Selective Reactions of Transition Metals and their Complexes

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Mechanistic features of selective catalytic hydrogenation reactions of alkynes and of aromatic hydrocarbons are discussed. Catalysts considered include molecular mononuclear transition metal complexes, dinuclear complexes, clusters, and also metal surfaces. Particular attention is given to competitive reaction systems based on alkyne–alkene and on arene–alkene reaction mixtures.

Introduction

One of the many continuing scientific challenges within the broad area of inorganic chemistry is the development of the dynamic molecular features of chemical reactions.* It is on such bases that the full systematic details of inorganic chemistry will be founded. A major contributing factor to the scientific and intellectual challenge is the diversity and complexity [1] that certainly exceeds that of organic chemistry alone. Here the d-block elements contribute substantially to that overall diversity and complexity in generating bonding situations that have no strict analogs in organic chemistry. However, it is at the very interface of inorganic and organic chemistry that the diversity really develops, where the zoo of organometallic chemistry arises. Within this area of organometallic chemistry, the catalytic reactions are veritable bonanzas for the chemist interested in reaction mechanism. No catalytic reaction based on metals or metal complexes comprises solely one elementary step... indeed some are quite impressive in the context of number of elementary steps. An ostensibly simple catalytic reaction like olefin hydrogenation is minimally based on four elementary steps for those based on mononuclear metal complexes. Recently, we have examined an aromatic hydrocarbon catalytic hydrogenation reaction, based on a mononuclear cobalt complex, that has over twenty

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*I had the good fortune as an undergraduate student, to be exposed to this research area by two pioneers, Fred Basolo and Ralph Pearson. See reflections by R. G. Pearson, *J. Chem. Ed., 55*, 720 (1978).

elementary steps associated with the catalytic sequence. Thus a wealth of fundamental information about inorganic and organometallic chemistry can be obtained from reaction mechanism studies of catalytic reactions. For these reasons, I elected to discuss mechanistic aspects of some specific catalytic reactions as an illustration of one research subject of major interest to me and to members of my research group when I was invited to participate in the publication of this Jubilee issue of the 50th Volume of Inorganic Chimica Acta devoted to 'Perspectives in Inorganic Chemistry.' I make no claim that this research area is the most important one, now or in the future. It simply represents an area I find interesting, challenging and fun.

Selective Catalytic Hydrogenation Reactions

One aspect of reaction mechanism of general interest to our research group has been selectivity that arises in competitive catalytic hydrogenation reactions between compounds representative of different classes of organic unsaturated molecules. For example, all metal surfaces (investigated by us and others) when presented with a reaction mixture of hydrogen, an alkene (terminal or internal), and an arene such as benzene selectively catalyze the alkene hydrogenation. The relative rate of alkene hydrogenation alone compared to the arene hydrogenation rate is always larger for a given metal surface in the 0–100 °C range but is never more than two orders of magnitude greater for liquid phase reactions. We found the ratios of relative rates of $k_{alkene} : k_{arene}$ range from 3–20:1 for various transition metal surfaces. Rhodium, one of the most active surfaces examined by us, had a ratio of about 4:1 for the 1-hexene hydrogenation to the benzene hydrogenation rate at 20 °C (liquid phase). All molecular catalysts with the exception of the unique allycobalt tris(phosphite) and tris(phosphine) catalyst precursors show a total selectivity to alkene hydrogenation. The competitive catalytic hydrogenation of alkene–alkyne mixtures also has revealed interesting selectivity features. A class of polynuclear rhodium hydride

molecules selectively catalyzed alkyne hydrogenation in alkyne—alkene mixtures despite the fact that the rate of alkene hydrogenation alone was many orders of magnitude greater than that of alkyne hydrogenation alone.

Many plausible explanations can be advanced for these selectivities in competitive catalytic reactions. The issue is, of course, what is the molecular basis for these selectivities? Are there systematics and generalizations that may be drawn? I review in this article the status of our investigation of this general subject and an analysis of a selected set of studies reported by other researchers.

Hydrogenation of Alkynes and Competitive Hydrogenation of Alkyne—Alkene Mixtures

Catalytic hydrogenation reactions of alkenes have been extensively studied for both solid state and solution state catalysts*. However, no solution state catalyzed alkyne hydrogenation reaction has been mechanistically established until recent studies by our research group defined with fair rigor the elementary steps of several such reactions. Our studies do illuminate the potential elementary steps that can provide a totally selective hydrogenation of alkynes in an alkyne—alkene mixture but there is not a uniform mechanistic feature to these selective hydrogenation reactions. One comprises different pathways for alkene and for acetylene hydrogenations and several an inability of a catalyst intermediate to complex an alkene. Although mechanistic pathways differ, all owe their selectivity to a more effective coordinating capability of the acetylene with respect to either hydrogen or alkene.

