Stereochemistry of H₂ Oxidative Addition and Dihydride-Transfer Reactions Involving Iridium(I) Complexes

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I. Introduction

Hydride complexes of the transition metals are of great interest because of their unusual reactivity[1] and their potential as homogeneous catalysts.[2] Because it is one method of generating metal hydride complexes and is an essential step in homogeneous hydrogenation and hydroformylation reactions, the oxidative addition of H₂ to transition-metal complexes has been intensively studied. In spite of this intensive study, the factors that control the stereoselectivity of H₂ addition are not clearly understood. The major part of this article is an attempt to analyze the factors that influence the stereoselectivity of H₂ oxidative addition to d⁸ square-planar transition-metal complexes by examining H₂ addition to complexes of the type IrX(CO)P₂. A later section of this review will discuss a different aspect of iridium(I) chemistry, namely the ability of IrX(CO)-(dppe) to abstract dihydrogen from metal polyhydride complexes by dihydride transfer and the relationship of this dihydride transfer to H₂ oxidative addition.

## II. Stereochemistry of H₂ Oxidative Addition

A. Vaska's Complex

The classic example of oxidative addition to a d⁸ square-planar complex is the facile and reversible reaction of H₂ with *trans*-IrCl(CO)(PPh₃)₂, Vaska's com-

plex, forming IrH₂Cl(CO)(PPh₃)₂ (eq 1).[3] This reaction
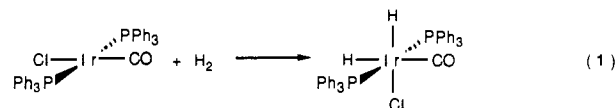
and the reaction of compounds of the general type *trans*-IrX(CO)P₂, where P is a tertiary phosphine ligand, have been the subject of intensive mechanistic study over the past 25 years, principally aimed at determining the kinetic and thermodynamic parameters of the reaction as a function of X and P.[4,5] The generally accepted mechanism, based on experimental and theoretical studies,[4-10] involves a concerted cis addition of H₂ along one of the ligand axes corresponding to a diagonal of the square-planar complex, as shown in eq 2. Addition along one diagonal or the other can lead
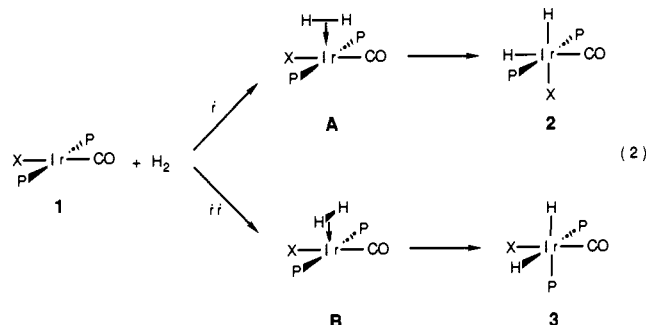
to the formation of two stereochemically different cis-dihydride products, but only the product with stereochemistry 2 is observed for IrH₂Cl(CO)(PPh₃)₂, as in eq 1. The cis disposition of the hydride ligands is unambiguously established by IR and ¹H NMR spectroscopic studies.[4] Kinetics studies show the reaction to follow clean second-order behavior, the rate law having a first-order dependence on the concentrations of both IrCl(CO)(PPh₃)₂ and H₂,[5] with a value for the second-order rate constant (k_2) of 0.93 M⁻¹ s⁻¹ in benzene at 30 °C.[5a] The reaction of IrCl(CO)(PPh₃)₂ with H₂ in benzene has an activation enthalpy ($\Delta H^\ddagger$) of 10.8 kcal/mol and an activation entropy ($\Delta S^\ddagger$) of −23 eu,[5a] this moderately negative value of $\Delta S^\ddagger$ being similar to that observed for substitution reactions in square-planar compounds. The small kinetic isotope affect observed for this reaction indicates little H–H bond breaking in the transition state ($k(H_2)/k(D_2) = 1.22$).[5a,k] On the basis of these and other observations, the addition is proposed to occur in a concerted manner involving a transition state resembling C, with the degree of trans ligand bending uncertain. While Vaska views the transition state as product-like,[5b] the reaction is exo-
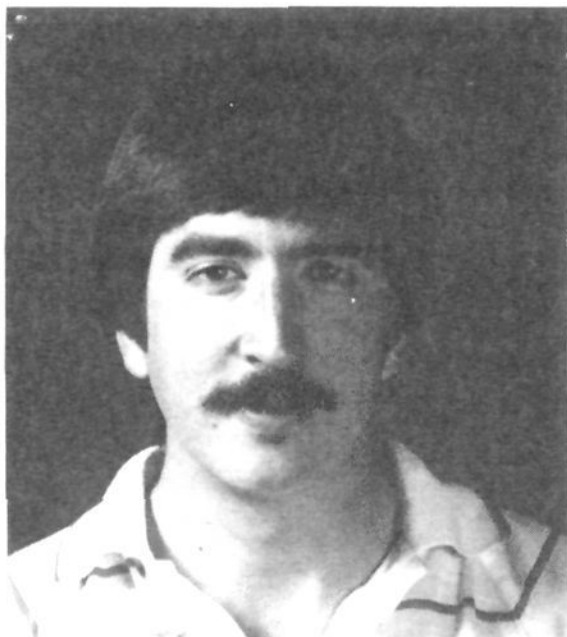
Paul Deutsch was born in Allentown, PA, in 1959 and received a B.S. degree in chemistry from Lehigh University in 1981. After spending 2 years at Air Products and Chemicals, he returned to Lehigh, where he received a M.S. in 1985 (with K. Klier). He then went on to continue studies toward a Ph.D. at the University of Rochester, where he won Sherman Clarke (1985–1988) and Elon Huntington Hooker (1987–1988) Fellowships.
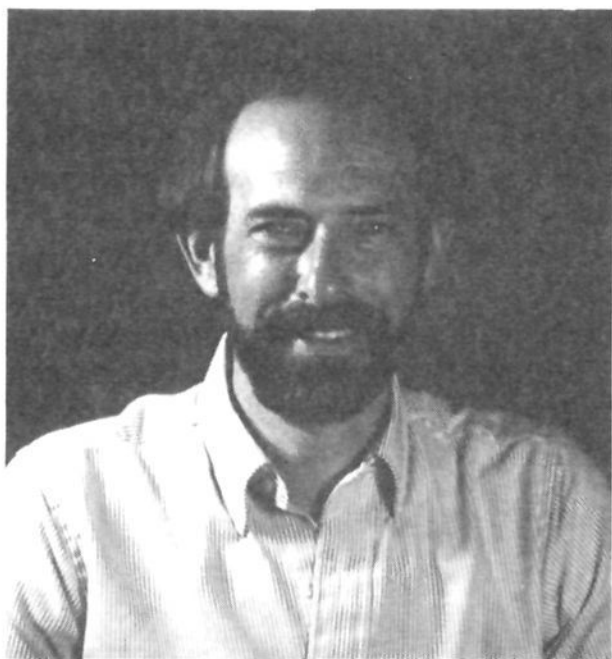
Rich Eisenberg was born in New York City in 1943 and graduated from Columbia University in 1963. After receiving a Ph.D. in 1967, also from Columbia, he joined the faculty at Brown University. He subsequently moved to the University of Rochester in 1973. Professor Eisenberg was an Alfred P. Sloan Fellow (1972–1974) and a John S. Guggenheim Fellow (1977–1978). He has served as Chairman of the Organometallic Subdivision of the Inorganic Division of the ACS (1982) and currently serves as a Councilor for the Inorganic Division of the ACS and as a member of the PRF Advisory Board. His research interests include the interaction of small molecules such as H_2, CO, CO_2, silanes, and unsaturated organic species with platinum group metal complexes, structure–function relationships in catalytically active systems, binuclear complexes, and catalysis of the reduction of CO_2.

$$H\text{---}H$$
$$Ir$$

C
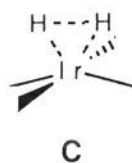
thermic ($\Delta H° = -14$ kcal/mol in chlorobenzene at 30 °C) and an earlier transition state seems more likely based on the Hammond postulate.[15]

B. H_2 Addition to *trans*-$IrX(CO)P_2$ Complexes

Many studies on the oxidative addition of H_2 to *trans*-$IrX(CO)P_2$ have focused on varying the halogen

X and the tertiary phosphine P and assessing their influence on the rate and stereochemistry of the reaction.[4-9] A wide variety of complexes have been studied, with X as a halogen or pseudohalogen (X = Cl, Br, I, NCO, NCS, N_3, NO_3, $SnCl_3$) and P as a triaryl, trialkyl, or mixed phosphine (PR_3 with R = C_6H_5, p-$C_6H_4CH_3$, m-$C_6H_4CH_3$, o-$C_6H_4CH_3$, p-$C_6H_4OCH_3$, p-C_6H_4F, p-C_6H_4Cl, C_6F_5, OC_6H_5, C_6H_{11}, i-$CH(CH_3)_2$, $CH_2C_6H_5$, C_4H_9, C_2H_5, and CH_3; $PR_2R' = P(C_6H_5)_2(C_4H_9)$, $P(CH_3)_2(C_6H_5)$, $P(C_2H_5)_2(C_6H_5)$, $P(CH_3)_2(o\text{-}C_6H_4OCH_3)$).[5] These reactions proceed along pathway i of eq 2, such that the phosphine ligands maintain their trans disposition.

In these studies it was found that the reactivity of the Ir(I) square-planar complex generally increases with increasing electron richness of the metal center. The carbonyl stretching frequency (ν_{CO}) of these complexes *trans*-$IrX(CO)P_2$ is a measure of this electron richness, which for lack of a better term is usually called metal basicity, and is a function of both X and P. For example, the second-order rate constants for H_2 addition were found to increase in the order Cl < Br < I ($k_2 = 0.93$, 14.3, and $>10^2$ M^{-1} s^{-1}, respectively, for X in $IrX(CO)(PPh_3)_2$[5a] at 30 °C in benzene)[5a] and $P(C_6F_5)_3 < P(C_6H_5)_3 < P(p\text{-}C_6H_4CH_3)_3 < P(p\text{-}C_6H_4OCH_3)_3$ ($k_2 = 0$, 1.2, 1.7, and 2.1 M^{-1} s^{-1}, respectively, for PR_3 in $IrCl(CO)(PR_3)_2$ at 30 °C in chlorobenzene).[5b]

The free energy for the oxidative addition reaction was found to be small, which is consistent with the reversible nature of the reaction ($\Delta G° = -6.3$, -7.6, and -11 kcal/mol for X = Cl, Br, I, respectively, in $IrX(CO)(PPh_3)_2$ at 30 °C in chlorobenzene).[5b] The reaction enthalpy was typically also small whereas the reaction entropy was consistently a relatively large negative value ($\Delta H° = -14$ kcal/mol, $\Delta S° = -26$ eu for $IrCl(CO)(PPh_3)_2$).[5b]

The observation of increasing reactivity with increasing metal basicity led Vaska to propose that donation of electron density from Ir(I) to the H_2 substrate is the controlling interaction in the oxidative addition process and that the addition of H_2 is oxidative in character with respect to the metal.[5b]

In addition to the above electronic effects, steric effects have been observed to greatly influence reactivity. A case in point is a study by Vaska and co-workers in which $IrCl(CO)(P(o\text{-tol})_3)_2$ was found to be unreactive toward H_2 addition whereas $IrCl(CO)(P(p\text{-tol})_3)_2$ reacted readily.[5j] Similarly, while $IrCl(CO)(P(C_6H_{11})_3)_2$ should be very reactive toward H_2 based upon high metal basicity, steric hindrance led to low reactivity ($k_2 = 0.0034$ M^{-1} s^{-1} for $IrCl(CO)(P(C_6H_{11})_3)_2$ vs 1.2 M^{-1} s^{-1} for $IrCl(CO)(PPh_3)_2$).[5b,j]

Examples of H_2 addition along pathway ii of eq 2 are also known. The complex $Ir(\sigma\text{-carb})(CO)(PPh_3)_2$, where σ-carb = 1,2- and 1,7-dicarbo-*closo*-dodecaborane(12), has been reported to add H_2 along both pathways of eq 2 to give initially both possible products in moderately polar solvents, with subsequent isomerization to yield only the isomer from pathway i, indicating that the reaction proceeds under kinetic control.[6] Steric factors arising from use of the bulky σ-carborane ligand were cited as influencing the course of this reaction.

