$Ru[C_6(CH_3)_6]_2$ and $H_4Rh_2[P(OR)_3]_4$, but there is only one known selective catalyst, actually a class of catalysts, the allylcobalt tris(phosphite) complexes. Selectivity, specifically stereoselectivity, requires the absence of certain reaction cycles: (1) significant displacement of the partially hydrogenated arene as a cyclohexene and (2) significant lifetimes for intermediates derived from alkyl-substituted arenes in which transformations from η^3-benzylmetal to η^1-benzylmetal would allow for rotation about the metal–carbon σ bond. We must design structures so as to disallow these processes. The presence of an electronically ambidentate ligand like the allyl ligand which can facilitate the generation of open coordination sites can also operate to minimize the formation of low hapticity interactions with a partially hydrogenated arene (e.g., η^1-benzylmetal) and also stabilize the last displaceable state before total hydrogenation, the cyclohexene state.

(38) There is no compelling technological need for longer-lived, more efficient or more active arene hydrogenation catalysts. Established solid-state catalysts meet present day practical needs.

We now seek alternative ambidentate ligands—e.g., chelate ligands that are more resistant to reduction.

Finally, we note here one of the most fascinating aspects of reactions catalyzed by discrete coordination compounds—and to us one of the most compelling reasons for studying such reactions. Many fundamental features of coordination chemistry can be revealed from the studies because of the multistepped character of the catalytic reactions. The allylcobalt class of complexes has been no exception to the generality—the number of elementary steps identified in the arene–hydrogen reaction catalyzed by the cobalt complexes is impressively large.

Iridium Compounds in Catalysis

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Why are metal surfaces (heterogeneous catalysts) so much more active than the metal complexes (homogeneous catalysts) which are their soluble counterparts? How can one set about the design of homogeneous systems that are much more active than those presently available?

These were the sort of questions that prompted us to look at the catalytic chemistry of some highly coordinatively unsaturated iridium species. These systems have proved to be far the most active homogeneous hydrogenation catalysts known. For example, they can reduce even tetrasubstituted olefins, such as $Me_2C=CMe_2$, at up to 4000 catalytic cycles per hour at 0 °C. These studies have also led to the isolation both of the first dihydrido olefin complexes, the active intermediates in catalysis, and of some unusual hydrogen-bridged cluster complexes formed in the deactivation of the catalysts.

High catalytic activity in an iridium-based system might be thought surprising, because transition metals of the third row had previously been found to be less active in catalysis than those of the first and, more especially, the second rows (see Figure 1). A char-

acteristic example is that of the complexes [MCl(PPh$_3$)$_3$]. Where the metal is rhodium, this complex is an efficient catalyst for the hydrogenation of unsaturated substrates.[1] The cobalt and iridium analogues are entirely inactive, but for different reasons. The cobalt complex fails to react with hydrogen,[2] while the iridium analogue reacts irreversibly with hydrogen to give a stable adduct [IrClH$_2$(PPh$_3$)$_3$]; this adduct, however, unlike the rhodium analogue, fails to dissociate PPh$_3$ to allow the substrate access to the active site.[3]

The mechanisms of olefin hydrogenation with [RhCl(PPh$_3$)$_3$], Wilkinson's catalyst, are known in some detail;[1,4] the major route is shown in Figure 2. Hydrogen addition (step a) gives a relatively unstable dihydride adduct in which solvent or PPh$_3$ (L') is labile, presumably due to the high trans effect of a hydrogen ligand. Solvent and substrate (step b) can compete for the available site. The presumed dihydrido olefin intermediate, which has never been observed, must undergo a hydride insertion, perhaps assisted by a ligand association (step c). A reductive elimination (step d) gives the product alkane and regenerates the catalyst.

Robert H. Crabtree was born in London in 1948. He studied at Oxford (B.A., M.A.), where he worked for a year with Malcolm Green, and then took his D.Phil with Joseph Chatt at the Unit for Nitrogen Fixation, Sussex University. With Hugh Felkin, at the Institut de Chimie des Substances Naturelles at Gif-sur-Yvette, near Paris, he was first a postdoctoral fellow, and then Attaché de Recherche. In 1977, he took up an assistant professorship in Inorganic Chemistry at Yale University.

(1) J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc. A*, 1711 (1966).
(2) N. Aresta, M. Rossi, and A. Sacco, *Inorg. Chim. Acta*, **3**, 227 (1969).
(3) M. A. Bennett and D. A. Milner, *J. Am. Chem. Soc.*, **91**, 6983 (1969).
(4) P. Meakin, J. P. Jesson, and C. A. Tolman, *J. Am. Chem. Soc.*, **94**, 3240 (1972); C. A. Tolman, P. Z. Meakin, D. L. Lindner, and J. P. Jesson, *ibid.*, **96**, 2762 (1974); J. Halpern and C. S. Wong, *Chem. Commun.*, 629 (1973).

Fe Co Ni
Ru Rh Pd
Os Ir Pt

Figure 1. The arrangement of the group 8 elements in the periodic table.

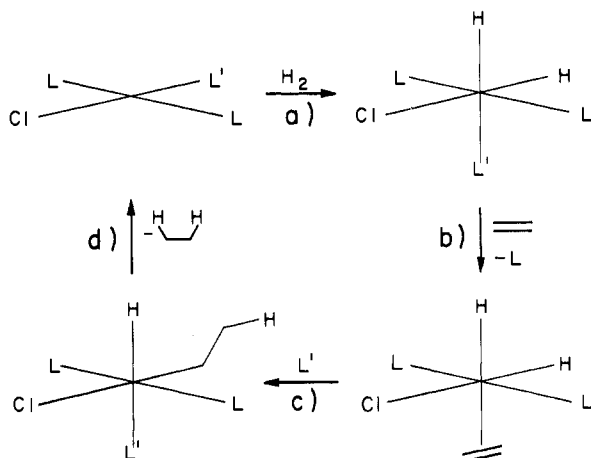**Figure 2.** A mechanism for the hydrogenation of olefins with Wilkinson's complex [RhCl(PPh$_3$)$_3$]. L' may be solvent or PPh$_3$ (for details see ref 4).