Alkynes rapidly react with $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4$ to form isolable and stable $(\eta^5\text{-}C_5H_5)_2(CO)_4(\mu_2\text{-}\eta^2\text{-}RC_2R)$ complexes with a tetrahedral framework, **1**,

composed of the two molybdenum atoms and the two acetylenic carbon atoms of the bridging alkyne ligand.** This type of alkyne complex is a catalyst precursor at 120–150 ℃ for the hydrogenation of alkynes to cis-olefins, including the conversion of C_2H_2 and D_2 to cis-$C_2H_2D_2$. These complexes are incapable of initiating alkene hydrogenation. In this dinuclear complex system, an alkene is totally ineffective as a $\mu_2\text{-}\eta^2$-ligand and explicably does not

compete with alkynes in the catalytic sequence [6]. No step in this dinuclear metal complex catalyzed alkyne hydrogenation involves Mo—Mo bond scission as established by cyclopentadienyl ligand labeling experiments. The key rate determining step is CO dissociation to give $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_3(\mu_1\text{-}RC_2R)$ [6]. No explicit molecular characterization of later species in the catalytic sequence was achieved. Consequently, the stereochemical features that then require selective cis-addition of hydrogen to give the cis-olefin rather than the thermodynamically favored trans-olefin are not precisely defined (see later discussions).

Formally similar to the molybdenum complexes discussed above are the coordinately unsaturated $(1,5\text{-cyclooctadiene})_2Ni_2(\mu_2\text{-}\eta^2\text{-}RC_2R)$ complexes [7] which have a tetrahedral $Ni_2\text{-}C_2$ (acetylenic carbon atoms) core structure, **1**, analogous to that of the molybdenum complex [8]. These nickel complexes also effect a selective catalytic hydrogenation of alkynes to cis-olefins and also are incapable of complexing olefins or effecting catalytic olefin hydrogenation [7]. Hence, like the molybdenum complex, the nickel complex expels the olefin as it is formed in the catalytic reaction. The full mechanistic details of this dinuclear nickel complex catalyzed alkyne hydrogenation sequence have not been defined.

The polynuclear complexes, $Ni_4(CNR)_4(\mu_3\text{-}\eta^2\text{-}RC_2R)$, R = aryl, are also totally selective catalysts for the conversion of alkynes to cis-olefins (see Figure 1 for the molecular structure of these clusters
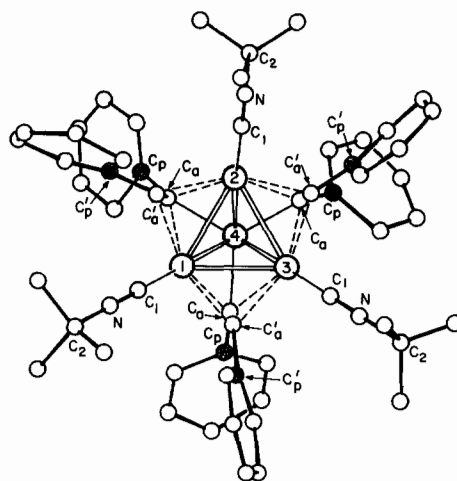

Fig. 1. Representation of the $Ni_4[CNC(CH_3)_3]_4(\mu_3\text{-}\eta^2\text{-}C_6H_5C_2C_6H_5)_3$ structure. The view is down along the idealized three-fold axis. The nickel atoms (large open circles numbered 1 through 4) form a tetrahedral array and each nickel atom has one terminal isocyanide ligand. The acetylenic carbon atoms, labelled C_a and C'_a, bridge three of the tetrahedral faces. The C_a acetylenic carbon atoms are within bonding distance of two nickel atoms and the C'_a carbon atoms are within bonding distance of three nickel atoms that describe the tetrahedral face.

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*For recent reviews of catalytic olefin hydrogenation reactions see references 2–5.

**See reference 6 for a discussion of structural features and for relevant structural references.

[9]). For example, over a day period at 20 °C, 3-hexyne was hydrogenated solely to *cis*-3-hexene [10, 11]. Although the reaction mechanism for this catalytic alkyne hydrogenation system has not been established, the gross basis for selectivity is fully defined. The nickel cluster catalyst precursor neither complexes olefins nor does it catalyze olefin hydrogenation. Like the dinuclear molybdenum alkyne complex described above, the alkyne in this nickel complex is a bridging ligand (bridging three nickel atoms as in 2 compared to two metal atoms, 1, in the
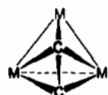
$$\text{2}$$

dinuclear species). There is no precedent for an analogous bridging by olefins in conventional, or at least coordinately saturated, metal clusters. In these nickel and molybdenum dinuclear and polynuclear reaction systems, the olefin once formed no longer binds to the complex and hydrogenation does not proceed further to give alkane or even isomerized olefin.