Harrod has also observed products from both possible addition pathways. The reactive four-coordinate intermediate "$IrH(CO)(PPh_3)_2$", generated in situ from

the corresponding styrene or triphenylphosphine adducts, reacts rapidly with H_2 to produce both *fac*- and *mer*-trihydride species (eq 3).[7] When the reaction was

$$ \text{(3)} $$

L = PPh₃, C₆H₅CH=CH₂
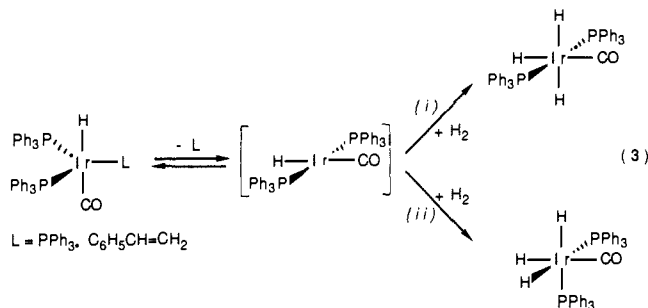
performed at -30 °C under D_2, the stereochemistry of the $IrHD_2(CO)(PPh_3)_2$ products was found to be consistent with cis concerted addition along paths i and ii of eq 2. Clearly the steric factors that were invoked for the σ-carborane system cannot be used to account for the difference in stereochemistry here. It was further observed that H/D scrambling occurred in the trihydrides at room temperature. This was explained in terms of formation of hydride-bridged binuclear species and will be discussed below in the context of dihydride transfer.

Recently, Crabtree and co-workers investigated H_2 oxidative addition to Vaska type complexes containing PMe_3 as the tertiary phosphine and σ-bonded alkyl and aryl ligands in place of halide.[8] They observed that addition of H_2 to $Ir(Ph)(CO)(PMe_3)_2$ at -80 °C produces $IrH_2(Ph)(CO)(PMe_3)_2$ along pathway ii, with isomerization to the other dihydride isomer occurring as this solution is warmed to room temperature (eq 4). Sim-

$$ \text{(4)} $$
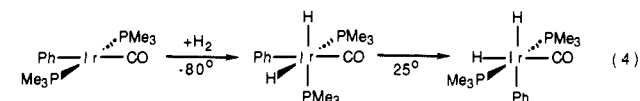
ilarly, reaction of $Ir(Me)(CO)(PMe_3)_2$ gives only the *cis*-dihydride having stereochemistry 3. At -80 °C, H_2 reacts with $Ir(Me)(CO)(PPh_3)_2$ along pathway ii to produce $IrH_2(Me)(CO)(PPh_3)_2$, which eliminates methane and reacts further with H_2 to produce *fac*-$IrH_3(CO)(PPh_3)_2$ as the solution is allowed to warm.[9] Replacement of the H_2 atmosphere over solutions of $IrH_2(Me)(CO)(PPh_3)_2$ with D_2 allowed the stereochemistry of D_2 addition to "$IrH(CO)(PPh_3)_2$" to be unambiguously determined. As shown in eq 5, the product arises from addition along pathway ii of eq 2.

$$ \text{(5)} $$
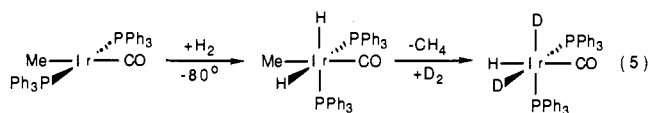
It is clear from these studies that preference for the reaction to proceed by one pathway over the other is a consequence of both electronic and steric factors that can change dramatically as the ligands X and L are varied. These factors thus control the stereochemistry of oxidative addition, and much effort is now being directed to elucidate them.

C. Factors Affecting Oxidative Addition of H₂

In terms of specific orbital interactions, three primary electronic interactions occur between the incoming H_2

molecule and the d^8 metal complex in the oxidative addition reaction.[10,11] The first interaction, shown as D, involves a σ donation from the bonding σ orbital of
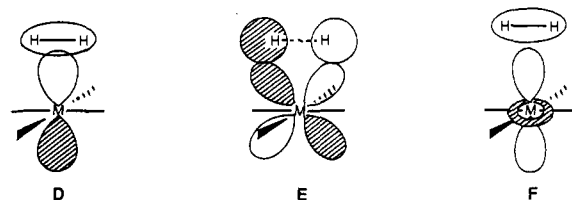
H_2, $\sigma(H_2)$, into the vacant p_z or p_z-d_{z^2} metal-centered acceptor orbital. The second, E, is a back-bonding interaction in which electron density from the filled metal d_{xz} or d_{yz} orbital is transferred into the antibonding orbital of H_2, $\sigma^*(H_2)$. Both of these interactions serve to weaken the H–H bond while creating M–H bonds. The third interaction, F, is a four-electron repulsive interaction between the filled σ orbital of H_2 and the filled d_{z^2} orbital on the metal center. While this third interaction does not affect the bonding in the dihydride product, it does contribute to the activation energy barrier of the reaction by its repulsive nature.

The ligands that surround the metal center can significantly affect the aforementioned orbital interactions. The relative σ-donor capacity of the ligands can raise or lower the energy of the p_d and d_{z^2} orbitals in the square-planar complex, thereby affecting the extent of interactions D and F but not discriminating between addition along pathway i or ii of eq 2. Ligands having π-acceptor (or π-donor) capabilities interact with and split the degeneracy of the metal d_{xz} and d_{yz} orbitals, which can lead to discrimination between the two pathways. However, experimental[5] and theoretical[10] studies indicate that in the transition state for this reaction, the metal complex is no longer square planar but rather has a pair of trans ligands that are bent away from the incoming H_2 molecule to some extent, as in C. At this point, the σ-donor and π-acceptor (or π-donor) capacities of the ligands in the bending plane can affect all three orbital interactions, D, E, and F. Determining which interaction affects the direction of H_2 addition most is difficult since the problem involves comparison of both σ and π effects of one pair of initially trans ligands with those of the other pair on the three orbital interactions D–F in an activated complex of uncertain geometry.

The ligands surrounding a metal center may also influence the path that the reaction follows due to steric repulsions between ligands and the incoming substrate. These steric interactions, which are most pronounced for phosphine ligands, have been described by Tolman in terms of ligand cone angles.[12] The ease with which one can compare the steric effects of the ligands is of limited help since experimental evidence seems to indicate that steric factors play a much smaller role than electronic factors in the stereochemistry of H_2 addition.

It is evident from these and other studies that there exists much difficulty in evaluating the individual ligand effects that determine the stereochemical outcome of the oxidative addition of H_2 to *trans*-$IrX(CO)P_2$. The widely varying electronic and steric effects of the three ligands, X, CO, and P make a precise analysis of ligand influences in the H_2 + *trans*-$IrX(CO)P_2$ reaction system very difficult. However, changing the square-planar geometry from trans phosphine donors to cis

renders the analysis more tractable.

## D. Stereochemistry of H₂ Addition to Cis Analogues of Vaska's Complex

With cis phosphine analogues of $IrX(CO)P_2$, the influence of the phosphine ligands, P, in H_2 oxidative addition can essentially be eliminated and the ligand effects of X versus CO can be probed directly. As with trans-$IrX(CO)P_2$, two possible pathways for H_2 addition to cis-$IrX(CO)P_2$ exist, the stereochemical consequences of which are shown as pathways iii and iv in eq 6. In

$$(6)$$
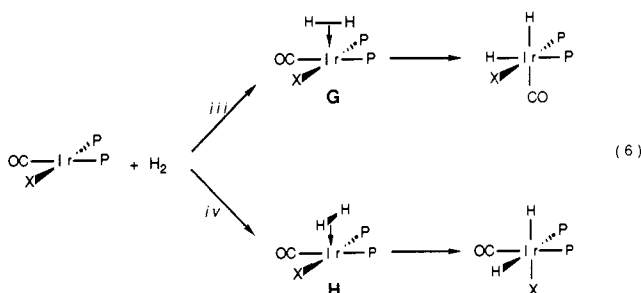
each of the two possible dihydride products, one hydride ligand is trans to one phosphine while the other hydride ligand is cis to both phosphines. Therefore, the phosphine ligands in cis-$IrX(CO)P_2$ exert the same influence on the H_2 substrate regardless of the pathway followed, iii or iv.

In order to prepare cis phosphine analogues of Vaska's complex, a chelating di(tertiary phosphine) ligand such as 1,2-bis(diphenylphosphino)ethane (dppe) is employed. By studying the stereochemistry of H_2 oxidative addition to the cis phosphine complexes IrX-(CO)(dppe), Eisenberg and co-workers have analyzed more fully the electronic and steric effects of the X and CO ligands.[13] In catalytic reactions, these influences go beyond simple oxidative addition since different dihydride isomers can display different reactivities. Therefore, control of the stereochemistry of H_2 oxidative addition leading to different dihydride intermediates may be important in controlling the rate and stereochemistry of the subsequent hydrogenation reaction.

