(Pentamethylcyclopentadienyl)rhodium and -iridium Complexes: Approaches to New Types of Homogeneous Catalysts

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Considerable research over the last 15 years has centered on complexes of the platinum metals which, in homogeneous solution or heterogeneously when supported on a suitable carrier, have good catalytic properties.[1]

Most of these new catalysts have involved complexes of the platinum metals with tertiary phosphines and similar ligands. The need for such ligands, especially in reactions which occur under reducing conditions, arises from the ease with which irreversible decomposition to the metals otherwise occurs. Phosphines are *soft* ligands that bind well to the platinum metals in both low and intermediate oxidation state complexes, and their presence inhibits decomposition on reduction. One example is the classical "Wilkinson complex" hydrogenation catalyst, $[Rh(Ph_3P)_3Cl]$.[2]

However, a catalytic system which had good activity, under useful conditions, combined with high specificity and long life, and which in addition did not contain such labile phosphine ligands would have some distinct additional advantages. For example, since phosphines and similar ligands have themselves high reactivity toward electrophiles, oxygen, and oxidizing agents, their absence from any catalytic system wherein free ligand is generated should result in an increase in versatility.

The design of such a catalyst poses some difficulties since, in order for it to be active homogeneously, the metal–ligand bonds must be able to survive the necessary changes in oxidation state and coordination number that occur during the catalytic cycle. In principle, this can be achieved through the use of sufficiently bulky *and* strongly bound ligands, but unfortunately such ligands can also seriously inhibit the desired reactions at the metal to the degree that the complexes become catalytically useless. It is therefore essential to make a careful choice of ligand in order to arrive at the best overall compromise between stability and reactivity.

The chemistry of some new types of rhodium and iridium compounds is reviewed here; apart from their unusual chemical properties, they also act as very efficient catalysts, and although their potential has not yet been fully explored, it is clear that we have succeeded in arriving at a catalytic system that meets the requirements outlined above.

η^5-Pentamethylcyclopentadienylrhodium and -iridium Complexes

The pentamethylcyclopentadienyl (η^5-C_5Me_5) half-sandwich complexes of Rh and Ir [e.g., $[Rh(C_5Me_5)Cl_2]_2$, **1**] offer a quite exceptional blend of stability and reactivity seldom found even among phosphine complexes. This arises from the strong C_5Me_5–metal bond (which survives acidic and basic as well as reducing and oxidizing conditions) on one side and from the lability of the ligands on the other which allows useful reactions to occur. The C_5Me_5 ligand also acts as a useful NMR probe (singlet in the ^{1}H spectrum) and confers good solubility character to its complexes as well as making them generally easy to crystallize. The complexes, particularly in the III oxidation state, are normally air-stable.

But why *pentamethyl*cyclopentadienyl? Won't the unsubstituted and simpler cyclopentadienyl do? In fact it will not. $[Rh(C_5H_5)Cl_2]_n$ is known but, in contrast to $[Rh(C_5Me_5)Cl_2]_2$, it is amorphous and insoluble in all but powerfully coordinating solvents and is probably polymeric. Reliable and reproducible synthesis of $[Rh(C_5H_5)Cl_2]_n$ is difficult; however, worst of all once the Rh–C_5H_5 bond has been formed, it turns out to be quite reactive and easily cleaved by a variety of reagents (including hydrogen) which do not affect the Rh–C_6Me_5 bond. For all its esoteric appearance, the synthesis of $[Rh(C_5Me_5)Cl_2]_2$ is very simple: it merely involves refluxing in methanol the commercially available $RhCl_3\cdot xH_2O$ with hexamethylbicyclo[2.2.0]hexadiene [hexamethyl(Dewar benzene), **2**], which may be bought or made directly from 2-butyne.[3]

Kang's discovery of the complex **1a** was in part serendipitous. We were interested in the reactivity of Dewar benzenes toward transition metals and the disclosure of a simple route to the Dewar benzene **2**[4] prompted us to explore its reactivity toward rhodium chloride. We obtained, in high yield, a red crystalline solid which was diamagnetic and showed only a singlet

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(1) See, for example, B. R. James, "Homogeneous Hydrogenation", Wiley, New York, N.Y., 1973; P. N. Rylander, "Organic Syntheses with Noble Metal Catalysts", Academic Press, 1973; "Catalysis, Heterogeneous and Homogeneous", Elsevier, Amsterdam, 1975; "Aspects of Homogeneous Catalysis", R. Ugo, Ed., Carlo Manfredi, Milan, and D. Reidel, Boston, Mass.: Vol. 1 (1970), 2 (1974).

(2) J. A. Osborne, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc. A*, 1711 (1966); J. Halpern and C. S. Wong, *J. Chem. Soc., Chem. Commun.*, 629 (1973); J. Halpern, T. Okamoto, and A. Zakhariev, *J. Mol. Catal.*, 2, 65 (1977).

(3) J. W. Kang, K. Moseley, and P. M. Maitlis, *J. Am. Chem. Soc.*, 91, 5970 (1969); see also B. L. Booth, R. N. Haszeldine, and M. Hill, *J. Chem. Soc. A*, 1299 (1969), and *J. Organometallic Chem.*, 16, 491 (1969).