Figure 3. Typical hydrogen absorption curves for [Ir(cod)-(PMePh$_2$)$_2$]PF$_6$ (0.5 mM) in CH$_2$Cl$_2$ at 0 °C for various alkenes (0.5 M) [p(H)$_2$ = 620 mmHg]. The figures refer to the maximum rates expressed in mol of H$_2$ (mol of Ir)$^{-1}$ h^{-1}.

Osborn and co-workers made the important observation that cationic rhodium(I) complexes having two phosphines per rhodium were also active hydrogenation catalysts. These experiments were undertaken in coordinating solvents, such as ethanol, acetone, or tetrahydrofuran (THF), and the active species in each case were found to be the isolable solvates 2[5] (see eq 1).

$$[Rh(cod)L_2]^+ \xrightarrow[\text{solv}]{H_2} [RhH_2(solv)_2L_2]^+ \qquad (1)$$
$$\underset{1}{} \qquad\qquad\qquad \underset{2}{}$$
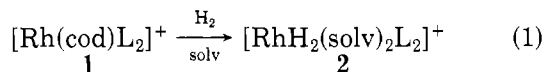
cod = 1,5-cyclooctadiene; L = PR$_3$;
solv = acetone, ethanol, or THF

These systems require dissociation of a solvent ligand rather than, as in the Wilkinson case, of a phosphine before the olefin substrate can gain access to the active site. This process is relatively rapid for the rhodium complexes 2, which are good catalysts, but displacement seems to occur slowly if at all for the analogous iridium complexes,[6] which are almost inactive as catalysts. This inertness to substitution of the iridium solvates is reminiscent of the behavior of [IrClH$_2$(PPh$_3$)$_3$], discussed above. Only the rhodium systems, therefore, were examined in detail by these authors.[5] Both systems were studied exclusively in coordinating solvents.

It seemed to us that since heterogeneous catalysts, which are simply metal or metal oxide surfaces, do not require ligand dissociation for substrate binding, this dissociation step of the solvent or a phosphine might be the limiting factor on catalyst activities in many homogeneous systems. In designing a catalyst system which would allow the substrate free access to the active site, we had to strike a compromise between the stability of the precursor, which should be conveniently isolable, and free availability of unoccupied sites in the active catalyst itself. We therefore decided to examine
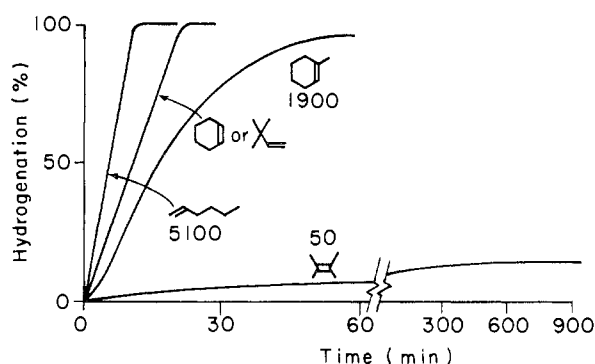
the effect of *irreversibly creating active sites in a noncoordinating solvent.*

The Iridium Catalysts

The complexes [Ir(cod)L$_2$]PF$_6$ (3, cod = 1,5-cyclooctadiene; L = tertiary phosphine), first studied by Osborn, presented a test of these ideas. Our initial experiments in solvents like benzene, toluene, or hexane, that we thought might prove noncoordinating, were disappointing: only catalytically inactive precipitates were formed under hydrogen.

It was George Morris, a graduate student who worked with me in Paris, who found the way forward. Since the unpromising precipitates he had obtained only dissolved in dichloromethane, he tried it as a solvent for the catalytic reaction itself. The chlorinated solvents, CHCl$_3$, C$_6$H$_5$Cl, and, best of all, CH$_2$Cl$_2$, are the only viable solvents for catalytic hydrogenation with these cationic iridium catalysts, presumably since they all have high polarity but negligible coordinating power.

This result was surprising since CHCl$_3$, and to some extent CH$_2$Cl$_2$, normally oxidize and deactivate the low valent catalysts involved in hydrogenation. Hence, these solvents have generally been avoided by workers in the field.[1] We were later to discover that both the precursors and the catalysts themselves are stable to other oxidizing reagents, such as O$_2$ or EtI, that instantly deactivate all other hydrogenation catalysts that we have used, or of which we are aware. We shall return below to this unusual oxidative stability of the catalysts.

Typical hydrogenation curves[7] for a catalyst of type 3 in CH$_2$Cl$_2$ under H$_2$ are shown in Figure 3. The catalysts are so active at 25 °C that all our experiments were done at 0 °C to get rates slow enough to be measurable. The catalyst is tolerant of several functional groups, such as CO$_2$R, on the olefin, but those which are good ligands, such as CH$_2$OH, or strong bases, such as NR$_2$, can cause a loss of activity in the catalyst. Deliberate deprotonation of the catalyst system with NEt$_3$ leads to the formation of [IrH$_5$L$_2$], known to be a poor catalyst.[8]

We tried several related complexes as potential catalysts. [Ir(cod)py$_2$]PF$_6$ (4, py = pyridine) was entirely inactive, apparently because it fails to add hydrogen.
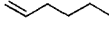
(5) R. R. Schrock and J. A. Osborn, *J. Am. Chem. Soc.*, **98**, 2134, 2143, 4450 (1976).

(6) (a) J. R. Shapley, R. R. Schrock, and J. A. Osborn, *J. Am. Chem. Soc.*, **91**, 2816, (1968); (b) J. R. Shapley and J. A. Osborn, *ibid.*, **92**, 6976 (1970).