The reaction of H_2 with the d^8 square-planar complexes IrX(CO)(dppe), where X = Cl (4a), Br (4b), or I (4c), has been found to produce sequentially the isomeric dihydrides 5a–c and 6a–c (eq 7).[13] These

$$(7)$$
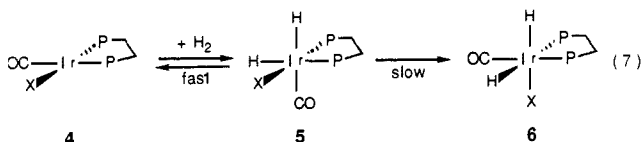
complexes are readily identified and distinguished by ^1H NMR spectroscopy. All of the isomers contain two different hydride resonances in their respective ^1H NMR spectra, one resonance showing both cis- and trans-phosphorus couplings. The chemical shifts of the hydride resonance showing only cis-P coupling is definitive for the nature of the ligand trans to that hydride (X vs CO), thus making the stereochemical assignment complete based on the ^1H NMR spectrum alone; see Figure 1. However, further evidence for the assignment is obtained from IR spectroscopy and is confirmed by an X-ray crystal structure of complex 6b.[13c]
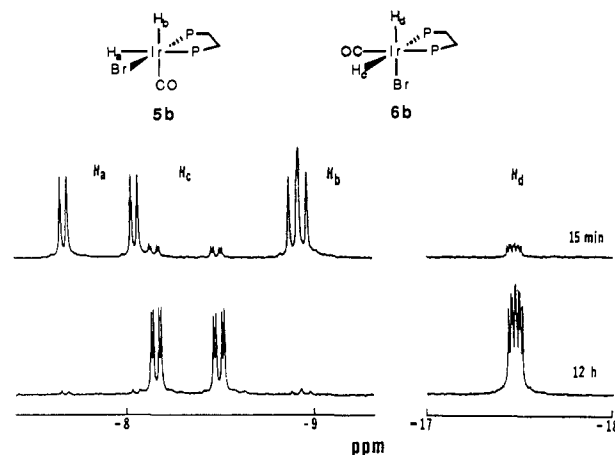

Figure 1. ^1H NMR spectra (400 MHz) in the hydride region for the reaction IrBr(CO)(dppe) (4b) with H_2 in benzene solution.
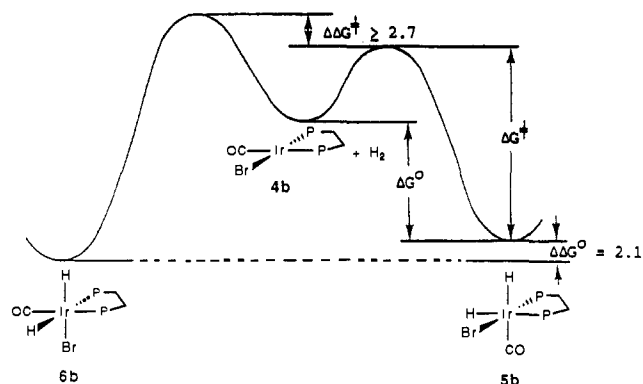

Figure 2. Reaction coordinate diagram for the system IrBr-(CO)(dppe) + H_2. Values in kcal/mol.

The reaction of H_2 with 4a–c to form the initial dihydrides 5a–c occurs rapidly and with >99% stereoselectivity. This facile reaction is readily reversible, as indicated by formation of 4a–c when solutions of 5a–c are placed under vacuum and by rapid formation of 5a–c-d_2 when the H_2 atmosphere above the solutions is replaced by D_2. The reaction of H_2 with 4a–c thus proceeds under kinetic control with initial stereoselective formation of 5a–c followed by isomerization to give 6a–c over time. A thermodynamic equilibrium between 5 and 6 is eventually reached, with K = 41, 35, and 13 for X = Cl, Br, and I, respectively. The initial >99% stereoselectivity toward formation of 5 over 6 indicates that H_2 oxidative addition to 4 via pathway iii is kinetically favored over pathway is by >2.7 kcal/mol $(\Delta\Delta G^\ddagger)$, but the final equilibrium ratio K = 35 for X = Br indicates that 6b is thermodynamically more stable by $\simeq$2.1 kcal/mol $(\Delta\Delta G^\circ)$; see Figure 2.

The cyano complex Ir(CN)(CO)(dppe) (4d) also reacts rapidly with H_2 to form initially only the cis-dihydride isomer resulting from addition along pathway iii. With time, this isomer, 5d, slowly equilibrates with two other dihydride isomers, 6d and 7d, to give a final equilibrium composition of 89% 5d, 5% 6d, and 6% 7d.

$$(8)$$
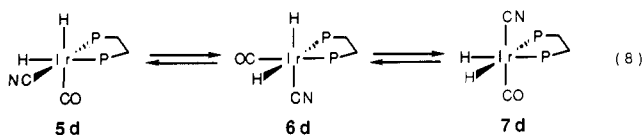
The addition of H_2 to Ir(CN)(CO)(dppe) is therefore

similar to that of the halide complexes from a kinetic standpoint with initial, stereospecific formation of an isomer of type **5**, but it differs in that **5d** is also thermodynamically preferred.

The very reactive complex "IrH(CO)(dppe)" (**4e**) can be generated in situ by either photolysis or thermolysis of solutions of IrH₃(CO)(dppe) or IrH(CO)₂(dppe). To produce "IrH(CO)(dppe)" in a manner suitable for following its H₂ oxidative addition, complex **4e** was produced by low-temperature dehydrohalogenation of **6b** and was reacted in situ with D₂. Predominant

$$(9)$$
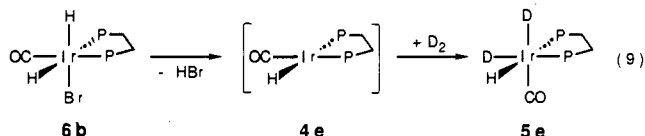
formation of the facial trihydride complex IrHD₂-(CO)(dppe) was observed, corresponding to D₂ addition along pathway iii only. Subsequent rearrangement in IrHD₂(CO)(dppe) led to randomization of the H/D positions, but no isomer having stereochemistry corresponding to **6** was ever observed. In this respect, the hydride and cyanide complexes are similar. Small amounts of the d_0 isotopomer of IrH₃(CO)(dppe) (**5e**) and the bromo complex **5b** were also observed to form in this reaction by dihydride transfer of the type discussed below involving IrH(CO)(dppe) and the thermodynamic dihydride isomer **6b**.

The cationic complex Ir(PPh₃)(CO)(dppe)⁺ (**4f**), in which X is replaced by triphenylphosphine, also undergoes stereoselective oxidative addition of H₂ along pathway iii to form IrH₂(PPh₃)(CO)(dppe)⁺ (**5f**) exclusively. This product is both the kinetically and thermodynamically preferred isomer; no product having stereochemistry for H₂ addition along pathway iv is observed by ¹H NMR spectroscopy.

$$(10)$$
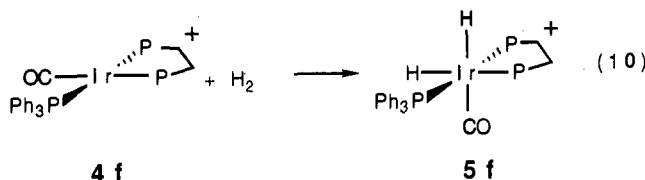
E. Basis for Stereoselectivity of H₂ Addition

The complexes IrX(CO)(dppe) for X = Cl, Br, I, CN, H, and PPh₃ all undergo stereoselective oxidative addition of H₂, with pathway iii of eq 6 the kinetically preferred channel. The same stereoselectivity has also been reported for the analogue with X = 7-phenyl-1,7-dicarbo-*closo*-dodecaborane (**4g**).[14] The concerted cis oxidative addition of H₂ to all of the complexes **4a–g** appears to occur by the same process, with the substrate molecule approaching so that the H–H bond axis is parallel to the P–Ir–CO diagonal of IrX(CO)(dppe), shown as I. The approach and reaction along this

I
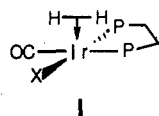
diagonal of IrX(CO)(dppe) as opposed to the X–Ir–P diagonal are favored by at least 2.7 kcal/mol based upon the >99% stereoselectivity observed for the reaction.

It should again be noted that the stereoselectivity of H₂ oxidative addition is a kinetic phenomenon, with subsequent isomerization of the kinetic isomers **5a–c** to the more stable isomers **6a–c** indicating that the initial path for addition is not controlled by product stability.

As discussed earlier, the cis disposition of the phosphine ligands in the IrX(CO)(dppe) system requires the phosphines to exert the same influence on the incoming H₂ molecule regardless of the pathway of addition, thus making any stereoselectivity the result of steric and/or electronic effects of the X and CO ligands only. On the basis of the range of sizes for the X groups from the bulky carborane and PPh₃ to the much smaller CN and hydride ligands, steric effects do not appear to contribute significantly to the observed stereochemical preference for addition along pathway iii of eq 6. This preference must therefore be the result of electronic influences of X and CO, and their relative contributions to the σ donation, back-bonding, and four-electron repulsive interactions in H₂ oxidative addition shown as D, E, and F, respectively.

The σ-donation interaction, D, and the two-orbital, four-electron repulsion, F, do not in and of themselves have an influence on the stereoselectivity of H₂ addition since the metal orbitals involved, p_z and d_{z^2}, are cylindrically symmetric about the z axis, the direction of H₂ approach. The back-bonding interaction, E, however, could give rise to a preference for H₂ addition along pathway iii or iv of eq 6 since there are two separate and distinct metal-centered orbitals of appropriate symmetry for interaction with σ*(H₂). In IrX(CO)-(dppe), the two metal d_π orbitals, d_{xz} and d_{yz}, are not degenerate because of the lower symmetry of the complex resulting from the X and CO ligands bound to the metal center. The d_{yz} orbital (along the OC–Ir–P diagonal) is stabilized relative to the d_{xz} orbital (along the X–Ir–P diagonal) by the interaction of d_{yz} with the π* orbital on CO, K.[10] One would therefore expect d_{xz} to
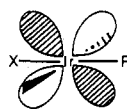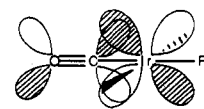
J   K

serve as a better π donor to σ*(H₂), resulting in preferential addition along the X–Ir–P diagonal. However, this is exactly opposite to what is observed, and a rationalization based on the back-bonding interaction, E, cannot be invoked to account for the stereoselectivity of H₂ addition.

Since the addition of H₂ to these complexes is exothermic, the transition state occurs early in the reaction and should be more reactant-like in character, as suggested by Hammond.[15a] For a square-planar d⁸ complex, the overall interaction of the metal center with the approaching H₂ molecule is repulsive due to a large contribution from interaction F between σ(H₂) and the filled metal d_{z^2} orbital. While the transition state should be reactant-like in character, a slight bending of a diagonal of the four-coordinate metal complex does not require high energy and according to Sevin[10b] and Hoffmann[10a] leads to an overall attractive interaction between H₂ and the metal center.

Changes in the previously described electronic interactions occur when a pair of trans ligands is allowed

to bend back. In the σ-bonding interaction, D, the metal acceptor orbital rehybridizes slightly, L, allowing for increased overlap with $\sigma(H_2)$. Deviation from
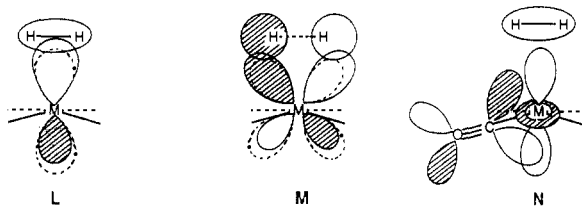
planar geometry leads to enhanced overlap in the back-bonding interaction, E, as well. Specifically, as a pair of trans ligands bends, their σ-donor orbitals begin to interact with the metal d_π orbital along the diagonal of bending. This results in destabilization and rehybridization of that metal orbital and leads to enhanced overlap between the metal d_π orbital and $\sigma^*(H_2)$, as shown in M. The increased π donation into $\sigma^*(H_2)$ that stems from this bending and rehybridization is proportional to the σ-donor strength of the ligands involved.

The repulsive interaction, F, can also be affected by bending of a pair of trans ligands. In the case where one of the trans ligands is a π acid, the ligand π^* orbital can interact with and withdraw electron density from the filled d_{z^2} orbital, shown as N. This will reduce the repulsion between $\sigma(H_2)$ and d_{z^2}, and thereby lower the activation barrier for the reaction.

