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MOLECULAR METAL CLUSTERS AS CATALYSTS

Earl L. Muetterties

October 1980

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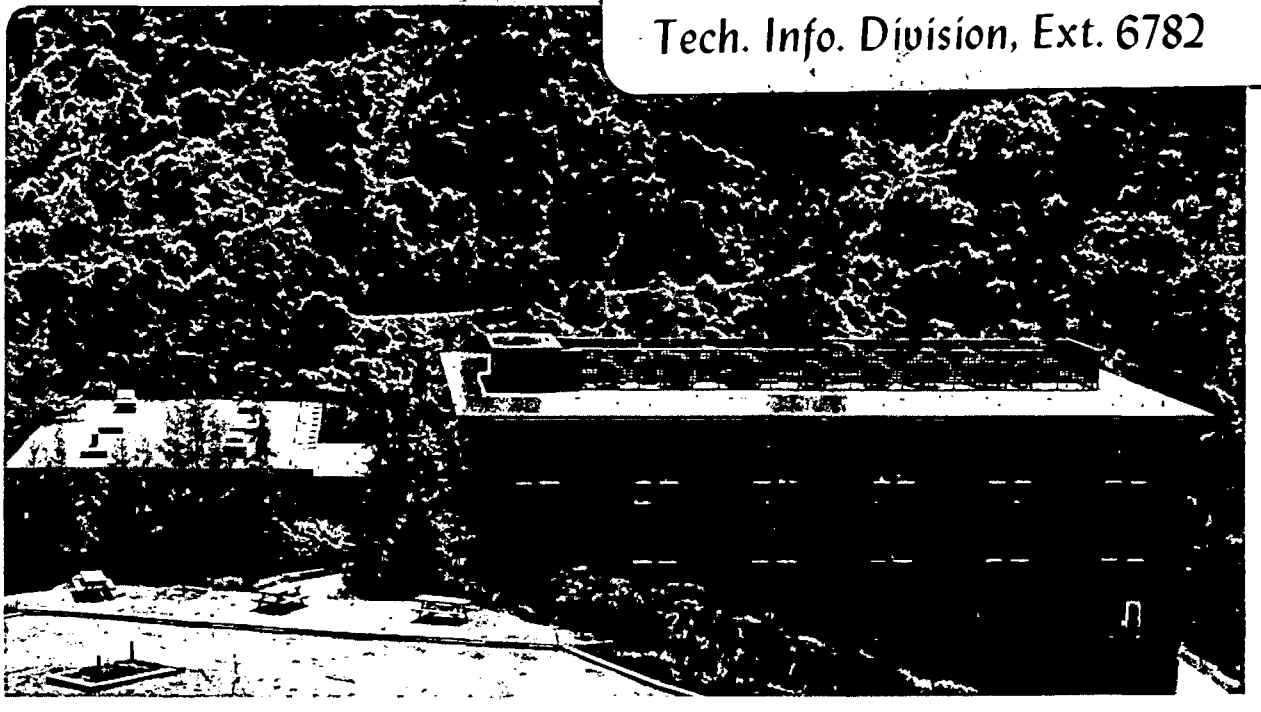

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Molecular Metal Clusters As Catalysts

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Abstract

Experimental and theoretical models for structural and electronic features requisite for catalytic activity in metal clusters are critically examined. Specifically, the catalytic activity of the coordinately unsaturated class of clusters, $\{HRh[P(OR)_3]_2\}_n$ is discussed for the hydrogenation of olefins, acetylenes, arenes and carbon monoxide. Reaction mechanistic features of these catalytic reactions are described. Catalytic hydrogenation of carbon monoxide is also examined in the context of the dissociative pathway, [M(surface)-CO $\longrightarrow$ M(surface)-O + M(surface)-C], and of cluster models of intermediates in metal surface catalyzed CO hydrogenation reactions. The reactivity of low-coordinate and exposed carbide carbon atoms in molecular metal carbide clusters is critically evaluated.

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Introduction

In earlier analyses,[1-8] we have established a correlation between metal clusters and metal surfaces with chemisorbed molecules in the specific contexts of (1) the metal frameworks wherein the metal cluster core structures are fragments of cubic and hexagonal close packed or body centered cubic metal bulk structures, (2) ligand stereochemistry where the geometric features of ligands bound to clusters and to metal surfaces are similar, (3) thermodynamic features where the average bond energies for ligand-metal and metal-metal bonds are very similar, for a specific metal, in the metal cluster and the metal surface regime, and (4) mobility of ligands bonded to metal cluster frameworks and to metal surfaces. Nevertheless, there are sharp distinctions between surfaces and clusters. The average coordination numbers for metal-metal interactions and for metal-ligand interactions are distinctly different for clusters and for surfaces: generally, the former are larger for surfaces and the latter are larger for clusters. Additionally, the surface state is typically differentiated from the cluster state in the degree of coordination saturation--the metal atoms in the surface state are typically less coordinately saturated even for the states in which molecules or molecular fragments are chemisorbed at the surface than those metal atoms at the periphery of a molecular metal cluster. In the crucial chemical issue, metal surfaces are far more reactive than metal clusters. Metal surfaces exhibit a wide range and high level of catalytic activity whereas most metal clusters are catalytically inert at least under modest reaction conditions. Most reported clusters are relatively stable and nonreactive; they are not the products of sophisticated synthesis procedures designed to generate highly reactive metal clusters. They commonly have been the products of reaction mixtures run at forcing conditions and are thermodynamically controlled not kinetically controlled products.

I often encounter the question, "what have metal clusters done (in a catalytic context) better than the established molecular mononuclear metal complexes?" The answer simply is nothing. A few clusters have been shown to be catalyst precursors but for these systems there has been no unique catalytic activity and there has been no definitive mechanistic study.

Why should there be an interest in molecular metal clusters in catalysts? What are the expectations? Consider the conventional, coordinately saturated metal cluster. For such a species to be catalytically active, a bond must be broken either in a preequilibrium step before the catalysis substrates begin to coordinate to a specific metal atom site or in a concerted (associative) step whereby catalysis substrates coordinate to a specific metal atom site. Bond scission may comprise a metal-ligand or metal-metal bond cleavage. If the latter prevails, the cluster may only serve as a source of reactive mononuclear metal complex fragments. However, even if the former prevails, the catalytic sequence may directly involve only one of the metal atoms in the cluster framework. If conceptually a unique reactivity, either stoichiometric or catalytic, is to be realized in metal clusters,[1-3,8,9] a cluster reactivity predicated on contiguous multiple metal atom sites should be sought. The issue then is the design of a cluster that presents the possibility of consecutive reactions at different metal atom sites in a molecular cluster. Such reactivity is not necessarily achieved by simply heating (or literally pyrolyzing) a cluster, by photoactivation or through the use of a heteronuclear, yet coordinately saturated, metal cluster.

One class of cluster structure that might possess a reactivity sequentially centered on contiguous metal atoms would have weak field

ligands like acetonitrile or ethers bonded to these contiguous metal atoms. Facile displacement of such weak field ligands from mononuclear and polynuclear metal complexes is well established.[9,10] However, only two clusters, $Os_3(CO)_{10}(NCCH_3)_2$ and $Os_3(CO)_{10}(olefin)_2$[9] have been reported with the requisite placement of two weak field ligands at adjacent metal atom sites.[11] This approach to clusters with multiple metal atom site reactivity should prove successful especially with multidentate, weak field ligands but no such cluster and associated catalytic chemistry has been reported to date.

An alternative approach to cluster catalysts with contiguous metal atom site reactivity is the design of metal clusters with all or most metal atoms coordinately unsaturated. This synthetic approach to reactive metal clusters is presently a major thrust in our research and is discussed, in some detail below, for a set of coordinately unsaturated, polynuclear rhodium hydrides.

A catalytic reaction of considerable scientific charm is the catalytic hydrogenation of carbon monoxide.[6] The reactant is a diatomic molecule with a bond energy that exceeds that of any other bond in any known molecule. Yet carbon monoxide can be hydrogenated to a variety of species such as methanol, alkanes, alkenes, arenes, etc. by such catalytic agents as metal surfaces,[12] metal oxide surfaces,[12] and a few mononuclear metal carbonyls.[13,14] Of particular interest to us has been the mechanism of CO hydrogenation reactions in which the C-O bond is cleaved, at some step, so as to give products that are hydrocarbons -- alkanes, alkenes, or arenes or a mixture thereof. Contemporary evidence indicates that these reactions often occur by a first step of dissociative CO chemisorption to give chemisorbed carbon and oxygen atoms. Subsequent steps of C-H and C-C bond formation occur in some

order to give the conventional products of the catalytic methanation or the Fischer-Tropsch reaction; the chemisorbed oxygen atoms are converted to CO_2 and/or water in parallel reaction sequences. The initial steps in this pathway of CO hydrogenation to hydrocarbons raises questions about model reactions or intermediates in molecular metal clusters. We explore in the second section of this article model reaction steps or intermediates in CO hydrogenation reaction sequences.

Discussion

Coordinately Unsaturated and Catalytically Active Metal Clusters

A class of coordinately unsaturated metal clusters was discovered in our research group by sheer accident. It had been established that η^3-allylcobalt tris(trialkyl phosphite) and tris(trialkylphospine) complexes were unique stereoselective catalysts for the hydrogenation of aromatic hydrocarbons.[15] In an attempt to extend this chemistry to rhodium, Andrew Sivak found that hydrogen rapidly cleaved the alkyl-rhodium bond in η^3-$C_3H_5Rh[P(OR)_3]_2$ to give, among other products, polynuclear $\{HRh[P(OR)_3]_2\}_x$ complexes with x = 2 or 3.[16-18] These polynuclear rhodium hydrides have proven to be catalysts of widely ranging chemistry and of extremely high reactivity for some simple hydrogenation reactions.[18] The significance of this chemistry lies not in the value of the catalytic reactions because none is unique but in the mechanistic information about reaction sequences in clusters in which contiguous metal atoms are involved and in the possible insights provided by analogy to mechanistic features of similar reactions that proceed on metal surfaces.