(7) R. H. Crabtree, H. Felkin, and G. E. Morris, *J. Organometal. Chem.*, **141**, 205 (1977).

(8) R. Zanella, F. Canziani, R. Ros, and M. Graziani, *J. Organometal. Chem.*, **67**, 449 (1974); M. G. Clerici, S. di Gioacchino, F. Maspero, E. Perotti, and A. Zanobi, *ibid.*, **84**, 379 (1975).

Table I
Rates[a] of Hydrogenation of Variously Substituted Olefins with Active Catalysts of Different Types

catalyst precursor	temp, °C	solvent	⟋⟍⟋⟍	⬡	⬡⟋	⟩=⟨	ref
[Ir(cod)PCy₃(py)]PF₆	0	CH₂Cl₂	6400	4500	3800	4000	7
[Ir(cod)(PMePh₂)₂]PF₆	{ 0	CH₂Cl₂	5100	3800	1900	50	7
	0	Me₂CO	~10	0	0	0	7, 10
[Rh(cod)(PPh₃)₂]PF₆	25	CH₂Cl₂	4000	10	–	0	11
[RuHCl(PPh₃)₃]	25	C₆H₆	9000	7	–	0	12
[RhCl(PPh₃)₃]	{ 25	C₆H₆/EtOH	650	700	13	0	1, 10
	0		60	70	–	0	

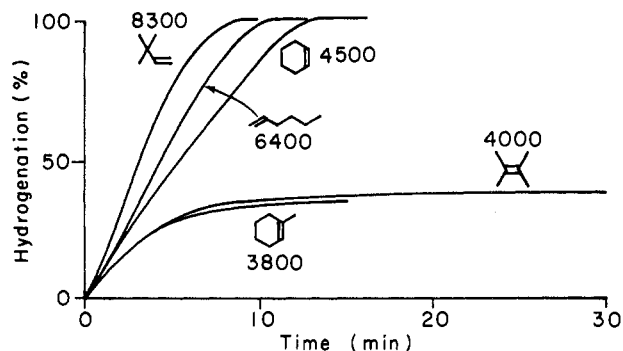[a] In mol of substrate reduced (mol of catalyst)⁻¹ h⁻¹.

Figure 4. Typical hydrogen absorption curves for [Ir(cod)(P-*i*-Pr₃)(py)]PF₆ (conditions as in Figure 2).

The mixed-ligand complexes [Ir(cod)L(py)]PF₆ (5),[9] however, proved to be the most active catalysts of any we have tried, particularly for hindered substrates, such as Me₂C=CMe₂ (see Figure 4).

Table I compares the rates of reduction of some variously substituted olefins by a number of the most active hydrogenation catalysts. The catalysts derived from **3** and **5** are surprisingly insensitive to substitution at the olefin, a feature in which they resemble heterogeneous catalysts far more than they resemble any other homogeneous system. One should allow about an order of magnitude rate differential to account for the 25 °C temperature difference between the measurements made at 0 °C (complexes **3**, **5**, and Wilkinson's catalyst) and those made at 25 °C in Table I.

The catalysts derived from **3** and **5** are entirely homogeneous, colorless and yellow solutions, respectively, and they have no tendency to deposit metallic iridium even after prolonged contact with hydrogen. In noncoordinating solvents only, they are much more active than their rhodium analogues.[5,10-12]

Deactivation

It will be seen from Figures 3 and 4 that the reduction of the more hindered olefins does not proceed to completion. This is due to an irreversible deactivation process, which occurs even for unhindered olefins when the substrate has been consumed. Catalysts derived from **3** turn yellow on deactivation. Unsuccessful efforts were made to prevent deactivation using coordinating solvents or weakly coordinating ligands, or by changing

(9) R. H. Crabtree and G. E. Morris, *J. Organometal. Chem.*, **135**, 395 (1977).
(10) R. H. Crabtree and G. E. Morris, unpublished observations.
(11) R. H. Crabtree, A. Gautier, G. Giordano, and T. Khan, *J. Organometal. Chem.*, **141**, 113 (1977).
(12) P. S. Hallman, B. S. McGarvey, and G. Wilkinson, *J. Chem. Soc. A*, 3143 (1968).

Table II
1-Methylcyclohexene Reduction Rates for a Variety of Iridium Catalysts

catalyst	rate[a]	extent[b]	time[c]
[Ir(cod)(PMePh₂)₂]PF₆	1900	940	60
[Ir(cod)P(*i*-Pr)₃(py)]PF₆	3800	350	15
[Ir(cod)(dpe)]PF₆ [d]	640	720	120
[Ir(cod)(PMePh₂)₃]PF₆ [d]	370	650	150

[a] In CH₂Cl₂ solution at 0 °C (except where stated), catalyst 0.5 mM, substrate 0.5 M, p(H₂) = 60 cmHg, rate in mol of substrate reduced (mol of catalyst)⁻¹ h⁻¹. [b] Of hydrogenation of 1-methylcyclohexene in mol of substrate reduced (mol of catalyst)⁻¹ (max:1000). [c] When hydrogenation ceased (min). [d] At 20 °C, 15-min induction period.
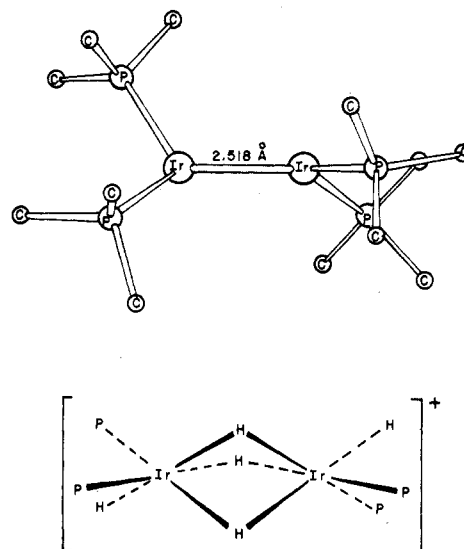

Figure 5. (a) (Upper) Partial X-ray crystal structure of the cation [Ir₂H₅(PPh₃)₄]⁺. (b) (Lower) Structure we assign to the dinuclear cation, including the bridging and terminal hydrogen ligands.

the number and type of ligands in the precursor complex (Table II).

