with a medium-pressure Hanovia lamp. No evidence of exchange was observed in the ^{1}H NMR spectrum (Brüker 200).

Dihydrido Olefin and Solvento Complexes of Iridium and the Mechanisms of Olefin Hydrogenation and Alkane Dehydrogenation

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Abstract: Tests for homogeneity are applied to the catalysts [Ir(cod)L$_2$]A/CH$_2$Cl$_2$/H$_2$ (cod = 1,5-cyclooctadiene; A = BF$_4$; L = PPh$_3$, PMePh$_2$) and their possible generality is discussed. [Ir(cod)L$_2$]A (L = PPh$_3$) reacts with H$_2$ and S (S = solvent) to give the isolable complexes [IrH$_2$S$_2$L$_2$]A (**1**) in which the displacement order of the M–S groups is H$_2$O ≈ THF < *t*-BuOH < *i*-PrOH < Me$_2$CO < EtOH < MeOH < MeCN. The utility of this order in understanding our alkane activation system based on **1** and the effects of S on catalytic hydrogenation are discussed. **1** (S = H$_2$O) reacts at –80 °C with olefins to give [IrH$_2$(ol)$_2$L$_2$]A (ol = C$_2$H$_4$, C$_3$H$_8$) and [IrH$_2$(ol)(H$_2$O)L$_2$]A (ol = PhCH=CH$_2$, C$_5$H$_8$, *t*-BuCH=CH$_2$). Their role in hydrogenation is discussed in the light of stepwise catalytic ^{1}H NMR studies at –80 to +25 °C, in which they appear to be intermediates in catalysis. A catalytic cycle is proposed. Selectivity in competitive experiments is discussed. The rhodium analogues do not exhibit similar properties.

Introduction

In this paper we discuss rigorous tests of the homogeneity of hydrogenation catalysts, in particular [Ir(cod)L$_2$]A (cod = 1,5-cyclooctadiene; L = PR$_3$; A = BF$_4$), as well as the synthesis and properties of two classes of related complexes [IrH$_2$S$_2$L$_2$]A and [IrH$_2$(ol)$_2$L$_2$]A (S = solvent; ol = olefin). The dihydrido olefin complexes are intermediates in the catalytic reaction and can be detected when the reaction is run in an NMR experiment in a stepwise fashion. A mechanism is proposed. Finally, the relevance of these results to our alkane dehydrogenation system is also discussed.

[Ir(cod)L$_2$]A (cod = 1,5-cyclooctadiene; L = PMePh$_2$; A = BF$_4$) and related compounds are alkene hydrogenation complexes of an unusual type.[3,4] The reaction is highly solvent sensitive: in CH$_2$Cl$_2$ the system is very active and reduces even tetrasubstituted olefins very rapidly, but in EtOH it is almost inactive. In contrast, the Rh analogue shows a much less significant solvent dependence.[3] The rates (in catalytic cycles h^{-1}) for the reduction of 1-hexene by the following systems expressed as (metal, solvent) are as follows: (Ir, CH$_2$Cl$_2$), 5000 > (Rh, CH$_2$Cl$_2$), 4000 > (Rh, EtOH), 600 > (Ir, EtOH), 5. For hindered olefins, e.g., 1-methylcyclohexene, the rate advantage for the iridium system becomes even more marked: (Ir, CH$_2$Cl$_2$), 1900 ≫ (Rh, CH$_2$Cl$_2$),

(Rh, EtOH), (Ir, EtOH), ≃1. These results cannot be understood by restricting oneself to considering the nature of the catalyst precursor charged into the reactor at the outset, but rather in terms of the properties of all the species present under catalytic conditions. In the cases we shall discuss, one species (the principal species) seems to predominate (>95%) in the reaction mixture. This may often be the case, since (as long as there are no dead-end side equilibria on the catalytic cycle) the occurrence of a markedly slow step in the catalytic cycle will tend to lead to a buildup of the preceding species. In the catalytic cycle shown, for example,
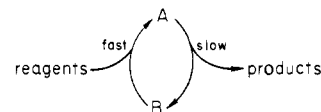
A will be the principal species. We will address the question of the nature of the principal species in the iridium catalyst in this paper. Other unusual properties of the system are the selectivity and insensitivity both to oxidizing functionality in the solvent or substrate and to the presence of air, and we shall also discuss the origin of some of these effects.

We have also developed a closely related alkane dehydrogenation system[4] involving [IrH$_2$S$_2$L$_2$]BF$_4$ (S = H$_2$O or Me$_2$CO, L = PPh$_3$), which may share some intermediates with the hydrogenation system mentioned above.

It was suggested to us by several colleagues[5] that all these properties are very unusual for a homogeneous system, so unusual,

(1) Yale University.
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(3) Crabtree, R. H.; Felkin, H.; Morris, G. E. *J. Organomet. Chem.* **1977**, *141*, 205. Crabtree, R. H.; Morris, G. E. *Ibid.* **1977**, *35*, 395.
(4) (a) Crabtree, R. H. *Acc. Chem. Res.* **1979**, *12*, 331. (b) Crabtree, R. H.; Mihelcic, J. M.; Quirk, J. M. *J. Am. Chem. Soc.* **1979**, *101*, 7738. (c) Crabtree, R. H.; Mellea, M. F.; Mihelcic, J. M.; Quirk, J. M. *Ibid.* **1982**, *104*, 107.

(5) Ibers, J. A.; DiCosimo, R.; Whitesides, G. M. *Organometallics* **1982**, *1*, 13.

indeed, that one should consider the possibility that precipitated or colloidal metal is responsible for both hydrogenation and dehydrogenation. In our paper on alkane activation,[4c] we were able to exclude this possibility by using a variety of tests we had developed. In this paper, we successfully apply similar methods to the case of the hydrogenation system.

Having established their homogeneity, we consider the synthesis and reactions of [IrH₂S₂L₂]A and conclude with a discussion of the mechanism of hydrogenation and dehydrogenation in this system.

Results and Discussion

Heterogeneous Mechanisms. The fact that a soluble metal complex appears to catalyze a liquid-phase organic reaction does not establish that the complex is a homogeneous catalyst. The complex may have partly or wholly decomposed to deposit metal on or in the reaction flask or to give a metallic colloid. This may be a more common occurrence than is generally believed.

Maitlis et al.[6] have addressed the question of precipitated or deposited metal. We have now applied our minor modification of their method to the [Ir(cod)(PMePh₂)₂]PF₆-based catalyst previously described.[3] A catalyst preparation that has been successfully used for olefin reduction is passed through a micropore filter, which would retain any precipitated metal, and the filter washed with fresh CH₂Cl₂ (the reaction solvent). The filter was examined microscopically for metal; none was observed. The filter was then placed in the original flask in which the catalytic reaction was run. The filter and flask failed to catalyze cyclohexene hydrogenation, as expected if precipitated metal is absent. Iridium black, in contrast, shows hydrogenation activity under these conditions. The catalyst therefore does not contain precipitated metal.

Metal particles of colloidal size (10–1000 Å) readily pass through micropore filters, and these could easily have been present in the active catalyst and be responsible for the catalytic activity. We have met this problem before in our work on alkane activation[4c] and so were able to apply the same tests to the problem.

Preparations of colloidal iridium[4c,7] are pale yellow and completely clear and transparent. They resemble genuine homogeneous solutions yet typically have on the order of 100 m² of metal surface per mL of the preparation. They can be exceptionally catalytically acitve.[8] If one is deliberately synthesizing a colloid, a polymer is usually added to stabilize the system. Otherwise the metal tends to precipitate. Polyvinyl alcohol (PVA) is most commonly used for this purpose. The tendency to precipitate increases as one goes to the less polar solvents (such as the chlorinated solvents we use).

There are three general types of experiments that can help distinguish homogeneous from heterogeneous catalysis. Homogeneous catalysis is indicated if: (1) the selectivity pattern for the catalytic reaction resembles those of authentic homogeneous catalysts but differs from those of all known heterogeneous catalysts, (2) authentic metal colloids catalyze a test reaction which is *not* catalyzed by the supposed homogeneous catalyst in question, and (3) light-scattering studies suggest colloids are absent. Test 1 is the most powerful. A colloid might pass test 2 in the unlikely event that it had been selectively poisoned for the test reaction. A colloid might pass test 3 if it were of very small diameter (<20 Å) or very dilute (<1 nM).[4c] The iridium system passes all these tests and is therefore definitively homogeneous.