A much more fascinating molecular catalyst system for selective alkyne hydrogenation *vis-a-vis* alkene hydrogenation is that of the polynuclear rhodium hydrides, $\{HRh[P(OR)_3]_2\}_n$. These polynuclear rhodium hydrides catalyze alkene hydrogenation at rates approaching diffusion controlled rates at 20 °C and also catalyze alkyne hydrogenations, to give *cis*-olefins, but at rates that are many orders of magnitude lower than for alkene hydrogenation. Yet, presented with a hydrogen, alkene, and alkyne mixture, these hydrides produce chiefly the *cis*-olefin derived from the alkyne until the alkyne is consumed [12, 13]. Spectroscopic studies of these systems have delineated virtually all sequences in the alkene and the alkyne hydrogenation sequences and clearly establish the key selectivity feature in the competitive hydrogenation reactions. To illustrate the mechanistic details, I focus solely on the simplest polynuclear rhodium hydride, the dinuclear $\{HRh[P(O-i-C_3H_7)_3]_2\}_2$ complex although in a formal sense the reactions catalyzed by the trinuclear complexes, $\{HRh[P(OR)_3]_2\}_3$ R = CH_3 or C_2H_5, are fully analogous.
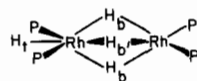
The dimer has the bridged square planar geometry of 3 with all rhodium, bridging hydrogen, and phos-
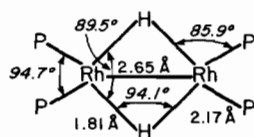
$$\text{3}$$

phite phosphorus atoms coplanar [14, 15]. This dimer does not react, except in a very slow and complex manner, with alkenes but reacts instantaneously with precisely one mole of hydrogen to give a new dimeric hydride 4 with three bridging hydride

$$\text{4}$$

hydrogen atoms. This tetrahydride is stereochemically nonrigid with facile intramolecular hydride hydrogen atom site exchange that proceeds in two steps. In the low energy process, there is selective exchange between the one terminal hydride and the unique bridging hydride hydrogen atom of 4 whereby the intermediate or transition state shown in 5 is unique-
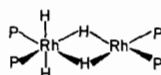
$$\text{5}$$

ly determined by the character of the NMR line shape changes. This excited state, 5, is presumed to be the species that interacts with the alkene and the resultant olefin complex was implicated by low temperature NMR studies. Above ~−80 °C, the olefin complex rapidly yields alkane and the original dinuclear rhodium hydride. An overall sequence for the alkene hydrogenation reaction is illustrated in 6.
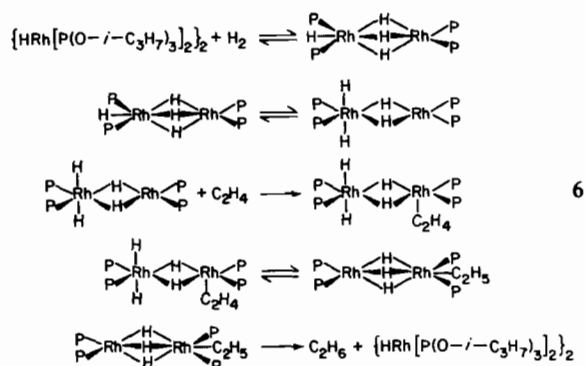
$$\text{6}$$

In contrast to alkenes, alkynes do react − and react instantaneously − with the dinuclear rhodium hydride, 3. In fact, the alkynes are selectively complexed, with respect to hydrogen by the dimer, $\{HRh[P(O-i-C_3H_7)_3]_2\}_2$. The product is a vinyl bridged dimer 7 as judged by NMR studies; a single
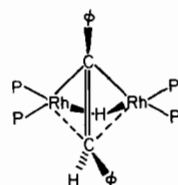
$$\text{7}$$

crystal of 7 based on diphenylacetylene is under X-ray crystallographic study to substantiate the putative structure 7. Hydrogen reaction with 7 is slow—slow relative to the alkene hydrogenation sequence. Thus

the slow but selective hydrogenation of acetylenes catalyzed by these rhodium hydrides can be fully rationalized by a much higher reactivity of the catalyst precursor toward alkynes relative to either hydrogen or an alkene and to a different hydrogenation sequence for the alkyne relative to the alkene. Selective formation of the *cis*-olefin (as observed) from the bridged vinyl intermediate 7 is not necessarily required assuming the geometry as shown in 7 is correct. However, reductive elimination of the olefin in 7 was not observed at least at rates that would be consistent with the observed rate of catalytic alkyne hydrogenation. The rate determining step in the catalytic sequence is apparently hydrogen addition to 7 where the product should be 8, a simple σ-vinyl