The polynuclear rhodium hydrides $\{HRh[P(OR)_3]_2\}_x$ are a dimer with triisopropyl phosphite ligands and trimers with trimethyl and triethyl

phosphite ligands. X-ray and neutron diffraction studies[17,19] of the dimer established that the $P_4Rh_2H_2$ framework atoms were coplanar within experimental error; see 1 below.

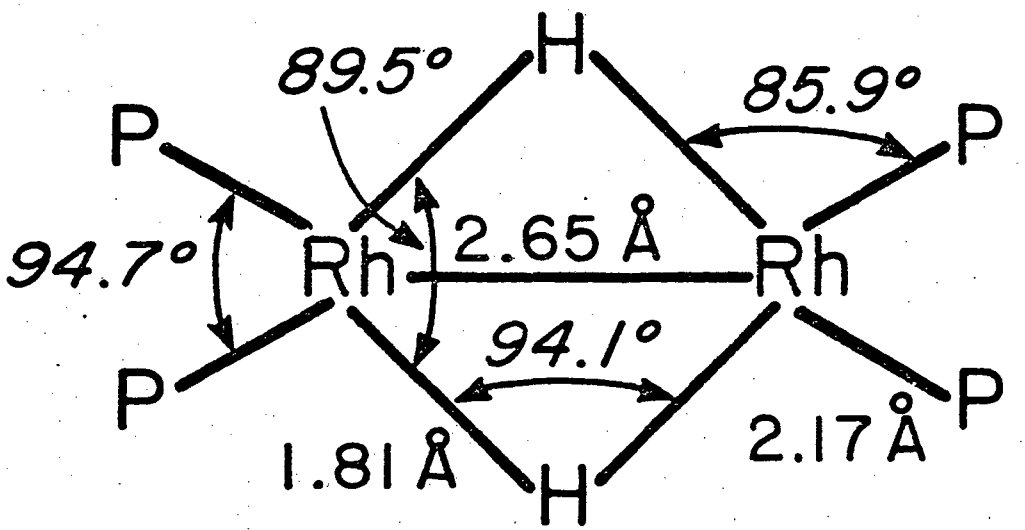
1

The coplanarity of the core structure, and the near 90° coordination angles rigorously establish the square planar coordination geometry about each rhodium atom. This dimer has only 28 valence electrons and is coordinately unsaturated.

X-ray and neutron crystallographic studies of the trimer $\{HRh[P(OCH_3)_3]_2\}_3$ established a core structure that was a nearly equilateral array of rhodium atoms with hydrogen atoms bridging the triangular edges. The immediate coordination sphere about each rhodium atom was square planar with two hydride hydrogen atoms and two phosphite phosphorus atoms. All interbond angles about each rhodium atom were close to the 90° required for square planar geometry (see Figure 1). The cluster is coordinately unsaturated and has only 42 valence electrons; 48 is the number for a nominally saturated trinuclear cluster.

These dimeric and trimeric rhodium hydrides were extremely active catalyst precursors for terminal olefin hydrogenation to alkanes. In fact, the rates were, or nearly were, diffusion controlled at 20°C. The scientific issue is "how do the reactions proceed?" Neither dimer nor trimer reacted rapidly with an olefin; these reactions were extremely slow and complex in character. Reaction with hydrogen was virtually instantaneous and was visually apparent in the transition from green-black (dimer) or brown-black

1



(trimer) to bright red. We had expected that hydrogen addition would convert these polynuclear hydrides to mononuclear metal hydrides, equations (1) and (2); however, the stoichiometry established in each case was precisely one

$$2H_2 + \{HRh[P(O\text{-}i\text{-}C_3H_7)_3]_2\}_2 \rightleftharpoons 2H_3Rh[P(O\text{-}i\text{-}C_3H_7)_2]_2 \qquad (1)$$

$$3H_2 + \{HRh[P(OCH_3)_3]_2\}_3 \rightleftharpoons 3H_3Rh[P(OCH_3)_3]_2 \qquad (2)$$

mole of H_2 per mole of cluster, equations (3) and (4). There was no evidence of a mononuclear species in this hydrogen reaction system.[18] NMR spectroscopic

$$H_2 + \{HRh[P(O\text{-}i\text{-}C_3H_7)_3]_2\}_2 \rightleftharpoons H_4Rh_2[P(O\text{-}i\text{-}C_3H_7)_3]_4 \qquad (3)$$

$$H_2 + \{HRh[P(OCH_3)_3]_2\}_3 \rightleftharpoons H_5Rh_3[P(OCH_3)_3]_6 \qquad (4)$$

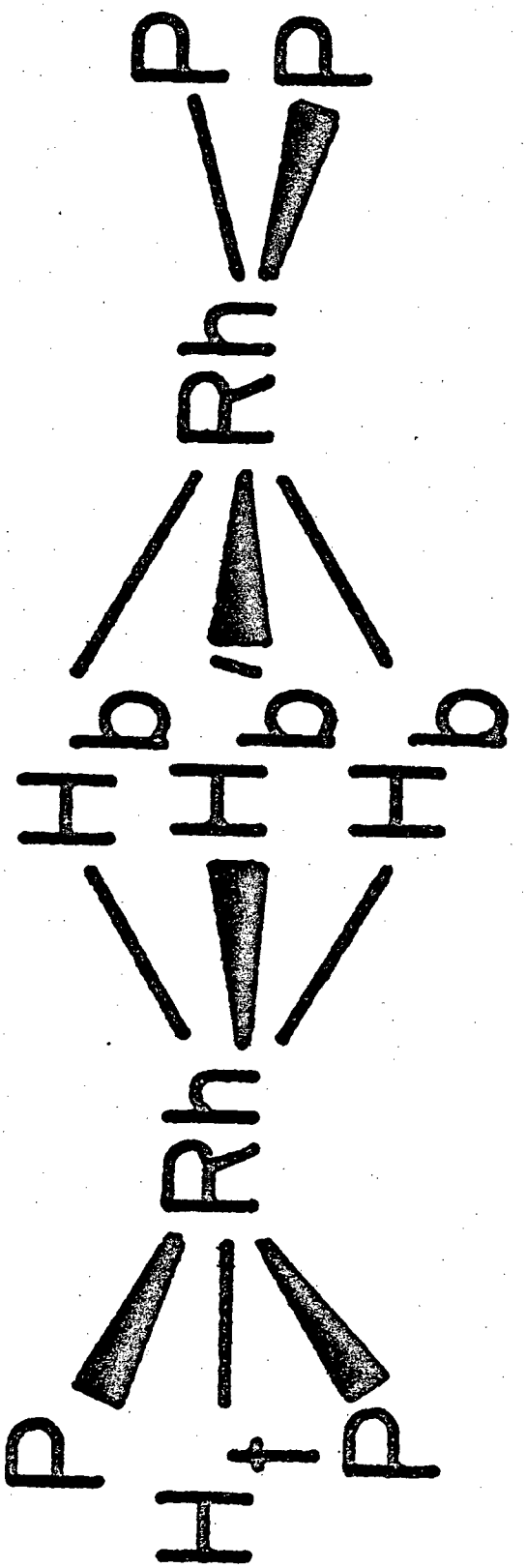
studies established the dimer adduct to have the stereochemistry shown in 2.[18]

2

This dimer hydrogen adduct was stereochemically nonrigid. Hydride hydrogen atom site exchange was slow at -90°C: there was one terminal and two discrete bridged-hydride ^1H NMR resonances. On warming, hydrogen atom exchange between sites H_t and H_b occurred first. The character of the line shape changes of the low temperature process established structure 3 as the exchange intermediate or transition state for the overall process 4.

3

4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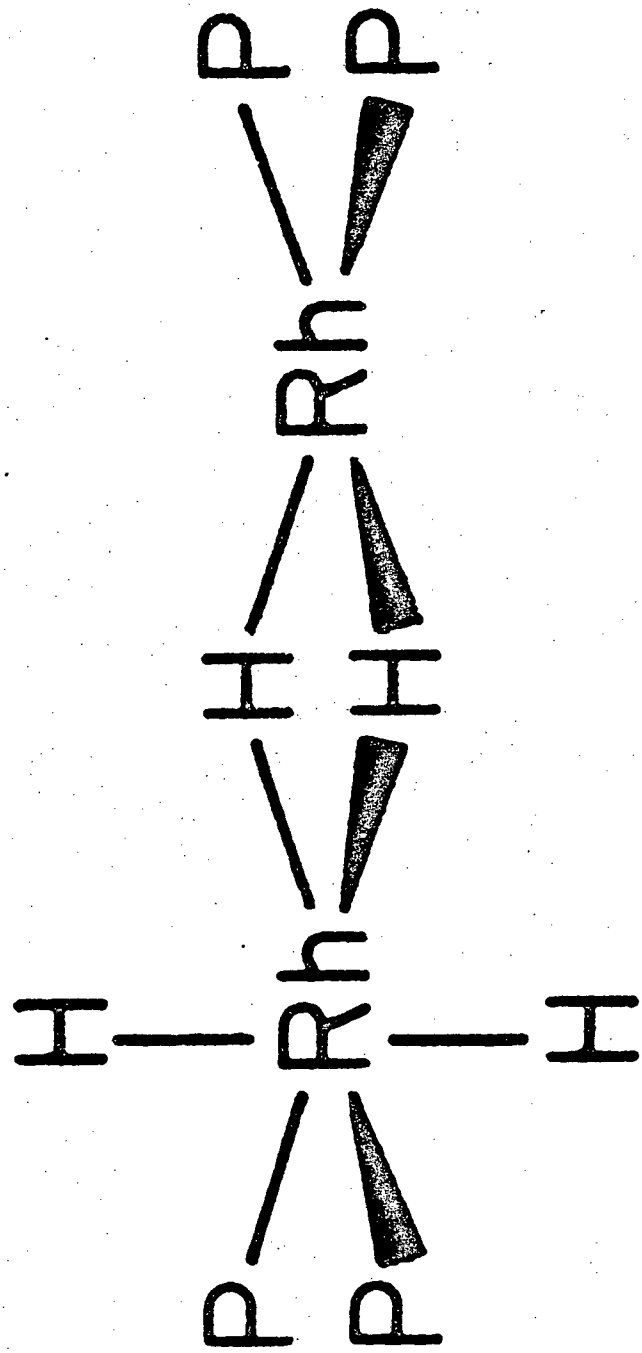