We soon recognized that we had to characterize the yellow metal complexes formed in this process in order first to understand and then to prevent deactivation. It was over a year before we had fully characterized [7,13] [Ir₂H₂(μ-H)₃(PPh₃)₄]PF₆ (6) obtained in the deactivation of **3** (eq 2, L = PPh₃) by a combination of X-ray

$$2[Ir(cod)L_2]PF_6 + 7H_2 \rightarrow$$
$$\textbf{3}$$
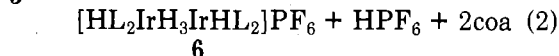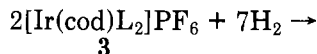
$$[HL_2IrH_3IrHL_2]PF_6 + HPF_6 + 2coa \quad (2)$$
$$\textbf{6}$$

L = PPh₃, coa = cyclooctane

crystallography, manometry, and low-temperature ^{1}H NMR spectroscopy.

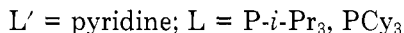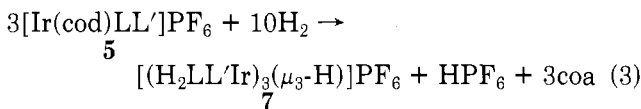The X-ray results (Figure 5a) show that the Ir–Ir distance in **6** is 2.52 Å, the shortest known, and that the stereochemistry around the metal atoms is distorted. Clearly, some of the ligands in the complex have escaped detection in the X-ray experiment, and these ligands can only be hydrogens. The hydride resonances in the ^{1}H NMR spectrum at –80 °C, two triplets[14] and a doublet, provide the evidence we needed for the location of these ligands. The stereochemistry around each iridium is octahedral, as expected for Ir(III), and each metal shares a face which contains the three bridging hydrogen atoms (Figure 5b). Each iridium also bears a terminal hydrogen. A triplet hydride resonance arises from the bridging hydrogen trans to two PPh$_3$ ligands (^{31}P, 100%, spin 1/2), a doublet from the two bridging hydrogens trans to a single PPh$_3$ ligand, and the other triplet from the terminal hydrogens which are cis to two PPh$_3$ ligands. The $J_{\text{PH(cis)}}$ coupling constant,[14] 18 Hz, is in the normal[15] range (10–30 Hz), but the $J_{\text{PH(trans)}}$ couplings of 65 and 85 Hz, which involve the bridging hydrogens, were exactly one-half of the normal values (130–180 Hz). This reduction may be related to the fractional bond order ($^1/_2$) that we believe is associated with the bridging MHM system.

The shortness of the M–M distance does not necessarily mean that we are dealing with a *direct* MM multiple bond, as we ourselves first thought.[13] The metals are perhaps best considered as being held together with three M–H–M bridge bonds. These bonds seem to be 2-electron, 3-center systems, not unlike those in the boranes.[16] The M–M distance is short because M–H bonds are short (ca. 1.6 Å). By making a model, one finds that in an octahedral L$_3$MH$_3$ML$_3$ system, an M–H distance of 1.6 Å geometrically requires an M–M distance of 2.5 Å.[7]

More recently, we also characterized[17] the yellow complexes, **7**, formed in the deactivation of the mixed ligand catalysts, **5** (eq 3).

$$3[\text{Ir(cod)LL}']\text{PF}_6 + 10\text{H}_2 \rightarrow$$
$$\textbf{5}$$
$$[(\text{H}_2\text{LL}'\text{Ir})_3(\mu_3\text{-H})]\text{PF}_6 + \text{HPF}_6 + 3\text{coa} \quad (3)$$
$$\textbf{7}$$

$$\text{L}' = \text{pyridine; L} = \text{P-}i\text{-Pr}_3, \text{PCy}_3$$

The X-ray crystal structure of **7** (Figure 6a, L = PCy$_3$) shows the triangular arrangement of metal atoms, with Ir–Ir distances of 2.76 Å. In spite of the problems associated with bond-length arguments, especially in hydrogen-bridged clusters, we believe that the structure can best be interpreted in terms of metal–metal bonds

Figure 6. (a) (Upper) X-ray crystal structure of the [Ir$_3$H$_7$-(PCy$_3$)$_3$(py)$_3$]$^{2+}$ cation. Only the heavy atoms in the immediate coordination sphere of the metal are shown. (b) (Lower) Our assignment of the full coordination sphere of the metal atoms, including bridging and terminal hydrogen ligands.

of unit order; most examples of such bonds have Ir–Ir distances of 2.7–2.8 Å.[18]

Once again, we assigned the hydrogen ligands on the basis of the ^{1}H NMR data, interpreted in the light of the manometric and X-ray results (Figure 6b). Only one hydrogen shows J_{PH} coupling with all three phosphorus ligands in the ^{1}H NMR spectrum, and the coupling constant, 50 Hz, is one-third of that normally associated with a *trans*-HMP arrangement. As in the analogous case of the binuclear hydride, **6**, this reduction in coupling constant may be associated with the fractional M–H order ($^1/_3$) of each of the 2-electron, 4 center M–H bonds in the M$_3$H bridging arrangement.[17b] Each metal atom bears two inequivalent hydrogen ligands, each giving rise to a narrow doublet in the ^{1}H NMR spectrum. Unexpectedly, the molecule shows no sign of fluxionality.

