

Iridium Compounds in Homogeneous Hydrogenation

By Robert H. Crabtree

Sterling Chemistry Laboratory, Yale University, New Haven, Connecticut

Iridium is generally considered to be a less effective catalyst than the other platinum metals but when highly co-ordinatively unsaturated species of it are prepared they appear to be exceptionally active hydrogenation catalysts, even for reduction of sterically hindered olefins. A mechanism for this reaction has been postulated based on low temperature magnetic resonance evidence. As the reaction proceeds, catalytically inactive hydrogen bridged cluster compounds are formed but work is in progress to counter this deactivation by physically separating the catalytic centres on a polymer support.

The generally accepted order of catalyst activities for the elements of the transition series and their compounds is 2nd row \geq 1st row \geq 3rd row. A characteristic example is that of the complexes $MCl(PPh_3)_3$. Where $M = Rh$, this complex is a versatile homogeneous catalyst for hydrogenation (1), decarbonylation (2), and cyclisation (3). The cobalt and iridium analogues are entirely inactive for these catalytic reactions. In the case of homogeneous hydrogenation, the cobalt complex is inactive because it does not react at all with hydrogen (4) while the iridium analogue reacts with hydrogen to give $[IrH_2Cl(PPh_3)_3]$, which, unlike the rhodium analogue, fails to dissociate PPh_3 to allow the substrate access to the active site (5).

We believed that once access of the substrate to the active site was assured, compounds of third row elements might prove to be highly active catalysts. What was needed was a ligand which would occupy a co-ordination site on a metal, and give readily isolable, stable complexes for use as catalyst precursors. However, this ligand would have to be irreversibly removed from the co-ordination sphere under the conditions of the catalytic reaction. Osborn briefly described (6) the catalyst precursors $[Ir(cod)L_2]^+$ (i);

where $cod = 1,5$ -cyclo-octadiene; $L =$ tertiary phosphine. He found that under H_2 and in a co-ordinating solvent, the complexes $[IrH_2(solvent)_2L_2]^+$ (ii), ($solvent = Me_2CO$, $EtOH$ or thf) were formed. These were moderately active hydrogenation catalysts but less active than the rhodium analogues which were studied in much more detail (7).

Cod might therefore serve as such a ligand, since it was irreversibly removed by hydrogenation to cyclooctane in the catalytic reaction. However, in a co-ordinating solvent, the cod was merely replaced by a different co-ordinating ligand, the solvent itself.

We decided to look at the behaviour of complexes such as (i) in polar, but non-co-ordinating, solvents, such as CH_2Cl_2 . The results were strikingly different from those found in co-ordinating solvents, showing the profound effect of solvent on a process as complicated as catalysis. No solvate such as (ii) was formed, instead, when (i) reacts with hydrogen in CH_2Cl_2 , highly co-ordinatively unsaturated species were formed. In the presence of olefin, the resulting solutions constitute hydrogenation catalysts of unprecedented activity. They are even capable of rapidly reducing tetrasubstituted olefins such as $Me_2C=CMe_2$. The Table shows some

Comparative Rates for the Reduction of Cyclohexene and 1-Methylcyclohexene by a Number of Catalysts

Catalyst(a)	Cyclohexene		1-Methylcyclohexene	
	Rate(b)	Extent of hydrogenation(c)	Rate(b)	Extent of hydrogenation(c)
[Ir(cod) (PMePh ₂) ₂]PF ₆	3700	100	1900	94
[Ir(cod)Pi-Pr ₃ (py)]PF ₆	4500	99.5	3800	35
[Ir(cod) (dpe)]PF ₆ (d)	1300	100	640	72
[Ir(cod) (PMe ₂ Ph) ₃]PF ₆ (e)	1200	100	370	65
[Rh(cod) (PPh ₃) ₂]PF ₆	10	100	0	—
[RhCl(PPh ₃) ₃] (f)	700	100	12	100

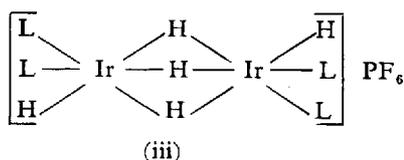
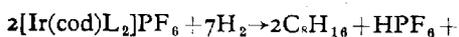
(a) catalyst: 0.5 mM; substrate: 0.5 M in CH₂Cl₂ at 0°C unless stated; p(H₂)=60 cm/Hg. dpe=Ph₂PCH₂CH₂PPh₂; py=pyridine. Data from Ref. 8.

(b) in mol H₂ absorbed per mol catalyst per hour (c) until deactivation occurs.

(d) induction time: 15 min. (e) induction time: 30 min. (f) in benzene at 25°.

of the results obtained with different catalysts (8). The corresponding rhodium catalysts [Rh(cod)L₂]⁺ can be seen to be far less active, in sharp contrast to their behaviour in co-ordinating solvents.