$$P{\gt}Rh{\lt}^H_H{\gt}Rh{\lt}^P_P{\lt}^R_{C-R} \qquad \mathbf{8}$$

derivative analogous to the ethyl intermediate, $[(i\text{-}C_3H_7O)_3P]_2Rh(\mu_2\text{-}H)_3Rh[P(O\text{-}i\text{-}C_3H_7)_3]_2C_2H_5$, in the olefin hydrogenation sequence shown in **6**. Reductive elimination of olefin from 8 can directly yield only the *cis*-olefin and $\{HRh[P(O\text{-}i\text{-}C_3H_7)_3]_2\}_2$. The latter does not interact with an olefin; and accordingly, neither olefin isomerization nor hydrogenation can occur as long as an alkyne is present to capture the dimeric hydride.*

Although the selective acetylene hydrogenation systems catalyzed by dinuclear metal complexes differ in detail, the selective feature is based on a more effective complexation of the acetylene at some step. Is the latter feature a general aspect of transition metal chemistry? Is the equilibrium constant for the complexation of some coordinately unsaturated transition metal complex ML_x with an alkyne always substantially greater than for an alkene? Will an alkyne displace either hydrogen or an olefin from some H_2ML_x or ML_x (olefin) complex? Simple EHMO theory suggests that alkynes will complex more strongly with single metal centers than will alkenes but does not provide a reliable quantitative measure of bond strengths. Since these fundamental questions are experimentally unanswered for simple** hydrocarbon alkenes and alkynes, they are questions we seek to answer in full quantitative detail.

One ostensible example of a fully selective acetylene hydrogenation to *cis*-olefin by a molecular mononuclear transition metal complex has been reported. Schrock and Osborn [17] have described monomolecular rhodium complexes, specifically

species derived from the cationic complex Rh(nonbornadiene)(PR$_3$)$_2$]$^+$ and hydrogen in ketones or ethers, that convert alkynes to *cis*-olefins with total selectivity. Since these same species convert alkenes to alkanes, there must be some difference in mechanistic pathways for alkyne and for alkene hydrogenation or else the alkyne simply competes for the transition metal complex intermediates far more effectively than does the alkene. Low temperature NMR studies may provide a definitive elucidation of reaction mechanism in this mononuclear rhodium system and we plan to explore these possibilities. A presumably related system is based on $H_4Ru_4(CO)_{12}$ as the catalyst precursor where 1-pentyne and 2-pentyne are cleanly converted to 1-pentene and *cis*-2-pentene early on ($\sim$10% conversion), but later isomerized pentenes and also pentane are produced. The cluster is also a catalyst precursor for olefin hydrogenation and isomerization [18]. These results cleary show a competitive complexation of alkynes and alkenes without a large difference in equilibrium constants. No mechanistic details of this catalytic system have been established. Since the alkene effectively competes with the alkyne in this system, the alkyne (and the olefin as well) probably bonds to a single metal center.

Another mononuclear metal complex catalyzed alkyne hydrogenation system has been reported by Pregaglia, Andreetta, Ferrari and Ugo [19]. The catalysts are the analogous $HCo(CO)_2[P(n\text{-}C_4H_9)_3]_2$ and $HCo(CO)[P(n\text{-}C_4H_9)_3]_3$ complexes, the latter the more active and selective of the two. Both complexes are catalyst precursors for olefin and for alkyne hydrogenation reactions (no comparison of relative rates of olefin and alkyne hydrogenation rates were presented). Both display a relatively high selectivity to *cis*-olefin formation in the alkyne hydrogenation reaction up to relatively high alkyne to olefin conversions although alkane and isomerized olefin products appear in later stages of the reaction. An interesting feature of this catalytic system is that if the starting complex is $DCo(CO)_n[P(n\text{-}C_4H_9)_3]_{4-n}$ ($n = 2$ or 1) and H_2 is the reactant, olefin hydrogenation or isomerization can be run to high conversions without substantial depletion of deuterium in the cobalt catalyst precursor.*

Alkyne hydrogenation on metal surfaces can be relatively selective to *cis*-olefin formation especially by pretreatment of the surfaces with sulfur or with nitrogen compounds as in the Lindlar catalyst [20] which is prepared by treating palladium metal with quinoline. There has been a presumption that the sur-

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*Reaction mechanism features in this system appear to be very sensitive to the substituent atoms or groups on the acetylenic carbon atoms.

**J. A. Connor [16] has reported that fluoroalkyne of iridium are more stable than the fluoroalkene complexes.

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*This result is explicable if the catalyst intermediate is $DCo(CO)_2(PR_3)$, or $DCo(CO)(PR_3)_2$. Such low concentration intermediates could effect many catalytic turnovers leaving the bulk of the catalyst precursor unchanged as the D−Co species.

face pretreatment poisons sites for olefin hydrogenation but there are no surface studies that provide a definitive molecular characterization of the surface pretreatment.