This last interaction, N, appears to dominate in the IrX(CO)(dppe) system. Clearly, CO will be able to withdraw electron density from d_{z^2} because of its π acidity, leading to H_2 addition along the P–Ir–CO axis. The only ligand X that is a significant π acid is CN⁻, but it is weaker than CO in this regard, and addition occurs along P–Ir–CO preferentially. The back-bonding argument, M, would predict bending along the axis containing the two best σ-donor ligands, which would affect the involved metal d_π orbital most. This rationalization would lead to the prediction of H_2 oxidative addition along the X–Ir–P axis for X = H, PPh₃, and possibly CN, but this is not observed. Thus, while all of the influences are important and their interplay leads to the observed stereoselectivity of H_2 addition, it is reduction of the repulsive interaction via N that dominates in the IrX(CO)(dppe) complexes. A recent theoretical study by Jean and Lledos, using cis-RhX-(CO)(PH₃)₂ as a model complex, supports this conclusion.[10d]

## F. Cis Additions of Other Substrates as Stereochemical Probes

Further support for the basis of stereoselectivity in H_2 addition comes from a study of the oxidative addition of trialkylsilanes (R₃SiH) and hydrogen halides to the IrX(CO)(dppe) complexes.[16]

The oxidative addition of silanes to iridium(I) complexes has been well studied.[17,18] This reaction, which represents a required step in hydrosilation catalysis, proceeds as a concerted cis addition. In an elegant series of investigations, Harrod and co-workers studied silane oxidative addition to IrH(CO)(PPh₃)₃ (eq 11) stereochemically and kinetically.[17] Use of a deuteriated silane substrate showed unambiguously that silane addition to IrH(CO)(PPh₃)₂ proceeds in a cis manner.


$$(11)$$
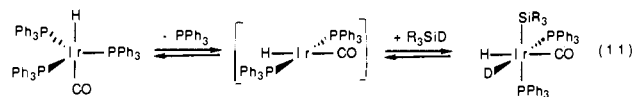
Through an analysis of the activation parameters of eq 11, they concluded that silane oxidative addition and phosphine addition are mechanistically similar processes with similar activation enthalpies. They proposed that this similarity is due to the notion that ΔH^* arises mainly from deformation of the square-planar complex prior to addition. Support for the concerted nature of Si–H oxidative addition comes from the work of Sommer et al., in which it was observed that the isotope exchange between optically active Si*–H and racemic Si–D catalyzed by IrCl(CO)(PPh₃)₂ occurs with complete retention of stereochemistry on the chiral silane.[18a]

The mechanism of hydrogen halide addition to IrCl(CO)(PPh₃)₂ and its analogues has also been investigated.[19,20] Vaska observed that gaseous hydrogen halide, HX′, oxidatively adds to trans-IrX(CO)(PPh₃)₂ in the solid state to form cis addition products.[19b]


$$(12)$$
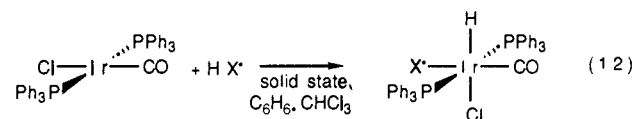
Blake and Kubota also found that the cis stereochemistry of addition is maintained for the reaction in benzene or chloroform solution but that mixtures of cis and trans HX′ addition products are formed in the presence of more polar solvents such as MeOH, MeCN, H_2O, and DMF.[20b] The stereochemistry and mechanism of HX′ addition to IrX(CO)P₂ thus depend on the reaction conditions, with cis addition occurring in nonionizing solvents and the solid state.
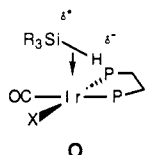
For the cis phosphine complexes IrX(CO)(dppe), the cis concerted oxidative addition of an unsymmetrical substrate HY can lead to the production of four different isomers, depending upon the orientation of the substrate and the pathway of addition (eq 13). Addition along the P–Ir–CO axis, pathway v, produces a diastereomer either with hydride trans to CO, 8, or with hydride trans to phosphine, 9, while addition along the P–Ir–X axis gives a product with hydride trans to X, 10, or hydride trans to phosphine 11.

$$(13)$$
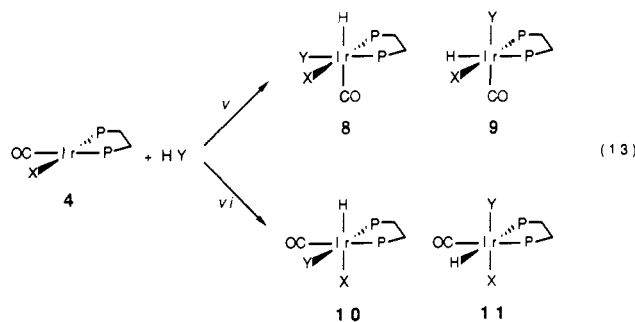
For trialkylsilane substrates, the oxidative addition to IrX(CO)(dppe) (X = Br, CN) proceeds stereospecifically along pathway v to give only isomer 8.[16] As with H_2, the reaction proceeds under kinetic control, with subsequent isomerization to the more stable 10 isomer occurring when X = Br (eq 14). The preference for geometry 8 as opposed to 9 is probably steric in
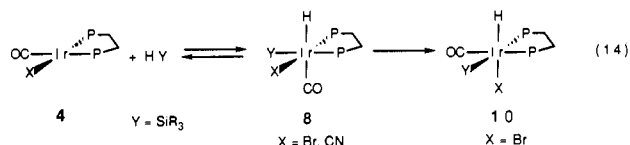
nature, involving minimization of nonbonding interactions between the silyl group and the phosphines. The steric interactions may also alter the approach of the Si–H bond and cause it to tilt, with the H end directed toward the metal center, indicated by O. This is con-


sistent with Harrod's view of silane oxidative addition as being similar to addition of an electron pair donor. The donor ability of the Si–H bond increases the importance of the σ-donation interaction from substrate to metal and the repulsive interaction between d_{z^2} and the donor Si–H orbital, while decreasing the importance of the back-bonding interaction in determining the stereochemistry of oxidative addition. Reduction of the four-electron repulsion, interaction F, thus appears to be the key factor in controlling the direction of addition along the P–Ir–CO axis.

Addition of hydrogen halides, HBr and HI, to IrX-(CO)(dppe) (X = Br, I) proceeds stereospecifically along pathway vi to give isomer 10, which is opposite to that obtained with H₂ and R₃SiH addition. While H₂ and
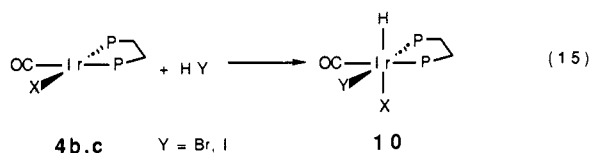
R₃SiH resemble two-electron donors and their approach to the metal center is nucleophilic, the hydrogen halides approach as electrophiles. This type of approach, shown as P, resulting from the "protic" nature of the
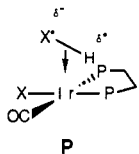

hydrogen in HX′, emphasizes the electronic interactions in which electron density is transferred from the metal to the substrate and decreases the importance of interactions in which electron density is transferred from substrate to the metal center. Bending of the complex along the diagonal containing ligands that can best enhance the donor ability of the metal center would thus be expected to control the stereoselectivity, and in fact does.

G. Stereoselective H₂ Addition in Other Systems

Fryzuk and MacNeil have recently been studying the chemistry of complexes containing a tridentate amido phosphine ligand, N(SiMe₂CH₂PPh₃)₂⁻, and have reported the results of the reaction of H₂ with the square-planar iridium(I) complexes Ir[N-

(SiMe₂CH₂PPh₃)₂]L, with L = PMe₃ (12a), CO (12b), and cyclooctene (12c).[21] The reaction of 12a with H₂ led to addition along the P–Ir–P axis, giving rise to 13 (eq 16). However, no reaction between 12b and H₂ was
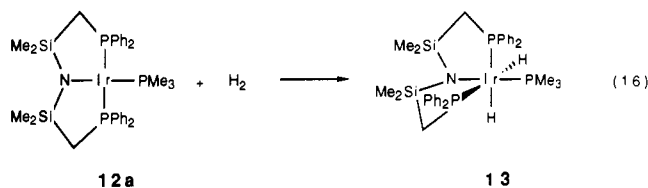

observed. The reaction of 12c led to novel chemistry involving what is proposed to be ligand-assisted heterolytic splitting of H₂. In benzene solution, 12c reacted with excess H₂ to produce free cyclootene and 14, which could be reversibly converted to 15 by removal of H₂ (eq 17). The reaction of 12c with H₂ in pentane led
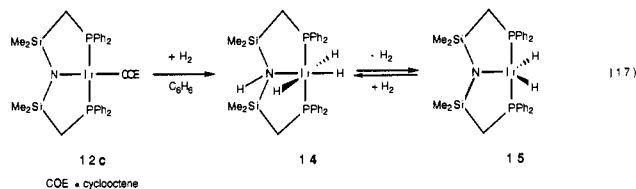
to formation of 16, the *fac* isomer of 14, and cyclooctene. Upon dissolution of 16 in benzene, slow conversion to 14 was observed (eq 18), which was proposed to occur by elimination and addition of H₂. Complex 15, which
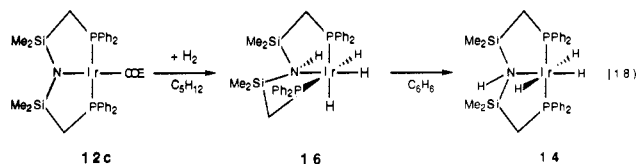
is a coordinatively unsaturated iridium(III) complex, was observed to react with added PMe₃ or CO to form 17 according to eq 19. It is of interest to note that the geometry of 17a, L = PMe₃, is different from that observed in the reaction of 12a with H₂. Also, while no reaction was found to occur between 12b and H₂, 17b is readily formed.
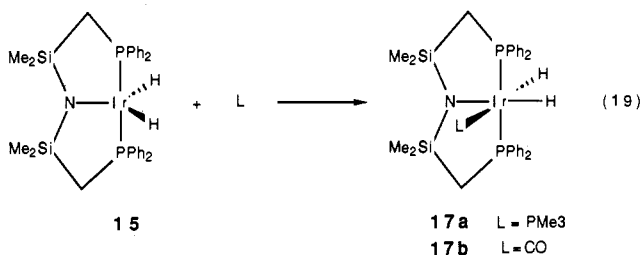
In their studies involving homogeneous hydrogenation of olefins and catalyzed by Ir(COD)LL′⁺, Crabtree and co-workers have been able to isolate and characterize a number of dihydride–olefin complexes of the type IrH₂(COD)LL′⁺ (COD = 1,5-cyclooctadiene; L, L′ = PR₃, pyridine, RCN, etc.).[22] Because of the cis disposition of the olefin groups of the cyclooctadiene ligand about the metal center, the steric and electronic influences of the COD ligand are eliminated as they are for the dppe ligand in the IrX(CO)(dppe) complexes discussed above. The addition of H₂ to Ir(COD)(PPh₃)-(RCN)⁺ (R = CH₃, C₆H₅, p-CH₃OC₆H₄, p-NO₂C₆H₅) at −80 °C in CD₂Cl₂ was reported to give only the di-

hydride complex 19, shown in eq 20, resulting from H_2

(20)