We were able to apply a test of type 1 in the course of an investigation on the reduction of steroidal dienones;[9] we reported that [Ir(cod)(PCy₃)(py)]PF₆ selectively reduces the relatively unhindered C=C double bond of Δ¹,⁴-androstanedione before it reduces the more hindered one. More significantly the hydrogen

is added exclusively from the α side of the molecule in the reduction of the second double bond. This is exactly what is observed for [RhCl(PPh₃)₃] but not for any heterogeneous catalysts, which give mixtures of the α and β product, the β predominating.[9] This test may have some generality.

Nitrobenzene is very rapidly reduced to aniline by H₂ in the presence of iridium colloids.[7] In contrast, our own catalyst system does not effect this reduction, even after 4 days at 25 °C (H₂, 1 atm). It is not known how general this test will prove to be, since several catalysts claimed to be homogeneous[10] also effect this reduction. Further work will show whether all these are indeed genuinely homogeneous or not.

Authentic colloids scatter light strongly.[11] In the dynamic light-scattering experiment, the scattered light is analyzed by means of its autocorrelation function in a way that allows the average sizes of any scattering particulate present to be determined. We have reported the full details of the application of this method to the case of our alkane activation system. As now applied to the catalytic hydrogenation system, test 3 shows that particulates (>20-Å diameter) are absent, at least to a detection limit of ca. 1 nM. We shall be publishing elsewhere a full account of the application of this method to other colloidal and catalytic systems.[12]

These tests firmly establish that the system is indeed homogeneous. Having ruled out one mechanism, we go on to consider what the real mechanism might be.

Role of the Solvent. A striking feature of the catalyst is the requirement for a relatively noncoordinating solvent, such as CH₂Cl₂, and the high sensitivity to inhibition by coordinating solvents, as mentioned in the Introduction.

This property of the system is probably due to the formation, in the presence of coordinating solvents, of [IrH₂S₂L₂]A (1, S = solvent; L = PPh₃; A = BF₄ or PF₆). These were briefly noted in 1969.[13] We have now isolated a wide variety of these as crystalline solids and find that, under certain conditions, the solvent can be replaced by other weakly bound ligands. This has led to the isolation of a number of unusual species, some of which are discussed below. Secondly, they are the key precursors in our alkane activation experiments,[4c] in which we were able to dehydrogenate a variety of alkanes to coordinated π ligands. This reaction is discussed in a later section. Thirdly, they seem to be intermediates in catalysis when the solvents S are present in the reaction mixtures or when the substrates contain ligating donor groups such as C=O.[9]

Synthesis of [IrH₂S₂L₂]A. Hydrogenation (1 atm, 0 °C) of [Ir(cod)L₂]A (L = PPh₃, A = BF₄) leads to loss of cyclooctane. In a coordinating solvent, the solvento complexes [IrH₂S₂L₂]A are formed.[13]

In addition to the previously known examples (S = Me₂CO, EtOH, and MeCN), we have investigated others (S = H₂O, THF, MeOH, i-PrOH, and t-BuOH). All the complexes are air-stable, pale buff-colored crystalline materials, and they tend to lose H₂ thermally, especially in solution. Perhaps for this reason, 1 (S = Me₂CO) requires an unusual degree of care to obtain good yields. The best yields are obtained if the initial isolation is carried out under H₂ at 0 °C. To this end, the minimum volume of solvent S was used in those cases (S = Me₂CO, MeCN) where the product is soluble in S, and Et₂O was added to precipitate the crude product after the reaction.

We were, of course, particularly interested in cases in which the S ligands were weakly bound, and we considered that the H₂O, THF, MeOH, i-PrOH, and t-BuOH complexes might prove more labile. In these cases, and in the known case S = EtOH, poor synthetic results were obtained by using a mixture of CH₂Cl₂ and S. Rather, a suspension of [Ir(cod)L₂]A in S was treated with H₂ at 20 °C. The red color of the starting complex gave way to a pale yellow suspension after 0.5 h. This consisted of the known[3]

(6) Hamlin, J. E.; Hirai, K.; Millan, A.; Maitlis, P. M. *J. Mol. Catal.* **1980**, *7*, 543.

(7) Dunworth, W. P.; Nord, F. F. *J. Am. Chem. Soc.* **1950**, *72*, 4192.

(8) Huckel, W. "Katalyse mit Kolloiden Metallen"; Akad-Verlag: Leipzig, 1927.

(9) Suggs, J. W.; Cox, S. D.; Crabtree, R. H.; Quirk, J. M. *Tetrahedron Lett.* **1981**, *22*, 303 and references cited therein.

(10) Marko, L. *Adv. Chem. Ser.* **1978**, *No. 173*, 26.

(11) Berne, B. J.; Pecora, R. "Dynamic Light Scattering", 1st ed.; Wiley: New York, 1976.

(12) Albaum, M.; Crabtree, R. H.; Eden, D. *J. Mol. Catal.*, in press.

(13) Shapley, J. R.; Schrock, R. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1969**, *91*, 2816.

Table I. NMR and IR Data for the Complexes $[IrH_2L^1L^2(PPh_3)_2]BF_4$

ligands		¹H NMR data[a]			IR data[b]	
L¹	L²	Ir-H	Ir-solv[c]	Ir-ol[c,d]	ν(Ir-H)	solv
Me₂CO[e]		-27.8, t (17)	1.8		2257, w	1666, 1713, w
MeCN		-20.7, t (16)	1.7		2207, w	2315, w
THF		-29.5, t (16)	1.7, 2.0, 3.6c			
H₂O		-29.8, t (16)	2.4		2280, w	1610, 3650, w
MeOH		-29.5, t (18)	1.2, 2.4			
EtOH		-29.4, t (16)	1.0, 2.4		2240, w	3415, s; 3040, m
i-PrOH		-29.5, t (17)	0.9, 1.3, 2.4			
t-BuOH		-29.9, t (16)	0.9, 2.4		2290, w	3050, w; 3660, m
coe	H₂O[f]	{ -10.3, dd (4, 16) { -31.9, dd (4, 16)	2.4	4.1, 4.3		
C₅H₈	H₂O	{ -10.4, dd (4, 20) { -31.4, dd (4, 17)	2.5	3.9, 4.2		
PhCH=CH₂	H₂O	{ -10.2, dd (4, 16) { -31.4, dd (4, 17)	2.4	3.9, 4.1, 4.5		
t-BuCH=CH₂	H₂O	{ -10.5, dd (4, 17) { -31.6, dd (4, 16)	2.4	4.0, 4.1, 4.5d		
C₂H₄		-11.8, t (16)		3.2		
C₃H₆		-14.2, t (14)		3.2, 3.5		
PhCH=CH₂		-13.6, t (18)		3.9, 4.1, 4.5		

[a] In CD_2Cl_2 at -80 °C. Resonances reported: position (δ), multiplicity (t = triplet, d = doublet) (coupling constant, Hz). A complex set of peaks at 7.1-7.4 assigned to PPh₃ appears in all cases. [b] In CH_2Cl_2 at 25 °C given as: position (cm⁻¹), intensity. In all cases bands due to PPh₃ and BF₄⁻ were also observed. [c] Broad resonances $\omega_{1/2} \approx 5$ Hz due to exchange. [d] The excess of olefin leads to the obscuring of some resonances. [e] $\nu(Ir-H) = 2230$ and 2250 cm⁻¹ (w); $\nu(C=O) = 1710$ and 1660 cm⁻¹ (s). [f] Resonances $(CD_2Cl_2, -80 °C)$ assigned to Ir(ol)-(H₂O)L₂⁺: 2.4-2.5 (in all cases, H₂O), and 4.1 and 4.3 (coe), 4.0 and 4.2 (C₅H₈); 3.9, 4.1, 4.5 (PhCH=CH₂); no complex of this type observed (t-BuCH=CH₂). For Ir(ol)₂L₂⁺: 3.2 (C₂H₄); 3.2, 3.5 (C₃H₈).

