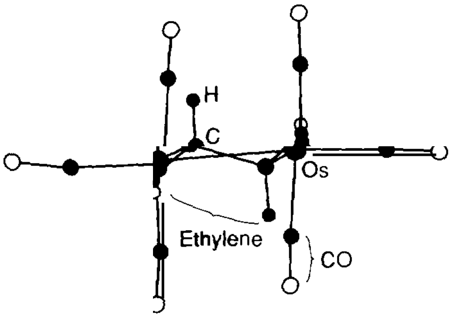


TWO KINDS OF ETHYLENE LIGANDS

Fig. 6. Ethylene can form two distinctly different types of ligand bonds with metal atoms. (a) The π-bonded type involves the formation of a symmetric sigma-like bond between a *single* metal atom and a π-bond orbital of the ethylene molecule, a configuration in which the planar nature of the ethylene molecule is retained. (b) The di-σ-bonded type involves the formation of two sigma-like bonds between the carbon atoms and two adjacent metal atoms. As a result, the carbon-carbon bond in the ethylene becomes a single u bond and the hydrogen atoms move out of the molecular plane and assume an approximate tetrahedral arrangement about the carbon atoms.

The planar configuration of the ethylene molecule is obviously drastically altered by its association with the osmium carbonyl cluster. Simply replacing the two osmium atoms with hydrogen atoms would produce the geometry found in ethane, the product of hydrogenation of ethylene. The twist observed in the cluster-bonded ethylene is tending toward the bond angles normally found in ethane.

In this example, the osmium cluster can be considered a model of either an isolated fragment of a metal surface (as in heterogeneous catalysis) or an individual catalytic molecule (as in homogeneous catalysis). In either case, osmium is not necessarily unique in completing with ethylene. Other metal atoms have different electrons at different energy levels, so the degree of activation and distortion may differ from one complex to another. However, all of them should have a tendency to activate ethylene to one degree or another by forming a complex of this kind.



AN ETHYLENE-BRIDGED COMPLEX

Fig. 7. An example of the di-σ-bonded type of ethylene ligand (Fig. 6b) may be found in the osmium complex $Os_2(CO)_8(C_2H_4)$. Not only has the carbon-carbon bond in the ethylene ligand lengthened, but the ligand has twisted, allowing the hydrogen atoms (blue) and the two osmium atoms (red) to assume a more tetrahedral grouping about each central carbon atom (green).

Binding of Molecular Hydrogen to a Metal

In this final example we shall go back one step in the hydrogenation reaction and focus on the reaction of molecular hydrogen with a metal atom, the reaction that precedes its dissociation into hydrogen atoms. As mentioned earlier, most small molecules can bind chemically to complexes containing one or more metal atoms, often in ways that roughly resemble the chemisorbed state of the molecule. The coordinated molecule and the metal atom or atoms share electrons to some extent; as a result, some bond angles or bond lengths in the bound molecule are changed. Molecular hydrogen has always been a notable exception; until recently it was found to bind only dissociatively, that is, as two individual hydrogen atoms. Observation of chemically bound molecular hydrogen would offer enormous potential for understanding on the basis of first principles the process that eventually results in dissociative binding of hydrogen.

A few years ago, G. J. Kubas and collaborators isolated the tungsten complex $W(CO)_3(PCy_3)_2H_2$ (where Cy is cyclohexyl, a 6-carbon alkane ring) that may represent the long-sought intermediate in the oxidative addition of hydrogen to a metal. Since then, many additional molecular-hydrogen complexes with central metal atoms other than tungsten and ligands other than tricyclohexylphosphine have been identified. The hydrogen in these complexes is apparently reversibly bound to the metal, as can be demonstrated by passing hydrogen gas into a solution of, for example, the precursor of the above tungsten-tricyclohexylphosphine complex at room temperature. The solution, which is originally purple. turns yellow, and light yellow crystals of the H_2 complex can be precipitated from it. If the hydrogen stream is replaced by a chemically inert gas such as argon, the purple color returns, implying the dissociation of H_2 from the complex. An interesting feature of these compounds is that formation of a stable hydrogen complex apparently requires organophosphine ligands that are large and bulky. The structure of the purple precursor contains a clue to the role these ligands may play: the P–W–P axis is distorted and the organic portion of one phosphine appears to fill the hole left by the absent molecule of hydrogen.

Neutron-scattering techniques have played a decisive role in characterizing the dihydrogen ligand of the complexes in terms of both its structural and dynamical properties. This information has then been used to work out a detailed quantitative picture of the bonding of the hydrogen molecule to the metal, as will be described in the following sections.