This increase in activity, gained by using highly unsaturated iridium species as catalysts, is accompanied by a loss of catalyst stability. When the olefin has been consumed, or, in the case of olefins which are poor ligands, nearly consumed, the catalyst deactivates to give a series of remarkable hydrogen-bridged cluster complexes which are catalytically inactive. For example:



(L = PPh₃ or PMePh₂)

This complex (iii) has the shortest iridium-iridium distance known (8). The bridge bonding probably resembles that in diborane so that both iridium atoms can achieve completed valence shells (9). The complexes

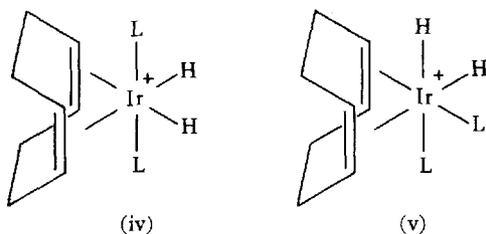
[Ir(cod)LL']PF₆ (10) (L=tertiary phosphine, L'=pyridine) react with hydrogen to give a yellow crystalline substance, which preliminary spectral and crystallographic evidence suggests is an unusual trimeric iridium complex, [(IrLL'H₂)₃(μ₃-H)](PF₆)₂, in which the unique hydrogen atom bridges three iridium atoms.

By keeping the catalyst species apart from one another, deactivation can be prevented or, at least, slowed down. Since the catalyst precursors and the catalysts themselves appear to be entirely air-stable, one effective method is to inject the catalyst solution into the reaction vessel drop by drop. Choosing ligands L so large that they prevent dimerisation 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. Work along these lines is in progress.

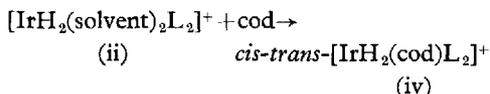
While co-ordinatively unsaturated iridium species can be much more reactive than their rhodium analogues, co-ordinatively saturated complexes of iridium are often more stable than the rhodium or cobalt analogues. We uncovered a striking example of this effect in

our catalytic systems. When cod itself is used as a substrate for the catalyst system, co-ordinatively saturated species are rapidly formed and the catalysis slows down abruptly. The unexpected product of this reaction is *cis-trans*-[IrH₂(cod)L₂]⁺ (iv) which can be isolated as a crystalline solid (11).

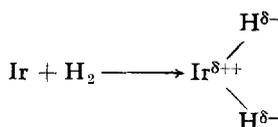
At -80°C another isomer of (iv), namely *cis*-[IrH₂(cod)L₂]⁺ (v) is formed by the direct addition of hydrogen to (i) (12). On heating this solution to room temperature in the presence of cod, hydrogenation proceeds rapidly and then slows abruptly with the formation of (iv).



These complexes are the first examples of dihydrido olefin complexes. Such complexes had been assumed (1, 13) to be intermediates in the hydrogenation of olefins but never directly observed. They may be formed either, as above, by hydrogen addition to an olefin complex or by olefin addition to a hydride complex (11):



The direct addition of H₂ to an olefin complex had been considered unlikely (1). The olefin, as an electron-withdrawing ligand, was considered to deactivate the metal towards the "oxidative" addition of hydrogen, so called because the metal was assumed to be partially oxidised in the product, implying the presence of hydridic hydrogens.

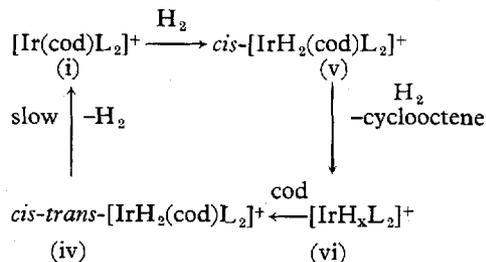


We now know that [Ir(cod)₂]⁺, containing only olefinic ligands, reacts readily with H₂

at -80°C to give a complex type (v) (L₂=cod) (11). In contrast [Ir(cod)(pyridine)₂]⁺, in which a cod ligand of [Ir(cod)₂]⁺ has been replaced by two strongly donor ligands, fails to add H₂ at any temperature. This may mean that the addition of hydrogen does not greatly affect, or even slightly lowers the partial positive charge on the metal, and that the addition of H₂ is not oxidative, at least in the case of this iridium system. Certainly, the Pauling electronegativity of all the platinum metals (2.2-2.3) is very close to that of hydrogen (2.2), so that one would not expect a large charge separation in any platinum metal-hydrogen bond.

In the catalytic solutions themselves, the intermediates may well be of the type [IrH_{6-2x}(mono-olefin)_xL₂]⁺ (x=0, 1, 2 or 3). They are probably formed by both of the routes mentioned above.

It is significant that the crystalline *cis-trans*-complex (iv) decomposes thermally at about 80°C to give largely (i) and hydrogen while (v) decomposes at around -20°C to give largely cyclooctene. Similarly, in a hydrogenation of cod by (i) (see Scheme below), the initially formed intermediate, (v), readily hydrogenates the co-ordinated cod. Free cod subsequently co-ordinates to give the *cis-trans*-isomer (iv) and the hydrogenation rate falls 40-fold. It would seem that coplanar M(C=C)H arrangement is required in order for the olefin to insert into the metal-hydrogen bond, since (v) possesses this arrangement, while (iv) does not.