We have recently begun to examine metal surface catalyzed competitive hydrogenations of alkyne-alkene mixtures. Preliminary results with rhodium on silica at 25 °C showed a fair selectivity (about 6:1) toward the alkyne for a 1:1 molar mixture of 3-hexyne and *cis*-2-pentene early in the reaction; the products from the 3-hexyne included *cis*-3-hexene, *trans*-3-hexene, 2-hexenes and hexane. *Cis*-3-hexene was predominant only at low conversions. These preliminary results for the competitive reaction was anticipated because even the untreated second and third row Group VIII transition metals are relatively selective in converting acetylene to ethylene—the range is from 55% for iridium to 97% for palladium (Table I) [21]. We [11] have also found that untreated nickel metal at 20 °C was relatively selective in catalyzing the hydrogenation of 2-butyne, the products were *cis*-2-butene, *trans*-2-butene, 1-butene and butane in the molar ratios of $\sim$16:0.4:0.5:1.0 with the percent *cis*-2-butene in the total product about 89%. This type of selectivity has been assumed to be a reflection of the fact that acetylene is more strongly chemisorbed than ethylene. Ostensibly, the selectivity of a metal surface for the reaction of alkyne $+ H_2$ to give an olefin is a function of the rate of olefin hydrogenation and the relative concentrations of the alkyne and olefin on the surface [22].

TABLE I. Selectivity in the Metal Surface Catalyzed Hydrogenation of Acetylene [21].

Metal	Reaction Temperature °C	Molar % C_2H_4 in Product
Ir	150	55
Os	150	60
Ru	150	75
Rh	100	78
Pt	100	80
Pd	0	97

None of the molecular features of the catalytic sequence for alkyne hydrogenation on metal surfaces is established [23]. However, the nature of the products produced do establish key points. The major product is the *cis*-olefin whereas the *trans*-olefin is

overwhelmingly the favored product. Clearly, there is a stereochemical control in these surface reactions whereby the two hydrogen atoms add to one side of the bound alkyne—any viable mechanism proposed to explain molecular features must naturally account for this stereochemical fact. Then, the chemisorbed *cis*-olefin produced may dissociate (or be displaced by an alkyne) or if the lifetime of this state is long relative to rates of olefin isomerization and olefin hydrogenation processes, then alkane and also alkene isomers will be produced.

Interestingly, the surface chemistry of alkenes and alkynes on clean metal surfaces of well defined crystallography is not really *rigorously* established in a structural and stereochemical fashion despite extensive studies of ethylene and acetylene chemisorbed on single crystal surfaces of metals like iridium, nickel and platinum. Many proposals have been advanced based on photoelectron spectroscopic, electron energy loss (vibrational) spectroscopic, and low energy electron diffraction data but no single study and no collective set of studies rigorously defines the chemisorption state or states. One major problem is that both acetylene and ethylene chemisorb irreversibly on these clean surfaces (at submonolayer coverages); only with the less reactive metals like platinum can even a small fraction of either acetylene or ethylene be thermally desorbed at elevated temperatures.* Also we [24] have been unsuccessful in all our attempts to displace either acetylene or ethylene (sub monolayer coverages) with strong field ligands like phosphines, PF_3 and CH_3NC from clean platinum or nickel surfaces or even from these same metal surfaces that contain $\sim$0.1 to 0.3 of a monolayer of carbon or sulfur. Facile carbon–hydrogen bond breaking is a common phenomenon [25]; and on some metal surfaces, ethylene chemisorbed at low temperatures undergoes dehydrogenation to presumably give acetylene (still chemisorbed) at temperatures well below 20 °C. In fact, in the absence of hydrogen, ethylene can be converted to a mixture of ethane and acetylene over transition metal surfaces [23].

Because of the implication, from the discussion of mechanisms in alkyne hydrogenation [23], that acetylene can displace an olefin chemisorbed on a metal surface, we have attempted such displacements on Pt(111) surfaces (submonolayer coverages – ultra high vacuum system). We have seen no evidence of displacement – the end result was a surface with chemisorbed species derived from both acetylene and ethylene. Results with 1,2-disubstituted derivatives like 2-butyne and 2-butene have been analogous [24].

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*This result is explicable if the catalyst intermediate is $DCo(CO)_2(PR_3)$, or $DCo(CO)(PR_3)_2$. Such low concentration intermediates could effect many catalytic turnovers leaving the bulk of the catalyst precursor unchanged as the D–Co species.

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*Another complication is that acetylene and ethylene chemisorb on these metal surfaces to generate more than one kind of chemisorbed species.