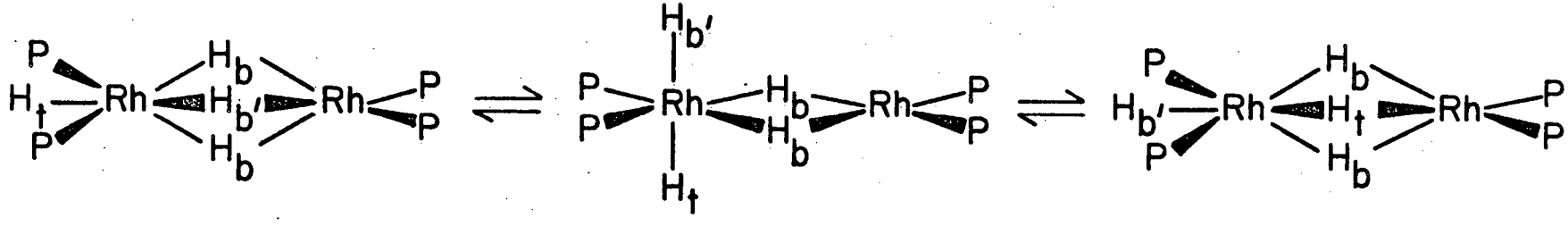
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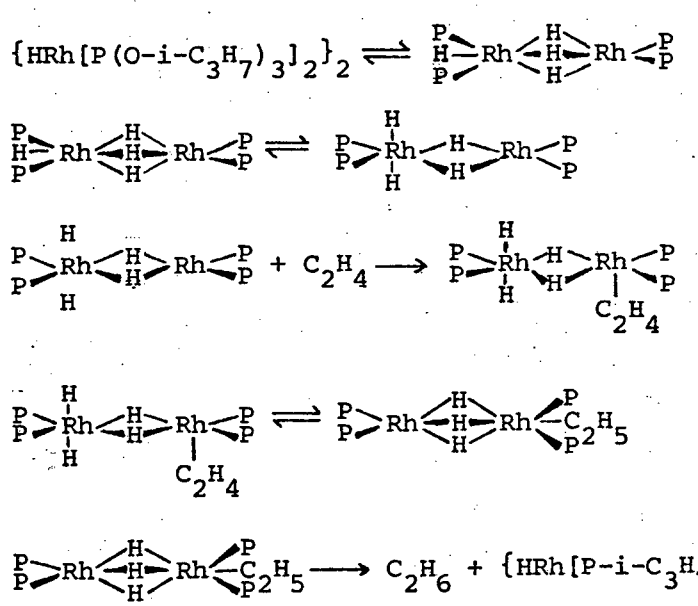
Also stereochemically nonrigid was the trimer hydrogen adduct, $H_5Rh_3[P(OCH_3)_3]_6$. Because an unambiguous structural interpretation of the ^1H NMR spectrum for this trimer hydrogen adduct was not possible, a discussion of structural and exchange phenomena is deferred until crystallographic data are available for this complex. Analogous crystallographic data are being sought for the dimer hydrogen adduct, $H_4Rh_2[P(OCH_3)_3]_4)$.[18]

A fairly precise definition of mechanism is available for the hydrogenation of alkenes catalyzed by the polynuclear rhodium hydrides. The first step was hydrogen addition: olefins like ethylene reacted very slowly with either $\{HRh[P(O\text{-}i\text{-}C_3H_7)_3]_2\}_2$ or $\{HRh[P(OCH_3)_3]_2\}_3$ but hydrogen reacted instantaneously with the dimer and trimer as noted above. Both dimer and trimer hydrogen adducts reacted with olefins to rapidly form alkane and the dimer and trimer, respectively. Low temperature NMR studies with the dimer hydrogen adduct, $H_4Rh_2[P(O\text{-}i\text{-}C_3H_7)_3]_4$, showed that the adduct formed a complex with ethylene at -100°C. This olefin complex rapidly eliminated ethane to reform the dimer, $\{HRh[P(O\text{-}i\text{-}C_3H_7)_3]_2\}_2$, at temperatures above ∿ -80°C. All these data[18] strongly implicate the following reaction scheme (5) - (9):



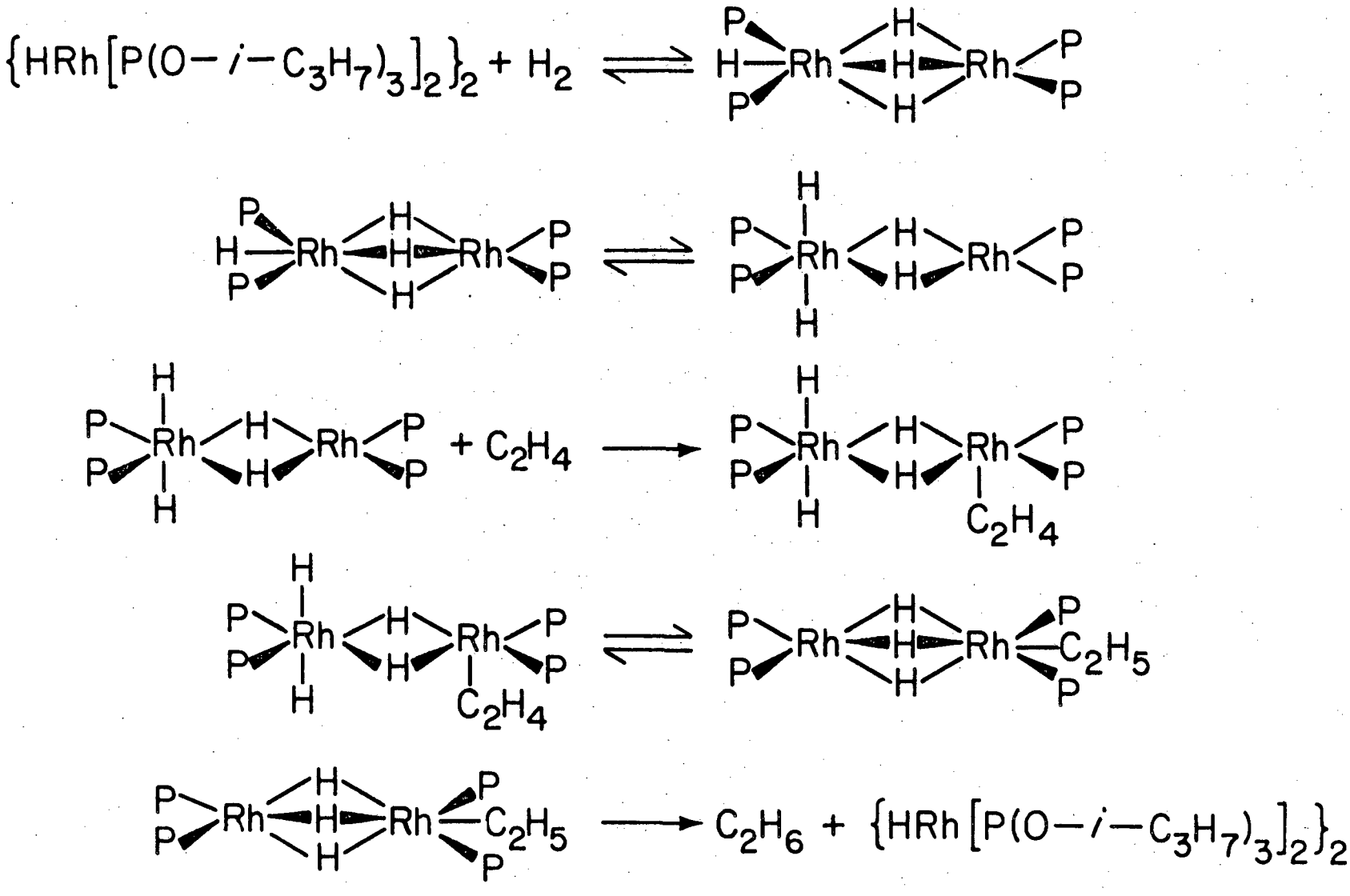
(5)

(6)

(7)

(8)

(9)


{HRh[P(O-i-C3H7)3]2}2 + H2
+ C2H4
C2H4
C2H5
C2H6 + {HRh[P(O-i-C3H7)3]2}2

Because step (8) to (9) was extremely fast, no information about the postulated ethyl intermediate can be obtained. The precise stereochemistry of the olefin complex (step 7) cannot be established from the NMR data: the stereochemistry can be established only if this thermally reactive intermediate can be isolated by low temperature techniques as a single crystal susceptible to a low temperature X-ray or neutron diffraction study. Accepting the qualifying remarks about the stereochemistry of some intermediates, the catalytic reaction sequence has features that are important. Effectively, the sequence shows hydrogen addition to one rhodium atom and olefin addition to the other rhodium atom, i.e., one type of chemistry at one metal site and another at the second site -- the very type of reactivity that we seek in the chemistry of reactive, coordinately unsaturated polynuclear metal complexes. A similar chemistry can be postulated for the trimer but more specific crystallographic data, as noted above, are required; a possible intermediate prior to olefin addition is shown in 5 where one rhodium atom is square planar, coordinately unsaturated,

5

and presumably the site of subsequent olefin addition.