The unusual intermediate (vi) can only be isolated where L is a bulky ligand such as PCy₃, which is known (14) to stabilise unusual hydride complexes. Where L is a

smaller phosphine (vi) rapidly dimerises to give (iii). From NMR and hydrogen evolution studies, the value of x seems to be six, in which case (vi) is a unique example of heptavalent iridium. Treatment of (vi) with NEt_3 gives the known (15) complexes IrH_5L_2 .

Iridium therefore seems to be an element whose catalytic potential has yet to be fully realised. Given the right conditions, in

particular, co-ordinative unsaturation, iridium can provide catalysts as active as those of any other element.

Acknowledgements

I would like to thank Hugh Felkin for many discussions. This work was performed at the Institut de Chimie des Substances Naturelles, C.N.R.S., Gif-sur-Yvette, France, and is taken, in large part, from the doctoral thesis of George E. Morris (Orsay, 1976).

References

- 1 J. A. Osborn, F. H. Jardine, J. F. Young and G. Wilkinson, *J. Chem. Soc. (A)*, 1966, (12), 1711
- 2 J. Tsuji and K. Ohno, *Tetrahedron Lett.*, 1965, (43), 3969
- 3 K. Sakai, J. Ide, O. Oda and N. Nakamura, *Tetrahedron Lett.*, 1972, (13), 1287; K. Sakai and O. Oda, *Tetrahedron Lett.*, 1972, (42), 4375
- 4 N. Areata, M. Rossi and A. Sacco, *Inorg. Chim. Acta*, 1969, 3, (2), 227
- 5 M. A. Bennett and D. A. Milner, *J. Am. Chem. Soc.*, 1969, 91, (25), 6983
- 6 J. R. Shapley, R. R. Schrock and J. A. Osborn, *J. Am. Chem. Soc.*, 1969, 91, (10), 2816
- 7 R. R. Schrock and J. A. Osborn, *J. Am. Chem. Soc.*, 1976, 98, (8), 2134, 2143; *J. Am. Chem. Soc.*, 1976, 98, (15), 4450
- 8 R. H. Crabtree, H. Felkin and G. E. Morris, *J. Organometal. Chem.*, 1977, 141, (2), 205
- 9 C. A. Tolman, *Chem. Soc. Rev.*, 1972, 1, (3), 337
- 10 R. H. Crabtree and G. E. Morris, *J. Organometal. Chem.*, 1977, 135, (3), 395
- 11 R. H. Crabtree, H. Felkin, T. Khan and G. E. Morris, *J. Organometal. Chem.*, 1978, 144, (1), C15
- 12 R. H. Crabtree, H. Felkin and G. E. Morris, *J. Chem. Soc., Chem. Commun.*, 1976, (18), 716
- 13 C. A. Tolman, P. Z. Meakin, D. L. Lindner and J. P. Jesson, *J. Am. Chem. Soc.*, 1974, 96, (9), 2762
- 14 H. D. Empsall, E. M. Hyde, H. Mentzer, B. L. Shaw and M. F. Uttley, *J. Chem. Soc., Dalton Trans.*, 1976, (20), 2069
- 15 B. E. Mann, C. Masters and B. L. Shaw, *J. Chem. Soc., Chem. Commun.*, 1970, (11), 703

Commercial Catalytic Processes

Handbook of Catalyst Manufacture BY MARSHALL SITTIG,

Noyes Data Corporation, Park Ridge, New Jersey, 1978, 474 pages, \$48

This book gives an account of 417 patents issued in the United States since 1974 that deal with catalysts and their commercial technology. The contents comprise chapters on general topics (with useful information on catalytic reactors), alkylation, ammoxidation, aromatisation, cracking, dehydrogenation, disproportionation (metathesis), isomerisation, oligomerisation, oxidation, hydroformylation, reforming, steam reforming and methanation. There is also a lengthy section on hydrogen processing, as befits recent and current interest in this subject.

The book delivers both more and less than the title promises: more in the sense that subjects other than catalyst manufacture are discussed (especially reactor design and construction), less in the sense that no overview

of the methods and problems of catalyst manufacture is provided, and thus in no real sense is it a handbook. Anyone aspiring to make a good catalyst solely with the information provided in this book would be well advised not to start. The book has all the defects of its congener, also recently reviewed in this journal (*Platinum Metals Rev.*, 1978, 22, (1), 24): most sadly lacking is a subject index, without which any search for a specific piece of information tends to be rather a hit-or-miss affair. Since the work is classified on the basis of the process rather than the catalyst, it is more a handbook on catalysed processes than of catalyst manufacture. It will therefore be more useful to those who are strictly process-oriented than to those whose horizons are wider. G. C. B.