18   **19**
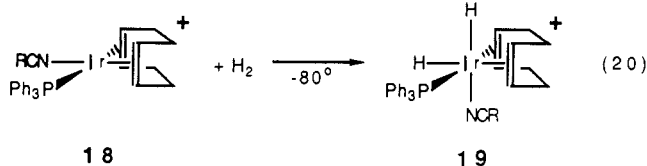
addition along the olefin–Ir–NCR diagonal of 18.[22e] In contrast to the IrX(CO)(dppe) complexes, H_2 addition to these cationic Ir(I) complexes 18 occurs with bending of the complex diagonal containing the weaker π acid, RCN being a weaker π acid than PPh_3. While steric factors may have an influence on the course of H_2 addition to 18, they can be essentially eliminated in Ir-(COD)LL$'^+$ by carefully choosing L and L$'$. The H_2 oxidative addition to $Ir(C_8H_{12})(Ph_2POCH_2CH_2PPh_2)^+$ (20) was examined by Crabtree and Uriarte,[22f] with formation of only the cis-dihydride product 21 observed to occur (eq 21). The steric influence of the two ends

(21)

20   **21**
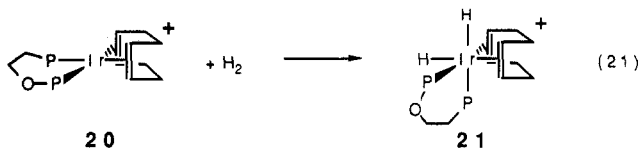
of this chelating phosphine ligand should be similar, but the relative electronic effects will differ and thus account for the stereoselectivity of H_2 addition. Addition of H_2 occurs along the complex diagonal containing the phosphine end ($Ph_2PCH_2^-$) of the chelating ligand, the phosphine being a weaker π acceptor than the phosphinite (Ph_2PO^-). The stereoselectivity of H_2 addition to these complexes is opposite to that observed for the IrX(CO)(dppe) complexes discussed above, and it has been suggested that the electronic interaction between the metal d_π orbital and $\sigma^*(H_2)$, as in M, governs the reaction.[22f,8] On the basis of spectroscopic data and reactivity patterns, Crabtree has suggested that H_2 addition to $Ir(COD)LL'^+$ is reductive in character with respect to the metal center, and not oxidative as with $IrX(CO)L_2$ and $IrX(CO)(dppe)$.[22a] This difference in the nature of H_2 addition may account for the different interactions M and N giving rise to the stereoselectivities for H_2 addition to $Ir(COD)LL'^+$ and $IrX(CO)$-(dppe), respectively.

One of the most elegant applications of homogeneous catalysis is the synthesis of chiral organic products from nonchiral starting materials using transition-metal complexes containing chiral phosphine ligands. The greatest success along these lines has been in the asymmetric hydrogenation of (acylamino)cinnamic or -acrylic acids or esters using rhodium(I) complexes containing chiral chelating bis(phosphine) ligands.[23] Intensive investigation of this reaction has led to a proposed mechanism involving (a) olefin coordination to the metal center, (b) oxidative addition of H_2 to give an olefin–dihydride complex, (c) addition of one hydrogen atom to the bound olefin to give a σ-alkyl-hydrido–metal intermediate, and (d) reductive elimination of the alkane and regeneration of the active catalyst species; see Scheme I. In studies involving the hydrogenation of phenylalanine precursor substrates using $Rh(chiraphos)S_2^+$ as a catalyst, where chiraphos is $(2S,3S)$-bis(diphenylphosphino)butane, it has been

SCHEME I. Proposed Mechanism for the Asymmetric Hydrogenation of Methyl (Z)-α-Acetamidocinnamate Catalyzed by $(Rh[(R,R)$-dipamp])$^{+}$[23a]

P * P = (R,R)-1,2-bis(o-methoxyphenylphenylphosphino)ethane
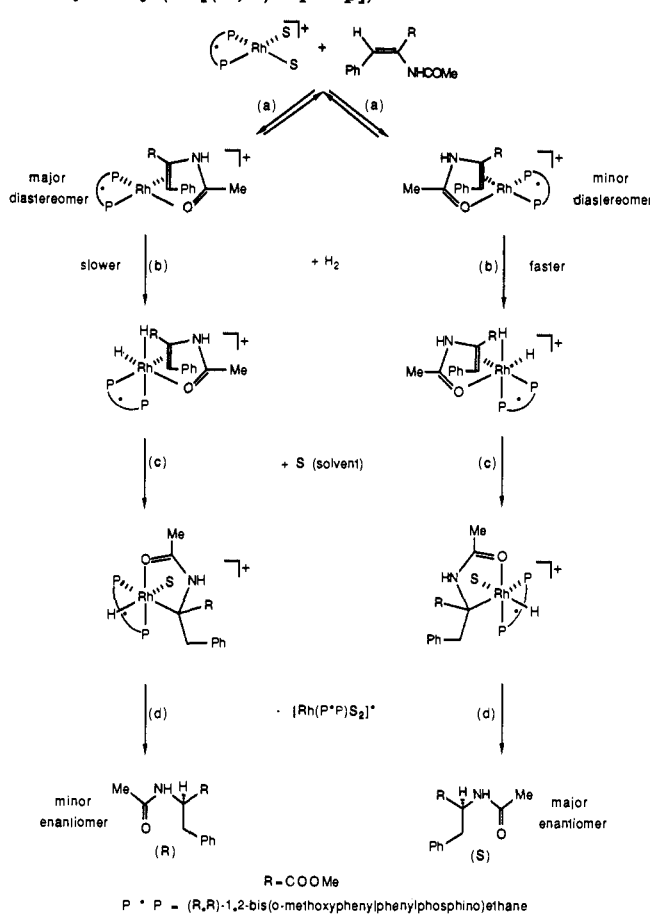
found that the predominant Rh(chiraphos)(substrate)$^+$ diastereomer observed in solution (>95%) does not correspond to the diastereomer that would yield the correct enantiomer of the observed phenylalanine type product. It has therefore been suggested that the first irreversible step, the oxidative addition of H_2 to Rh-(chiraphos)(substrate)$^+$ species, is the enantioselective step.[24] The asymmetric hydrogenation catalysis thus proceeds under Curtin–Hammett control, with the two diastereomers of Rh(chiraphos)(substrate)$^+$ in rapid equilibrium and the minor diastereomer reacting with H_2 more rapidly to give rise to the predominant product enantiomer. However, while H_2 oxidative addition is the enantioselective step in the catalysis, the olefin-dihydride species resulting from it has not been directly observed.

Toward this end, Brown and Maddox[25] have investigated Ir(dipamp)(substrate)$^+$ complexes (dipamp = 1,2-bis((o-anisylphenyl)phosphino)ethane) and their reactions with H_2 to allow observation of stable analogues of the dihydride–olefin intermediates and subsequent alkyl hydrides. The stereochemistries of these model compounds were established by using a variety of NMR spectroscopic techniques.

In the first of two studies,[25a] the substrate employed was the (S)-menthyl ester of α-acetamidocinnamate. The two diastereomers 22a and 22b were prepared independently and each was reacted at low temperature with H_2. For the more stable diastereomer, 22a, the conversion to the alkyl hydride 23a occurred slowly with no discernible intermediates, while for 22b the reaction
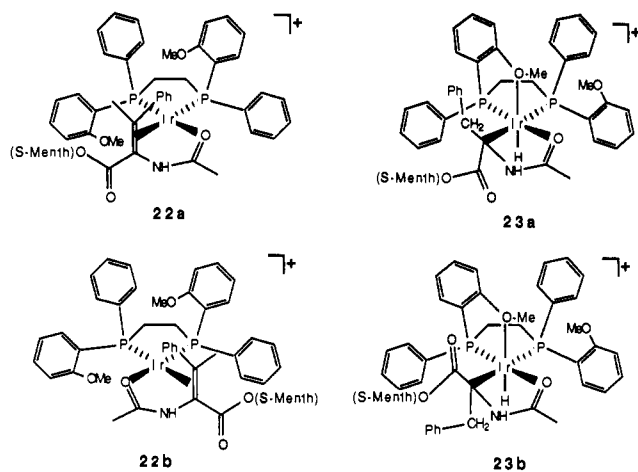
with H₂ at -70 °C was rapid, leading to initial formation of two transient alkyl hydrides in a 6:1 ratio followed by conversion to **23b** at -40 °C. A key difference between **23a** and **23b** is the relative positions of the benzyl group and the Ir hydride ligand; in **23a** the benzyl group and hydride ligand are on opposite sides of the iridium bis(phosphine) plane whereas in **23b** they are on the same side. This structural feature and the slowness in forming **23a** indicate that **23a** does not form simply by H₂ oxidative addition and olefin insertion without some rearrangement. The faster reaction of **22b** with H₂ and the 6:1 ratio of alkyl hydride intermediates leading to **23b** provide evidence that the minor diastereomer, **22b**, is the more reactive one, in accord with Scheme I, and that diastereoselective H₂ oxidative addition is occurring. However, the intermediate olefin–dihydride complexes were still not observed, and the factors controlling the stereoselectivity of H₂ addition could not be analyzed.

In the second study employing a different substrate, Brown and Maddox[25b] prepared complex **24** and, upon its reaction with H₂ (eq 22), observed dihydrides **25a**
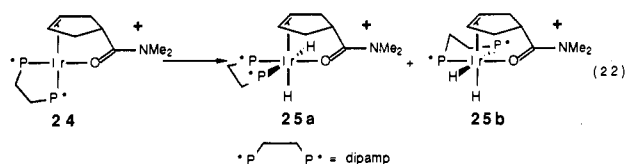
and **25b**, indicating stereoselective H₂ oxidative addition. Complexes **25a** and **25b** are diastereomers formed by H₂ oxidative addition along the P–Ir–olefin axis. The isomeric dihydrides corresponding to addition along the P–Ir–O axis, **26a** and **26b**, form subsequently (eq 23) and are apparently more stable, although further
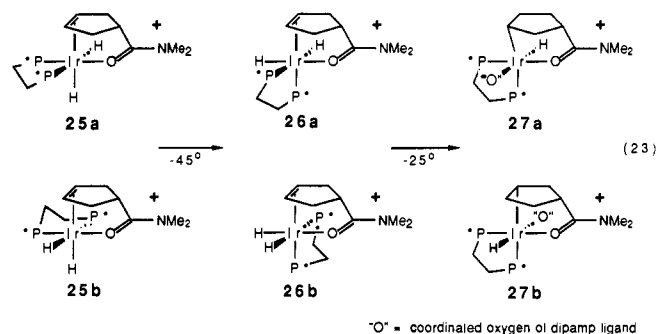

rearrangement to alkyl hydride structures **27a** and **27b**, respectively, precludes this determination. The basis

of the stereoselectivity leading to **25a** and **25b** has been put forth by Brown as analogous to that proposed by Johnson and Eisenberg with the π*(olefin) orbital replacing π*(CO) in the analysis. Thus interaction N may control the kinetic stereoselectivity of H₂ addition to **24**.