The fact that the deactivation products are polynuclear clusters suggests that by keeping the catalyst species apart from one another, deactivation can be prevented or at least slowed down. One effective method is simply to inject a dilute catalyst solution dropwise into the reaction vessel as the hydrogenation proceeds. The air stability of the catalyst, both in the form of the precursor and of the active species itself, simplified the experimental procedure. Choosing ligands, L, so large that they prevent dimerization also works, but at the cost of almost complete loss of activity.

A more elegant solution would be to use a polymer support, incorporating relatively widely spaced phosphine groups to anchor the catalyst precursor. Our efforts in this area have not yet met with success, but work continues.

(13) R. H. Crabtree, H. Felkin, G. E. Morris, T. J. King, and J. A. Richards, *J. Organometal. Chem.*, 113, C7 (1976).

(14) J. Quirk (unpublished observations, 1979) has resolved the triplet resonance of the terminal hydride in this complex, which we had not done before (ref 7 and 13). The molecule is fluxional at room temperature.

(15) J. Chatt, R. S. Coffey, and B. L. Shaw, *J. Chem. Soc.*, 7391 (1965).

(16) M. L. H. Green, personal communication (1976); M. Berry, N. J. Cooper, M. L. H. Green, and S. J. Simpson, *J. Chem. Soc., Dalton Trans.*, in press; R. H. Summerville and R. Hoffmann, *J. Am. Chem. Soc.*, in press.

(17) (a) D. F. Chodosh, R. H. Crabtree, H. Felkin, and George E. Morris, *J. Organometal. Chem.*, 161, C67 (1978). (b) The possibility that the unique hydrogen is mono- or bicoordinate and fluxional, which might be consistent with the NMR data, was rejected on the basis of the close approach of the cluster to 3-fold symmetry and the absence of abnormal thermal parameters in the solid state.
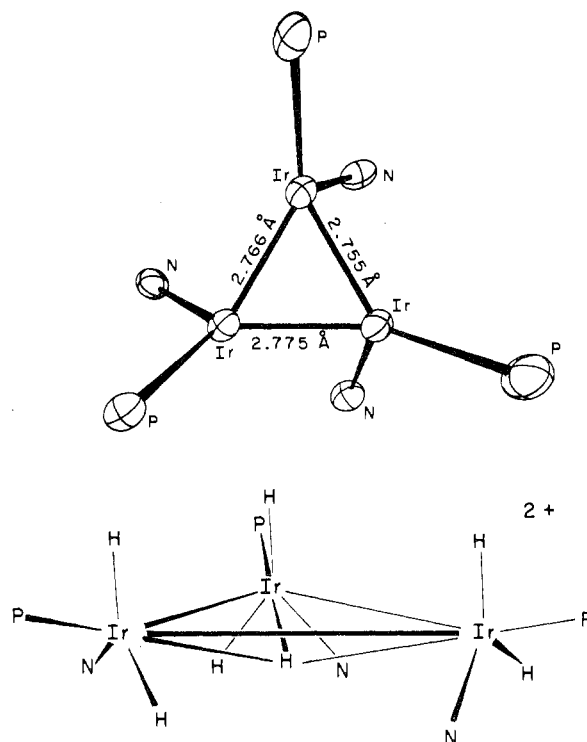
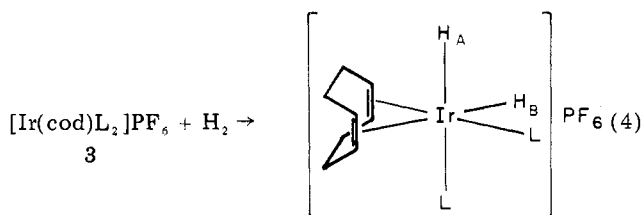(18) V. Albano, P. Bellon, and V. Scatturin, *Chem. Commun.*, 730 (1967).

The Dihydrido Olefin Intermediates

Our original thoughts in starting work in iridium chemistry were that we might be able to isolate catalytic intermediates for iridium, the rhodium analogues of which, having never been isolated, were presumed to be highly reactive and unstable. On the other hand, we did not expect to find a high catalytic activity for iridium species.

The high catalytic activity that we in fact found seemed, at first sight, to indicate that intermediates would not be likely to be isolable in the same system. We now know, however, that in spite of the unprecedented activity of the iridium catalysts, a variety of intermediates of the dihydrido olefin type can indeed be isolated from these systems, particularly at low temperatures.

The original clue came from an important early observation by George Morris. He knew that the catalyst precursor 3, as a red CH_2Cl_2 solution, decolorizes on admission of hydrogen to the reaction flask. One day, he decided to see what would happen if he immediately pumped the hydrogen away again. He found that the color of the solution turned back to red. The color changes could even be cycled four or five times by admitting and then removing the hydrogen. Complex 3 could be reisolated unchanged, and in moderate yield, after the cycle of color changes. This suggested that a colorless intermediate might be formed in the reaction and might be stable enough at least to observe, if not to isolate.

A concentrated solution of 3 in CD_2Cl_2 in an NMR tube also decolorizes rapidly at -80 °C on passing hydrogen for a few seconds, and the solution is stable for at least several hours at -80 °C. We were delighted to find, from the ^1H NMR spectrum at that temperature, that the product is the simple cationic adduct[19] *cis*-$[IrH_2(cod)L_2]^+$ (see eq 4). This was the first example known of a dihydrido olefin complex. Such complexes had been presumed to be the key intermediates in homogeneous hydrogenation, but had never been observed.