(4) W. Schäfer and H. Hellman, *Angew. Chem., Int. Ed. Engl.*, 5, 518 (1967).

in the ^{1}H NMR spectrum (at δ 1.6) and which we therefore supposed to be a rhodium complex of *hexamethylbenzene*, formed by a metal-assisted valence isomerization of the Dewar benzene **3**. However, the analytical data did not fit any reasonable combination of C_6Me_6, Rh, and Cl and we were finally forced to abandon this line of thought and to accept the surprising conclusion that a ring contraction to give a π-pentamethylcyclopentadienyl complex had taken place.[5]

The reason for this strange occurrence came somewhat later when Paquette and others found that the Dewar benzene **2** underwent a reaction with acid (e.g.,
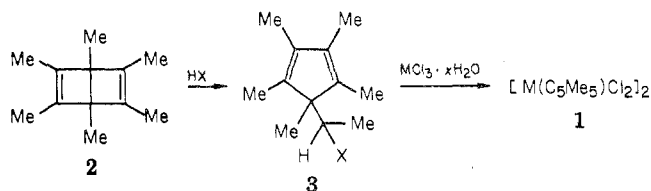
HCl) to give the 1-substituted ethylpentamethylcyclopentadiene (**3**).[6]   In the reaction of **2** and $RhCl_3\cdot xH_2O$ to give **1a**, the compound (**3**, X = Cl or OMe) is generated in situ; the acid comes from partial hydrolysis of the $RhCl_3\cdot xH_2O$ and which was shown to give an acid solution in water.[3]

Attempts to prepare the C_5Me_5–iridium analogue (**1b**) directly from the Dewar benzene **2** were not successful, but we obtained it again in high yield when **3** (X = Cl) was first prepared from **2** and then reacted with $IrCl_3\cdot xH_2O$ in methanol.[3]

The chief role of the metal ion in these reactions appears to be to complex the cyclopentadiene **3** and to assist the cleavage of the CH_3CHX- side chain; the driving force for the overall process must be the very high stability of the C_5Me_5–metal bond in **1**. Moseley found that a byproduct of these reactions was dimethyl acetal, $[MeCH(OMe)_2]$, which arose through methanolysis of the CH_3CHX- side chain.[3]

It is also possible to synthesize **1** from pentamethylcyclopentadiene, but unhappily a simple, convenient, *and* inexpensive route to this precursor is still lacking.   However, a satisfactory synthesis of ethyltetramethylcyclopentadiene[7] has recently been reported, and the C_5Me_4Et analogues of **1** have now become available;[8] their properties are very similar to those of **1a** or **1b** but they are more soluble, especially in less polar solvents.

If the C_5Me_5 ring is assumed to occupy three coordination sites about the metal in **1** then, together with the three chlorine ligands (two bridging, one terminal), each metal atom has pseudooctahedral coordination (sometimes termed "three-legged piano stool") as shown by the X-ray crystal structures of the isostructural complexes **1a** and **1b** (Figure 1).[9]   Six-coordination is almost invariably found for low-spin (d^6) Rh(III) and Ir(III) complexes.

Replacement of the chloride ligands occurs very easily; amines and tertiary phosphines cleave the
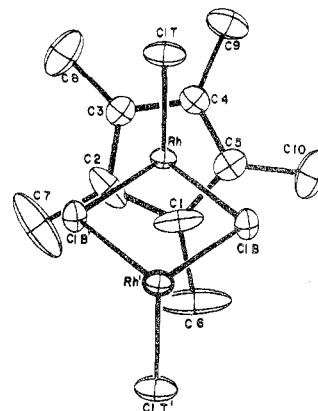
Figure 1. A portion of the $[Rh(\eta^5\text{-}C_5Me_5)Cl_2]_2$ molecule projected onto one C_5Me_5 ring, showing the "three-legged piano-stool" arrangement of ligands about Rh; the other C_5Me_5 ring is omitted for clarity. (Reproduced from ref 9.)

chlorine bridges to give the monomeric $[M(C_5Me_5)Cl_2L]$ (**4**, Scheme I).   Another reaction of some interest is the formation of salts; it seems likely that in solution there is an equilibrium,

$$[Rh(C_5Me_5)Cl_2]_2 \rightleftharpoons [\{Rh(C_5Me_5)\}_2Cl_3]Cl$$
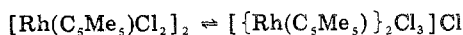
and the tris-μ-chloro binuclear cation (**5**) is easily obtained on adding $Na[BPh_4]$ to a solution of **1a**.[10]

A nice illustration of the surprising stability of these organometallics is that the rhodium complex **1a** dissolves in hot aqueous sodium hydroxide; from this solution the tris-μ-hydroxo compound (**6**, X = Cl) may be obtained as large orange crystals.[10]   The formation of binuclear cationic complexes with three bridging ligands is a recurrent feature of these C_5Me_5–metal compounds; similar complexes are also now being found elsewhere,[11] and it appears that such systems are easily formed and have a high stability.