Complexes **25a** and **25b** are diastereomers differing by chirality at the metal center in a complex having a chelating chiral bis(phosphine). These diastereomers form in an initial 4:1 ratio, indicating that there is a difference in activation energy for H₂ approaching the square-planar complex from above or below the molecular plane. This differentiation is primarily steric in origin since the H₂ axis is parallel to P–Ir–olefin for each diastereomer. Similarly, in the formation of **26a** and **26b** one diastereomer appears to predominate overwhelmingly (>95%). From these studies one can conclude that both electronic and steric factors influence the diastereoselectivity of H₂ oxidative addition, which may be crucial in determining the success of asymmetric hydrogenation catalysis.

In an attempt to ascertain the effects of a chiral bis(phosphine) ligand alone on the diastereoselectivity of H₂ addition, Kunin et al.[27] synthesized an analogue of **4** using the ligand chiraphos. In complexes of type **4** containing the nonchiral ligand dppe, approach of H₂ from above or below the plane of the complex is equally likely, leading to formation of racemic mixtures of dihydrides **5** and **6**. When the chiral bis(phosphine) chiraphos is substituted, these approaches are no longer equivalent and the formation of diastereomers of potentially different stability occurs.

The complex IrBr(CO)(chiraphos) (**28**) reacts rapidly with H₂ in acetone, in a manner similar to that of **4**, to first produce diastereomers **29a** and **29b** with >99.5% stereoselectivity followed by slower formation of a more stable pair of diastereomers **30a** and **30b**, as shown in eq 24. At -25 °C, the kinetic diastereomers **29a** and
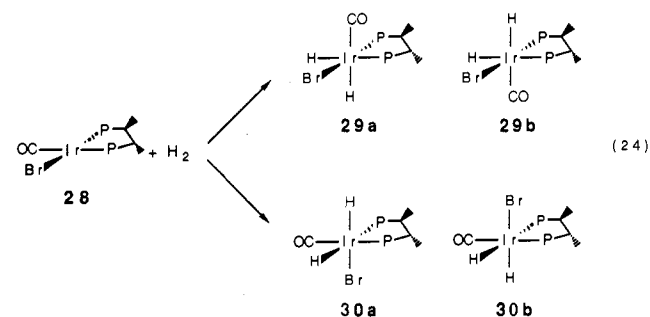
29b form in a 2.1:1 ratio, which remains constant for extended periods of time, with lack of H₂/D₂ exchange into species **29** indicating that the observed ratio of diastereomers corresponds to kinetic differentiation.[28] Isomerization to diastereomers **30** does not occur at -25 °C under excess H₂. When the temperature is allowed to rise to room temperature, the ratio of **29a** to **29b** changes within 5 min to 1.2:1, rapid H₂/D₂ exchange occurs, and the thermodynamic diastereomers **30** start to grow in slowly. During early stages of the isomerization the observed ratio of **30a:30b** is 2.4:1, while at equilibrium the ratio is 1.3:1, with diastereomers **30** comprising 85% of the total hydride species present. At equilibrium, the ratio of **30a:29a** is 7.2:1.

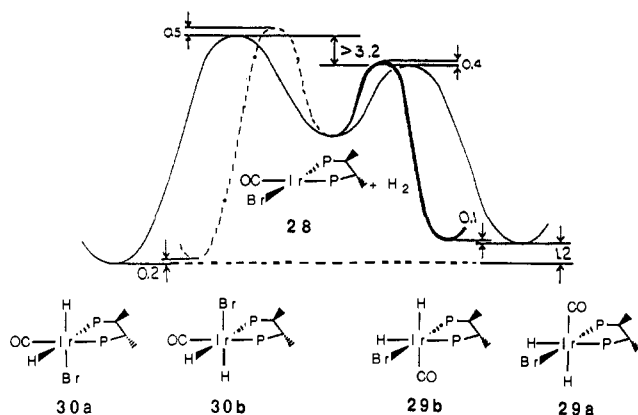The experiments show that in addition to the stereoselective, kinetically controlled H₂ oxidative addition

Figure 3. Reaction coordinate diagram for the system IrBr-(CO)(chiraphos) + H_2. Values in kcal/mol.

originally seen for 4, diastereoselection for 29 and 30 occurs due solely to the influence of chiraphos on the developing chirality at the metal center as the cis oxidative addition proceeds. The kinetic differentiation expressed as $\Delta\Delta G^{\ddagger}$ for 29a:29b and 30a:30b is 0.40 and 0.50 kcal/mol, respectively. From the initially observed ratio of >200:1 for 29:30, it was concluded that $\Delta\Delta G^{\ddagger}$ between the formation of 29a and 30a must be >3.1 kcal/mol. Thermodynamic differentiation between the diastereomers was obtained from the ratio of 29a:29b as 30 started to form and the ratios 30a:30b and 30a:29a after equilibrium had been reached. A reaction coordinate profile of the 28 + H_2 system summarizing all of these results is given in Figure 3.

The oxidative addition of Ph_3SiH to 28 was examined and was also found to proceed stereoselectively under kinetic control. The reaction occurred as shown in eq 25, with initial formation of diastereomers 31 (>99.5%)

(25)
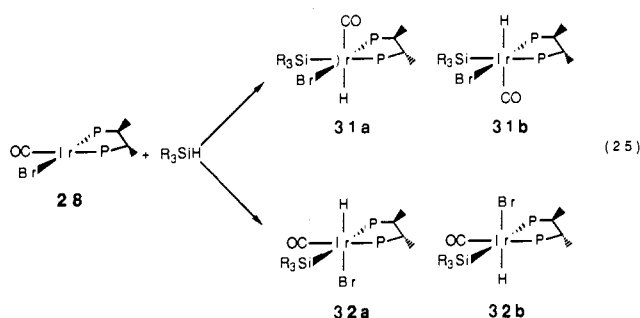
followed by isomerization to the more stable diastereomers 32.[29] A preference for formation of 31a over 31b was observed at -70 °C, corresponding to $\Delta\Delta G^{\ddagger}$ = 0.9 kcal/mol, as evidenced by a 4.5:1 ratio of diastereomers. At room temperature, the ratio rapidly changed to 1:1 as equilibration of diastereomers 31 occurred, followed by slower isomerization to 32. A striking kinetic differentiation between diastereomers 32a and 32b was observed, $\Delta\Delta G^{\ddagger}$ = 1.5 kcal/mol, as evidenced by a ratio 32a:32b of 12:1 observed early in the isomerization. The equilibrium ratio of these diastereomers was found to be 1:1, indicating little thermodynamic differentiation.

The kinetic preference for the formation of 29 over 30 and 31 over 32 is the same as that observed for the dppe complexes above, indicating that the same electronic interaction, N, dictates which isomer is formed. In addition to this, there is a steric interaction due to the chiraphos ligand that gives rise to a kinetic pref-

erence for the formation of one configuration of each pair of diastereomers. Analysis of these reactions using space-filling molecular models indicates a kinetic preference for the formation of the Δ configuration in each pair of diastereomers but also shows little thermodynamic differentiation within each pair of diastereomers, consistent with the initial and equilibrium ratios observed for each pair of diastereomers. The fact that there is little thermodynamic preference for one diastereomer of each pair while there is a large kinetic differentiation lends support to the transition state of the reaction being reactant-like—i.e., with little deformation of the complex from square-planar geometry as M–H bonds form and the H–H bond weakens.

H. Isomerization of $IrH_2X(CO)(dppe)$: Reductive Elimination/Oxidative Addition vs Dihydride Transfer

As described above, the oxidative addition of H_2 to IrX(CO)(dppe) (X = Cl (4a), Br (4b), I (4c)) proceeds under kinetic control with the initial stereoselective formation of the cis-dihydride isomer 5a–c followed by slow conversion to the more stable isomer 6a–c. This isomerization reaction between the two dihydride isomers 5 and 6 has been studied mechanistically for X = Br.[30]

The kinetic results of the isomerization of 5b to 6b in acetone under a large excess of H_2 reveal that the reaction proceeds by a clean first-order process, as indicated by linear plots of ln [5b] vs time. The isomerization of 5b to 6b was found to have a half-life of 35 h at 25 °C and 62 min at 55 °C, corresponding to observed rate constants (k_{obsd}) of 5.50×10^{-6} s and 1.85×10^{-4} s^{-1}, respectively. On the basis of the fact that the initial oxidative addition of H_2 to 4 is facile and reversible, the isomerization mechanism was proposed to be a reductive elimination/oxidative addition sequence (eq 26). The rate law for this mechanism, given

(26)
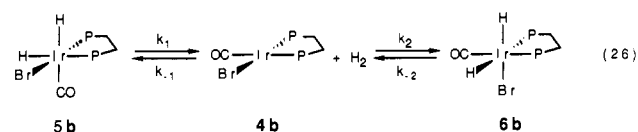
as eq 27, depends only on the concentration of 5b and shows no H_2 dependence. The high stereoselectivity

$$\frac{-d[5b]}{dt} = k_{obsd}[5b] = \frac{k_1 k_2 [5b]}{k_{-1} + k_2} - \frac{k_1 k_2 [5b]}{k_{-1}} \quad (27)$$

for the initial oxidative addition (>99%) indicates that k_{-1} is much greater than k_2, and the rate law corresponds to that of a system with a preequilibrium.

Through a kinetic study of the D_2 exchange into 5b, a value for k_1 in eq 27 of 1.15×10^{-3} s^{-1} at 25 °C was determined. From the values for k_{obsd} and k_1, the stereoselectivity for H_2 oxidative addition (k_{-1}/k_2) can be calculated. Since $k_{-1}/k_2 = k_1/k_{obsd} = 210$, the stereoselectivity for the formation of 5b at 25 °C is 99.5%. From k_1 and k_1/k_{obsd}, exact values of $\Delta G^{\ddagger}$ for reductive elimination from 5b and $\Delta\Delta G^{\ddagger}$ for H_2 oxidative addition in Figure 2 can also be determined, $\Delta G^{\ddagger}$ = 21.4 kcal/mol and $\Delta\Delta G^{\ddagger}$ = 3.2 kcal/mol (cf. >2.7 kcal/mol from the original estimate of >99% stereoselectivity).

The notion of isomerization of an Ir hydride complex via reductive elimination/oxidative addition had been

previously established by Harrod et al. in the interconversion of *mer* and *fac* isomers of IrH₃(CO)(PPh₃)₂ (eq 28).[31] These investigators observed that the rate
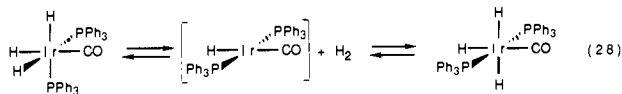
of isomerization was nearly the same as the rate of PPh₃ substitution into IrH₃(CO)(PPh₃)₂ to form IrH(CO)-(PPh₃)₃, with both reactions appearing to proceed via rate-determining reductive elimination of H₂.

An intramolecular isomerization mechanism not involving reductive elimination/oxidative addition is also consistent with the observed first-order kinetics. However, while this type of isomerization has been demonstrated for Ir hydrides of the type *cis*- and *trans*-IrH₂(dppe)₂⁺ [32] and IrHCl(dppe)₂⁺,[33] it was considered less likely for the IrH₂X(CO)(dppe) complexes given that the rate of H₂ reductive elimination is much faster than the rate of isomerization.