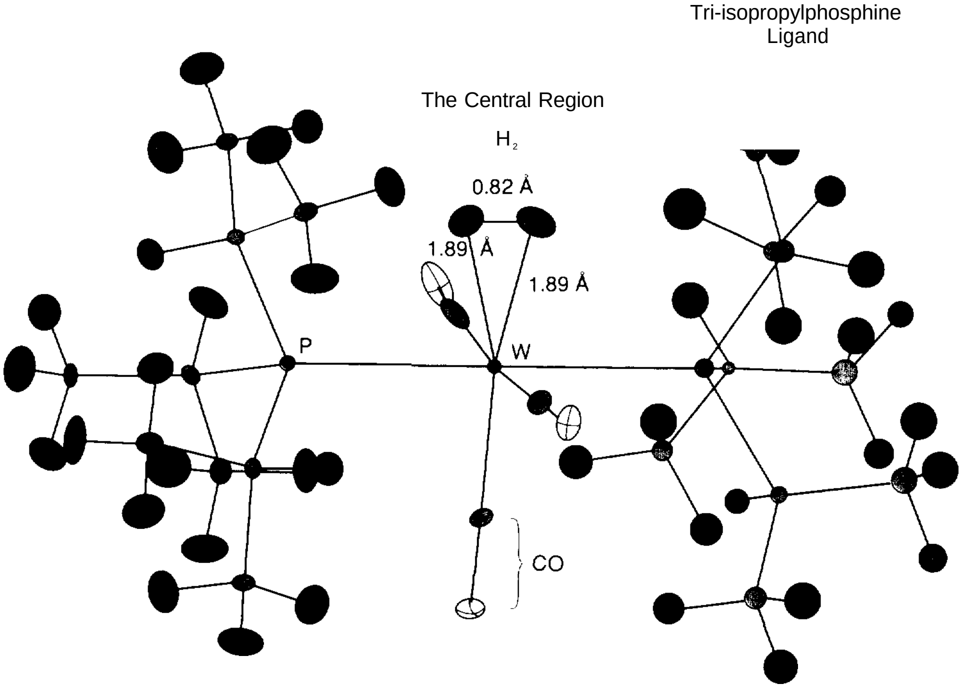
A Sigma-Bond Complex. In the early stages of the investigation of the complexes, it was absolutely essential to locate the dihydrogen ligand and ascertain whether, in fact, it retained its molecular identity. Although some initial evidence for the molecular-hydrogen binding came from x-ray diffraction, conclusive evidence required the use of neutron diffraction because of its sensitivity to scattering from hydrogen. The first structure determined for a molecular-hydrogen complex is shown in Fig. 8. The complex is the same as the one we have been discussing except the tricyclohexylphosphine ligands (PCy_3) have been replaced with less bulky triisopropylphosphine ligands ($P(i\text{-}Pr)_3$, where i-Pr represents $CH(CH_3)_2$). Probably the most important features of this structure are the two equal W–H distances of 1.89 A and the increase in the H–H distance by some 10 percent over that in free H_2 (0.82 A versus 0.74 A). These facts clearly suggest the formation of a three-center metal-dihydrogen bond (that is, some of the electrons are shared between the metal atom and the two hydrogen nuclei) and a substantially weakened H–H bond.

The dihydrogen ligand was also found to have a well-defined equilibrium orientation (Fig. 8c), one in which the H–H axis is parallel to the P–W–P axis of the complex. This fact might be ex-

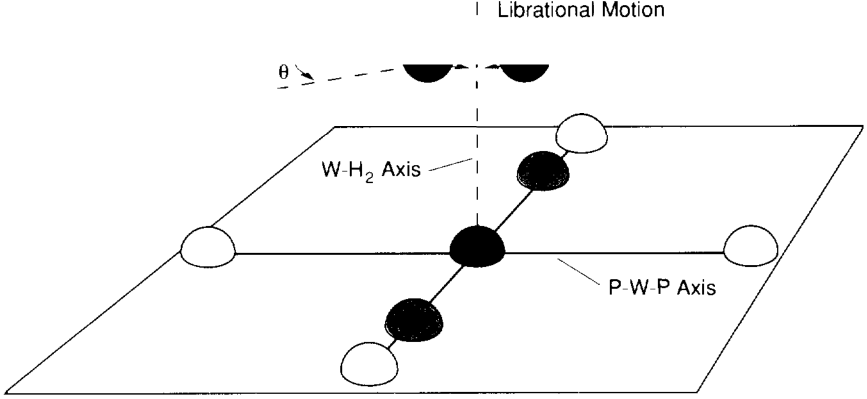
A DIHYDROGEN COMPLEX

Fig. 8. (a) $W(CO)_3(P(i\text{-}Pr)_3)_2H_2$, the first molecular-hydrogen complex to have its structure determined, has two bulky tri-isopropylphosphine ligands (orange, blue, and green) located on opposite sides of a tungsten atom (red). The central region between the opposing phosphorus atoms (orange) contains three carbonyl ligands (green and yellow) and the molecular-hydrogen ligand (blue). The fact that the H-H bond length (0.82 A) is longer than in free H_2 (0.74 A) and the fact that the two W–H bond lengths are equal (1.89 A) suggest a three-center metal-dihydrogen bond and a substantially weakened H–H bond. (b) The preferred orientation of the H_2 ligand is parallel to P–W–P axis, suggesting that there is a barrier to rotation of the H_2 ligand about the W–H_2 axis. (c) A potential-energy curve for rotation of the H_2 ligand in a plane perpendicular to the W–H_2 axis with one degree of angular freedom (the angle θ) has minima for the identical orientations of O and 180 degrees from the P–W–P axis. Because the ground-state wave functions (dashed lines) for each potential well overlap (shaded areas), there is tunneling between potential wells and, as a result, the energy levels split.

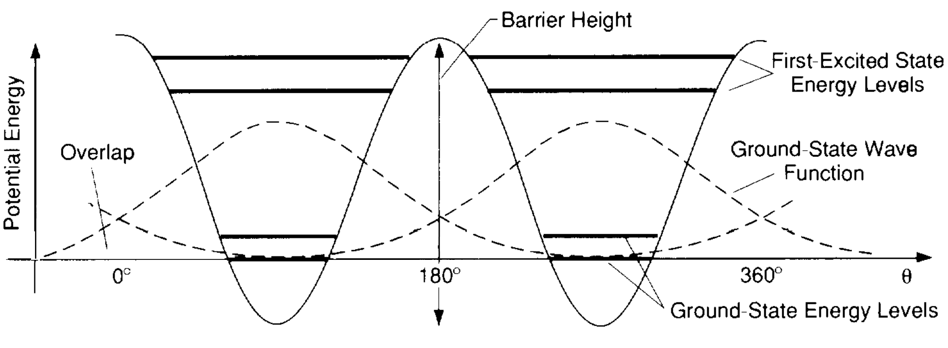
(a) The $W(CO)_3$ $(P(i\text{-}Pr_3)_2$ H_2 Complex



(b) H_2-Ligand Dynamics



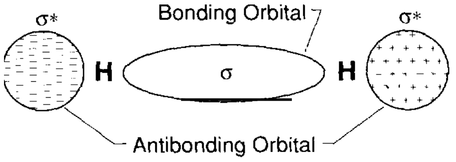
(c) Potential-Energy Barrier to Rotation



plained on the basis of interactions between the dihydrogen ligand and other ligands bound to the metal that would make alignment *perpendicular* to the P–W–P axis (and parallel to the OC–W–CO axis) energetically less favorable than alignment parallel to the P–W–P axis. We also observed that the hydrogen atoms of the bulky organophosphines formed a pocket around the region of the dihydrogen ligand, but the orientation of these organic groups is very accommodating and would not be expected to constrain the H_2 molecule.