Mechanistic Generalizations for the Selective Acetylene Hydrogenation Reactions

Selective formation of *cis*-olefins as the initial product of alkyne hydrogenation reactions may well be a general feature of catalytic alkyne hydrogenation reactions. Appearance of some *trans*-olefin in the products may be the result of a subsequent reaction, olefin isomerization, of the bound *cis*-olefin. Initial formation of a *cis*-olefin for alkyne hydrogenation reactions catalyzed by a molecular mononuclear metal complex is virtually a required feature for this class of mononuclear metal coordination catalysis. The alkyne-metal complex may be formally considered as a metallacyclopropene structure, **9**. Hydro-


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gen atom transfer to either acetylene carbon atom must yield a σ-vinyl complex **10**, which must yield the *cis*-olefin complex **11**, on the transfer of the

   10   **11**
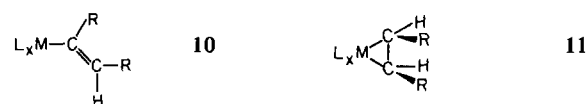
second hydrogen atom to the other carbon center. Then if another alkyne molecule is quickly captured by **11**, then the *cis*-olefin should be displaced—if not, then olefin isomerization or hydrogenation may ensue at some competitive level.

For alkyne hydrogenation reactions catalyzed by molecular di- or polynuclear metal complexes, the above comments on *cis*-olefin formation from mononuclear metal complex catalysts holds if the alkyne is simply bound in a conventional η^2 manner to a single metal center within the polynuclear complex. However, if the alkyne is a μ_x-bridging ligand, as in **1** or **2**, above, there are at least two plausible scenarios and one of these leads to the initial formation of a *trans*-olefin. In one, the initial μ_x-alkyne ligand on the first hydrogen atom transfer to an acetylene carbon atom may form a nonbridging vinyl derivative as schematically illustrated in **12**, specifically for the dinuclear

   12
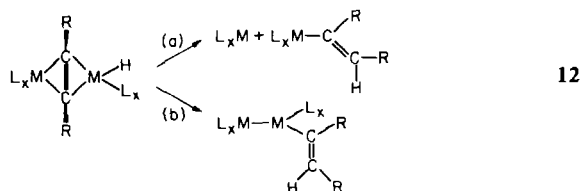
case with two different subsequent pathways, either of which must then on the second hydrogen atom transfer yield a *cis*-olefin metal complex or the free uncomplexed *cis*-olefin. Alternatively, a dinuclear

metal complex with a μ_2-alkyne ligand may first rearrange to a nonbridging alkyne ligand whereby subsequent steps would be analogous to those discussed above for mononuclear metal intermediates.

A different type of intermediate in the hydrogenation sequence for a catalytic intermediate with a bridged alkyne ligand could lead to the initial formation of a *trans*-olefin (or *cis*-olefin) product. This possible sequence is illustrated in **13**. A stepwise hydrogen atom addition is illustrated in **13** although a
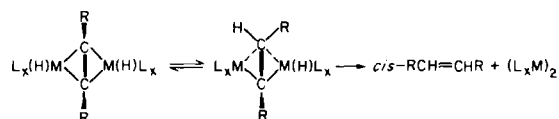
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concerted addition of two hydrogen atoms, if symmetry allowed, could also account for the postulated stereochemistry of the olefin product.

The experimentally established facts for dinuclear or polynuclear coordination catalyst precursors or intermediates with bridging alkyne ligands are that *cis*-olefins are the invariable products. Available data suggest that subsequent intermediates involve non-bridged vinyl intermediates (whether mononuclear as implicated for $(1,5\text{-cyclooctadiene})_2Ni_2(\mu_2\text{-RC}_2R)$ [7] or dinuclear as established for $(C_5H_5)_2Mo_2(CO)_4$-$(\mu_2\text{-RC}_2R)$ [6] and for $\{HRh[P(O\text{-}i\text{-}C_3H_7)_3]_2\}_2$ [12, 13]) that then require initial formation of the *cis*-olefin (or complexed *cis*-olefin). However, I take note of the stoichiometric production of substantial quantities of a *trans*-olefin (*trans* to *cis*-olefin product ratio of 9 to 1) in the reaction of hydrogen with $(OC)_6Fe_2(\mu_2\text{-RC}_2R)$ [7]. The lowest unoccupied molecular orbital in this iron complex is largely π^* in character so that the complex basically has σ and π metal—metal bonds. The lowest unoccupied orbital is relatively low lying and contains a sizeable contribution from the acetylene carbon atoms and is bonding between the iron and acetylene—carbon atoms. This orbital provides a likely site for the initial addition of a hydrogen molecule to the bridged vinyl complex as shown in **14**. The resultant complex could yield either a *cis*- or *trans*-olefin.
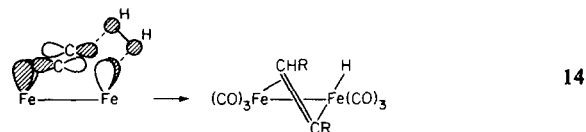
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Now to turn to the other issue of selectivity—selective formation of the *cis*-olefin from a mixture of an alkyne and an olefin, *i.e.* selective hydrogenation of the alkyne, consider the generalizations that naturally evolve from the available mechanistic data. One obvious generalization for dinuclear or polynuclear metal complexes with a bridge bonded alkyne