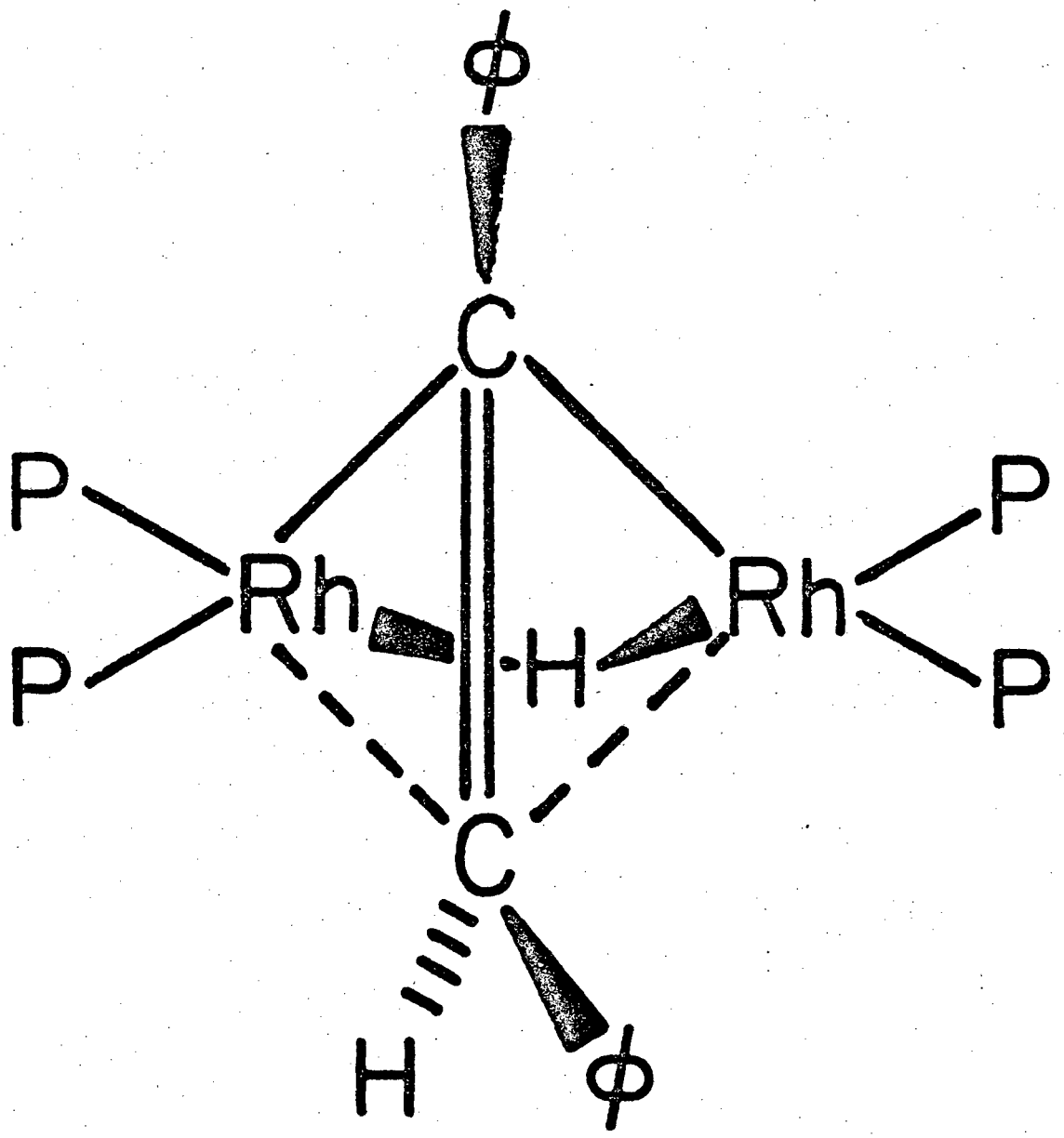
Olefin hydrogenation catalyzed by the polynuclear rhodium hydrides was extremely fast while acetylene hydrogenation catalyzed by these species was relatively slow -- yet the product of the acetylene hydrogenation reactions was an olefin, specifically the cis - olefin, in reactions that were run short of completion.[18] This observation, not uncommon for molecular and for surface catalyzed reactions, is explicable only if the mechanisms of olefin and of acetylene hydrogenations are sequentially differentiable. In our rhodium

system, acetylenes unlike olefins reacted rapidly (and preferentially with respect to hydrogen) with the polynuclear rhodium hydrides to form intermediate complexes.[21] The intermediate complexes and the thermal reactivity of the intermediates were a sensitive function of the substituents on the acetylenic carbon atoms.[21] In the specific case of diphenylacetylene, the initial reaction product with the dimeric $\{HRh[P(O\text{-}i\text{-}C_3H_7)_3]_2\}_2$ complex was a dimeric species with a bridging hydride hydrogen atom and a vinyl, $C(C_6H_5{=}CH(C_6H_5)$, ligand that appeared to be bridging, **6**.[21] A crystallographic

6

analysis of this intermediate should be completed soon. The rate determining step in acetylene hydrogenation was the hydrogen addition step to a species like **6** to give the <u>cis</u> alkene and the rhodium hydride dimer. Because of the generality of selective acetylene hydrogenation, we are presently investigating mechanistic features of acetylene hydrogenation reactions catalyzed by molecular and metal surface catalysts. Interestingly, the mechanistic features of no acetylene hydrogenation reaction has been definitively established with the exception of those catalyzed by $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4(\mu_2\text{-}RC_2R)$[22].

The $\{HRh[P(O\text{-}i\text{-}C_3H_7)_3]_2\}_2$ dimer also is a catalyst for arene hydrogenation but the reaction was extremely slow. This reaction is not mechanistically characterized but is presumed to involve monomeric $HRh[P(O\text{-}i\text{-}C_3H_7)_3]_2$ species that are not kinetically important in the olefin or acetylene hydrogenation reactions.[18,21] In the analogous cobalt system, monomeric $HCo[P(OR)_3]_2$ is presumed to be the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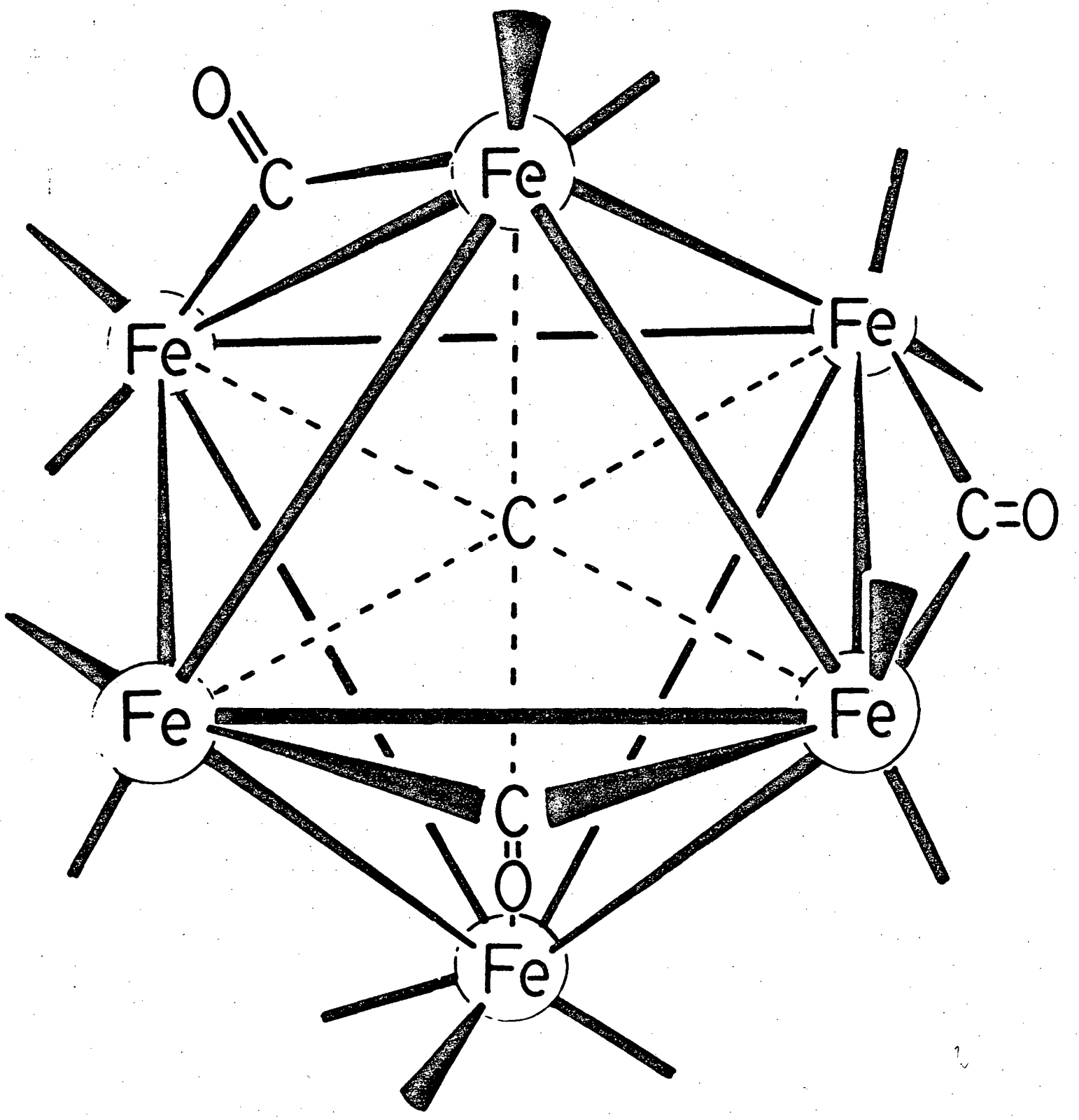
key catalytic species and reacts with benzene to form $HCo[P(OR_3]_2(n^4-C_6H_6)$.[23]