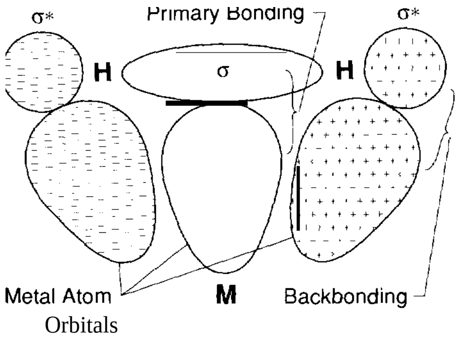
Theoretical analysis is necessary to derive a more quantitative picture of the metal-ligand bonding than that indicated by the structural results. The most fundamental types of calculations can, in fact, derive structural parameters such as the H–H or W–H distances; comparison with experimental values then serves as a check on the validity of the theory. The current problem, however, is sufficiently complex that structural information is used as input to simplified theoretical models. Whether or not the theoretical model is derived from first principles or from a combination of structural data and a theoretical model, it is highly desirable to have other experimental information on the nature of the chemical bonding that can be used to gauge the theoretical picture.

The nature of the bonding between the dihydrogen ligand and the transition metal is of major significance because the complex represents the first example of a *sigma-bond complex,* that is, a complex in which the ligand binds through interaction of a metal center with a o-bonding electron pair. Theoretical studies of this three-center, two-electron bond indicate that both the bonding and antibonding orbitals of hydrogen (Fig. 9) may be involved. The primary interaction between H_2 and the metal atom is donation of electron density from the H–H σ bond to an empty orbital in the metal atom (Fig. 10); however, the same studies indicate that, to a lesser degree, backbonding between a metal orbital and the H_2 antibonding sigma orbital (σ^*) also occurs. Backbonding stabilizes the side-on orientation shown in Figs. 8 and 10 rather than an end-on orientation (in which the H_2 molecule would have its bonding axis pointed straight at the tungsten atom with one hydrogen atom much closer to the metal atom than the other). The side-on coordination ultimately facilitates cleavage of the H–H bond to give dihydride complexes in oxidative addition reactions. These theoretical predictions, of course, require experimental confirmation.



MOLECULAR-HYDROGEN ORBITALS

Fig. 9. The usual theoretical picture of H-H bonding has the two electrons in the hydrogen molecule occupying a low-energy σ-bonding orbital whose electron-density map (here pictured schematically in a *cross-*sectional view) generally occupies the space between the two hydrogen nuclei. However, there is also a higher-energy σ^*-antibonding orbital that is usually unoccupied and whose electron-density map has a node between the two hydrogen nuclei. (The plus and minus patterns in the antibonding orbital are there to indicate the antisymmetric nature of the orbital.)



BONDING OF MOLECULAR-HYDROGEN LIGAND

Fig. 10. Although the main bonding between the dihydrogen ligand and the metal atom is due to an interaction between an empty metal-atom orbital and the σ orbital in the hydrogen molecule (here shown in a cross-sectional view), there is evidence for some *backbonding,* which is an interaction between an antisymmetric metal-atom orbital and the hydrogen σ^*-antibonding orbital. Both of these interactions weaken the H-H bond and strengthen the M-H bond. The former interaction donates electron density from the o-bonding orbital of H_2 to the metal atom, whereas the latter interaction puts electron density from the metal atom into the H_2 antibonding orbital.

Rotational Dynamics. Hydrogen in the side-on coordination mode can undergo a remarkably wide variety of ligand dynamics, including torsional oscillations, or *librations,* about its equilibrium orientation and much slower 180-degree reorientations by tunneling through the rotational barrier. Establishing the presence of a significant electronic energy barrier to rotation would provide confirmation of metal-to-H_2 backbonding. Such a barrier is too small to be observed by standard nuclear-magnetic-resonance techniques. Inelastic neutron scattering, however, is highly sensitive to hydrogen motions because of the very large neutron-scattering cross section of protons and the typically large amplitude of the motions. In fact, this technique is routinely used to study rapid rotational motion (for example, of methyl groups and of solid or liquid hydrogen or molecular hydrogen in zeolites).