ligand is that the olefin cannot bond in an analogous bridge-bonded fashion so that the olefin simply cannot compete in the hydrogenation sequence. This mechanistic feature is extant for $(C_5H_5)_2Mo_2(CO)_4$-$(\mu_2\text{-}RC_2R)$ [6], $Ni_4(CNR)_4(\mu_3\text{-}RC_2R)_3$ [7, 10, 11], and $(1,5\text{-cyclooctadiene})_2Ni_2(\mu_2\text{-}RC_2R)$ [7]. None of these is a catalyst precursor for either olefin isomerization or olefin hydrogenation—the olefin simply cannot complex with the precursor or any intermediate in the catalytic alkyne hydrogenation cycle.

A more interesting mechanistic exemplar is that based on the $\{HRh[P(OR)_3]_2\}$ complexes, in particular $\{HRh[P(O\text{-}i\text{-}C_3H_7)_3]_2\}_2$. The dimer does not react with olefin but does react rapidly with either hydrogen or alkyne to give, respectively, a hydrogen adduct, 4, or a bridged vinyl complex, 7. Although the former can react with an olefin to rapidly form an alkane, the vinyl complex, 7, is formed preferentially to the hydrogen adduct, 4, from mixtures of H_2, alkyne, and olefin. Conversion of 7 to the *cis*-olefin is slow. Thus despite the fact that olefin hydrogenation is catalyzed at rates many orders of magnitude greater than for alkyne hydrogenation, the complex is selective to alkyne to *cis*-olefin hydrogenation for alkene—alkyne reaction mixtures. Reaction sequences are different for alkyne and for olefin hydrogenation with alkyne addition the first step for the former and hydrogen addition the first step for the latter—the selectivity feature then arises from the fully selective (competitive) complexation of alkyne over hydrogen addition by the initial catalyst precursor, $\{HRh[P(OR)_3]_2\}_2$.

For the fully or partially selective alkyne hydrogenation catalyzed by mononuclear metal complexes, no generalizations are appropriate because the catalytic sequence for the alkyne hydrogenation has not been established (is H_2 addition or alkyne complexation the first step?). Also no generalizations are appropriate in the metal surface catalyzed selective hydrogenation reactions for alkyne—alkene mixture—the molecular details of neither the alkyne nor the alkene catalytic hydrogenation cycle have been established. These issues remain scientific challenges.

Another possible mechanism for isomerization of a *cis*-olefin complex formed from the hydrogenation of an alkyne is through a methylene or carbene metal complex as schematically illustrated in 15 [26]. No
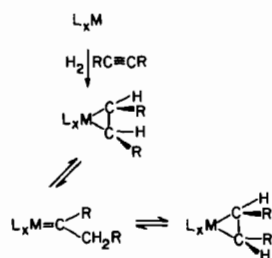
such reaction sequence has been established for any catalytic reaction but there is a purely formal precedent in stoichiometric reactions as in the reaction of alkynes with methylnickel complexes where through a CH_3—Ni alkyne addition reaction both *cis* and *trans* vinylnickel complexes result (postulated carbene complex stabilized by a phosphine ligand initially attached to the nickel atom) [27] and also in the sequential protonation of and hydride addition to $Fe_2(CO)(\mu\text{-}CO)(\mu\text{-}n^1, \eta^3\text{-}C(O)C_2H_2)(\eta^5\text{-}C_5H_5)$ to give $Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}C(H)CH_3)(\eta^5\text{-}C_5H_5)$ [28].

Selective Features of Arene Hydrogenation Reactions

An ubiquitous feature of arene hydrogenation reaction is a relatively selective *cis* addition of hydrogen in the formation of the cyclohexane product. Selectivities vary substantially for metal surfaces (Table II) [29] and for most molecular metal com-

TABLE II. Dimethylcyclohexane Products from the Metal Surface Catalyzed Hydrogenation of *p*-Xylene [26].