Two hydride resonances were observed, a triplet, due to H_B coupling to two cis phosphorus nuclei, and a doublet of doublets, due to H_A coupling to one trans and one cis phosphorus nucleus. Four sharp resonances, due to the four inequivalent (cod) vinyl protons, were also present; these resonances have proved to be a reliable guide to the structure of a variety of types of iridium complex containing 1,5-cyclooctadiene, and we now have over 30 examples. The $PMePh_2$ complex also showed two PMe doublets, as expected for two inequivalent cis ligands.
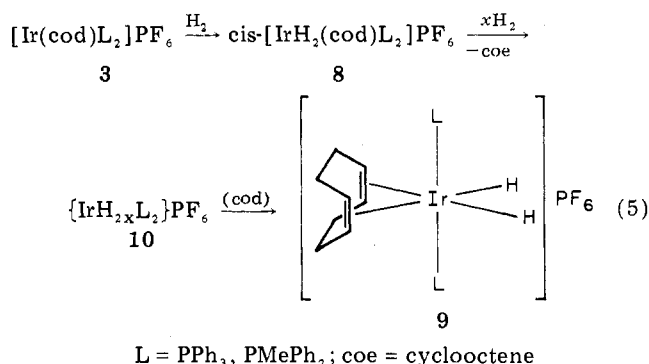
The cis complexes (8) were also formed with chelating phosphines as ligands [e.g., where L_2 = 1,2-diphenyl-

phosphinoethane (dpe)]. We even found one example[20] in which the metal has no tertiary phosphines at all in the coordination sphere: *cis*-$[IrH_2(cod)_2]^+$, formed by H_2 addition to $[Ir(cod)_2]^+$ at -80 °C. This example is particularly interesting, because it had been thought that hydrogen addition to an olefin complex was forbidden, since an olefin is an electron-withdrawing and therefore deactivating ligand. We will return to this important point.

In one case (L_2 = dpe), we isolated the crystalline adduct with Et_2O at -80 °C. The IR spectrum of the solid, which is just stable at room temperature, shows two Ir-H vibrations, as expected for a cis arrangement of these ligands.

When the solution is warmed to -20°, in the *absence* of excess H_2, hydrogen is in part lost to give 3. Some hydrogen is transferred to the coordinated olefin to give $[Ir_2H_5L_4]PF_6$, cyclooctane, and HPF_6, according to eq 2; the yield of hydrogenation products, only ca. 5% based on iridium, is nearly 20% when based on hydrogen, the true limiting reagent. In the presence of excess H_2 the complexes are completely hydrogenated on warming.

We wished to discover whether $[IrH_2(cod)L_2]^+$ might be an intermediate in the reduction of *excess* (cod) as substrate by the catalyst precursor 3. The initial activation of the precursor 3 ($L = PPh_3$ or $PMePh_2$) does indeed give the cis hydrogen adduct 8 (eq 4). Unexpectedly, however, once the initial mole of (cod) originally coordinated to the metal has been hydrogenated via 8, a new cation[20] succeeds 8 as the principal iridium-containing species in solution (see eq 5). This

$$[Ir(cod)L_2]PF_6 \xrightarrow{H_2} \textit{cis-}[IrH_2(cod)L_2]PF_6 \xrightarrow[-coe]{xH_2}$$

3   8

$$\{IrH_{2x}L_2\}PF_6 \xrightarrow{(cod)} \qquad (5)$$

10   9

$L = PPh_3$, $PMePh_2$; coe = cyclooctene

cation is *cis,trans*-$[IrH_2(cod)L_2]^+$ (9), the (cod) ligand of which derives from the excess (cod) used as substrate for the catalyst.

The same cation 9 can also be conveniently prepared by the displacement of acetone from $[IrH_2(ace-tone)_2L_2]^+$ (11) by (cod) (eq 6).

$$[Ir(cod)L_2]^+ \xrightarrow[H_2]{acetone} [IrH_2(acetone)_2L_2]^+ \xrightarrow{cod}$$

3   11

$$\textit{cis,trans-}[IrH_2(cod)L_2]^+ \quad (6)$$

9
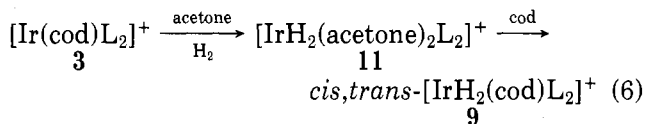
In contrast to the cis isomer 8, the *cis,trans*-dihydride 9 does not readily transfer its hydrogen to the coordinated olefin. The complexes appear to be stable in solution, at least over short periods, at ca. 40 °C. One example (9a, $L = PMePh_2$) can be isolated with Et_2O as a white crystalline solid, which only decomposes rapidly in air at ca. 85 °C.


(19) R. H. Crabtree, H. Felkin, and G. E. Morris, *J. Chem. Soc., Chem. Commun.*, 716 (1976).

(20) R. H. Crabtree, H. Felkin, T. Khan, and G. E. Morris, *J. Organometal. Chem.*, 144, C15 (1978); 168, 183 (1979).

The stereochemistry of complex **9a** follows from the ^{1}H NMR spectra: a triplet hydride resonance is due to coupling with two cis phosphorus nuclei, a virtually coupled[21] triplet resonance can only arise from trans PMePh$_2$ groups, and a single resonance due to the equivalent (cod) vinyl protons is also observed. The triphenylphosphine analogue has similar spectra and chemical properties.

We believe that the difference in properties of the two complexes with regard to decomposition via metal hydride insertion into the cis metal–olefin group is due to the coplanarity of this M(C=C)H system in the cis complex **8**, leading to facile insertion in this isomer. In the cis,trans complex **9** each M–H bond is orthogonal to the M(C=C) unit, and the insertion is therefore forbidden.

The cis dihydride **8** also undergoes loss of H$_2$ to give **3**, by a simple reversal of the formation reaction. The application of this same reverse pathway (eq 7) to the

$$\diagup\!\!\!\!_\mid^\mid\!\!\text{Ir}\diagup + H_2 \;\rightleftharpoons\; {>}\text{Ir}\text{---}\diagup^H_H \;\rightleftharpoons\; {>}\text{Ir}{<}^H_H \quad (7)$$
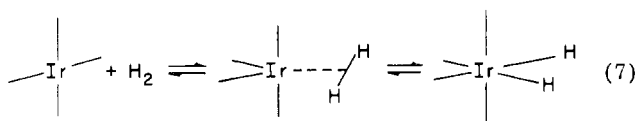
case of the cis,trans isomer **9** would lead to a transition state in which (cod) would be called upon to chelate to two incipiently trans sites, an unfavorable situation. Similarly, we have never observed the cis,trans dihydride **9**, even in traces, in any direct addition of hydrogen to **3**, but only via eq 5 or 6.