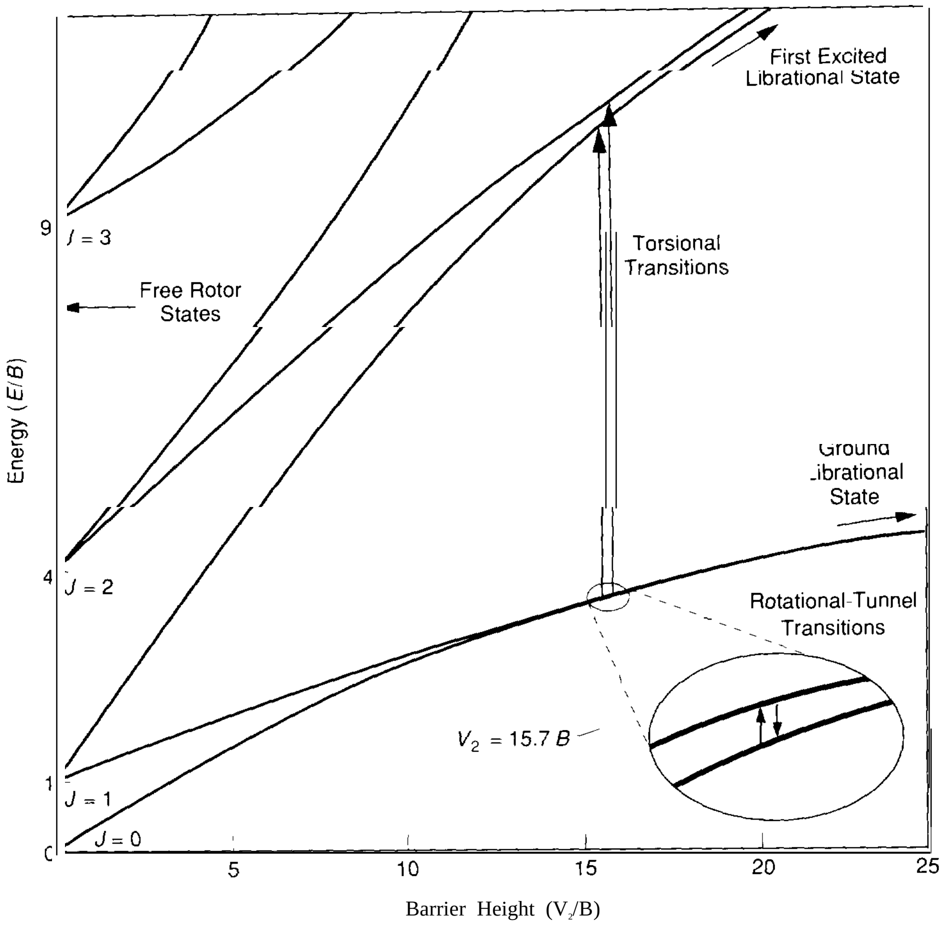
The nature of the rotational motion of the bound hydrogen molecule may be described with the aid of a diagram that shows the energy levels that the dihydrogen ligand may occupy as a function of the height of the barrier hindering the rotation. These levels are the solutions to the Schrodinger equation chosen to represent the rotational motion of the bound hydrogen molecule. In particular. the equation includes only one angular degree of freedom because we assume that the relatively strong three-center metal-dihydrogen bond keeps the hydrogen ligand essentially in a plane during its rotational motion. The complex may, in fact, be the first example of hydrogen rotation with only one degree of rotational freedom, a situation first described by Pauling as an approximation for solid hydrogen. If any mixing with vibrational modes can also be neglected, the Schrodinger equation for the rotational motion is

$$\left[-B\frac{\partial^2}{\partial\phi^2}+\frac{1}{2}\sum_{n} V_{2n}(1-\cos 2n\phi)\right]\Psi = E\Psi, \quad (1)$$

where B is the rotational constant *(B = h^2/21,* where I is the moment of inertia of the molecule for the rotation in question), ϕ is the angle of rotation about the O–C–W–H_2 axis, V_{2n} represents the barrier-height potential energy for a potential with $2n$ minima, and Ψ and E are, respectively, the wave function and energy of the allowed rotational states.

In the present case, as we've already pointed out. crystal-structure studies as well as theoretical calculations have shown the dihydrogen ligand to have a well-defined orientation parallel to the P–W–P axis. The hydrogen molecule in this complex should then have two equivalent orientations located at potential minima that are 180 degrees apart (Fig. 8c), and we may assume that the term with n = 1 (a simple double-minimum potential) will dominate. Equation 1 can then be reduced to the Mathieu equation, for which solutions are tabulated. The resulting energy-level diagram as a function of barrier height V_2 is shown in Fig. 11, in which both the energies and barrier heights are given in terms of *B*.

The energy levels corresponding to $V_2 = 0$ (left axis in Fig. 11) are those of a free rotor with one degree of freedom ($E_J = BJ^2$, where J is the rotational quantum number, yielding levels at energies of 0, *B*, 4B, 9B. . .). introduction of a barrier to this rotation ($V_2 >$ O) changes the level spacing drastically and removes some degeneracies. In the limit of very high barriers (suggested by the arrows on the right side of Fig. 11), the states approach a set of equally spaced energy levels characteristic of essentially harmonic torsional oscillations.