Intermediates in CO Hydrogenation Reactions

There is a current scientific fascination with CO hydrogenation reactions, a fascination predicated on technological features of potential importance. The ready generation of $CO + H_2$ mixtures from coal reserves has served to focus attention on the potential importance of catalytic reactions that can convert these mixtures to useful hydrocarbons or hydrocarbon intermediates. The value of the $CO + H_2$ conversions to methanol is of substantial technological and economical importance and should remain so. Improvements in this basic catalytic reaction will probably come slowly. The primary limitation in the best processes today is heat removal. For this reason, there is an interest in a homogeneous catalytic process where this heat removal problem might be resolved without sacrifice in space time yields of methanol and in catalyst lifetimes. Alternatively, methane can be produced as a fuel from CO and H_2 but at an energy expenditure in the C-O bond cleavage reaction. Another alternative is the conversion of CO and H_2 to a mixture of hydrocarbons or hydrocarbon derivatives--the basic Fischer-Tropsch reaction. The future economics of this type of reaction is questionable--it is energy consumptive and, as we know it today, nonselective. Alternatives are selective syntheses of specific hydrocarbons, or hydrocarbon derivatives, e.g., ethylene or ethanol, from CO and H_2 but these possibilities are not established to date. I see the academic issue in catalytic $CO + H_2$ reactions as one of establishing reaction mechanism sequences. Establishment of reaction mechanisms for $CO + H_2$ reactions is not only scientifically challenging but also of potential long range technological value for a rational design of new selective hydrocarbon syntheses. Here I wish to address specific aspects of catalytic $CO + H_2$ reactions in which CH_4 or hydrocarbons (Fischer-Tropsch reactions) are produced.

The chemisorption behavior of carbon monoxide on metallic surfaces is dependent upon the electropositive character of the metal. At the one extreme, the chemisorption and thermal desorption processes for CO on the more electronegative metals like platinum and iridium appear to be fully molecular (associative). For example, we have found that the chemisorption of ^{13}CO and $C^{18}O$ mixtures on platinum (111) surfaces at 20 to 250°C led to a chemisorption state that on thermolysis yielded only ^{13}CO and $C^{18}O$, no cross product $^{13}C^{18}O$.[24] There was no evidence of C-O bond cleavage under these reaction conditions. However, the chemisorption of CO on iron surfaces, good catalysts for Fischer-Tropsch reactions, is dissociative in character to give disjoint carbon and oxygen atoms chemisorbed on the surface. Similar evidence has been presented for ruthenium,[25] cobalt,[25] and nickel[25,26] surfaces, which are also good catalysts for hydrocarbons from $CO + H_2$. Thus, the Fischer-Tropsch reactions and also the methanation reaction (methane producing reaction) often appear to initially involve as a sole or a contributing hydrocarbon synthesis sequence the dissociative chemisorption of CO to give M(surface)-C and M(surface)-O species. Evidence has been presented that the M(surface)-C species are reactive towards hydrogen, to give hydrocarbons, at temperatures as low as 25°C.[27] Some investigators are directly addressing mechanistic features of such $CO + H_2$ catalytic reactions.[27-31] We are attempting to establish analog or model reactions of such surface reaction sequences in molecular metal clusters. These attempts are described below.

Reaction of $Fe(CO)_5$ and $Fe(CO)_4^{2-}$ yields $Fe_6C(CO)_{16}^{2-}$, an octahedral iron cluster, **7**, with a carbide carbon atom at the center of the octahedron.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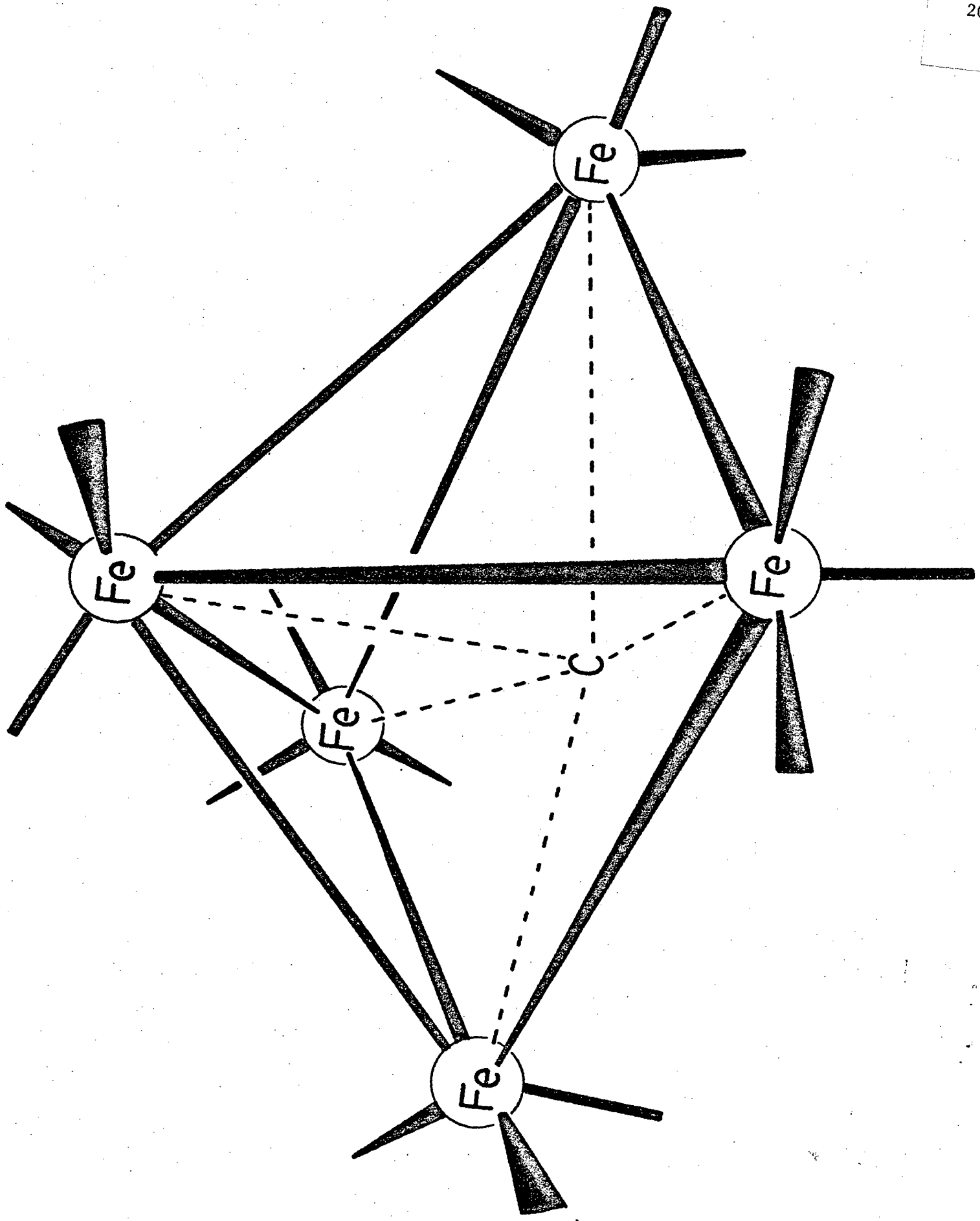
Formation of this interstitial or cage carbide from carbon monoxide established in cluster chemistry a capability for the conversion of CO to a carbide carbon atom but the product has not an exposed but a cage carbide carbon atom. Subsequent carbide hydrogenation, in further pursuing the analogy, would require an exposed carbide carbon atom. However, an intermediate in this reaction may be $Fe_5C(CO)_{14}^{2-}$, a square pyramidal iron cluster with an exposed carbide carbon atom located in the square base, because the conversion of $Fe_5C(CO)_{14}^{2-}$ to $[Fe_6C(CO)_{16}^{2-}]$ with iron carbonyls has been demonstrated. The structure of the parent $Fe_5C(CO)_{15}$ carbide cluster with an exposed carbide carbon atom is shown in 8.[32]