[Ir₂H₅L₄]A (ca. 5%) and the desired complex. Recrystallization from CH₂Cl₂/Et₂O gave the solvento complexes in pure form in 80-85% yield. It was important not to have additional coordinating solvent present in the crystal lattice, as this would interfere with our subsequent work. For this reason CH₂Cl₂/Et₂O was used for recrystallization; indeed, many of the compounds crystallized as CH₂Cl₂ solvates.

The fact that this reaction went well even in H₂O, in which the organometallic complexes are insoluble, suggested that H₂ might be able to react directly with solid crystalline [Ir(cod)L₂]A in the absence of solvent. This proved to be true, [Ir₂H₅L₄]A being formed in good yield over 0.5 h at 25 °C at 1 atm pressure.

An alternative synthetic route to 1, protonation of IrH₅L₂ with HBF₄ in acetone or in the other solvents, was slightly less convenient and was not explored in detail.

A number of compounds which do not usually act as ligands also coordinate to form similar complexes. One of these, o-diiodobenzene,[14] gives a rare[15] example of a complex of an organic halide. Other organic halides also seem to coordinate to 1, but more weakly.[16] Organic nitro compounds, esters,[14] enones, and dienones[9] also bind well, especially when part of an extended conjugated π system (e.g., PhNO₂, PhCH=CHCO₂Et). These will be described elsewhere.

The stereochemistry of the complexes 1 follows from the empirical finding[17] that the position of an IrH resonance depends on the nature of the trans ligand. For PR₃, H, or C=C, a resonance at δ -10 to -15 is expected. The observed resonance positions are in the region of δ -29 to -30 for all the alcohol and ether complexes, δ -27.8 for the acetone complex, and δ -20.7 for the softest S ligand of the group, MeCN (see Table I). This indicates stereochemistry 1 and provides a resonance position range (27-30 ppm) for Ir(III) complexes with oxygen donor ligands trans to H. In confirmation of the stereochemistry, a cis ²J(P,H) coupling constant of 16-18 Hz is observed in all cases.

In the IR of CH₂Cl₂ solutions of the complexes, a broad ν(Ir-H) absorption is observed (Table I). The more strongly coordinating the S ligand, the lower the Ir-H stretching frequency, as would

be expected from trans-influence considerations. The bands shift in the expected manner in the corresponding cis-dideuterio complex, suggesting that these vibrations are not extensively coupled with those due to S. Vibrations assigned to coordinated MeCN (ν(CN)), Me₂CO (ν(CO)), and ROH (ν(OH)) are lowered in frequency on coordination compared to the free ligands, as expected.

Reactions of [IrH₂S₂L₂]A. We recently described the first examples of olefin dihydride complexes, such as [IrH₂(cod)L₂]⁺, formed from cod and 1.[18] We also proposed the complex as an intermediate in cod hydrogenation by 1. We wished to extend our studies to the more common olefins to see if other features of interest emerged. We found that similar complexes are formed and that the coordinated olefins were rapidly dehydrogenated above 40 °C. This suggested attempting the previously unknown dehydrogenation of alkanes, which we successfully achieved in 1979.[4b] We now return to the chemistry of the system in more detail and describe the reactions of 1 with olefins from -80 to +25 °C, where dehydrogenation does not usually occur. This work throws light on the mechanisms of hydrogenation and dehydrogenation.

At low temperatures (-80 to -50 °C), simple olefins, such as cyclooctene (coe) in CD₂Cl₂, displace the more labile S ligands of the solvento complexes. We have studied the case S = H₂O, as this is the most labile member of the series. All the reactions have been followed by NMR spectroscopy, as the complexes have proved to be even less thermally stable than the cod analogues. These first examples of monoolefin dihydride complexes have not, therefore, been fully characterized. The NMR spectra of the reaction mixtures nevertheless allow us to determine the ligand environment and stereochemistry of the major organometallic species present. No more than ca. 5% of other species was present in the cases reported here except where noted.

The reactions were carried out by adding 10 M equiv of olefin to 1 (S = H₂O) at -80 °C in CD₂Cl₂ and recording the ¹H NMR spectra over the ranges of δ +10 to -40 and -80 to +20 °C. The resonances observed could be ascribed to the species 1-3 (eq 1). In the cases of the most strongly binding olefins, ethylene and propylene, 3 (ol = ethylene, 3a; propylene, 3b; styrene 3c) was

(14) Crabtree, R. H.; Mellea, M. F.; Faller, J. W.; Quirk, J. M. *Organometallics* **1982**, *1*, 1361.

(15) Lawson, D. N.; Osborn, J. A.; Wilkinson, G. *J. Chem. Soc. A* **1966**, 1733.

(16) Martin, E.; Wiberg, K. B., personal communication, 1981.

(17) Green, J. C.; Green, M. L. H. In "Comprehensive Inorganic Chemistry"; Emeleus, H. J., Ed.; Pergamon Press: Oxford, 1973; Vol. 4.

(18) Crabtree, R. H.; Felkin, H.; Fillebeen-Khan, T.; Morris, G. E. *J. Organomet. Chem.* **1979**, *168*, 183.

(19) Some of this work was mentioned in a short note.[4b] We have since found that some complexes we then thought were diolefin complexes now prove to be monoolefin monosolvento complexes.

$$I \quad\quad\quad 2 \quad\quad\quad 3 \quad\quad (1)$$

(L = PPh$_3$, ‖ = olefin, S = H$_2$O)
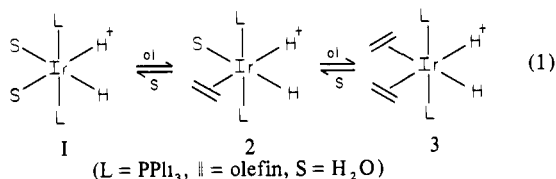
formed directly, no other species being observed. Styrene also gave some **3c** (ca. 50%) at −80 °C, but on warming to −50 °C, no **3c** was left and the equilibrium shifted toward **2**. Bulkier olefins, such as cyclooctene, cyclopentene, and *tert*-butylethylene, gave only the mixed-ligand derivatives **2** in equilibrium with **1**.

The complexes were identified from their ^{1}H NMR spectra (Table I). Taking the simplest case first, the introduction of C$_2$H$_4$ into a solution of **1** at −80 °C leads to the replacement of the coordinated H$_2$O. The original triplet resonance at δ −29.8 assigned to the hydride ligands in **1** is cleanly replaced by a new triplet resonance of equal intensity at δ −11.8. A new peak at δ 3.2 is assigned to coordinated C$_2$H$_4$. A resonance due to free water was not seen, possibly because it is obscured by other peaks.

Exactly the same resonances are observed in the case of the acetone complex **1** (S = Me$_2$CO), but in this case a peak corresponding to free acetone at δ 2.09 is also seen.

The stereochemistry of **1** and **2** shown in eq 1 is certain, but that for **3** could not be unambiguously distinguished from the closely related all-trans isomer, although by analogy with **1** and **2** the one shown in eq 1 is very likely.

Propylene behaves in the same way, but styrene behaves differently. As mentioned above, at −80 °C only **2c** and **3c** are observed, but on warming, **3c** disappears and only **2** is left. The evidence for the assignment of the new species as **2** is as follows. All the new resonances due to **2** rise and fall in concert on heating or cooling the sample. The IrH resonances trans to S show exactly the same sort of dependence on the nature of S as do the corresponding resonances in **1**. The resonances for the inequivalent IrH groups are mutually coupled (^2J(H,H) = 4 Hz), showing that these two groups are present in the same molecule and must be mutually cis. A resonance for coordinated S is observed and addition of excess S changes the equilibrium in favor of the more highly S-substituted species **1** and **2**. Resonances for coordinated olefin are also seen (see Table I for data).