A wide variety of other metathesis reactions have also been carried out by Kang, Rigby, and others: chloride can be replaced by carboxylate,[10] other halides,[3] NO_2, N_3,[12] etc., and some of these are shown in Scheme I.

Dicationic Complexes $[M(C_5Me_5)L_3]^{2+}$: Soft Centers and Hard Shells

Very useful dicationic mononuclear complexes are also easily made.   For example, we found that treatment of **1** with $AgPF_6$ in the presence of a solvent (s = acetonitrile, pyridine, acetone, THF, methanol, etc.) gives complexes of type **7**; when the ligands bind reasonably strongly (s = MeCN, Me_2SO, pyridine,[13] $(MeO)_3P$[14]) these tris complexes can be isolated and characterized.[13]

The solvent molecules are easily displaced (e.g., reaction with arenes gives **8**), and therefore the more labile solvent complexes (especially **7**, s = acetone) are valuable intermediates for the synthesis of dicationic sandwich compounds and related complexes.   Many

(5) J. W. Kang and P. M. Maitlis, *J. Am. Chem. Soc.*, **90**, 3259 (1968).
(6) L. A. Paquette and G. R. Krow, *Tetrahedron Lett.*, 2139 (1968); R. Criegee and H. Grüner, *Angew. Chem., Int. Ed. Engl.*, **6**, 467 (1968).
(7) D. Feitler and G. Whitesides, *Inorg. Chem.*, **15**, 466 (1976).
(8) J. Burrows, G. Fairhurst, C. White, and P. M. Maitlis, unpublished results.
(9) M. R. Churchill and S. A. Julis, *Inorg. Chem.*, **16**, 1488 (1977); M. R. Churchill, S. A. Julis, and F. A. Rotella, *Inorg. Chem.*, **16**, 1137 (1977).

(10) J. W. Kang and P. M. Maitlis, *J. Organometal. Chem.*, **30**, 127 (1971).
(11) E. A. Kelley, P. M. Bailey, and P. M. Maitlis, *J. Chem. Soc., Chem. Commun.*, 289 (1977). See also R. O. Gould, C. L. Jones, D. R. Robertson and T. A. Stephenson, *ibid.*, 232 (1977).
(12) W. Rigby, J. A. McCleverty, and P. M. Maitlis, unpublished results.
(13) C. White, S. J. Thompson, and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 1654 (1977).
(14) C. White, S. J. Thompson, and P. M. Maitlis, *J. Organometal. Chem.*, **136**, 87 (1977).

Scheme I

quite stable compounds of type **8** are known, and we may regard them as having soft centers and hard shells

$$[\text{M}(\text{C}_5\text{Me}_5)\text{Cl}_2]_2 + 4\text{AgPF}_6 \xrightarrow{\text{s}} [\text{M}(\text{C}_5\text{Me}_5)\text{s}_3]^{2+} \xrightarrow{\text{arene}}$$
$$\underset{\textbf{1}}{} \qquad\qquad\qquad \underset{\textbf{7}}{}$$
$$[\text{M}(\text{C}_5\text{Me}_5)(\eta^6\text{-arene})]^{2+}$$
$$\underset{\textbf{8}}{}$$
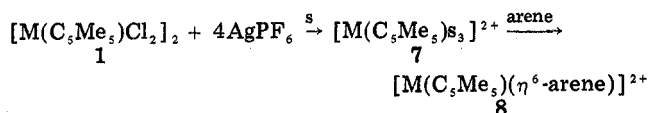
in that they π-bond easily to unsaturated hydrocarbons and yet have a high positive charge overall. This rather unusual combination of properties has allowed White and Thompson to investigate the chemistry of a variety of organic ligands in highly positively charged environments.

A more quantitative insight into the state of the metal here is given by the dimethyl sulfoxide complexes $[\text{M}(\text{C}_5\text{Me}_5)(\text{Me}_2\text{SO})_3](\text{PF}_6)_2$; IR studies indicate the rhodium complex to be only O-bonded both in solution [$\nu(\text{SO})$ 935 cm^{-1}] and in the solid [$\nu(\text{SO})$ 926 cm^{-1}], but the iridium complex is both O- and S-bonded in the solid [$\nu(\text{SO})$ 901, 1135 cm^{-1}] and only S-bonded in solution [$\nu(\text{SO})$ 1128 cm^{-1}].[13] Clearly therefore the iridium is a *softer* center than the rhodium, a point which is well borne out by the greater stability of the dicationic iridium sandwich complexes by comparison with their rhodium analogues.

The reaction **7** → **8** can also be reversed in suitable cases, and an order of stability for these η^6-arene complexes can be obtained. The η^6-arene rhodium complexes are more labile than the iridium ones, and for each series stability is enhanced in proportion to the number of alkyl substituents on the benzene. For example, *p*-xylene in [Rh(C$_5$Me$_5$)(*p*-xylene)]$^{2+}$ is displaced by dimethyl sulfoxide at 20 °C to give **7** (M = Rh, s = Me$_2$SO), and the analogous η^6-benzene complex is rapidly solvolysed by acetone at 20 °C; by contrast, [Ir(C$_5$Me$_5$)(benzene)]$^{2+}$ is stable in Me$_2$SO solution.[13]

This observation is not unexpected since, even on very qualitative arguments, it may be anticipated that electron-releasing substituents (methyl groups) on the organic ligands would stabilize highly positively charged complexes.