8

In the CO dissociative chemisorption pathway to hydrocarbons from CO + H_2 reactants on metal surfaces, the second step is ostensibly surface hydrogen atom transfer to the carbide carbon atom to initially form a chemisorbed CH fragment that subsequently through a series of C-H and C-C bond formation reactions leads to hydrocarbon formation ala the Fischer-Tropsch reaction. Can this second step of hydrogen atom addition to a carbide surface atom be modeled in molecular cluster chemistry? Such a reaction step requires a second step of hydrogen oxidative addition and then hydrogen atom migration to the carbon center to form a methylidyne, CH ligand. We have attempted to add hydrogen to the $Fe_5C(CO)_5$ cluster, 8, but with no success up to temperatures of ∿ 80 - 90°C where thermal decomposition of the cluster was relatively rapid.[33] In addition,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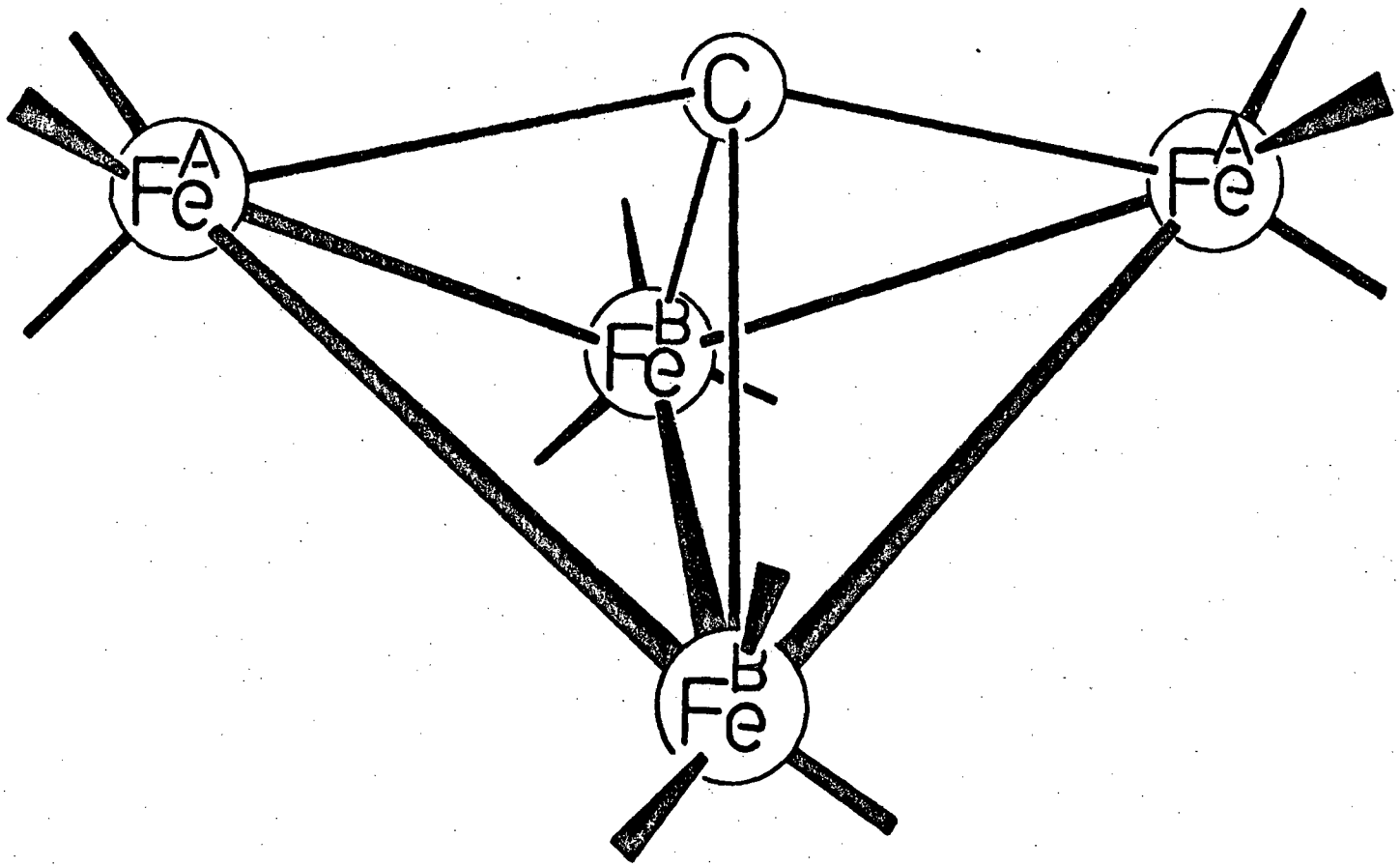
the exposed carbide carbon atom of 8 appeared to have little or no donor character; attempts to protonate the carbide carbon atom of 8 were also unsuccessful. Activation of 8 towards hydrogen addition is also being sought through photoactivation (possible generation of the coordinately unsaturated $Fe_5C(CO)_{14}$ cluster) and by substitution of CO by phosphine or phosphite ligands. Nevertheless, it is clear that the carbide carbon atom in the coordinately saturated $Fe_5C(CO)_{15}$ molecule is not especially reactive and does not model the reactive carbon atoms generated on metal surfaces by dissociative CO chemisorption reactions.

Actually, the low reactivity of the Fe_5C cluster was to be expected. First, $Fe_5C(CO)_{15}$ is coordinately saturated although this feature, in principle, could be circumvented simply by thermal or photo-dissociation of a carbonyl ligand. Secondly and most critically, the carbide carbon atom in $Fe_5C(CO)_{15}$ has a coordination number of five--the carbon atom is within bonding distance of all five iron atoms--a feature that undoubtedly lowers the reactivity of the carbide carbon atom. All other previously known metal carbide clusters with exposed carbide carbon atoms are structurally analogous to $Fe_5C(CO)_{15}$ (square pyramidal M_5 core structures with the carbide carbon atom located in the basal plane or displaced slightly from this plane away from the unique apical metal atom). However, a surface carbide carbon atom generated from CO dissociative chemisorption typically should have a metal coordination number of three or, maximally, four. Thus, a cluster carbide model if it is to have high reactivity should have the carbide carbon atom bonded to only three or four metal atoms. Our research has been directed to the synthesis of such clusters and we have obtained one cluster that has provided substantial insight to carbide based cluster chemistry and possibly to metal surface chemistry.[34] The cluster is $Fe_4C(CO)_{12}^{2-}$ which has the iron carbon framework illustrated in 9; the

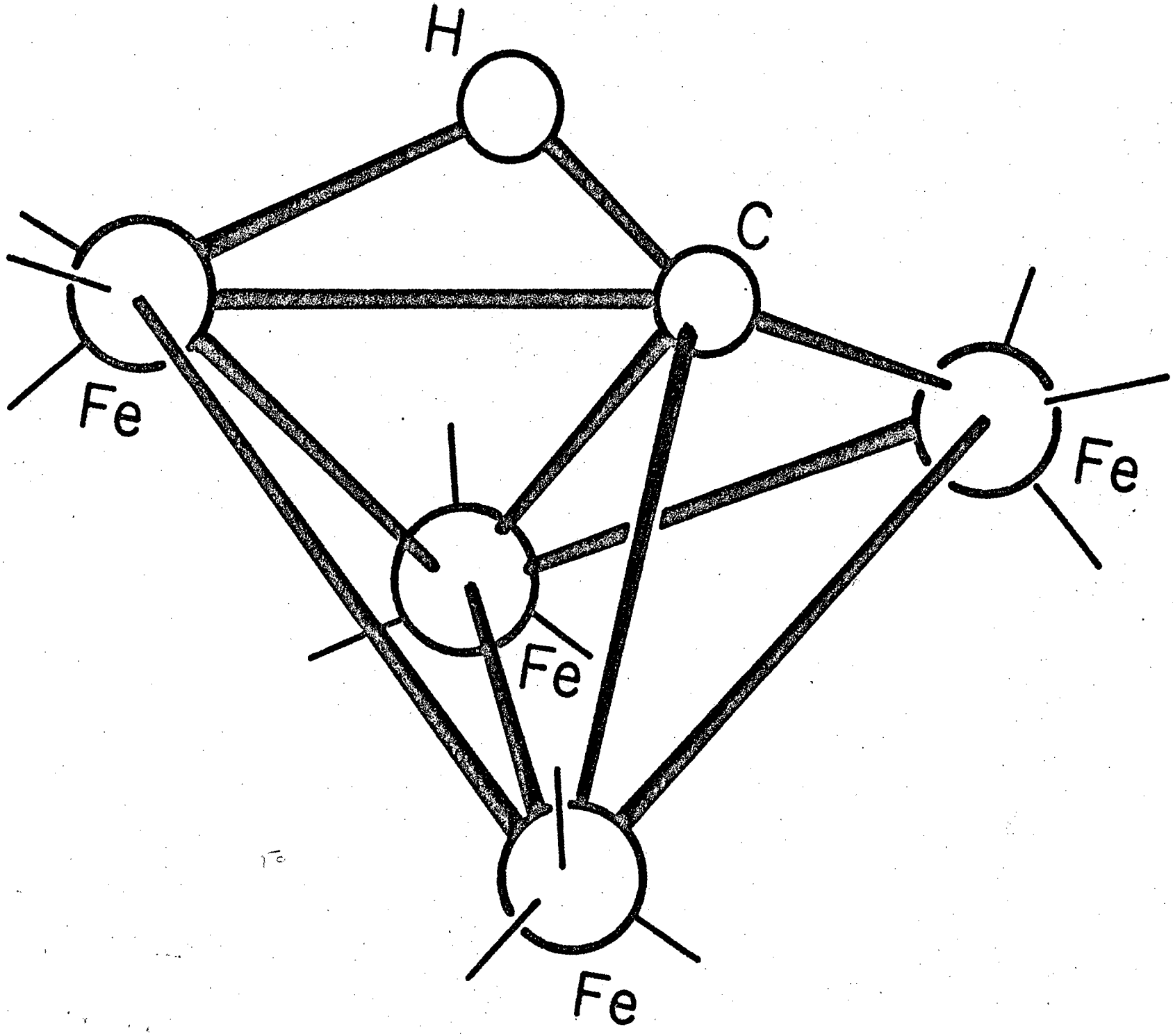
2 -



iron atoms are in a butterfly array with the carbide carbon atom nestled above the wings.[35,36] The carbide carbon atom is within bonding distance of all four iron atoms. This four-coordinate carbide cluster is coordinately saturated and explicably underwent no reaction with hydrogen at least under mild conditions.[34] However, oxidation of $Fe_4C(CO)_{12}^{2-}$ with silver ion at ∿ 0°C yielded the very reactive $Fe_4C(CO)_{12}$ cluster which in fact reacted with H_2 and D_2 to form respectively the clusters $HFe_4(\eta^2\text{-}CH)(CO)_{12}$ and $DFe_4(\eta^2\text{-}CD)(CO)_{12}$.[34] Thus, facile hydrogenation, at least to the methylidyne stage, of a carbide carbon atom in a cluster has been demonstrated. Understandably, this is not part of a catalytic cycle but it does present a viable model of the first step in a carbide carbon atom hydrogenation sequence. In addition, the methylidyne cluster product has provided some valuable information about the bonding of a methylidyne fragment to an aggregate of metal atoms and of the chemical character of the methylidyne hydrogen atom.[34]