Still more bulkly olefins, such as cyclopentene, cyclooctene, and *tert*-butylethylene give only an equilibrium mixture of **1** and **2**; **3** was never observed. In the cases of cyclopentene and cyclooctene, two CH vinyl resonances are observed. Probably olefin rotation is "frozen out" at −80 °C and it adopts the electronically preferred configuration shown in eq 1, for which the two termini of the C=C group become inequivalent. This configuration is probably adopted so that the C=C group can avoid sharing d orbitals with the good π acceptor PPh$_3$ groups.[20] This configurational preference leads to the complexes **2** and **3** tending to have coplanar M(C=C)H groups, an arrangement that we have already shown[18] leads to the most rapid hydrogenation. This favorable conformation may help account for the activity of our catalyst.

On warming of the reaction mixtures obtained from **1** and olefins to room temperature, olefin hydrogenation takes place, and the resulting alkanes can be detected in solution (NMR, GC). The organometallic products depend on the olefin. For C$_2$H$_4$ and C$_3$H$_6$, [Ir(ol)$_2$L$_2$]$^+$ seems to be formed, this complex is discussed in detail below. Addition of H$_2$ at −80 °C gives **3**. For styrene, the unusual product [(η^6-PhEt)IrL$_2$]A is obtained. As has been reported elsewhere,[21a] this reaction probably involves η^3-benzyl intermediates.

The reaction mixtures formed from cyclopentene and cyclooctene also give hydrogenation on warming. The organometallic products show NMR resonances at −80 °C both from coordinated

(20) Schilling, B. E. R.; Hoffmann, R.; Faller, J. W. *J. Am. Chem. Soc.* **1979**, *101*, 592.

(21) (a) Crabtree, R. H.; Mellea, M. F.; Quirk, J. M. *J. Chem. Soc., Chem. Commun.* **1981**, 1217. (b) Crabtree, R. H.; Quirk, J. M. *J. Organomet. Chem.* **1980**, *199*, 99.

Table II. The Cyclohexene Hydrogenation Activity of Solutions of [Ir(cod)(PMePh$_2$)$_2$] A in CH$_2$Cl$_2$, Containing 1.0 molar equiv mol^{-1} of Ir of Various Solvents, S

S	rate,^{a} %
none	100
t-BuOH	94
Me$_2$CO	85
i-PrOH	58
PhCl	58
EtOH	40
MeCN	0

^{a} Maximum rate as a percentage of the rate in pure CH$_2$Cl$_2$ (3800 mol of H$_2$ mol^{-1} of Ir at 0 °C in a constant-pressure apparatus (pH$_2$ = 62 cmHg, [olefin] = 0.5 M, [catalyst] = 0.5 mM)).

olefin at δ 4.2 and from coordinated H$_2$O at δ 2.4. These products may be [Ir(ol)(S)L$_2$]$^+$ although we cannot exclude the formation of the related 18-electron complexes [Ir(ol)$_{3-x}$S$_x$L$_2$]$^+$. At 20 °C, ligand exchange is rapid and the peaks due to coordinated olefin are no longer seen. The complexes do not add H$_2$, at least at −80 °C, perhaps because of the increased electron density present at the metal, which would inhibit an addition having reducing character.[21b] Under catalytic conditions, no S ligands are present and different behavior is expected (see below). 1,2-Di-*tert*-butylethylene (trans + cis) does not react at all with **1** at any temperature, no doubt because of its great bulk.

Analogous solvento complexes [IrH$_2$S$_2$(PCy$_3$)(py)]A from the related mixed-ligand catalysts [Ir(cod)(PCy$_3$)(py)]A (py = pyridine) appear to be formed in situ for S = Me$_2$CO but decompose on attempted isolation, and no monoolefin derivatives were ever obtained. We imagine the lower stabilty of these solvento complexes may be due to the more electron-releasing character of the ligands in this system, compared to the case where L = PPh$_3$, quenching part of the Lewis acid character. The details of this work will appear elsewhere.

Displacement and Catalytic Studies. To obtain an idea of the relative stabilities of the different S ligands in the complexes [IrH$_2$S$_2$L$_2$]$^+$ (**1**), we performed displacement studied by adding 2 equiv of one solvent (e.g., EtOH) to a CD$_2$Cl$_2$ solution of a complex of type **1** containing a different solvento ligand (e.g., **1**, S = H$_2$O). In this case, the resonances of **1** (S = H$_2$O) are completely replaced by those due to **1** (S = EtOH). From experiments like this we were able to obtain the following order of stability: H$_2$O $\simeq$ THF < *t*-BuOH < *i*-PrOH < Me$_2$CO < EtOH < MeOH < MeCN. In some cases what appeared to be mixed solvento complexes were obtained, as evidenced by the appearance of ^2J(H,H) cis coupling of 5 Hz between the now inequivalent hydrides, e.g., [IrH$_2$(MeOH)(Me$_2$CO)L$_2$]$^+$, but these were not studied in detail.

This order was most helpful to us in our attempts to use these complexes for alkane activation and for studies on the reactions of olefins with solvento complexes. We chose **1** (S = H$_2$O) for most of our subsequent studies, because this was the most labile of the series, but **1** (S = Me$_2$CO) was also useful on occasion.

We wished to discover whether the hydrogenation catalyst formed from [Ir(cod)L$_2$]A (**4**) and H$_2$ in CH$_2$Cl$_2$ was also inhibited by the solvents S, and whether the order of relative effectiveness of these solvents bore a relation to the displacement order obtained above. One problem arises at this point. Well-characterized complexes of type **1** can only be obtained for L = PPh$_3$, yet **4** (L = PPh$_3$) is a rather poor catalyst. We decided to study the catalyst **4** (L = PMePh$_2$) in pure CH$_2$Cl$_2$, and in CH$_2$Cl$_2$ to which a known amount of S had been added. In table II are listed the relative rates of hydrogenation of cyclohexene by **4** (L = PMePh$_2$) in the presence of only 1 M equiv per mol of Ir of some coordinating solvents, S. As can be seen the percentage inhibitions are surprisingly high, illustrating the high sensitivity of the catalyst to change of solvent. The order of relative rates is almost exactly that which we established above from displacement studies. In the case of the most strongly coordinating S ligand, MeCN, 1 M equiv suffices completely to suppress the catalytic reaction. As discussed above, [Ir(ol)(S)L$_2$]$^+$ does not

seem to add H_2 so that the formation of this complex (S = MeCN) would account for the observed inhibition.

Observation of Intermediates under Catalytic Conditions. It seemed plausible that the olefin dihydride complexes might be intermediates in the catalytic reduction of olefins by [Ir(cod)L$_2$]A (**4**). The main difference between the conditions used to observe **2** and **3** above and the catalytic conditions (CH$_2$Cl$_2$, olefin, 0 °C), is the presence only in the former case of the excess S, wholly or partially dissociated from **1**. In order to eliminate this interfering S ligand, we were forced to work in conditions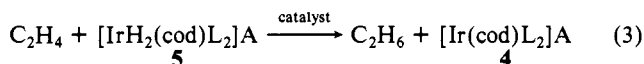 more closely approximating to the catalytic ones. One might think that simply hydrogenating **4** in CH$_2$Cl$_2$ containing the alkene, cooling to −80 °C, and observing the products by NMR should solve the problem. Unfortunately, this does not work, for the following reasons. The greater rate of hydrogenation by **4** of monoolefins compared to cod is such that for any moderate amount of added olefin, the reaction cannot be conveniently and reproducibly stopped at a point suitable for making measurements. Adding a large amount of olefin naturally introduces large olefin peaks into the NMR spectrum. These lead to complications in observing the weaker peaks of interest.

We therefore devised an experimental arrangement that allowed us to run the catalytic reaction reproducibly in steps. Products were observed after each step, and the catalytic cycle could be kept under strict control. A solution of **4** and a moderate amount (e.g., 10 equiv) of olefin is first cooled to −80 °C in an NMR tube. H_2 is passed at that temperature. The complex takes up H_2. The excess H_2 is then swept out of the NMR tube with N_2. The mixture is then allowed to warm up to room temperature. The only H_2 present is that bound to Ir, thus guaranteeing that only 1 equiv of olefin can be hydrogenated. This cycle is repeated as desired. Results using C_2H_4 as the added substrate are described below.