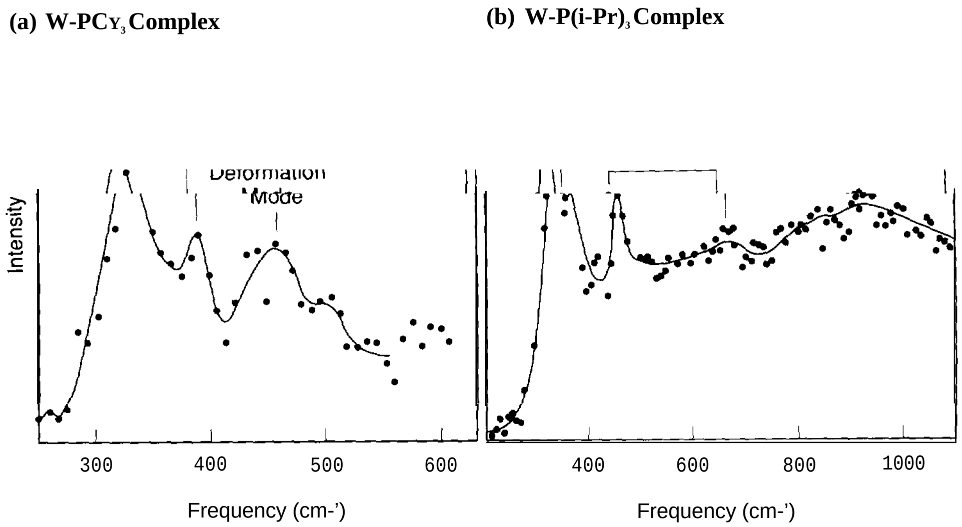


ROTATIONAL ENERGY-LEVEL DIAGRAM

Fig. 11. A dumbbell molecule (such as hydrogen) constrained to rotate in a plane has one rotational degree of freedom and rotational states J = O, 1, 2, 3, . . at energies of 0, *B*, 4B, *9B,...* if there is no barrier to the rotation (that is, if V_2 = O). On the other hand, if V_2 is very high (that is, beyond the right side of the figure), the molecule will occupy a set of equally spaced torsional oscillator levels. For intermediate barrier heights we find a series of split Vibrational states. The observed transitions (indicated by arrows) are of two types: transitions within the Vibrational ground state called rotational-tunnel transitions (in which $\Delta I = \pm 1$) and transitions from the ground to the first excited Vibrational state called torsional transitions. Because photons do not couple with nuclear moments, optical spectroscopy cannot be used to observe the tunneling transitions directly and can be used to observe only the torsional transitions between levels that have identical values of total nuclear spin (ΔI = O). The observed values for the transition energies are scaled by a value for B of 49.5 cm–' rather than the 60 cm $^{-1}$ value for free H_2 to reflect the increased H-H bond length (0.82 A) relative to free H_2 (0.74 A). The transitions shown are for a complex with a barrier height V_2 equal to 15.7 B.

The molecular hydrogen complexes being discussed here have intermediate barriers, and for these, we find a series of vibrational states, each of which is split relative to the torsional oscillator levels. This splitting arises from the fact that the barrier is *not* overly high, allowing the amplitude of the libations of the hydrogen molecule to be relatively large—large enough, in fact, for the wave functions that correspond to the molecule's being located in either of the two potential minima to overlap (Fig. 8c). To satisfy the Pauli principle, the degenerate states corresponding to these two orientations must split into two states, each with a slightly different energy (Fig. 11 inset). The splitting is called *tunnel splitting* because it is due to the overlap of wave functions through a potential barrier. The size of the splitting decreases rapidly with increasing barrier height and is thus an extremely sensitive measure of barrier height.

The two resulting states are characterized by their symmetry. For exam-



VIBRATIONAL-ROTATIONAL SPECTRA

Fig. 12. The high-frequency transitions associated with torsional, or rotational, motion of the dihydrogen ligand have been identified for the two complexes (a) $W(CO)_3(PCy_3)_2H_2$ and (b) $W(CO)_3(P(i\text{-}Pr)_3)_2H_2$ by using the Filter Difference Spectrometer at LANSCE. Unrelated frequencies in the spectra were **eliminated by taking the difference between the scattering spectrum for the complex with a dihydrogen ligand and that for the complex with a dideuterium ligand. The deformation modes include rocking and wagging of the dihydrogen ligand with respect to the complex. One piece of evidence that the assignment are correct is the fact that, for inelastic neutron scattering, the modes with the largest-amplitude motions of the hydrogen atoms have the highest intensity and the rotational modes involve more motion of the hydrogen atoms than the rocking modes.**

pie, 180-degree rotation corresponds to an odd permutation of identical spin-½ particles (the protons), with respect to which the total ground-state wave function must be antisymmetric. The low-temperature wave function can be constructed from linear combinations of nuclear-spin and rotational wave functions. Thus, a symmetric nuclear-spin wave function *(I* = 1, where *I* is the nuclear-spin-state quantum number) combines with an antisymmetric rotational wave function *(J* odd) and vice versa. These two cases correspond for zero barrier height to the two kinds of H_2 molecules referred to as ortho- and para-hydrogen, respectively. For finite barrier heights, *J* is no longer a "good" quantum number to describe the energy levels. The total nuclear spin of the molecule, however, must still change in a transition between the two lowest energy levels, that is, in a tunneling transition.

We note that transitions in which the total nuclear spin of the molecule changes cannot be observed in optical spectroscopy because photons do not couple to the nuclear spin. Neutrons, however, do couple and are quite useful for studying rotational transitions of this type. The neutron has a nuclear spin of ½, and a flip of the neutron spin during the scattering process will cause the total nuclear-spin state of the H_2 molecule to change also $(\Delta I = \pm 1)$. A spin-flip neutron-scattering process then allows direct observation of the ortho-para transition in hydrogen—for example, para-hydrogen (with *I* = 0 and *J* even) changing to ortho-hydrogen (with *I* = 1 and *J* odd). For a free hydrogen molecule with two rotational degrees of freedom, the transition that changes the rotational state from *J* = 0 to *J* = 1 has an energy of 2B, where ***B*** is the rotational constant. However, if the molecule is constrained to rotate in a plane with only *one* degree of rotational freedom, as is the case for our compounds, the transition has an energy of *B* for zero barrier height, that is, for free rotation. Moreover, as we discussed above, the energy for a tunneling transition rapidly becomes smaller with increasing barrier height until, at infinite barrier height, the splitting disappears and the two states become degenerate.

Experimental Confirmation. Now that we have selected an appropriate model for the rotational dynamics of the dihydrogen ligand in our system, it is a simple matter to relate the observed rotational transitions to the height of the rotational barrier. To observe both the high-frequency transitions to the excited Vibrational state (the longer arrows in Fig. 11) and the very-low-frequency transitions associated with rotational tunneling (the two short arrows in the exploded portion of Fig. 11), we had to perform experiments on two spectrometers, each located at a different neutron source. The high-frequency torsional transitions were measured on the Filter Difference Spectrometer at LANSCE by using two samples for each complex, one of which had dideuterium instead of dihydrogen ligands. Vibrational modes involving mainly the dideuterium ligand cannot be "seen" in the presence of the many more modes that include hydrogen motion (that is, those of the organophosphine ligands). The deuterium-substituted sample thus served as a "blank" for subtracting all the various vibrational modes except those of interest—the motions of the dihydrogen ligand. Figure 12 shows the results for two tungsten complexes: one with tricyclohexylphosphine ligands (PCy_3) and one with the less bulky tri-isopropylphosphine ligands ($P(i\text{-}Pr)_3$).