Apart from nucleophilic attack at the metal leading to total displacement of the η^6 ligand, both proton loss and nucleophilic attack at the ligand have been ob-

served. An interesting example of the former is the deprotonation of the η^6-phenol complex **9** to [Ir-
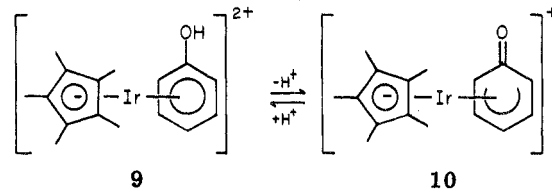
(C$_5$Me$_5$)(C$_6$H$_5$O)]$^+$, which is most satisfactorily described as an η^5-oxocyclohexadienyl complex, **10**.[15]

Another example is with indene; here deprotonation of the indene complex is accompanied by a change from η^6 coordination of the metal to the benzene ring, as in **11**, to an η^5 coordination of the five-membered ring, **12**.
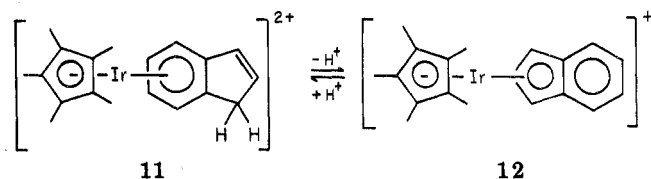
Indole undergoes analogous transformations.[13]

Nucleophilic attack occurs when the ligand is not easily deprotonated; for example, the η^6-hexamethylbenzene complexes give the η^5-hexamethylcyclohexadienyl complexes **13** with sodium borohydride.[16]

Attack by hydride and other nucleophiles at the ring always occurs exo to the metal.

The 18-Electron Rhodium(I) and Iridium(I) Complexes

In addition to the very wide chemistry that the (pentamethylcyclopentadienyl)rhodium and -iridium

(15) C. White, S. J. Thompson, and P. M. Maitlis, *J. Organometal. Chem.*, **127**, 415 (1977).

(16) C. White and P. M. Maitlis, *J. Chem. Soc. A*, 3322 (1971).

complexes display in the +III oxidation state, there is also an extensive chemistry in the +I (18-electron) oxidation state. Among the simplest complexes of this type are the carbonyls 14 which Kang obtained by

atmospheric pressure carbonylation of the chlorides in the presence of zinc metal (for 1a)[17] or sodium carbonate (for 1b).[3] These dicarbonyls undergo the oxidative addition reactions so characteristic of d^8 complexes; for example, methyl iodide gives the adduct 15 reversibly with the iridium carbonyl 14b and the acetyl complex 16 with the rhodium carbonyl 14a.

The other important class of formally five-coordinate compounds of the metal in the I oxidation state are the [M(C$_5$Me$_5$)diene] complexes discussed below.

Bridged Hydride Complexes and the Heterolytic Activation of H$_2$

Since metal hydrides are the active species in metal-catalyzed hydrogen-transfer reactions, the hydrides derived from 1 are of particular interest. Moseley

showed that the mononuclear iridium complex [Ir-(C$_5$Me$_5$)Cl$_2$(PPh$_3$)] (4, L = PPh$_3$, M = Ir) reacts in ethanol/base to give the expected mononuclear complex containing a terminal hydride [Ir(C$_5$Me$_5$)(H)(Cl)(PPh$_3$)] [ν(Ir-H) = 2090 cm^{-1}].[18] The dichlorides 1a and 1b are also readily reduced (by H$_2$/base or BH$_4^-$ or KOH/2-propanol), but in this case White obtained the *binuclear mono-μ-hydrido* complexes 17.[19]

The iridium complex 17b, under more vigorous conditions, can be further converted into the di-μ-hydride 18[20] and, finally, into the tri-μ-hydride cation 19. Similar series are generated on reaction of the acetates or the trifluoroacetates, and the complexes [{M(C$_5$Me$_5$)}$_2$HX$_2$]$^+$ and [{M(C$_5$Me$_5$)}$_2$H$_2$X]$^+$ (X = CF$_3$CO$_2$, CH$_3$CO$_2$) have been made. However, no rhodium analogues of 18 or 19 could be obtained, and

even the rhodium-di-μ-hydrido-μ-acetato and -μ-trifluoroacetato complexes were rather unstable.[19] These μ-hydrido complexes are, however, quite remarkably air-stable, particularly in the solid.