We find that the activation of the catalyst takes place via the formation of the known dihydride adduct that we have already reported,[18] the characteristic resonances of **5** appearing on H_2 addition to **4** at −80 °C (eq 2). The transfer of H_2 to the

$$Ir(cod)L_2^+ \rightarrow cis\text{-}[IrH_2(cod)L_2]^+$$
$$\mathbf{4} \qquad\qquad \mathbf{5} \qquad\qquad (2)$$
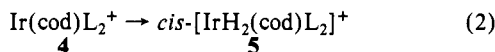
coordinated cod in **5** only takes place to the extent of ca. 20% in the first cycle. The activated catalyst then uses the H_2 in equilibrium with the initial H_2 adduct **5** to hydrogenate a part of the excess C_2H_4 (eq 3). This is complete by the time the mixture

$$C_2H_4 + [IrH_2(cod)L_2]A \xrightarrow{\text{catalyst}} C_2H_6 + [Ir(cod)L_2]A \quad (3)$$
$$\mathbf{5} \qquad\qquad\qquad\qquad\qquad \mathbf{4}$$

has warmed to room temperature. In this way, a part of the catalyst amounting to ca. 20% of the whole uses the H_2 from **5** to hydrogenate the excess of C_2H_4. We deduce from this that the hydrogen transfer to cod in **5** is ca. 5 times slower than to C_2H_4 in the activated catalyst (i.e., where cod is no longer present). This may perhaps be ascribed to the relative rigidity of the cod ligand.

The mixture is then cooled to −80 °C and H_2 is added. The 80% of the Ir that is present as **4** takes up H_2 to give [IrH$_2$-(cod)L$_2$]$^+$, as judged from the appearance of the resonances assigned to this species in our experiments.

Warming this solution leads to a further cycle of hydrogenation. As the cycles are repeated, less and less of the cod complexes **4** and **5** survive, and the C_2H_4-containing species replace them. After several cycles they built up to a point that we can identify proton resonances that we assign to coordinated C_2H_4 in the spectrum. The low-temperature form is **3a**, (ol = C_2H_4), and at high temperature the most reasonable assumption is that [Ir(C_2H_4)$_x$L$_2$]$^+$ (**6a**) is present. The value of x is probably 2, because the intensity of the resonance for coordinated C_2H_4 is unchanged on adding H_2 at −80 °C, when [IrH$_2$(C_2H_4)$_2$L$_2$]$^+$ is formed. The red color of the solutions that contain **6** confirms this idea because empirically, 16-electron complexes tend to be red, but 18-electron complexes tend to be colorless or light yellow. It remains possible that [Ir(ol)$_3$L$_2$]$^+$ (**7**) is in equilibrium with **6** for the smaller olefins C_2H_4 and C_3H_6. The trans structure for **6** is supported by the

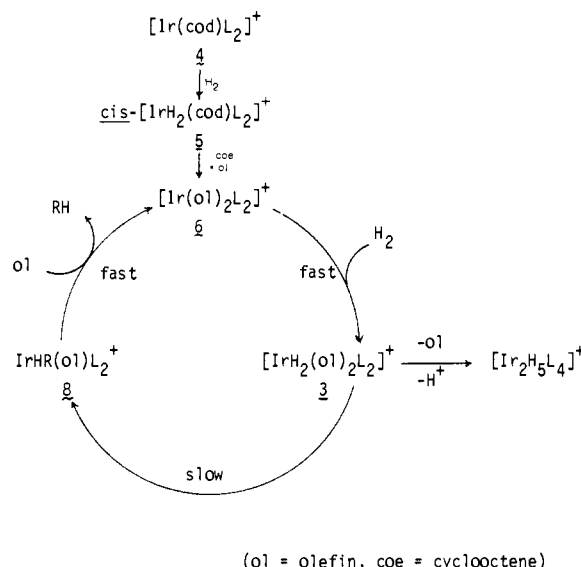$$(ol = olefin, coe = cyclooctene)$$

Figure 1. Proposed catalytic cycle for hydrogenation. Square brackets have been placed around species that have been observed. The upper part of the scheme represents catalyst activation, and the lower part represents the cycle itself.

failure to observe a $^2J_{P,C}$ coupling in a ^{13}C NMR spectrum, obtained on a similar sample in CDCl$_3$. For an olefin trans to PPh$_3$, such a coupling is usually observed.[21]

Consistent with this assignment, H_2 addition to **6a,b** at −80 °C gives the previously observed isomer of **3a,b** (eq 4). H_2 addition

$$(4)$$

$$\mathbf{6} \qquad\qquad\qquad \mathbf{3}$$
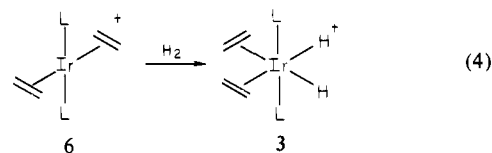
to **6** could, in principle, give another isomer of **3** in which the bulky L ligands were cis. This is not observed, possibly due to steric effects. We have no evidence about the conformational orientation of the olefin groups in **3** and **6** but show in eq 4 those to be expected.[20]

We can now write a plausible catalytic cycle for C_2H_4 hydrogenation based on the reactions we have observed. Figure 1 shows this cycle for a generalized olefin (ol).

Following rapid H_2 addition to **6a** to give **3a**, a slow transfer of coordinated H_2 to the coordinated olefin probably occurs. This transfer probably takes place in a stepwise fashion. In Figure 1, we postulate that an intermediate alkyl hydride IrHR(ol)L$_2^+$ (**8**) is formed. All attempts to trap **8** by adding ligands or using low temperature failed. Reductive elimination of RH from **8** should be very rapid. Some olefin isomerization accompanies hydrogenation. This must arise by β-elimination in **8** to give **3** (ol = isomerized olefin).

Competitive with hydrogenation is irreversible deactivation to the hydride-bridged dimer, [Ir$_2$H$_2$(μ-H)$_3$L$_4$]A.[3,4] This occurs when olefin has been consumed or, if the olefin is a poor ligand, when the olefin concentration begins to fall below a certain finite value (see ref 3). In this case, we imagine that an Ir−H group of a second molecule of an iridium hydride coordinates to **3** in preference to a molecule of substrate (Figure 1). Once in proximity to each other, a (μ-H)$_3$ bridging system can form and lead to irreversible deactivation.

It is here that the CH$_2$Cl$_2$ probably plays a role. It may be sufficiently coordinating to help prevent deactivation but not so much as to exclude substrate.

A more strongly coordinating solvent than CH$_2$Cl$_2$, Me$_2$CO completely inhibits deactivation, when present in CH$_2$Cl$_2$ at 1.0 equiv/mol of Ir, but causes a serious rate drop for hydrogenation of the more hindred tri- and tetrasubstituted olefins. Initial results[16] suggest that aromatic halides also help inhibit deacti-
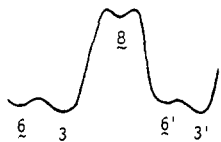
Figure 2. Qualitative free energy profile for the hydrogenation. The exothermicity of the reaction is so great that **6'** and **3'** lie far below **6** and **3**; for clarity, this has not been shown.

vation. The system completely reduces mono- and disubstituted (unhindered) olefins, but deactivation is competitive with reduction of tri- and tetrasubstituted (hindered olefins). No solvent has been found which completely inhibits deactivation but not the reduction of hindered olefins. We can therefore postulate that the species of catalytic interest compete with each other for binding in the order: unhindered olefins (0.5 M, i.e., standard conditions[3]) > Me$_2$CO (1 molar equiv/Ir) > hindered olefins (0.5 M) > Ir–H (5 mM) > CH$_2$Cl$_2$ (ca. 15 M). In this system, the intrinsic coordinating ability of CH$_2$Cl$_2$, together with its high concentration, combine to make it only slightly less coordinating than either Ir–H (deactivation) or hindered substrates. This may well be the optimum situation: the use of less coordinating solvents such as CHCl$_3$ leads to a sharp increase in the ratio of deactivation to reduction,[3] which is detrimental to the effectiveness of the catalyst. CH$_2$Cl$_2$ can therefore be said to coordinate sufficiently to maximize reduction of hindered olefins relative to deactivation.