The isomerization reaction of **5b** to **6b** proceeded much more rapidly in benzene solution, but consistently reproducible kinetics could not be obtained. However, the existence of other isomerization pathways seemed likely. This was supported by the observation that the conversion of **5b** to **6b** proceeded more rapidly in acetone when less H₂ was present. Since the proposed isomerization mechanism possessed no kinetic dependence on H₂, eq 27, the isomerization was investigated further as a function of H₂ pressure.

The kinetics for the isomerization under successively lower pressures of H₂, but with H₂ still in excess, were approximately first order. However, plots of ln [**5b**] vs time began to show increasing deviations from linearity, and the rate of isomerization was observed to increase progressively as the H₂ pressure was decreased. This variation in reaction rate was inconsistent with the reductive elimination/oxidative addition sequence, eq 26, and its rate law, eq 27. When the isomerization was studied with <1 equiv of hydrogen in the system, the rate increased significantly, with isomerization typically complete in <15 h. Also, large deviations from linearity were observed in plots of ln [**5b**] vs time. A second-order treatment of the experimental data at these low concentrations of H₂ was more successful in that plots of 1/[**4b** + **5b**] vs time were linear. Furthermore, a linear correlation was observed when k_{obsd} was plotted against 1/[H₂]. An isomerization mechanism that is second order in complex and possesses an inverse [H₂] dependence was thus found to predominate under low pressures of H₂.

Under conditions in which <1 equiv of H₂ is added to the reaction system, both the square-planar starting complex, IrBr(CO)(dppe) (**4b**), and the kinetic dihydride, IrH₂Br(CO)(dppe) (**5b**), are present in significant concentrations. A bimolecular mechanism involving these two species was proposed to explain the isomerization process under these conditions.[30] The mechanism, which is consistent with the kinetic data, involves dihydride transfer between iridium species via a binuclear intermediate, **33**, as shown in eq 29.

The proposal of a dihydride-bridged binuclear intermediate has precedents in other, closely related studies. Druoin and Harrod[7a] proposed a dihydride-bridged dimer species in their attempts to convert the
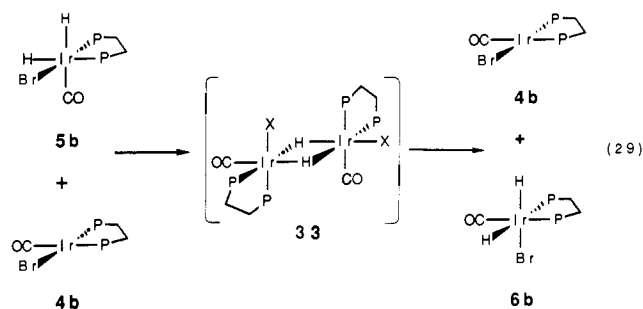
complex IrH₃(CO)(P(p-ClC₆H₄)₃)₂ (**34**) into the unsaturated complex IrH(CO)(P(p-ClC₆H₄)₃)₂ (**35**). When the trihydride **34** was placed under a stream of nitrogen to displace H₂, ¹H NMR evidence revealed the occurrence of an equilibrium proposed to involve **36**, as shown in eq 30.
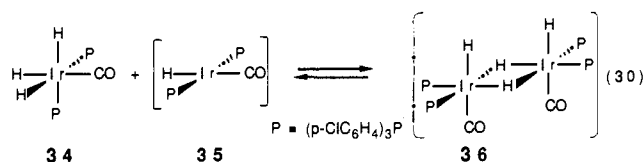
In the investigation of D₂ addition to IrH(CO)(dppe) (**4e**) generated in situ (eq 31), the observation of equimolar amounts of IrH₃(CO)(dppe) and **5b**-d_2 in addition to the major product IrHD₂(CO)(dppe) suggested the occurrence of dihydride transfer. Since the
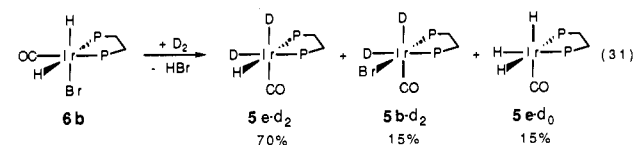
thermodynamic dihydride **6b** was known not to reductively eliminate H₂ on the time scale of the experiment, the formation of **5b**-d_2 was proposed to occur by direct dihydride transfer from IrH₂Br(CO)(dppe) (**6b**) to IrH(CO)(dppe) forming the trihydride **5e** and IrBr(CO)(dppe), which then reacted with D₂. The dihydride transfer was thought to proceed via a bridged intermediate similar to **33**.

Additional support for the bimolecular isomerization pathway arose from a low-temperature experiment which demonstrated that isomerization of **5b** to **6b** can occur in the H₂-deficient regime even when the reductive elimination/oxidative addition path is completely shut down. It was observed that D₂ does not exchange into **5b** at -23 °C, indicating that reductive elimination of H₂ does not occur at this temperature. However, in the low H₂ pressure regime, isomerization of **5b** was still found to occur at -23 °C, confirming that a pathway other than reductive elimination/oxidative addition must exist under these conditions.

The rate law for the bimolecular isomerization pathway is shown in eq 33, a full derivation of which has been reported.[30] The equilibrium between [**4b**] and [**5b**] is dependent upon [H₂], eq 32, and gives rise to the complex [H₂] dependence of the rate law.

$$\frac{[\mathbf{5b}]}{[\mathbf{4b}][H_2]} = \frac{k_{-1}}{k_1} = K_{eq} \qquad (32)$$

$$\text{rate via bimolecular path} = \frac{k_3 K_{eq}[4b + 5b]^2[H_2]}{(1 + K_{eq}[H_2])^2} \tag{33}$$

The kinetics data from a study of the isomerization under intermediate pressures of H_2 indicate that both the reductive elimination/oxidative addition mechanism and the bimolecular mechanism are operative. The complete rate law for the isomerization must therefore include both components, as given in eq 34.

$$\text{obsd rate} = \frac{k_2[5b]}{K_{eq}} + \frac{k_3 K_{eq}[4b + 5b]^2[H_2]}{(1 + K_{eq}[H_2])^2} \tag{34}$$

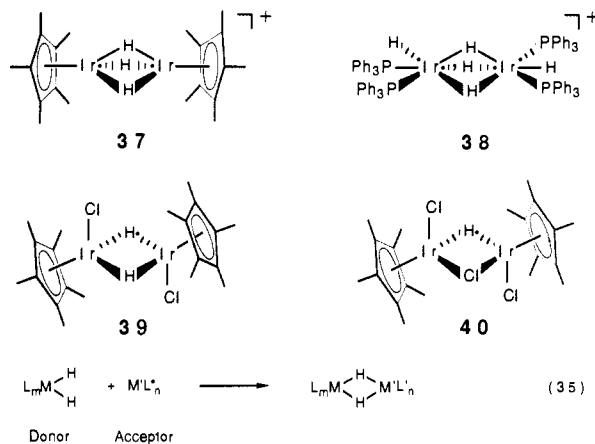Fitting of the data to the combined rate law allowed estimates of K_{eq} and k_3 to be made: $K_{eq} \simeq 2.8 \times 10^4$ M^{-1} and $k_3 \simeq 3.5 \times 10^{-3}$ M^{-1} s^{-1}. This large value of K_{eq} is consistent with that observed for complexes of the type $IrX(CO)(PPh_3)_2$[5b] and is indicative of a very favorable reaction. From this value of K_{eq}, $\Delta G°$ for the formation of 5b from 4b and H_2 at 25 °C and 670 Torr of H_2 is determined to be -6.1 kcal/mol, thus completing the reaction coordinate diagram shown in Figure 2.

Kinetic data for the reversible reaction of hydrogen with transition-metal complexes have been used to estimate M–H bond strengths.[5b,32] Pearson estimates an upper limit for M–H bond energies, D_0, from the activation enthalpy for the reductive elimination of H_2 from metal hydride complexes using $D_0 \le (103 + E_a)/2$ kcal/mol.[34] From this relation, values for $D_0(Ir-H)$ in $IrH_2X(CO)(PPh_3)_2$ where X = Cl, Br, and I have been estimated to be 59, 56, and 54 kcal/mol, respectively. If one assumes that $\Delta S^{\ddagger}$ for the reductive elimination of H_2 from 6b is small, as it is for the $IrH_2X(CO)(PPh_3)_2$ complexes, a value for Ir–H strength in 6b can be estimated to be $D_0(Ir-H) \le 64$ kcal/mol using this relation. This value is an upper limit estimate and ignores both $\Delta S^{\ddagger}$, which is assumed to be small, and the reorganizational energy of the iridium center. In order to determine a more accurate value for the Ir–H bond strength in 6b, precise thermochemical or kinetic measurements directed toward determining $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ would have to be made.

III. Dihydride Transfer

A. Hydride-Bridged Complexes

One of the most interesting aspects of the chemistry of Ir(I) Vaska type complexes and IrX(CO)(dppe) in particular revealed by the above studies is their ability to abstract hydrogen from other hydride complexes by dihydride transfer. Evidence for this behavior was given by the bimolecular isomerization of IrH_2Br-(CO)(dppe) (5b), discussed above, the exchange reaction of $IrH_3(CO)(P(p-ClC_6H_4)_3)_2$, shown as eq 30, and the dehydrohalogenation study of 6b under D_2, eq 31. Stable hydride-bridged binuclear species are not uncommon, a few pertinent examples of which are shown as 37,[35] 38,[22b] 39,[35] and 40.[35] In a recent review of bridging hydride complexes,[36] Venanzi describes the formation of binuclear hydride-bridged complexes in terms of a hydride-donor/hydride-acceptor scheme (eq 35). A dihydride complex, L_mMH_2, acting as a ligand,

$$L_mM\begin{matrix}H\\H\end{matrix} + M'L^*_n \longrightarrow L_mM\begin{matrix}H\\H\end{matrix}M'L_n \tag{35}$$

Donor   Acceptor

can bind through the hydrides to a coordinatively unsaturated acceptor complex, L_nM', forming a bridged species that contains three-center, two-electron M–H–M bonds. This scheme can be applied to the formation of mono-, di-, or polyhydride-bridged species. In the case of the isomerization of $IrH_2X(CO)(dppe)$ complexes under H_2-deficient conditions, 5 acts as the hydride "donor" complex and 4 acts as the hydride "acceptor" complex. The unusual feature of the IrX-(CO)(dppe) system is that the bridged species, 33, is not stable and total transfer of two hydrides from one metal center to another occurs under mild conditions. If one applies Venanzi's three-center, two-electron M–H–M bonding scheme to the intermediate species 33, one finds the "donor" Ir(III) site to be an 18-electron metal center while the "acceptor" Ir(I) site is a 20-electron metal center due to formation of two three-center, two-electron interactions. This feature may explain the apparent instability of 33, but electron counting in these hydride-bridged complexes is not always straightforward, especially when three-center bonding is involved.

B. Applications of Dihydride Transfer

Since the loss of H_2 from polyhydride complexes to acieve coordinative unsaturation often requires forcing thermal or photochemical conditions,[37] an alternative approach to achieving this unsaturation based on the dihydride-abstracting ability of IrX(CO)(dppe) appears very attractive and is under current investigation.