The reaction of each of these complexes with molecular hydrogen formally involves a *heterolytic* activation (H$^+$···H$^-$) of H$_2$ by the metal in which the hydridic hydrogen then replaces another anionic ligand in the complex. In this case there is no net change in formal oxidation state of the metal, and it may be contrasted with the more usual *homolytic* activation where an oxidative addition of H$_2$ occurs and where the metal changes from, for example, square-planar d^8 to pseudooctahedral d^6, as in Vaska's complex.[21]

$$[Ir^I(PPh_3)_2(CO)Cl] + H_2 \rightarrow [Ir^{III}(PPh_3)_2(CO)(H)_2Cl]$$

Clearly then, as acid is formed in the heterolytic activation, such reactions are expected to be base-

$$mX_2 + H_2 \rightarrow m(H)X + H^+X^-$$
$$m = M(C_5Me_5)$$

promoted. Thus the activation of molecular H$_2$ by the chlorides 1 or by [M(C$_5$Me$_5$)(OCOCF$_3$)$_2$]$_n$ occurs at 20 °C and 1 atm only in the presence of base.

However, since acetic acid is a very weak acid the acetato complexes [M(C$_5$Me$_5$)(OCOCH$_3$)$_2$]$_n$ react even in the absence of base, and a very simple demonstration experiment can be performed to show this heterolytic activation. When [Rh(C$_5$Me$_5$)(OCOCH$_3$)$_2$]$_n$ is dissolved in a mixture of diethyl ether and hexane a yellow-brown solution is obtained; if this solution is now exposed briefly to H$_2$ under ambient conditions the solution immediately turns dark red and the ionic and insoluble dark-brown μ-hydrido complex 20 is precipitated out.

Air does not inhibit this reaction, and it is a remarkable indication of the readiness with which Rh–H bonds are formed in this activation of hydrogen that H$_2$ can be selectively sucked out of an air–hydrogen mixture above the surface of the solution.

The structures of these hydrido complexes were elucidated by normal spectroscopic means as well as by X-ray structure determinations of 17a,[22] 17b,[9] and [{Ir(C$_5$Me$_5$)}$_2$H(OCOCH$_3$)$_2$]PF$_6$[23] and by X-ray and neutron-diffraction determination of the tri-μ-hydride 19.[24] The M···M distances in the four molecules are 2.906 (1), 17a; 2.903 (1), 17b; 3.02, [(IrC$_5$Me$_5$)$_2$H-(OAc)$_2$]$^+$; and 2.455 (1) Å, 19, respectively. Particularly when these distances are compared with those in the dichloride dimers [3.719 (1), 1a, and 3.769 (1) Å, 1b[9]], it is clear that the bridging hydrides tie the metals together very effectively and that the greater the number of bridging hydrides the stronger is this interaction. Indeed it has been suggested that the complex 19 could be considered to possess a "triply protonated Ir≡Ir triple bond".[24] While there is no

(17) J. W. Kang and P. M. Maitlis, *J. Organometal. Chem.*, 26, 393 (1971).

(18) K. Moseley, J. W. Kang, and P. M. Maitlis, *J. Chem. Soc. A*, 2875 (1970).

(19) C. White, A. J. Oliver, and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 1901 (1973).

(20) D. S. Gill and P. M. Maitlis, *J. Organometal. Chem.*, 87, 559 (1975).

(21) L. Vaska and M. F. Wernecke, *Trans. N.Y. Acad. Sci.*, 31, 70 (1971).

(22) M. R. Churchill and S. W. Ni, *J. Am. Chem. Soc.*, 95, 2150 (1973).

(23) P. M. Bailey and P. M. Maitlis, unpublished results.

(24) R. Bau, W. E. Carroll, R. G. Teller, and T. F. Koetzle, *J. Am. Chem. Soc.*, 99, 3872 (1977).

chemical or physical evidence which suggests that the bridging H's in **19** have any protonic character (for example, it cannot be deprotonated by base), the very short Ir–Ir distance implies substantial metal–metal bond character. The C_5Me_5 ligands shield the metal atoms very effectively from one side; if, in addition, the metal atoms are pulled together and further shielded by bridging ligands, their reactivity may be anticipated to be greatly reduced. This is indeed found, as discussed below.
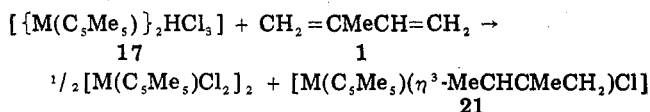
Stoichiometric Reactions with Diolefins

It was discovered early that the dichloride dimers **1** reacted readily with ethylene and a wide variety of diolefins in ethanol in the presence of base.[18] These are the conditions under which hydride formation occurs, and in the reactions with diolefins Moseley isolated enyl complexes that resulted from the addition of "H–M-(C_5Me_5)Cl" to the diene. Many of these enyl complexes then lose HCl to give the $M^I(C_5Me_5)(\eta^4\text{-diene})$ complexes, e.g., **21** → **22**,[25] and the complex isolated (η^3-enyl

$$[M(C_5Me_5)Cl_2]_2 + CH_2{=}CMeCH{=}CH_2 \xrightarrow[\text{base}]{\text{EtOH/}}$$
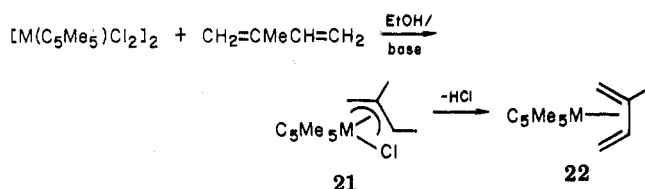
or η^4-diene) depends on the conditions of the reaction and on the number and nature of the allylic substituents.