For the reduction of unhindered olefins a more coordinating solvent can be used (e.g., 1 molar equiv of Me$_2$CO/mol of Ir in CH$_2$Cl$_2$). This has the advantage of very strongly suppressing deactivation, but without greatly affecting the reduction rate (see Table II).

Kinetic data are consistent with the identification of **3 → 8** as the slow step. The reaction is approximately zero order in [substrate] and [H$_2$] and first order in [catalyst] in the case of cyclohexene reduction by [Ir(cod)(PMePh$_2$)$_2$]BF$_4$. A slight dependence on [olefin] appeared for the more hindered olefins, perhaps due to competitive deactivation[3] in these cases. Since **6** is red and **3** colorless, the fact that the solutions are colorless under the catalytic conditions is also consistent with **3** being the principal species. The observation that H$_2$ reacts very rapidly with **6** to give **3** even at –80 °C suggests that it must be very fast indeed under catalytic conditions (0 °C), which is also consistent with these conclusions.

That the principal species is an Ir(III) complex, [IrH$_2$(olefin)$_2$L$_2$]$^+$ (**3**) to which oxidative addition cannot readily occur helps explain why the catalyst is stable to sensitive or oxidizing functionality, such as CBr, cyclopropane groups, CHCl$_3$, or O$_2$. Once an Ir(I) species, **6**, is formed, it must react very much more rapidly with H$_2$ than with the oxidizing functionality. As we have reported,[21b] [Ir(cod)L$_2$]$^+$, an isolable analogue of **6**, reacts only over 4 h with CH$_2$Cl$_2$, CHCl$_3$, and O$_2$, but very rapidly ($t_{1/2} \simeq 0.5$ s) with H$_2$, even at –80 °C. Our working hypothesis for the free energy profile of the catalytic reaction is shown in Figure 2. Complex **3**, as principal species is at the lowest point, in the scheme. **8** has never been observed and may well be the least thermodynamically stable.

The distinction[22a] usually made between a hydride pathway (e.g., 5a) and an "unsaturated" pathway (e.g., 5b) loses its meaning
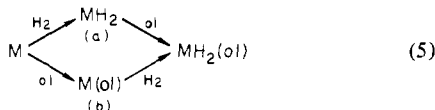
in this system, since the substrate is probably bound throughout the cycle.

Complications arise when groups are present in the substrate that can coordinate via lone pairs to the metal. C=O, for example, only binds weakly and C=C hydrogenation is slowed but not

(22) (a) Dolcetti, G.; Hoffman, N. W. *Inorg. Chim. Acta* **1974**, *9*, 269. (b) Tolman, C. A. *J. Am. Chem. Soc.* **1974**, *96*, 2780.

stopped. The greater the degree of unsaturation in conjugation with the C=O the tighter the Ir–O binding, probably because the Ir–O bonding is enhanced as the C=O π^* orbitals fall in energy.[9] In PhCH=CHCO$_2$Et, the binding is so tight[14] for **1** (L = PMePh$_2$) that no hydrogenation occurs at all.[3] The related mixed-ligand catalysts [Ir(cod)(PCy$_3$)py]A, which form far less stable solvento complexes, rapidly reduce this substrate. These effects also offer the attractive possibility of asymmetric induction by directing hydrogenation to one face of a chiral molecule via coordination of the catalyst to a C=O or OH group on one face of the molecule. Further work is in progress in this area.

Selectivity. An interesting feature of the catalytic system [Ir(cod)L$_2$]BF$_4$ (**1**, L = PMePh$_2$) is that it is selective. Cyclohexene (3700 catalytic cycles h^{-1}) and 1-methylcyclohexene (1900 cycles h^{-1}), when reduced in two separate experiments, gave a rate ratio of ca. 2:1. In a competitive experiment, an equimolar mixture of these olefins, exposed to only enough H$_2$ to hydrogenate half of the total, led to a product mixture of cyclohexane (93%) and methylcyclohexane (4%) in a ratio of 23:1.[3] The catalyst is therefore an order of magnitude more selective in a competitive experiment than one might be led to believe by a comparison of the rates for each olefin alone.

This illustrates once again that catalysis is a kinetic phenomenon in which effects are not additive and that the properties of catalyst will in general be strongly dependent on the nature of every component of the system. In this case, we imagine that the principal species, the olefin hydride complexes of type **3**, as the longest lived intermediates, have time to come to equilibrium with respect to the various olefins that may be present. In this case, cyclohexene is probably bound to a greater extent (ca. 10-fold if we consider that the intrinsic hydrogenation rate of a bound cyclohexene is 2.3 times that of a bound methylcyclohexene) than methylcyclohexene during the reaction. Since the ratio of the free olefins changes during the reaction, and methylcyclohexene is present in excess, especially during the later phase, the binding constant for cyclohexene must be ca. 100-fold greater than for methylcyclohexene, leading to a rough estimate of 2.8 kcal mol^{-1} for the difference in the free energy of binding. Differences of almost exactly this amount have been found by Tolman[22b] for the effect of methyl substitution on the binding of various olefins to Ni(0).

Interestingly, the less bulky olefins, C$_2$H$_4$ and C$_3$H$_8$, only give hydrogenation on warming to 10 °C. The bulkier olefins, cyclooctene and cyclopentene, undergo reaction at –10 to 0 °C. This is most probably the result of a greater relief of strain in going to the transition state of the olefin insertion in the cases of the bulkier substrates. A hindered olefin will bind more weakly to the metal, but this may help increase its rate of hydrogenation, *once it has successfully reached the active site.* In classical catalysts hindered olefins are reduced slowly, probably because they only very rarely get to the metal. In the iridium system, the olefin is bound throughout the catalytic cycle and the reduction rates for hindered olefins are comparable to those for unhindered ones.

If another ligand is present which competes with the olefin for the active site, this ligand will be a competitive poison. Examples are cyclohexene in the competition experiment mentioned above, excess PPh$_3$ in catalysts (such as RhCl(PPh$_3$)$_3$) that rely on dissociative equilibria of PPh$_3$ to open up sites at the metal, and coordinating solvents (e.g., THF, EtOH) in cases where these bind more strongly than the substrate. This helps to account for the greater sensitivity of hindered olefins to competitive poisoning by a coordinating solvent, or by a less hindered olefin when these are present. As is well established in enzyme kinetics, tight binding not of reagents or products but of the transition state for the catalyzed reaction is desirable for maximum catalytic rate enhancement. Indeed with a reaction rate of ca. 3 turnovers s^{-1} at 0 °C, the catalyst approaches the range of rates observed among enzymes (1–10^6 turnovers s^{-1} at 25 °C).

It is often said that true catalytic intermediates can rarely be directly observed and, conversely, complexes that are observed in catalytic systems are rarely intermediates. The present system

Table III. Temperatures of Olefin Substitution in NMR Experiments with $[RhH_2(Me_2CO)_2(PPh_3)_2]BF_4$

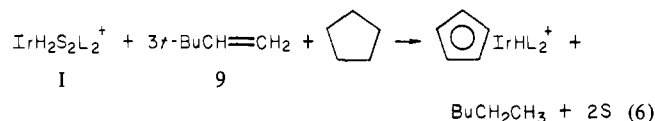| olefin[a]	temp,[b] °C	
	$(CD_3)_2CO$	CD_2Cl
nbd	−40	−78
cod	+25	−15

[a] Abbreviations: nbd = norbornadiene; cod = 1,5-cyclooctadiene. [b] Temperature of substitution in the solvent shown.

is an exception because there appear to be no side equilibria. Other factors are the low temperatures used to freeze out catalysis, the unusual kinetic stability of Ir(III) complexes in general, and the use of stepwise observations, in which only 1 molar equiv of H_2 per Ir is added in each cycle. The circumstances that make this study possible occur only rarely, and the stepwise method may not be generally useful.