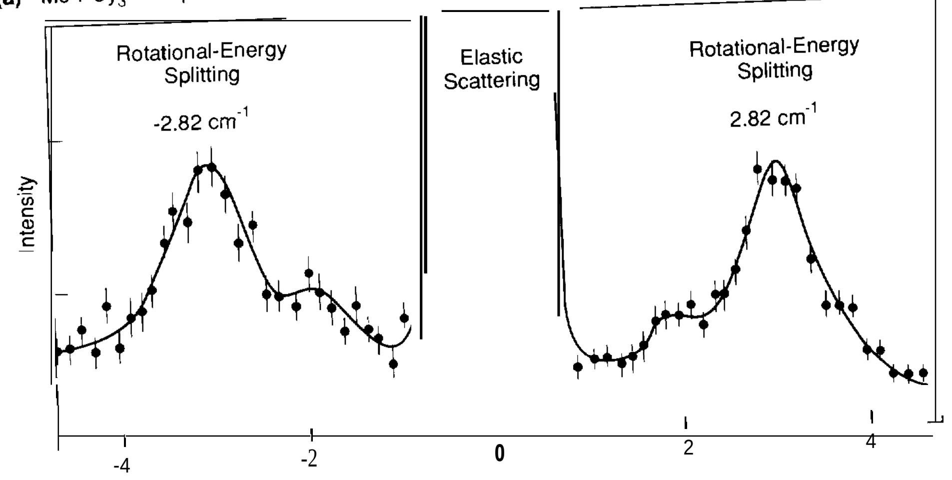
The low-frequency rotational tunneling spectra for three complexes (Fig. 13) were obtained on a cold-neutron time-of-flight spectrometer at the High Flux Reactor of the Institut Laue-Langevin in Grenoble, France. No "blank" sample was necessary in this case, since the other ligands were not expected to have observable excitations in the frequency range of interest for this experiment (which is less than 10 cm^{-1}).

For the two tungsten complexes with PCy_3 and $P(i\text{-}Pr)_3$ ligands, this type of analysis yielded a significant barrier height—one that was roughly 15

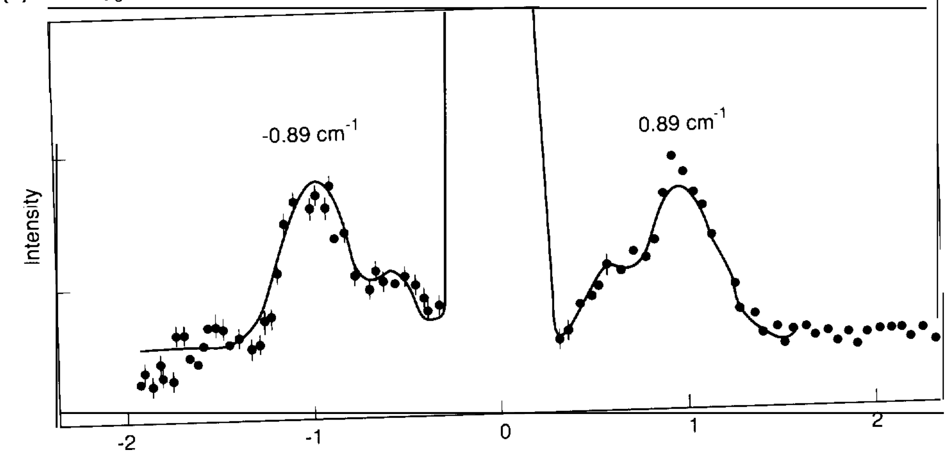
ROTATIONAL-TUNNELING SPECTRA

Fig. 13. The spectra for the low-frequency transitions associated with rotational tunneling are shown here for the three complexes (a) $Mo(CO)_3(PCy_3)_2H_2$, (b) $W(CO)_3(PCy_3)_2H_2$, and (c) $W(CO)_3(P(i\text{-}Pr)_3)_2H_2$. The strong central peak in each spectrum is an elastic-scattering line, whereas the peaks to both sides of that line are the inelastic-scattering transitions associated with rotational tunneling. The fact that the inelastic peaks have a doublet nature is most likely due to structural disorder in the crystals.

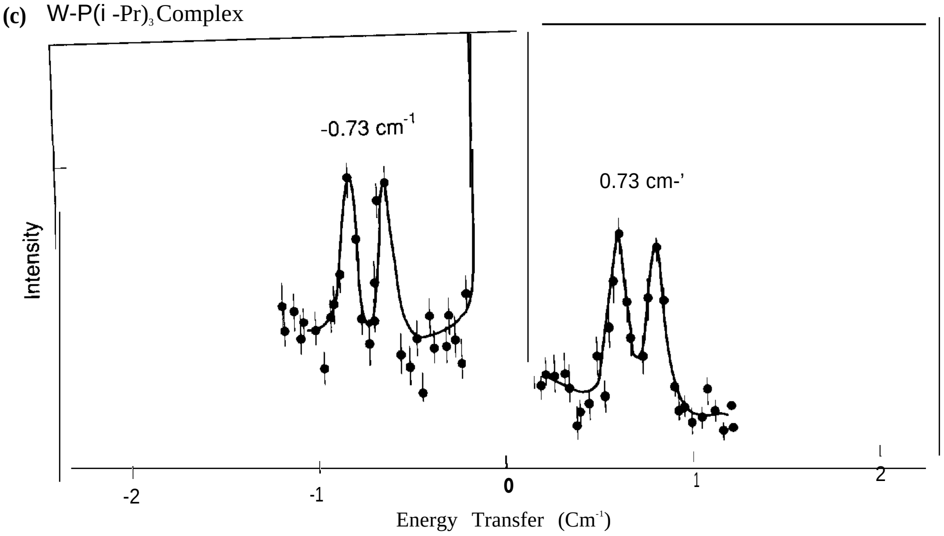
(a) Mo-PCy$_3$ Complex



(b) W-PCy$_3$ Complex



(c) W-P(i -Pr)$_3$Complex



times our derived rotational constant for bound H_2. Using the barrier heights and the energy-level diagram (Fig. 11), we were able to calculate the frequencies expected for the high- frequency transitions associated with the torsional motion of both complexes. The calculated values are in good agreement with the experimental values measured with the Filter Difference Spectrometer (Fig. 12), which suggests that the simple model of planar reorientation in a double-minimum potential is a reasonable description for the hydrogen motion in these systems.