In order to quantify the ratio of the activity of the cis and cis,trans complexes **8** and **9** as hydrogenation intermediates for (cod) reduction, we carried out a series of kinetic experiments.[20] We compared measurements of H$_2$ absorption (manometry) and (cod) reduction (GLC) with estimates of the amounts of the intermediates, **8** and **9**, present at various times, obtained from ^{1}H NMR measurements on aliquots of the catalytic solution cooled to –80 °C. We found that the initial hydrogenation rate, when only the cis complex **8** is present, is about 40 times greater than the hydrogenation rate observed at a later stage in the reaction, when only **9** can be detected in solution.

We do not yet have good evidence about the nature of the intermediate **10** in eq 5, but we suggest {IrH$_{2x}$L$_2$}$^+$ (x = 3) as a reasonable possibility. We know that some hydride, and not, for example, **3**, is the immediate precursor of the cis,trans isomer **9** in this system, since addition of H$_2$ to **3** would give the cis complex **8** (eq 4), which is not observed. The existence of an intermediate of type **10** (x = 3) would also account for the formation of [IrH$_5$L$_2$] on deprotonation of the catalyst with NEt$_3$. Curiously, neither **8** nor **9** deprotonates, even with NEt$_3$, although [IrH(cod)L$_2$] (**12**), the expected product, is known[6b] and is stable. At –40 °C, **12** protonates rapidly, however, to give only **8**, and no trace of **9**.

Very recently, Jennifer Quirk, a Yale graduate student, has been able to observe cis,cis,trans-[IrH$_2$(olefin)$_2$L$_2$]$^+$ (**13**, olefin = C$_2$H$_4$, PhCH=CH$_2$, or coe) which can be formed by hydrogen addition to [Ir(olefin)$_2$L$_2$]$^+$ or slow olefin addition to the solvated cations [IrH$_2$(acetone)$_2$L$_2$]$^+$ (**11**). We have not yet unraveled the full details of the chemistry of these systems, which is somewhat more complicated than that of the cyclo-

octadiene complexes **8** and **9**.

Nature of the Catalyst

The principal species present in classical homogeneous hydrogenation systems have to dissociate a solvent or other ligand before the olefin substrate can gain access to the active site.[22]

In the iridium system, in contrast, the principal species present seem to be dihydrido olefin complexes, probably various isomers of [IrH$_2$(olefin)$_2$L$_2$]$^+$ (**13**), which can collapse directly to alkane, without further associative or dissociative steps. In this they seem to resemble heterogeneous rather than homogeneous hydrogenation catalysts; this may account for their high activity. The corresponding rhodium complexes [Rh(cod)L$_2$]PF$_6$ are at least an order of magnitude less active under analogous conditions, and do not reduce tri- or tetrasubstituted olefins. Perhaps olefin dihydride complexes are not formed in the rhodium system; we have certainly not yet seen any. It is possible that the principal active rhodium species are similar to the catalytically active, hydrogen-bridged clusters [RhHL'$_2$]$_n$ (n = 2 or 3, L' = P(OR)$_3$) recently isolated by Muetterties[23] et al. and formed in the hydrogenation of [Rh(C$_3$H$_5$)L'$_2$].

Oxidative Addition Reactions of the Iridium Cations

Very many low-valent, 16-electron d^8 complexes, such as those of Pd(II), Pt(II), Rh(I), and Ir(I), are capable of oxidative addition.[24] In this reaction, illustrated in eq 8 for a Rh(I) or Ir(I) cationic center, both the co-

$$\text{ML}_4^+ + X_2 \rightarrow X_2\text{ML}_4^+ \qquad (8)$$
$$\mathbf{14} \qquad\qquad \mathbf{15}$$

$$M = Rh, Ir$$
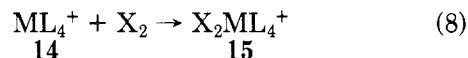
ordination number and the *formal* oxidation state of the metal increase by two units. Part of the driving force of this reaction comes from the dispersal, in the product **15**, of some of the relatively high electron density present at the metal in the low-valent, electron-rich complexes, **14**, that typically undergo the reaction.

Hence complexes of type **14** normally react more readily with the more oxidizing addenda. For example, O$_2$ and MeI generally give oxidative addition even in cases where H$_2$, a less oxidizing addendum, does not react.[25]

We were therefore surprised to find, in the complexes [Ir(cod)L$_2$]PF$_6$ (**3**), an example of a metal center of type **14** which only adds the less oxidizing addenda H$_2$ and HCl, but not the more oxidizing, O$_2$, MeI, or CHCl$_3$. Rather than showing a tendency to disperse electron density in their reactions, complexes of type **3** seem to show a tendency to attract electron density. For want of better terms, we have referred to the electron-attracting propensity of **3** as Lewis acid character, and to

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(22) G. Dolcetti and N. W. Hoffman, *Inorg. Chim. Acta*, **9**, 269 (1974).

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the more normal reactivity pattern as Lewis base character.

The Lewis acid character of the complexes 3 is particularly apparent in the unusual mechanism they adopt for the oxidative addition of the hydrogen halides. HX addition is normally either concerted, like hydrogen addition, or, particularly in ionizing solvents, ionic. Wherever the ionic mechanism has been examined in detail, it has been found that protonation precedes anion addition (eq 9).[26] This order of addition is

$$M \xrightarrow{H^+} MH^+ \xrightarrow{X^-} MHX \qquad (9)$$

understandable for a metal having Lewis base character.