Rhodium Analogues. Rhodium behaved very differently, and in no case were any of the rhodium analogues of **2–8** observed. In NMR experiments, $[RhH_2(Me_2CO)_2L_2]BF_4$ reacted with nbd or cod, directly to give [(diene)RhL$_2$]A and H_2, even when the solutions were warmed from −80 to +30 °C in 5° intervals. Table III shows the temperatures at which substitution occurred in these experiments. It will be seen that nbd substitutes more rapidly than cod and that in CD_2Cl_2 these reactions occur at much lower temperature than in $(CD_3)_2CO$. The mechanism of [Rh-(cod)L$_2$]A-catalyzed hydrogenation may therefore be substantially different than for the iridium analogue. The rate-determining step may perhaps be H_2 addition to the metal, which seems to be disfavored by olefin substitution, the reverse of the situation for iridium.
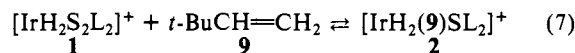
$[RhH_2(Me_2CO)_2L_2]BF_4$ also reacts with cyclopentene, but not cyclopentane, at 80 °C in $(CH_2Cl)_2$ to give $[RhCpHL_2]BF_4$. Further work is in progress.

Mechanism of Alkane Activation. The reaction of eq 6 is of

$$IrH_2S_2L_2^+ + 3t\text{-}BuCH{=}CH_2 + \text{⬠} \rightarrow \text{⬡}IrHL_2^+ +$$
$$\qquad\qquad I \qquad\qquad\qquad 9$$

$$BuCH_2CH_3 + 2S \quad (6)$$

considerable interest as the first example of a homogeneous alkane dehydrogenation. We have already published some of our mechanistic work which leads us to reject mechanisms involving carbonium ions, radicals, and colloidal or precipitated metal.[4c] We now discuss the possible role of complexes of type **2** in this reaction.

The starting complex $[IrH_2S_2L_2]BF_4$ (**1**) is unlikely to react directly with the alkane. We thought it more likely that the hydrogen acceptor $t\text{-}BuCH{=}CH_2$ (**9**) first coordinates. We have therefore studied the reaction of **9** with **1** by NMR spectroscopy

$$[IrH_2S_2L_2]^+ + t\text{-}BuCH{=}CH_2 \rightleftarrows [IrH_2(9)SL_2]^+ \quad (7)$$
$$\quad\textbf{1}\qquad\qquad\textbf{9}\qquad\qquad\qquad\textbf{2}$$

at −80 °C as described above and have observed resonances that can be assigned to $[IrH_2(9)(H_2O)L_2]^+$ (see Table I). This complex is a probable intermediate.

On warming of the solutions (5 min, 40 °C), these resonances are lost, and an as yet uncharacterized complex (**10**) is formed. This appears to be an iridium hydride, perhaps $[IrH_xL_2]^+$, and may well be an important intermediate in the reaction,[23] and further studies are in progress. **9** (1 M equiv) is hydrogenated in this reaction (NMR, GC), so it is reasonable to suppose that the hydrogen acceptor has stripped H_2 from **1**. These solvento complexes present an interesting example of the antisymbiotic effect,[24] in which the high trans effect of hydride stabilize the M–S bond. This throws light on the role of the hydrogen acceptor. When this abstracts H_2 from the metal, the M–S binding is
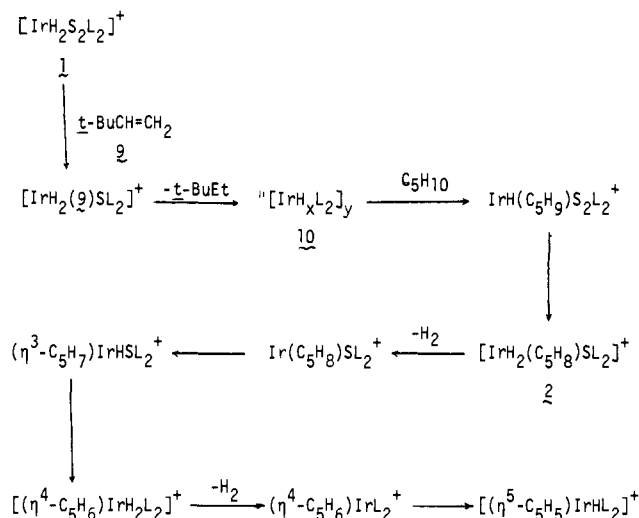
weakened (S = solvent), and the alkane may have easier access to the metal.

In view of all the evidence, the most reasonable mechanism to postulate for alkane activation (eq 5) is the reverse of the proposed mechanism for hydrogenation. Since the last step in hydrogenation is loss of alkane from a M(H)R species, an important step in alkane activation is probably "oxidative" addition to the metal.

For example, cyclopentane probably oxidatively adds to the iridium to give a cyclopentyl hydride complex. A β elimination would then lead to a cyclopentene dihydride of the type [IrH$_2$-(cyclopentene)SL$_2$]$^+$ (**2**). We have examined the reaction of cyclopentene with **1** by NMR at −80 °C to see if this complex can be prepared in this way. Indeed, resonances that can be assigned to **2** are found (Table I) in the spectrum of the reaction mixture, showing the complex can exist.

At this point, **2** can still revert to cyclopentane by a classical hydrogenation mechanism. For the reaction to proceed, H_2 probably first dissociates and is then scavenged by *tert*-butylethylene in a classical hydrogenation catalyzed by **1**, as discussed in a previous section, to give the observed *tert*-butylethane reaction product.[4c] Consistent with this mechanism is the observation that **2** (ol = cyclopentene) at 40 °C and in the presence of excess cyclopentene also gives the final organometallic product in the activation experiments, as well as cyclopentane, formed by hydrogen transfer to the cyclopentene. The metal presumably rapidly attacks the allylic CH_2 group to give a π-allyl hydride and then attacks the next CH_2 group to give a diene dihydride complex. Loss of H_2, followed by a further oxidative addition gives the product. None of these intermediates has been observed, suggesting that these steps are rapid.

The most difficult step of the proposed scheme is probably the first "oxidative" addition of a CH bond to the metal. The addition of a relatively unactivated CH bond to a transition metal has occasionally been observed intramolecularly.[25a] The iridium system provided the first example of an intermolcular attack on an alkane,[4b] other cases are now known.[25b]

The addition of cyclopentadiene (2 molar equiv) to **1** at ∼−80 °C leads to the appearance of a new triplet hydride resonance of low intensity at δ −13.4 (t, $J = 16$ Hz), consistent with the assumption that some $[IrH_2(cyclopentadiene)L_2]^+$ is formed in equilibrium with **1**. At −40 °C peaks due to $[CpIrHL_2]^+$ slowly appear. After 10 min at 0 °C, the cyclopentadienyl complex is the only organometallic product observed, but ∼1 molar equiv of cyclopentene was also seen. This suggests that the ease of CH

Figure 3. Postulated scheme for alkane dehydrogenation by **1**. Square brackets are placed around species observed.

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(23) Independently discovered by J. M. Brown, personal communication, 1980.

(24) Davies, J. A.; Hartley, F. R. *Chem. Rev.* **1981**, *81*, 79.

(25) (a) Bruce, M. I. *Angew. Chem., Int. Ed. Engl.* **1977**, *89*, 75. Omae, I. *Coord. Chem. Rev.* **1980**, *32*, 235. (b) Baudry, D.; Ephritikine, M.; Felkin, H. *J. Chem. Soc., Chem. Commun.* **1980**, 1245. Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1982**, *104*, 352. Hoyano, J. K.; Graham, W. A. G. *J. Am. Chem. Soc.* **1982**, *104*, 3723.

activation changes in the expected order: cyclopentane < cyclopentene < cyclopentadiene.

Conclusion

As Taube[26] has pointed out, organometallic complexes of such hard ligands as H_2O are rare. A positive charge on a complex seems best to stabilize such complexes, no doubt because this charge can be delocalized onto the protons of the coordinated H_2O. Yet too high a positive charge can lead to deprotonation.[27] Organometallic aquo complexes are unknown among the early transition metals, perhaps because of the strength of M=O bonds[28] in this part of the periodic table. The cationic iridium system avoids these problems, and a wide range of solvento complexes are available. As Hartley and Davies[24] have noted, such complexes are often labile, thus creating the active sites required for stoichiometric or catalytic reactions. Further, the lability of the system can be adjusted by choosing both the correct solvento ligand and reaction solvent.