The first application of this notion was the direct intermolecular transfer of H_2 between a rhenium trihydride complex and IrBr(CO)(dppe), described by Jones and Maguire.[38] Treatment of $(\eta^4-C_5H_6)Re$-$(PPh_3)_2H_3$ (41) with 1 equiv of 4b resulted in the formation of $(\eta^5-C_5H_5)Re(PPh_3)_2H_2$ (42) and the thermodynamic dihydride isomer of $IrH_2Br(CO)(dppe)$ (6b) as shown in eq 36. If the reaction had proceeded by
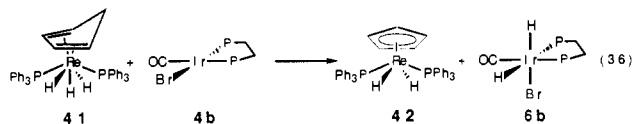

elimination of H_2 from 41 followed by H_2 addition to 4b, then dihydride isomer 5b would have been formed. Control experiments ruled out the possibility of H_2 loss from 41, and the results strongly supported the proposal that reaction between 41 and 4b proceeds via a dihydride-bridged binuclear intermediate, such as 43. The formation of strong Ir–H bonds and the thermo-

dynamic stability of **42** were proposed to be the driving forces for the reaction.
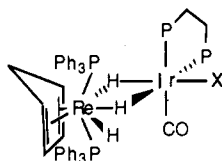

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Hydride abstraction has also been observed in the reaction of **4b** with Cp$_2$TaH$_3$ (**44**) (Cp = η^5-cyclopentadienyl).[39] This reaction was found to proceed
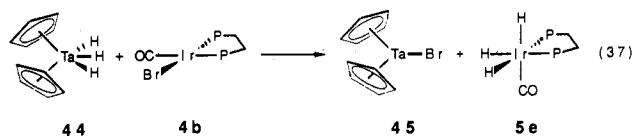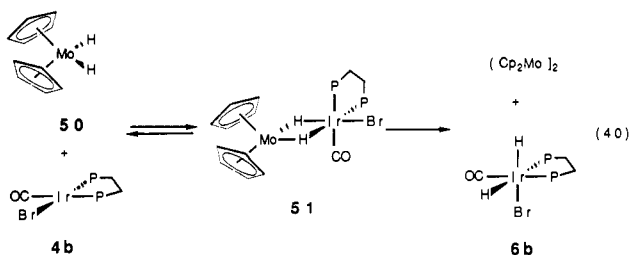

rapidly and cleanly to give IrH$_3$(CO)(dppe) (**5e**) and Cp$_2$TaBr (**45**) without the observation of any intermediates or products such as IrH$_2$Br(CO)(dppe) (**6b**) even when performed at low temperatures. The rapidity of the reaction and the observation of only **5e** and **45** as products indicate a bimolecular process is taking place, since H$_2$ loss from **44** normally occurs only above 80 °C.[40] However, since species such as **6b** are not observed, this process is a complex one and is not a single-step dihydride transfer. Neither IrHD$_2$(CO)(dppe) nor Cp$_2$TaHD$_2$ was observed when the reaction was carried out under D$_2$, and only **5e** and Cp$_2$TaBrL (**46**) were produced in the presence of added ligands, L = CO, C$_2$H$_4$, and C$_3$H$_7$C≡CC$_3$H$_7$, eq 38. The reaction is
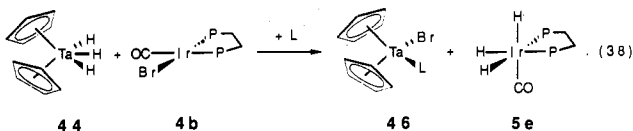
proposed to involve initial formation of a dihydride-bridged binuclear species such as **47**. Since intermediates of the type IrH(CO)(dppe), Cp$_2$TaH, and IrH$_2$X(CO)(dppe) are not observed and cannot be trapped out, it appears that the binuclear species must undergo subsequent rearrangement, similar to that shown in eq 39, with transfer of all three hydride ligands to the iridium center and transfer of X to the tantalum occurring before the species breaks up to form **5e** and **45**.
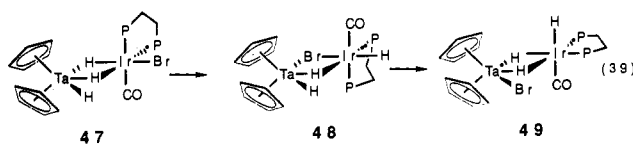

A dihydride-bridged species is observed in the reaction of Cp$_2$MoH$_2$ (**50**) with IrX(CO)(dppe).[41] Prelim-

inary studies show that an equilibrium between **50**, **4**, and the binuclear species, **51**, is rapidly established. When the reaction is performed in acetone, the bridged binuclear species slowly decomposes to form IrH$_2$X-(CO)(dppe) (**6**) and [Cp$_2$Mo]$_2$ species resulting from dihydride transfer. In addition to these two products, iridium trihydride **5e**, Cp$_2$MoHX, and other molybdenum products are formed to some extent in acetone and are the only products observed in benzene solution. These latter species appear to arise from a complex process perhaps similar to that involved in the reaction between Cp$_2$TaH$_3$ and IrBr(CO)(dppe).

While Cp$_2$MoH$_2$ reacts with **4**, the isoelectronic and isostructural complex Cp$_2$WH$_2$ does not. The difference in reactivity between these two species is likely due to the difference in M–H bond strengths, D_0(Mo–H) $\simeq$ 60 kcal/mol whereas D_0(W–H) $\simeq$ 73 kcal/mol.[34]

The experimental evidence in the above examples indicates that these reactions proceed via formation of dihydride-bridged binuclear intermediates. Other, closely related reactions between transition-metal hydrides and unsaturated metal complexes have recently been reported but are proposed to follow a quite different mechanism. Casey et al. have found that Vaska's complex, **1**, reacts with CpRe(CO)$_2$H$_2$ in the presence of PPh$_3$ to form mer-IrH$_2$Cl(PPh$_3$)$_3$ and CpRe(CO)$_3$.[42] These investigators propose that the reaction proceeds by oxidative addition of a Re–H bond to IrCl(CO)-(PPh$_3$)$_2$, giving **52**, which decomposes by transfer of the
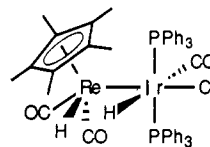
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second hydride to iridium with concomitant transfer of a carbonyl ligand from iridium to rhenium. A second reaction between CpReH$_2$(CO)$_2$ and Pt(C$_2$H$_4$)L$_2$ (L = PPh$_3$) yields the heterobimetallic complex **53** and is thought to proceed via oxidative addition of Re–H also. However, equivalence of the two hydrides in **53** is seen in solution, and this is proposed to occur through an equilibrium involving a bridged dihydride species, **54**, which might in fact be the initially formed species via dihydride transfer.

53   **54**
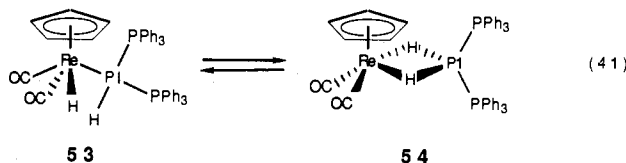
Casey's proposal of M–H oxidative addition rather than dihydride transfer leads to the conclusion that the two mechanisms are kinetically indistinguishable. To date, studies designed to differentiate one mechanism from the other have not been performed. Thus, while the stoichiometry of dihydride transfer is firmly established in reactions between metal hydrides and Ir(I) complexes, and the transfer of hydrides and other ligands between metal centers is well-known with platinum group systems, the mechanisms of these reactions are still not definitively known.

Even with this mechanistic ambiguity, the notion of dihydride transfer will continue to prove interesting as

a potential pathway to coordinative saturation.

C. Basis for Stereoselectivity of Dihydride Transfer

It is important to note that whereas the oxidative addition of H_2 to **4b** produces the kinetic isomer of $IrH_2(CO)(dppe)$, **5b**, the dihydride-transfer reactions between the hydride complexes **5b**, $(C_5H_6)Re(PPh_3)_2H_3$ **(41)**, and Cp_2MoH_2 **(50)** and the unsaturated complex **4b** give rise to the thermodynamic isomer of $IrH_2X(CO)(dppe)$, **6b**.

A detailed theoretical analysis of dihydride-transfer reactions, similar to those done for H_2 oxidative addition, has yet to be done. However, a general analysis of the factors that are involved in dihydride transfer can be performed. A key difference between H_2 oxidative addition and dihydride transfer from an electronic structural standpoint appears to be the fact that the MH_2 unit does not have an orbital similar to $\sigma(H_2)$ capable of interacting with d_{z^2} and p_z of the incoming Ir(I) center. While the stereoselectivity of H_2 oxidative addition to **4b** is governed by electronic effects that minimize the four-electron repulsion between the filled metal d_{z^2} orbital and $\sigma(H_2)$, it appears that the absence of a strong contribution from this four-electron repulsion leads to the immediate formation of the thermodynamic isomer of $IrH_2X(CO)(dppe)$, **6b**, in the dihydride-transfer reactions.

IV. Concluding Remarks

Hydrogen oxidative addition, one of the fundamental reactions in homogeneous catalysis, is a concerted cis addition in which the stereochemistry of the product is controlled by ligand electronic and steric effects. For the well-studied Vaska type complexes, $trans$-$IrX(CO)P_2$, the product dihydrides usually possess trans phosphine ligands, indicating H_2 oxidative addition with the H_2 axis parallel to the X–Ir–CO axis of the complex. The basis of stereoselectivity here is primarily steric although it remains difficult to sort out all factors for these systems.

For the cis-bis(phosphine) complexes $IrX(CO)(dppe)$, **4**, the addition proceeds under kinetic control stereoselectivity to give a cis-dihydride product with one hydride trans to CO and one hydride trans to phosphine, **5**. The stereoselectivity of H_2 addition to $IrX(CO)(dppe)$ appears to be governed by electron effects, and in particular, minimization of the four-electron repulsion between the filled metal d_{z^2} orbital and $\sigma(H_2)$ through interaction of the empty π^* orbital on CO with d_{z^2} in the transition state. Studies involving the oxidative addition of silanes and hydrogen halides support this proposal. The stereoselectivity of H_2 oxidative addition to d^8 complexes with chelating phosphines may have considerable importance in asymmetric hydrogenation in which for Rh catalysts H_2 addition appears to be the enantioselective step. Model Ir compounds are being studied in this context.

The kinetically produced cis-dihydrides $IrH_2X(CO)(dppe)$, **5a–c**, undergo subsequent isomerization to yield the thermodynamically favored dihydrides with one hydride trans to halide and the other hydride trans to phosphine, **6a–c**. Under an excess of H_2, this isomerization occurs via a reductive elimination/oxidative

addition process indicative of the stereoselectivity of H_2 addition, whereas a bimolecular process involving dihydride transfer appears to be operative under a deficiency of H_2.

Dihydride-transfer reactions involving iridium complexes have been observed in a number of instances. For transfer reactions between $IrX(CO)(dppe)$ and polyhydride complexes of other metals, the driving force to reaction may in part be the formation of very stable Ir–H bonds. The stereoselectivity of hydride-transfer reactions has not been fully established but in certain cases appears different from that of H_2 oxidative addition, consistent with the different electronic structures of H_2 and MH_2 as substrates.

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