The same dienes also reacted stoichiometrically with the mono-μ-hydrido complexes **17**; for example, with isoprene the major product, **21**, which arises by addition of M–H across the $-CH{=}CH_2$ bond, was isolated together with **1**.[26]

$$[\{M(C_5Me_5)\}_2HCl_3] + CH_2{=}CMeCH{=}CH_2 \rightarrow$$
$$\underset{\textbf{17}}{} \qquad\qquad \underset{\textbf{1}}{}$$
$$^1/_2[M(C_5Me_5)Cl_2]_2 + [M(C_5Me_5)(\eta^3\text{-MeCHCMeCH}_2)Cl]$$
$$\underset{\textbf{21}}{}$$

Kinetic studies by Lee of the reaction of the hydrides **17** with a variety of dienes showed that the rate of reaction was proportional only to the concentration of **17** and was independent of the concentration of and the nature of the diene.[27] The iridium complex **17b** reacted five times faster than the rhodium complex **17a**; there was no detectable isotope effect when the deuterio complex [$\{M(C_5Me_5)\}_2DCl_3$] was reacted, and the addition of base did not change the rate either. These data, together with the observed small negative $\Delta S^{\ddagger}$,[28] were consistent with the rate-determining step being a reorganization of **17** to create a vacant site. At +37 °C in dichloromethane the first-order rate constant, k_1, for reaction of dienes with the iridium mono-μ-hydride

(17b) was 7.6×10^{-4} s^{-1} ($t^1/_2$ ca. 910 s), but the iridium di-μ-hydride **18** did *not* react with dienes in dichloromethane to any observable extent,[20] and we conclude that the vacant site is not created (as might have been anticipated) by the breaking of what is formally a two-electron three-center M–H–M bond, but rather that it is the M–Cl–M bridge which is most easily broken. The transition state may therefore be represented as **23**, a result which further testifies to the unusual

23
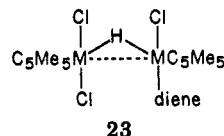
stability of the M–H–M bridge bond.

Olefin Hydrogenation Catalysts

Many of the (pentamethylcyclopentadienyl)rhodium and -iridium complexes show high activity as olefin hydrogenation catalysts at 20 °C and 1 atm H$_2$ pressure.[29,30] The activity is highest in weakly coordinating polar solvents such as 2-propanol, and the halide complexes [$M(C_5Me_5)X_2]_2$ as well as the hydrides [$\{M(C_5Me_5)\}_2HX_3$] (M = Rh, Ir; X = Cl, Br, or I) and [$Ir(C_5Me_5)HCl]_2$ (**18**) are strongly cocatalyzed by base (normally a noncoordinating amine, Et$_3$N, was used, but Na$_2$CO$_3$ was also effective). More detailed studies by Gill and White showed that coordinating ligands deactivated the catalyst and, for example, [Rh-($C_5Me_5)Cl_2PPh_3$] and [Rh($C_5Me_5)Cl(PMe_2Ph)_2$]$^+$ were quite inactive. The iridium complexes were usually 2–3 times as active as the analogous rhodium complexes, but they also caused isomerization of terminal to internal olefins to occur very much more rapidly than the rhodium complexes. The activity (in 2-propanol/base) decreased in the order X = Cl > Br > I but, surprisingly, the μ-hydride complexes were *less* effective hydrogenation catalysts roughly in direct proportion to the number of bridging hydride ligands present (Table I).

The requirement of base as cocatalyst arises mainly from the need to repress reactions such as

$$mHCl + HCl \rightarrow mCl_2 + H_2$$
$$m = M(C_5Me_5)$$
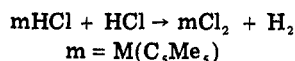
and since acid is generated in the heterolytic activation step (reverse of the above reaction) this needs to be removed before maximum catalyst efficiency can be attained.

For the rhodium complexes the activity rises with increase in concentration of base to plateau at about 4 equiv of triethylamine per rhodium atom. A similar increase in activity can be achieved with between 3 and 6 equiv of triethylamine per metal atom for the iridium complexes, but in this case further increase in amine concentration leads to a decrease in activity. At least part of this effect can be accounted for by the observations that the tri-μ-hydridoiridium complex [$\{Ir-(C_5Me_5)\}_2H_3$]$^+$, which is easily formed from other

(25) H. B. Lee and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 2316 (1975).

(26) A similar reaction presumably occurs with **1** and ethanol/base but in this case each dimer complex (**1**) forms two "M(C_5Me_5)H(Cl)" intermediates, both of which react with the diolefin.

(27) H. B. Lee, K. Moseley, C. White, and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, 2322 (1975).

(28) For the reactions of 1,5-cyclooctadiene with **17**, to give [M-(C_5Me_5)(1,3-η-cyclooctenyl)Cl] + **1**, the activation parameters in CH$_2$Cl$_2$ solution are: $\Delta H^{\ddagger}$ = 94 (M = Rh) and 90 (M = Ir) kJ mol^{-1} and $\Delta S^{\ddagger}$ = –9.5 J K^{-1} mol^{-1} (for M = Rh and Ir) [1 J = 4.184 cal].