Recent stopped-flow FT NMR studies[29] have led to quantitative data on solvent dissociation from **1** (S = Me_2CO) and some related complexes.

We have studied the reactions of **1** with olefins and also suggested mechanistic schemes for olefin hydrogenation and alkane activation with the iridium system, based on these results.

Experimental Section

NMR spectra were recorded on a Bruker HX-270 MHz instrument. Gas chromatography was performed on a Varian 920 instrument with a 3-m 5% Carbowax column. Standard Schlenk tube inert atmosphere techniques were used. Chlorinated solvents were distilled from CaH_2, and olefins deperoxidized (alumina column) before use. Cyclooctene was treated 5 times with 1 N AgNO₃ to remove traces of cyclooctadienes before use. Starting materials were prepared as previously described.[3,4]

Attempted Hydrogenation of Nitrobenzene with [Ir(cod)(PMePh₂)₂]A. [Ir(cod)(PMePh₂)₂]A (50 mg) was dissolved in CH_2Cl_2 (20 mL) and $PhNO_2$ (1 mL). The mixture was degassed and exposed to H_2 (1 atm, ca. 200 mL) in a sealed flask for 5 days. No trace of aniline was detected in the product (GC), nor was metal precipitated. An authentic Ir colloid rapidly reduced $PhNO_2$ under analogous conditions.[4c,7]

Light-Scattering Studies. [Ir(cod)(PMePh₂)₂]BF₄ (50 mg) in CH_2Cl_2 (16 mL) containing cyclohexene (1 mL) was degassed and exposed to H_2 for 5 min. Hydrogenation proceeded normally.[3] The mixture was then degassed and an aliquot (1 mL) prepared for the light-scattering experiment described previously.[4c] The catalytic solutions gave a completely flat autocorrelation function over the whole instrumental time range, implying that within the detection limits of the method no particulates (such as colloids) were present. An authentic Ir colloid, prepared by the method of Dunsworth and Nord,[7] could easily be detected at 1 nM concentration.[4c]

Dihydridodisolventobis(triphenylphosphine)iridium(III) Tetrafluoroborate. Method A, S = MeOH. [Ir(cod)(PPh₃)₂]BF₄ (500 mg) was suspended in MeOH (10 mL) and H_2 bubbled gently through the solution for 10 min at 0 °C. Et₂O (30 mL) was then added, while maintaining the H_2 stream, which led to the precipitation of a beige product.

Recrystallization from CH_2Cl_2/Et_2O gave a beige product (yield, 277 mg, 75%). Anal. Calcd for C₃₈H₃₂P₂O₂IrBF₄: C, 52.48; H, 4.64. Found: C, 52.20; H, 4.59.

S = THF and MeCN.[13] These were prepared similarly except that only 5 mL of solvent was used (yields 70–80%). S = THF: Anal. Calcd for C₄₄H₄₈P₂O₂IrBF₄·0.5CH₂Cl₂: C, 53.94; H, 4.98. Found: C, 53.91; H, 4.87. S = MeCN: Anal. Calcd for C₄₀H₃₈P₂N₂IrBF₄·0.25CH₂Cl₂: C, 53.19; H, 4.27. Found: C, 53.11; H, 4.08.

S = Me₂CO: This complex can be prepared by method A in 80% yield.[4b,13]

Method B, S = EtOH, i-PrOH, and t-BuOH. [Ir(cod)(PPh₃)₂]BF₄ (500 mg) was suspended in 10 mL of the coordinating solvent (S = EtOH, i-PrOH, or t-BuOH), and H_2 gently bubbled through the mixture (ca. 30 mL min⁻¹) until the suspension turned pale yellow (15–30 min). The product was filtered off and recrystallized from CH_2Cl_2/Et_2O (yield 80–85%). S = EtOH: Anal. Calcd for C₄₀H₄₄P₂O₂IrBF₄: C, 53.51; H, 4.94. Found: C, 53.48; H, 5.00. S = i-PrOH: Calcd for C₄₄H₅₂P₂O₂IrBF₄·CH₂Cl₂: C, 52.04; H, 5.20. Found: C, 51.71; H, 4.36. S = H₂O can be prepared by method B in 85% yield.[4b]

Reactions of Dihydridodisolventobis(triphenylphosphine)iridium(III) Tetrafluoroborate with Olefins. [IrH₂S₂L₂]BF₄ (S = H₂O, 15 mg) was dissolved in CD₂Cl₂ (0.5 mL) in an NMR tube. The sample was cooled to ca. –80 °C (dry ice) and the olefin (10 molar equiv/Ir) introduced by microsyringe. The sample was shaken until fully mixed and then introduced into the cooled NMR probe (~80 °C). Observations were made at 10 °C intervals up to 20 °C. The data appear in Table 1. In the case of *tert*-butylene, on warming of the solution (40 °C, 4 h), an as yet unidentified complex (**10**) was formed [NMR (288 K, CD₂Cl₂): δ 7.0–7.3 m; 2.79, s; –0.87, s; –25.9, t (16)], which was obtained as a microcrystalline white powder on adding Et₂O.

Reactions of (Cyclooctadiene)bis(triphenylphosphine)iridium(I) Tetrafluoroborate with H₂ and Olefins. To [Ir(cod)(PPh₃)₂]BF₄ (20 mg) in CD₂Cl₂ (0.5 mL) in an NMR tube was added C₂H₄ (50 equiv/Ir), and the sample cooled to ca. –80 °C (dry ice). H_2 was added until the color of the solution became pale yellow, and the excess H_2 was swept out with N₂. The resonances of cis-[IrH₂(cod)L₂]⁺ (**5**) are present at –80 °C, but on warming to 0 °C, these are replaced by a new peak at δ 0.95 due to C₂H₆. When the solution is cooled to –80 °C and H_2 added, the resonances of **5** reappear, but at ca. 80% of their former intensity. New peaks appear (Table I) that we ascribe to [IrH₂(C₂H₄)₂L₂]⁺ (**3**, ca. 20%). In successive repetitions of this cycle, **3** replaces **5** as the principal species. Attempts to trap alkyl hydride species by addition of other ligands (MeCN, PPh₃, bpy) failed.

Hydrogenations. Hydrogenations were performed with [Ir(cod)(PMePh₂)₂]PF₆ in a constant-pressure apparatus[3] (pH₂ = 60 cmHg; olefin 0.5 M; catalyst 0.5 mM; 0 °C; CH₂Cl₂). Coordinating solvents were added with a microsyringe. The data appear in Table II. Rates of hydrogen uptake in cyclohexene hydrogenation were observed in a constant-pressure apparatus previously described.[3] The product cyclohexane was observed by GC. The conditions mentioned above were used, but [olefin], pH₂, and [catalyst] were varied in separate experiments. No rate change was observed in the range [olefin] = 0.1–0.5 M (data reported as [olefin] (M), rate (mL of H₂ min⁻¹): 0.1, 10.7; 0.25, 10.8; 0.5, 10.9). The rate was proportional to [catalyst] in the range 0.1–0.5 mM (data reported as [catalyst] (mM), rate (mL of H₂ min⁻¹): 0.1, 2.1; 0.2, 4.3; 0.3; 6.5; 0.4, 8.7; 0.5, 10.8; and approximately independent of pH₂ (cmHg), rate (mL of H₂ min⁻¹ after reduction of the readings to the standard pressure (60 cmHg)): 32, 10.5; 42, 10.9; 52, 10.8; 62, 10.9).

(26) Taube, H. *Coord. Chem. Rev.* **1978**, *26*, 33.

(27) White, C.; Thompson, S. J.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1977**, 1654.

(28) Kepert, D. L. "The Early Transition Elements"; Academic Press: London, 1972.

(29) Howarth, O. W.; McAteer, C. H.; Moore, P.; Morris, G. E. *J. Chem. Soc., Dalton Trans.* **1981**, 1481.