The core structure of $HFe_4(\eta^2\text{-}CH)(CO)_{12}$ as established by a low temperature X-ray and neutron diffraction studies is illustrated in 10; not shown are

the twelve terminally bonded CO ligands--three are bonded to each iron atom in the cluster.[35,36] There are two cluster molecules in the asymmetric unit of the unit cell; and within near experimental error, there are no differences between the two molecules. Of focal interest to this discussion is the methylidyne ligand. The methylidyne carbon atom is within bonding distance, 1.83 to 1.93Å, of all four iron atoms in the cluster, and the methylidyne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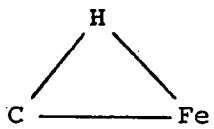
Fe
Fe

hydrogen atom is within bonding distance of the carbon atom and one of the apical iron atoms. Tight, closed three-center two electron bonding, analogous to established structures in boron hydride chemistry, is suggested by the bond distances in this three-center unit, **11**. The Fe-H distance is 1.75Å, only



11

slightly larger than the Fe-H distance (1.67Å) for the hydride hydrogen atom that bridges between the two basal iron atoms. The Fe-C distance is normal 1.93Å; and the C-H distance is unusually long, 1.18Å(aver), but still a bonding distance. The long C-H distance is consistent with structural, exchange, and chemical data cited below.

NMR studies of solutions of $HFe_4(\eta^2\text{-}CH)(CO)_{12}$ established a rapid switch of the methylidyne hydrogen atom from one apical iron atom to the other.[34] In addition, there was a slower site exchange of hydrogen atoms between the C-H-Fe site, **11**, and the Fe_{basal}-H-Fe_{basal} site.[34] Base removed the hydrogen atoms in $HFe_4(\eta^2\text{-}CH)(CO)_{12}$ as protons; the deprotonation occurred in stepwise fashion first to give $[HFe_4C(CO)_{12}^-]$ and then $[Fe_4C(CO)_{12}^{2-}]$. The "acidity" of the methylidyne hydrogen atom was clearly shown in the abstraction of the hydrogen atom by the weak base methanol to give $[HFe_4C(CO)_{12}^-]$.[34]

All previously reported molecular metal clusters with methylidyne ligands had the methylidyne carbon atom bonded to three metal atoms to form a compressed C_{3v} tetrahedral CM_3 core with the C-H bond colinear with the three-fold axis, e.g., $HCCo_3(CO)_9$ and related ruthenium and osminum clusters.[37,38] All these clusters were coordinately saturated. The iron butterfly would have been

coordinately unsaturated without the three-center C-H-Fe interaction, 11. Since metal atoms at a metal surface are typically coordinately unsaturated even with chemisorbed molecules on the surface, it seems reasonable to presume that a CH fragment bound to a metal surface would have the CH vector tipped with respect to the surface normal so as to develop multicenter C-H-M bonding. We have attempted to gain some understanding of such surface bonding features by a molecular orbital study of the bonding of simple CH_x fragments to a metal surface.[39] We found, for the face centered cubic nickel (111) surface, stereochemistry 12 with the methylidyne carbon atom over a

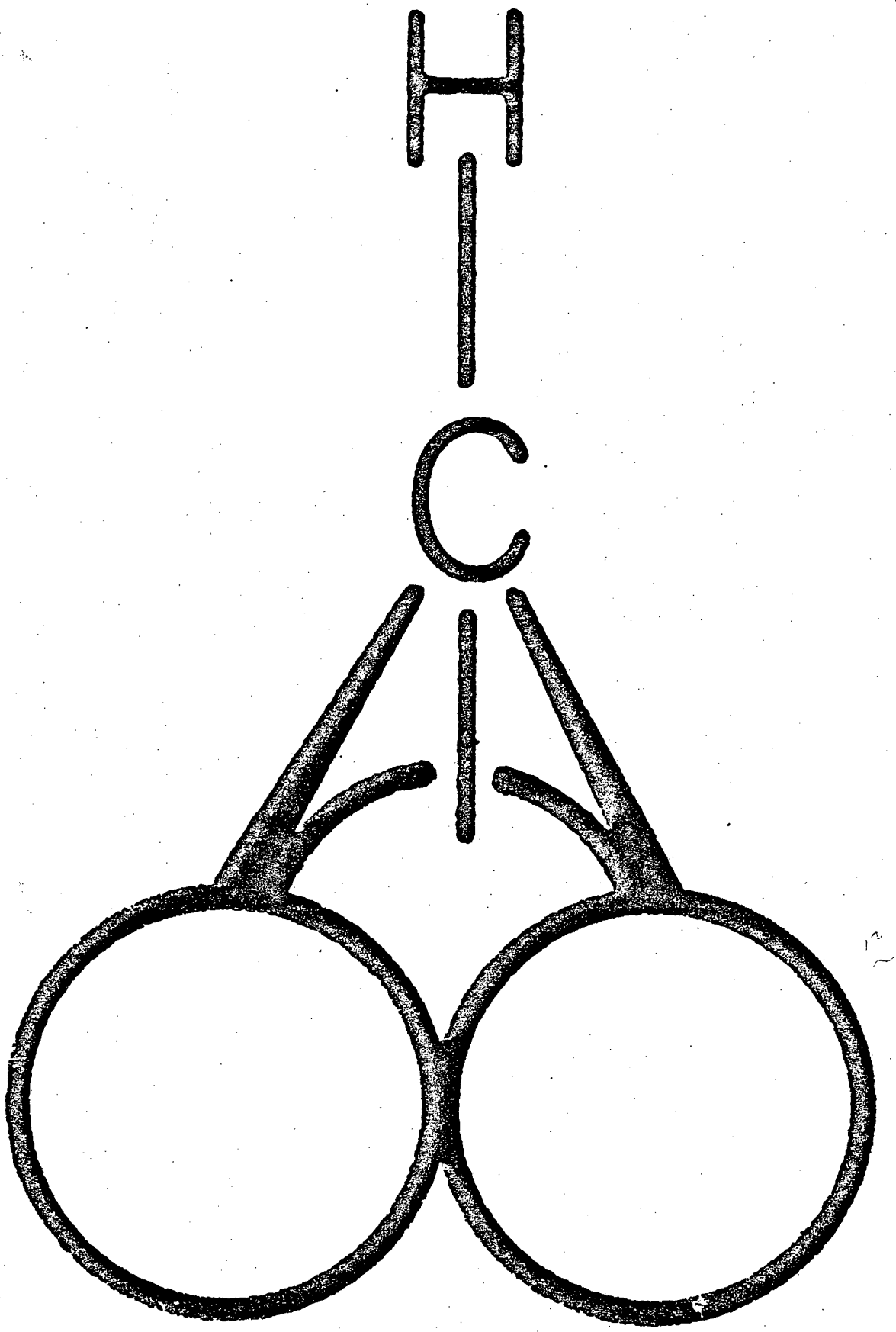
12

three-fold site to be of lower energy than for the carbon atom over a two-fold site or directly over a single metal atom.[39] However, of lowest energy is stereochemistry 13 with the carbon atom slightly off the three-fold site and with the C-H vector

13

tipped so as to generate a three-center C-H-Ni interaction. Of experimental significance is the spectroscopic evidence that chemisorbed CH on a Ni(111) surface has the C-H bond tipped with respect to the surface normal.[40] A stereochemical and bonding model of methylidyne as found for the iron cluster is apparently a model of potential significances for metal surfaces. The high lability of the methylidyne

12.



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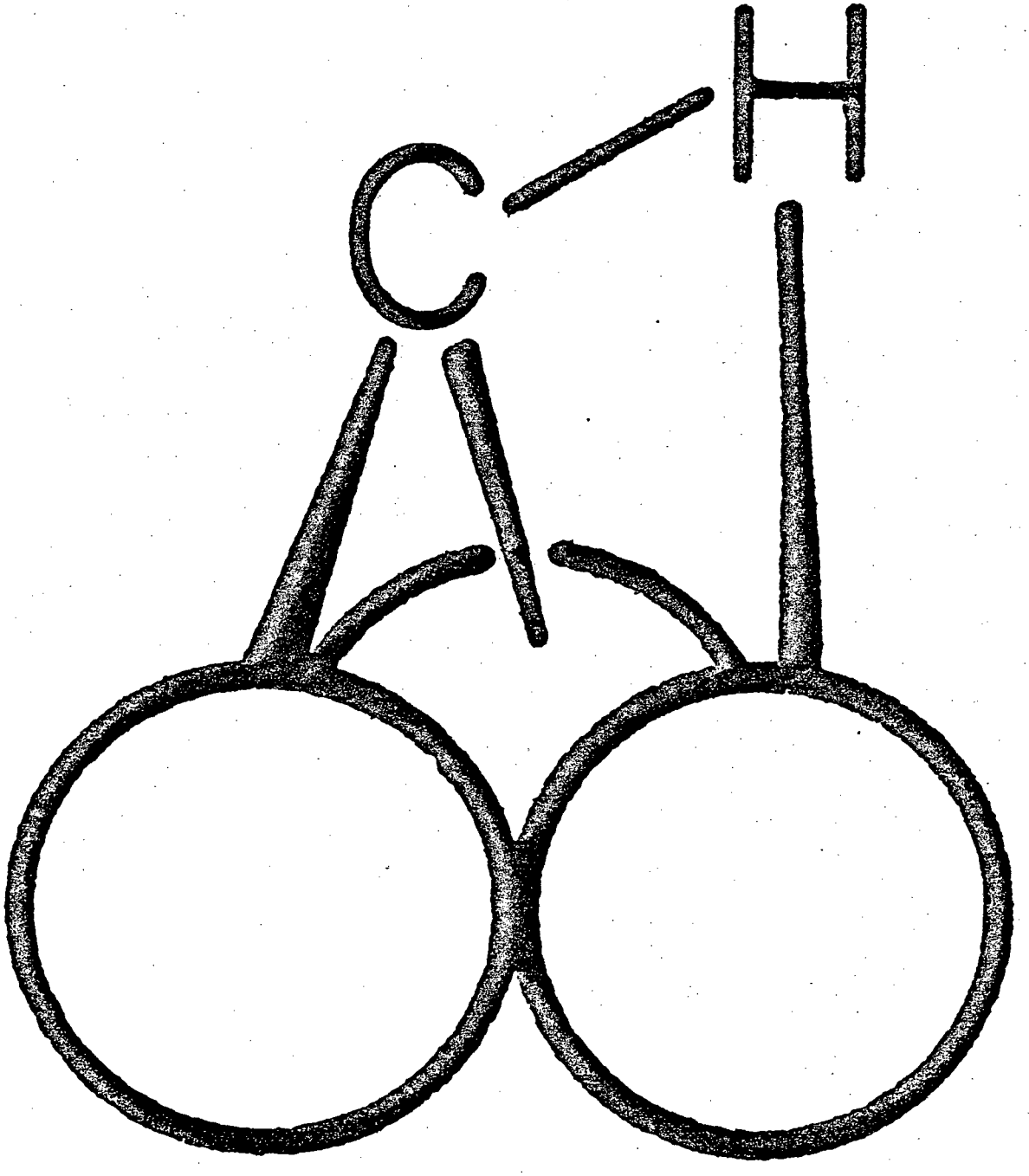