The crucial question at this point becomes what interactions give rise to the barrier to rotation. Two possible sources for the hindrance potential are *electronic* and *steric* effects. By an electronic effect we mean that the dihydrogen ligand may be constrained in its orientation because of the way the chemical bond is formed with the metal. In other words, the electron orbitals on the metal sharing electrons with those of the dihydrogen ligand have a symmetry that determines the orientation of the ligand.

Steric effects refer to the interactions of the dihydrogen ligand with the surrounding atoms of the other ligands. These are nonbonding interactions that may be described by van der Waals forces between pairs of atoms. They may be summed up for all pairs formed

Table 1

Barrier Heights to Rotation for the Dihydrogen Ligand

Complex		**Theoretical (keal/mole)**			**Observed (keal/mole)**
Metal Atom	Ligand	Molecular Mechanics	ab initio (pH_3)	Sum	
W	PCy_3	0.6	1.8	2.4	2.2
W	$P(i\text{-}Pr)_j$	1.4	1.8	3.2	2.4
Mo	PCy_3	0.6	0.6	1.2	1.5

by using either one of the H atoms on the dihydrogen ligand and any one of the surrounding atoms. As the dihydrogen ligand is rotated, the sum of these interactions shows an angular variation, which gives rise to an effective “steric” barrier.

In an attempt to sort out the relative effects of these two types of interactions, we performed separate measurements on the two tungsten complexes with PCy_3 and $P(i\text{-}Pr)_3$ ligands; then we replaced the tungsten atom in the PCy_3 complex with a molybdenum atom and took measurements on this third complex. Thus, we hoped to gauge the effects of changing the central metal atom and of replacing the large, bulky PCy_3 ligand with the less bulky $P(i\text{-}Pr)_3$ ligand.

The peaks in the spectra of Fig. 13 to the left and right of the strong elastic line represent the rotational-energy splitting associated with the H_2 molecule tunneling through the barrier from one 180-degree orientation to the other. The position of these lines is extremely sensitive to the height of the barrier. A comparison of the three spectra shows that replacement of tungsten (Fig. 13b) with molybdenum (Fig. 13a) changes the tunneling frequency by a factor of just over 3, from 0.89 to 2.82 cm^{-1}. On the other hand, replacing the PCy_3 ligand in the tungsten complex with the less bulky $P(i\text{–}Pr)_3$ ligand (Fig. 13c) changes the frequency by less than 20 percent, from 0.89 to 0.73 cm^{-1}.

The change that occurs when the central metal atom is replaced may be taken as reflecting the metal-dihydrogen bonding directly; that is, it is essentially an electronic effect. Replacing the PCy_3 ligands with $P(i\text{–}Pr)_3$ ligands, on the other hand, probably has little effect on the electronic state of the metal and therefore on the metal-dihydrogen bonding. These ligands most likely produce a steric component of the barrier to H_2 rotation through direct, nonbonded interactions. Thus, the experimental evidence, at least in these cases, strongly suggests that the barrier to H_2 rotation is determined more by electronic than steric effects. To test this conclusion, Jeff Hay, John Hall, and Caroline Boyle of the Theoretical Division at Los Alamos earned out two sets of calculations: an *ab initio* calculation—that is, from first principles—and a *molecular-mechanics* calculation.

The ab initio calculation treats primarily the electronic effects because a full set of one-electron wave functions for the whole molecule is used to compute the relative energy of a given configuration. The barrier to rotation was obtained from the difference in total energies for the structure with the H_2 aligned along the P–M–P axis and the structure with the H_2 aligned along the OC–M–CO axis. The calculation is rather extensive, and the bulky organophosphine ligands must be simplified to make it possible at all. When unsubstituted phosphine (PH_3) is used as a ligand instead of tricyclohexylphosphine or tri-isopropylphosphine, the calculation yields a barrier height of 1.8 kilocalories per mole for the tungsten complex and 0.6 kilocalorie per mole for the molybdenum complex.

The second type of calculation—the molecular-mechanics type—may be viewed as representing mainly steric effects. In this case, the pairwise, nonbinding interactions between the hydrogen atoms of the dihydrogen ligand and each of the other atoms of the molecule are summed. The summation is repeated for each orientation of the ligand, generating a curve of potential energy as a function of orientation. This calculation is not sensitive to the type of metal atom at the center of the molecule. The results show a barrier height of 0.6 kilocalorie per mole for the complexes with PCy_3 ligands and 1.4 kilocalories per mole for those with $P(i\text{ -}Pr)_3$ ligands.

If one makes the assumption that molecular mechanics treats only the steric effects and that the ab initio theory accounts primarily for the direct electronic interaction between H_2 and the metal, barrier heights from the two calculations may be added to arrive at an estimate of the effective total barrier. These assumptions are not unreasonable, because replacement of tungsten by molybdenum has no effect on the results of the molecular-mechanics case, whereas the ab initio theory uses the very small PH_3 ligands, rather than $P(i\text{-}Pr)_3$ or PCy_3 ligands, and thus essentially ignores steric effects. The sum of the two calculations for each of the complexes is shown in Table 1 along with the corresponding barrier height calculated from the observed inelastic neutron-scattering data.