(29) C. White, D. S. Gill, J. W. Kang, H. B. Lee, and P. M. Maitlis, *Chem. Commun.*, 734 (1971); P. M. Maitlis, C. White, J. W. Kang, and D. S. Gill, Canadian Patent 915 967 (filed May 25, 1971; issued Nov 28, 1972); U.S. Patent 3 849 459 (Nov 19, 1974).

(30) D. S. Gill, C. White, and P. M. Maitlis, *J. Chem. Soc., Dalton Trans.*, in press.

Table I
Activity of Hydrogenation Catalysts in 2-Propanol

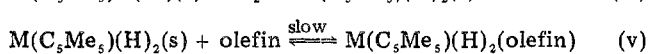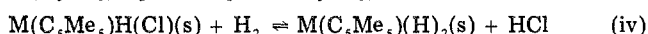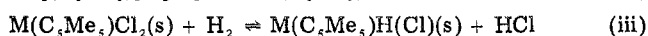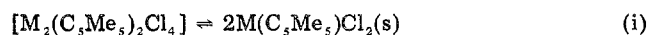| Catalyst	H₂, atm	Temp, °C	Relative rates	Substrate	Product
$[Rh(C_5Me_5)Cl_2]_2$ [a]	1	20	9.8[d]	Cyclohexene	Cyclohexane
$[Rh(C_5Me_5)Br_2]_2$ [a]	1	20	6.5[d]	Cyclohexene	Cyclohexane
$[Rh(C_5Me_5)I_2]_2$ [a]	1	20	0.6[d]	Cyclohexene	Cyclohexane
$[\{Rh(C_5Me_5)\}_2HCl_3]$ [a]	1	20	5.1[d]	Cyclohexene	Cyclohexane
$[Ir(C_5Me_5)Cl_2]_2$ [b]	1	20	27.3[d]	Cyclohexene	Cyclohexane
$[\{Ir(C_5Me_5)\}_2HCl_3]$ [b]	1	20	15.3[d]	Cyclohexene	Cyclohexane
$[\{Ir(C_5Me_5)\}_2H_2Cl_2]$ [b]	1	20	13.2[d]	Cyclohexene	Cyclohexane
$[\{Ir(C_5Me_5)\}_2H_3]^+$	1	20	0[d]	Cyclohexene	Cyclohexane
$[Rh(PPh_3)_3Cl]$ [c]	1	20	4.3[d]	Cyclohexene	Cyclohexane
$[\{Rh(C_5Me_5)\}_2HCl_3]$ [a]	1	20	9.1[d]	4-Methyl-1-pentene	4-Methylpentane
$[\{Rh(C_5Me_5)\}_2HCl_3]$ [a]	1	20	7.1[d]	1-Hexene	Hexane
$[\{Rh(C_5Me_5)\}_2HCl_3]$ [a]	1	20	5.1[d]	Cyclopentene	Cyclopentane
$[\{Rh(C_5Me_5)\}_2HCl_3]$ [a]	1	20	3.5[d]	4-Methylcyclohexene	Methylcyclohexane
$[\{Rh(C_5Me_5)\}_2HCl_3]$ [a]	1	20	2.8[d]	2-Methyl-1-pentene	2-Methylpentane
$[\{Rh(C_5Me_5)\}_2HCl_3]$ [a]	1	20	2.6[d]	cis-4-Methyl-2-pentene	4-Methylpentane
$[\{Rh(C_5Me_5)\}_2HCl_3]$ [a]	1	20	1.4[d]	trans-4-Methyl-2-pentene	4-Methylpentane
$[\{Rh(C_5Me_5)\}_2HCl_3]$ [e]	100	20	0.75[f]	Vinylcyclohexene	Ethylcyclohexane
$[\{Rh(C_5Me_5)\}_2HCl_3]$ [e]	100	20	4.0[f]	1,5-Hexadiene	Hexane
$[\{Rh(C_5Me_5)\}_2HCl_3]$ [e]	100	20	4.0[f]	Mesityl oxide	Methyl isobutyl ketone
$[\{Rh(C_5Me_5)\}_2HCl_3]$ [e]	100	20	10.0[f]	Vinyl acetate	Ethyl acetate (33%)
$[\{Rh(C_5Me_5)\}_2HCl_3]$ [e]	100	20	10.0[f]	Diphenylacetylene	Stilbene (70%) Dibenzyl (30%)
$[Rh(C_5Me_5)Cl_2]_2$ [g]	50	50	100[h]	Benzene	Cyclohexane
$[Rh(C_5Me_5)Cl_2]_2$ [g]	50	50	100[h]	Toluene	Methylcyclohexane
$[Rh(C_5Me_5)Cl_2]_2$ [g]	50	50	100[h]	o-Xylene	cis- and trans-1,2-dimethylcyclohexane (6.2:1)
$[Rh(C_5Me_5)Cl_2]_2$ [g]	50	50	60[h]	Ethylbenzene	Ethylcyclohexane
$[Rh(C_5Me_5)Cl_2]_2$ [g]	50	50	45[h]	tert-Butylbenzene	tert-Butylcyclohexane
$[Rh(C_5Me_5)Cl_2]_2$ [g]	50	50	100[h]	Acetophenone	Methyl cyclohexyl ketone
$[Rh(C_5Me_5)Cl_2]_2$ [g]	50	50	73[h]	N,N-Dimethylaniline	N,N-Dimethylcyclohexylamine