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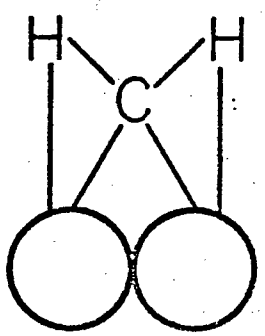
hydrogen atom with respect to H-D exchange with metal hydride hydrogen atom environments for the iron cluster is fully consistent with the metal surface observations for hydrocarbon - D_2 mixtures. Also notable is the long C-H bond distance for the methylidyne ligand in the cluster and the "protonic" character of the hydrogen atom. If the analogy between cluster and surface extends to such bonding and chemical detail, then basic sites on supported metal catalysts may substantially affect the catalytic reaction sequences for hydrocarbon reactions and for CO hydrogenation reactions that proceed through CH surface intermediates.

We now seek more detailed information about possible later steps in CO hydrogenation reactions (methanation or Fischer-Tropsch reactions) from cluster chemistry or cluster models of intermediates. Specifically, we seek structural and stereochemical definition of CH_2 and CH_3 bonding in coordinately unsaturated metal clusters. Multicenter C-H-metal bonding should also be important for CH_2 and CH_3 ligands. In fact, our molecular orbital calculations for CH_2 on a Ni(111) surface indicate that **14** is of lower energy than **15** simply because of the three-center C-H-metal bonding in **14**. Also, the

14 **15**

methyl ligands in the osmium cluster $H(CH_3)Os_3(CO)_{10}$ has multicenter $Os-\overset{H}{\underset{H}{C}}-H-Os$ bonding as shown in **16** and thereby the cluster achieves coordination saturation through this additional bonding interaction.[41]

14



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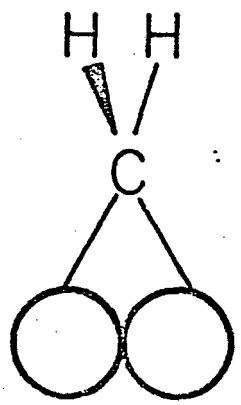

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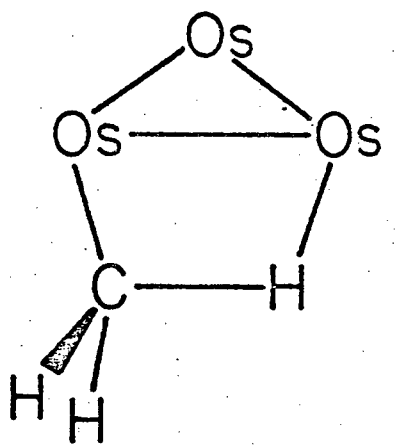

Chemistry for nitrogen (nitride clusters) analogous to the foregoing iron carbide chemistry has recently been developed and these clusters may provide insight to nitrogen conversion by hydrogen to ammonia.[42] The cluster $HFe_5N(CO)_{14}$, which has an exposed nitride nitrogen atom in the base of a square pyramid of iron atoms is isoelectronic and is structurally analogous to the previously cited $Fe_5C(CO)_{15}$ as established by an X-ray diffraction study. Two four-coordinate nitrides, $HFe_4N(CO)_{12}$ and $[Fe_4N(CO)_{12}^-]$ have also been prepared but their chemistry is not yet defined but all spectroscopic data indicate that these are analogous to $Fe_4C(CO)_{12}^{2-}$, **9**, with the hydride ligand in $HFe_4N(CO)_{12}$ bridging the basal (Fe^B) iron atoms.[42]

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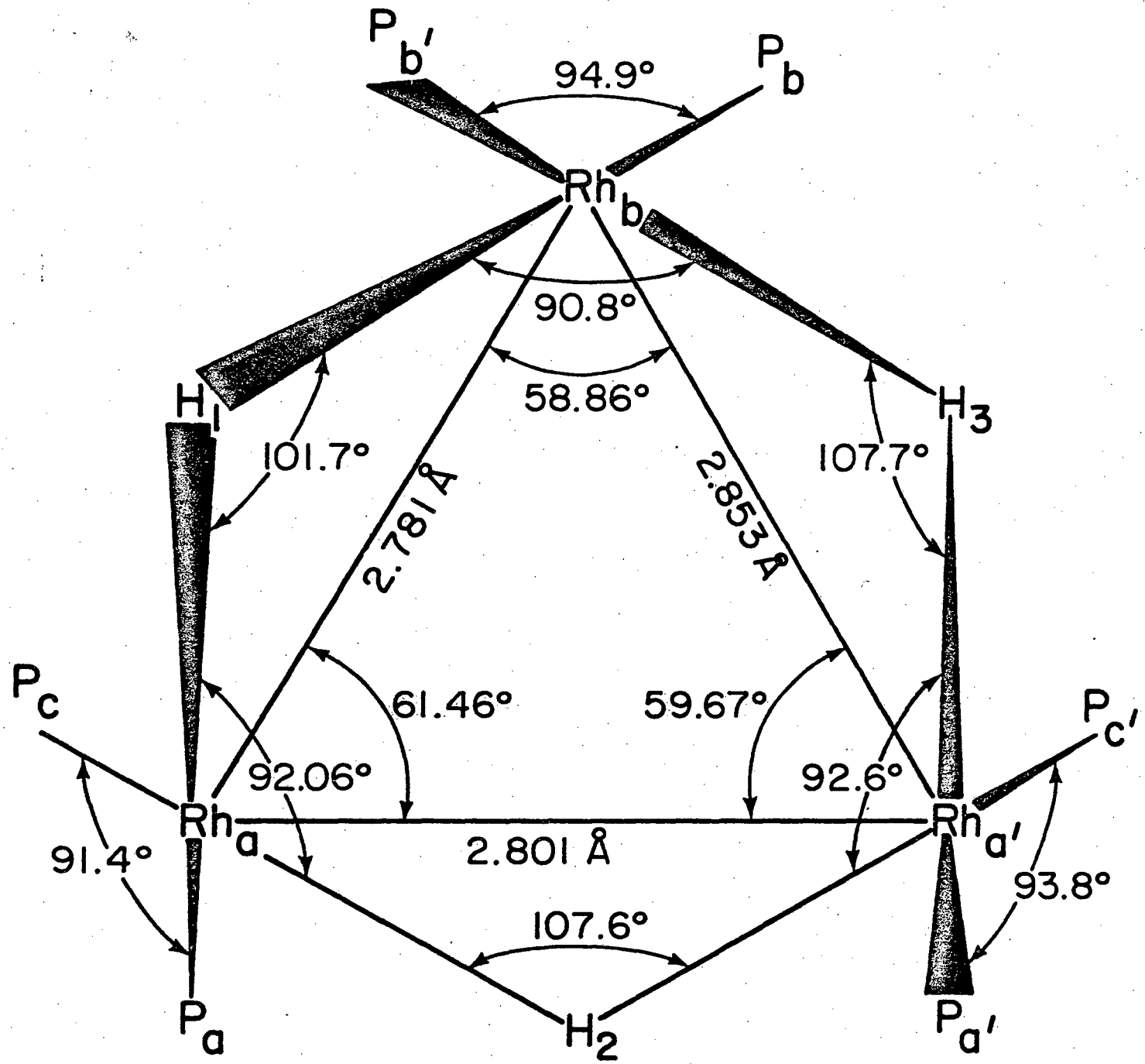
Figure 1: Schematic representation of the crystallographically determined structure of $\{HRh[P(OCH_3)_3]_2\}_3$ in the reduced context of the $H_3Rh_3P_6$cluster coordination sphere. Although the $H_3R_3P_6$ core structure is not coplanar (the core only has near C_2 symmetry), each rhodium atom has a near square planar coordination geometry with two hydride and two phosphorus (phosphite ligand) ligand atoms. Inspection of the figure shows that all interbond H-Rh-H, H-Rh-P, and P-Rh-P angles are nearly 90°.

FIGURE 1



Rh–H 1.77

Rh–P 2.16

P–Rh–H 80–94°

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