Metal Surface (t, °C)	Ratio of *cis* to *trans* Dimethylcyclohexene
Ni (180)	1:4
Pt black (200)	1:4
Rh/C (100)	1:2
PtO_2 (85)	1:2
Ru/C (100)	7:3
PtO_2	7:3
Pt black (20)	4:1

plexes. A unique class of molecular catalyst precursors are the allylcobalt tris(trialkyl phosphite) and tris(trialkylphosphine) complexes which effect a totally selective *cis*-hydrogen addition as in the formation of all *cis*-$C_6H_6D_6$ from $C_6H_6 + D_2$, *cis*-dimethyl-cyclohexanes from any of the xytenes, cis-trimethylcyclohexane from mesitylene, and *cis*-decalin from napthalene [29]. The established mechanistic features of this catalytic system are schematically illustrated in Fig. 2 [39]. Here the mechanistic features require an all *cis* addition of hydrogen atoms. In fact, absence of an all-*cis* addition of hydrogen to an arene seems anomalous for any homogeneous or heterogeneous catalytic system unless there is an intermediate unbound cyclohexene product which is later converted either to a *trans* or *cis* cyclohexane. In some metal surface and one molecular coordination complex catalyzed arene hydrogenation reactions, there is evidence for free cyclohexene intermediates (products) but not for all [30]. This feature of less than full stereochemical selectivity (less than full all *cis* hydrogen addition) for some catalytic systems remains to be established on a molecular mechanistic basis.
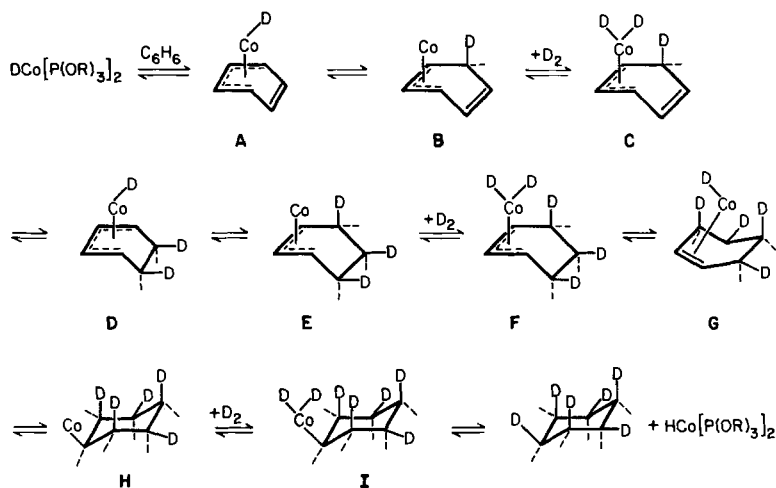
L_xM

$H_2 | RC{\equiv}CR$

$L_xM\big<^{C-^H_R}_{C-^H_R}$

15

$L_xM{=}C<^R_{CH_2R} \rightleftharpoons L_xM<^{C-^H_R}_{C-^R_H}$

Fig. 2. Reaction cycle for the hydrogenation of aromatic hydrocarbons catalyzed by the η^3-$C_3H_5Co[P(OR)_3]_3$ catalyst precursor. The active catalyst species is actually $HCo[P(OR)_3]_2$. Shown above are the key reaction steps in the hydrogenation cycle. The cycle requires an all-*cis* addition of hydrogen atoms to the ring. A complete discussion of the reaction mechanism is presented in reference 30.

All catalysts, surfaces or molecular species, with the exception of one class of molecular catalysts, selectively hydrogenate the alkene if presented with a reaction mixture of hydrogen, an alkene and an arene such as benzene [31]. The exceptional class is the aforementioned allylcobalt tris(trialkyl phosphite) and tris(trialkylphosphine) complexes. The key catalyst intermediate in this exceptional class is $HCo[P(OR)_3]_2$ or $HCo[PR_3]_2$, a fourteen-electron complex, which can complex an olefin, a diene or an arene (as an n^4-ligand)—and, in fact, there is with these catalysts a nearly equivalent rate of olefin and arene hydrogenation for hydrogen, olefin, and arene reaction mixtures [31].

The selective hydrogenation of olefins in olefin—alkyne reaction mixtures in all other homogeneous or heterogeneous catalytic systems cannot be fully explained with the presently available data. Our research is presently focused on the metal surface catalyzed reactions in an attempt establish the key features that lead to selective olefin hydrogenation for olefin—arene reaction mixtures. The only experimental finding of significance we can presently report is that neither do olefins displace benzene chemisorbed on clean or 'dirty' (carbon) nickel or platinum surfaces nor does benzene displace olefins chemisorbed on these same surfaces; there is a co-chemisorption of benzene and olefin [24]. However, these studies were done under ultra high vacuum conditions where the activity of H on the surface is low. Speculation, at this stage of our knowledge, would not appear to be constructive in regard to the mechanistic features of selective olefin hydrogenation for olefin—arene mixtures catalyzed by metal surfaces.

Acknowledgements

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