The calculated and observed barriers to H_2 rotation appear. at first glance, to agree only qualitatively. If, however. one takes into account the various limitations of the theoretical calculations, the agreement with experiment is remarkably good. For example, the necessary structural information is not known in detail for all three complexes in this experiment, and both types of calculations are normally used for barrier heights that are a factor of ten or so higher than the one in this study. Furthermore. comparison with experimental data does suggest that the molecular-mechanics calculation overestimates the steric part of the barrier, since replacement of the PCy_3 with $P(i\text{-}Pr)_3$ is found to change the barrier height by 0.8 kilocalorie per mole. which is four times the experimentally observed change. In view of these considerations, we can clearly conclude that the direct electronic binding of the dihydrogen ligand to the metal contributes significantly to the barrier, at least one-half to two-thirds of' the experimentally determined value.

The rotational tunnel splitting is an extremely sensitive measure of the barrier height—in fact, it depends *exponentially* on the value of the barrier. Such sensitivity has clear advantages. For example, the observation of a higher barrier in the tungsten complex than in the molybdenum complex is an indication of stronger binding of the hydrogen molecule to the metal atom. This conclusion can be reached both by observing the higher $M–H_2$ infrared stretch frequency in the tungsten complex or by observing the difference in rotational tunnel splitting. However. the change in infrared stretch frequency is only 10 percent, whereas the change in rotational tunnel splitting is more than 50 percent. It is therefore clear that rotational tunneling spectroscopy of side-on H_2 by inelastic neutron scattering can be used as a probe of the details of metal-to-H_2 binding.

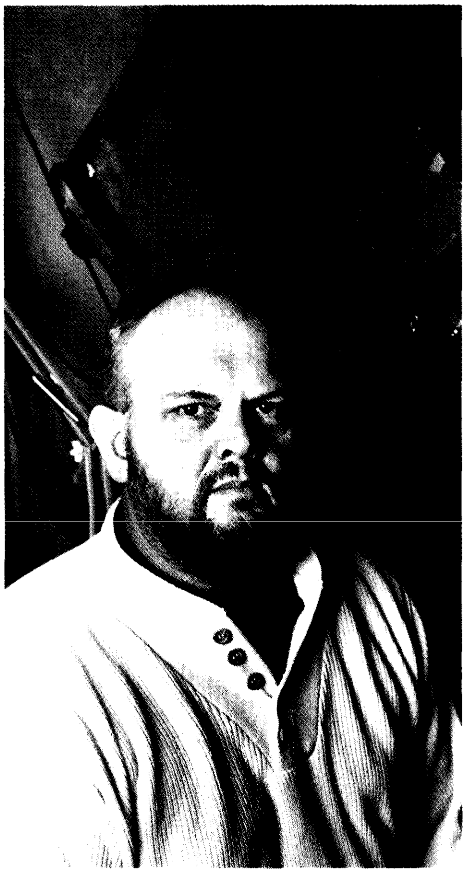
Given the fact that the directional properties of the electron wave functions that help optimize the electron flow between the dihydrogen ligand and the metal atom also seem to be largely responsible for the barrier to H_2 rotation, we feel that establishment of a significant electronic component to the barrier height is convincing evidence of σ^* backbonding between the metal atom and molecular hydrogen.

The latter conclusion, in particular, is a truly remarkable result of our neutron-scattering studies and illustrates the very fundamental details to which these catalytic model systems can be studied with such techniques. Apart from our model systems, many more realistic catalytic materials are being investigated by the same techniques—studies that are often greatly aided by previous work on model compounds. These more realistic systems include molecules adsorbed on dispersed metal particles, inside cavities of zeolites, or attached to many other active substrates. Although the level of detail that can safely be inferred from the “real” catalytic systems is somewhat lower than for the simpler model systems, significant progress can nonetheless be expected in understanding the catalytic function of these materials on an atomic scale. Neutron scattering will certainly play an important role in these studies. ■

Acknowledgments

It is a great pleasure to thank Greg Kubas, the person who first demonstrated the existence of molecular-hydrogen complexes, for our ongoing, fruitful collaboration. Of the many others who have made significant contributions to the work and the ideas discussed in this article, we would in particular like to mention Larry Dahl, Werner Press, Alberto Albinati, Guiliano Longoni, Tom Koctzle, Oren Anderson, and Jeff Hay).

Juergen Eckert earned his B.S. at Yale University and his Ph.D. at Princeton University in 1975. Most of the research for his doctoral thesis, which involved neutron-scattering studies of the lattice dynamics of solid neon. was carried out as a member of the neutron-scattering group in the Physics Department of Brookhavcn National Laboratory. After earning his doctorate, he remained at Brookhaven until 1979, when he accepted a staff membership atl Los Alamos to initiate neutron-scattermg research on the newly commissioned pulsed neutron source (WNR) at LAMPF. The focus of his work has steadily shifted towards applications of neutron scattering to chemistry, albeit from a physicist's perspective. He recently spent one year as a visiting scientist at the Institut Laue Langevin in in Grenoble, France. where some of the work described here was carried out.



Phillip J. Vergamini received his M.S. in inorganic chemistry from the University of Minnesota, Minneapolis, in 1968 after earning his B.S. at the University of Wisconsin, Superior. He completed his Ph.D. in inorganic chemistry at the University of Wisconsin, Madison, in the fall of 1971 and then joined the Isotope and Nuclear Chemistry Division at Los Alamos. His research there involved application of spectroscopic and x-ray crystallographic techniques to studying the synthesis and structure of inorganic and organometallic compounds. In the spring of 1980, he joined the neutron-scattering group at Los Alamos and took responsibility for the construction and use of the Single-Crystal Diffractometer, one of the first two LANSCE instruments to be placed into the international users program. With that diffractometer he has studied the structures of materials ranging from molecular-hydrogen complexes to the crystalline mineral in dinosaur bones.

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