In the case of the complexes 3, our own synthetic studies[27] as well as the independent kinetic results of Louw et al.[28] have unambiguously established that the addition proceeds by an ionic mechanism (eq 10) in

$$[Ir(cod)L_2]PF_6 \xrightarrow{X^-} [IrX(cod)L_2] \xrightarrow{H^+}$$

$$PF_6 \qquad (10)$$
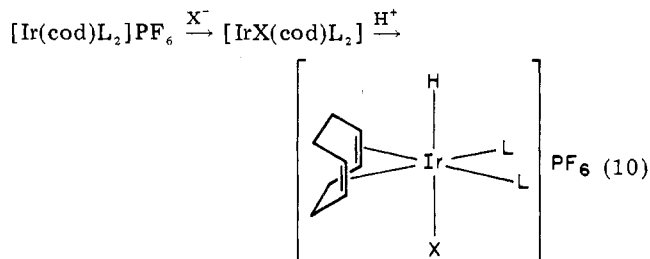
which halide ion addition is required *before* protonation can take place, the reverse of the normal order of addition.

We have isolated the intermediates 16 (X = I, Br) from the reaction mixtures themselves and prepared them (X = I, Br, and Cl) independently by halide ion addition to 3. Protonation of 16 gave the same isomer of the HX adduct 17 as is formed in the direct reaction 3 → 17. In contrast, 3 does not protonate at all with noncoordinating acids such as HPF_6.[29]

We have recently been looking at reactions of 3 with more oxidizing reagents, such as the halogens. In preliminary experiments Quirk has established that in a protic solvent, such as methanol, I_2 reacts with 3 to give a *hydrogen* iodide adduct in good yield. We do not yet understand the mechanism, but the overall reaction shows how resistant to oxidation is complex 3: The HI adduct, in which the metal is relatively less oxidized, has been formed to the exclusion of the expected, and more oxidized, I_2 adduct.

Hydrogen addition to d^8 complexes such as 13 is normally promoted by increasing the electron donor power of the ligands, consistent with the idea that the addition is oxidative.

We find just the opposite behavior for our iridium complexes: the addition is promoted by electron-withdrawing ligands and inhibited by electron donors.

$[Ir(cod)_2]^+$ and $[Ir(cod)L_2]^+$ (3), containing the relatively electron-withdrawing ligands, (cod) and tertiary phosphines, add hydrogen to give observable adducts. We have never observed the direct addition of hydrogen to $[Ir(cod)L(py)]^+$ (5), but 5 is a catalyst. Finally, the relatively strong donor ligands Cl$^-$ and pyridine (py) completely suppress addition (at -80 °C) and catalysis in $[Ir(cod)Cl(py)]$ and $[Ir(cod)(py)_2]^+$.

The addition of hydrogen to these complexes is therefore probably not oxidative, and may even be reductive in character.[30] Possibly, factors other than ligand basicity are involved in these effects, but whatever their origin, the unusual reactivity pattern that these complexes possess gives them and their derived catalytic systems a unique degree of resistance to oxidizing poisons.

The addition of hydrogen to an olefin complex (the unsaturated route) had been considered an unlikely formation reaction for dihydrido olefin intermediates, while olefin addition to a hydride complex (the hydride route) has been postulated in many catalytic schemes.[1,22] This view was held because it was believed an olefin, as an electron-withdrawing ligand, should deactivate the metal for hydrogen addition.

We have now found that both routes (eq 4 and 5) are viable, at least in these iridium systems, but believe that the hydride route is indeed more important[20] in catalysis.

Conclusions

It is evident from this Account that catalytic systems can be very sensitive to their environment, in which solvent and substrate play their part. A catalyst system can therefore only be specified by giving the full conditions: precursor, solvent, substrate, pressure, etc. The properties of the catalyst will be the properties, not necessarily of the precursor, but of the majority species actually present in solution under any particular set of conditions. We must therefore draw a distinction between the catalyst precursor, 3 in the cases above, and the majority species present in each case. Complex 3 in acetone gives, with H_2, a majority species [IrH_2-(acetone)_2L_2]^+ very different in properties from the catalyst formed from 3 in dichloromethane. Even in dichloromethane, adding hydrogen first and olefin only subsequently leads to a very different result, instant deactivation to give [Ir_2H_5L_4]^+, than does the reverse order of addition which gives [IrH_2(olefin)_2L_2]^+, the active species for hydrogenation.

Catalysis research presents a challenge because it is still so much of a "black art", but we are now beginning to see the outlines of an understanding of catalyst reactivity.

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(29) Louw et al.[28a] have found that the same mechanism operates for the neutral complexes, [IrCl(cod)(PEtPh_2)] (18), so that it is not the overall positive charge of 3 that decides the order of addition. 18 is, however, air-sensitive, so that the neutral complexes are less oxidation-resistant than their cationic counterparts.

(30) The distinction between a ligand addition (M + L → ML) and an oxidative addition (eq 8), which is often made, seems to me to be somewhat arbitrary. The addition of ethylene, for example, is a ligand addition if the adduct is considered as a metal–olefin complex, but an oxidative addition if considered as a metallacyclopropane. Apart from this fundamental ambiguity, there is some doubt as to the oxidizing character of "oxidative" additions such as 3 + H_2. The term 2-electron addition would unambiguously cover all these cases. A further division could be made according to the number of atoms forming bonds to the metal in the process: M + CO → MCO (1-center, 2-electron addition), M + C_2H_4 → M(C_2H_4), or M + H_2 → MH_2 (2-center, 2-electron). The same ideas could be applied to a variety of related processes: M + H^+ → MH^+ (1-center, 0-electron); M + e^- → M^- (0-center, 1-electron). This system has the advantage of being independent of the formal oxidation states of the complexes involved and of the electronegativity of the addendum.