[a] Catalyst (0.04 mmol), olefin (11.8 mmol), triethylamine (7.2 mmol) in 2-propanol.   [b] As for (a) except with 0.36 mmol of triethylamine.   [c] As for (a) except without triethylamine.   [d] Measured as H₂ uptake in mL min⁻¹.   [e] Catalyst (0.01 mmol), olefin (7.6 mmol) in 2-propanol (5 ml).   [f] Relative rates expressed in hours required for complete reaction. [g] Catalyst (0.05 mmol), arene (2 mL), triethylamine (1.5 mmol) in 2-propanol (18 mL) for 36 h.   [h] Rates expressed as percentages of product relative to benzene → cyclohexane which is 100% complete under these conditions.

iridium complexes in 2-propanol under conditions of high basicity, is totally inactive as a catalyst and that no rhodium analogue of this complex appears to exist.
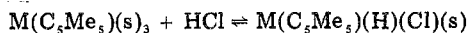
These results testify further to the kinetic inertness of M–H–M bridge bonds in these systems and suggest moreover that such bridges are absent in the most active catalysts. Evidence in favor of this comes from the observation that the most active systems were those based on the dichloride dimers $[M_2(C_5Me_5)_2Cl_4]$ which showed activity proportional to $[\text{catalyst}]^{1/2}$, implying that the actual catalysts involved were monomer complexes of the type $[M(C_5Me_5)H(X)s]$ (s = solvent or vacant site). Measurements during the first 10–20% of reaction indicated further that the rates were also proportional to $[p(H_2)]^2$ and that the olefin dependence was first order at low and zero order at high olefin concentration. The same dependence on $[\text{catalyst}]^{1/2}$ and on olefin concentration was observed for the iridium di-μ-hydride 18, but here the dependence on hydrogen concentration was of the form $[p(H_2)]^1$.

These data suggest that for the dichloride dimers (and for $[Ir(C_5Me_5)HCl]_2$) the reaction paths in eq i–vii are probably most significant.

In the first steps (i, ii) solvent-assisted cleavage into monomers occurs. In steps iii and iv these heterolytically activate H₂ to give the probable "true" catalyst, $[M(C_5Me_5)(H)_2(s)]$, which then reacts with olefin and more hydrogen in a cycle (steps v–vii). Steps vi and vii involve a formal reductive elimination ($M^{III} \rightarrow M^I$ + alkane) and an oxidative addition of H₂ to M^I, respectively, and this part of the process is broadly similar

$$[M_2(C_5Me_5)_2Cl_4] \rightleftharpoons 2M(C_5Me_5)Cl_2(s) \tag{i}$$

$$[Ir_2(C_5Me_5)_2H_2Cl_2] \rightleftharpoons 2Ir(C_5Me_5)H(Cl)s \tag{ii}$$

$$M(C_5Me_5)Cl_2(s) + H_2 \rightleftharpoons M(C_5Me_5)H(Cl)(s) + HCl \tag{iii}$$

$$M(C_5Me_5)H(Cl)(s) + H_2 \rightleftharpoons M(C_5Me_5)(H)_2(s) + HCl \tag{iv}$$

$$M(C_5Me_5)(H)_2(s) + \text{olefin} \underset{\text{slow}}{\rightleftharpoons} M(C_5Me_5)(H)_2(\text{olefin}) \tag{v}$$

$$M(C_5Me_5)(H)_2\text{olefin} \xrightarrow{\text{fast}} M(C_5Me_5)(s)_3 + \text{alkane} \tag{vi}$$

$$M(C_5Me_5)(s)_3 + H_2 \rightleftharpoons M(C_5Me_5)(H)_2(s) \tag{vii}$$

or

$$M(C_5Me_5)(s)_3 + HCl \rightleftharpoons M(C_5Me_5)(H)(Cl)(s)$$
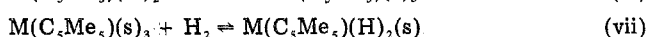
to the mechanism which has been deduced for olefin hydrogenation catalyzed by $[Rh(PPh_3)_3Cl]^2$.

On the other hand, the mono-μ-hydride complexes 17, which showed a first-order dependence on $[\text{catalyst}]^1$, largely appear to react by a path where intermediates analogous to 23 (olefin in place of diene) play a key role and where dissociation to monomer does not occur to a significant extent in the initial stages. Strong support for the idea that an initial olefin activation is important here comes from the observation that (in dichloromethane in the absence of hydrogen and base) $[\{Ir(C_5Me_5)\}_2HCl_3]$ is a very much better olefin isomerization catalyst than $[Ir(C_5Me_5)HCl]_2$ while $[Ir(C_5Me_5)Cl_2]_2$ is inactive.

Dienes and functional groups on the olefin tended to repress hydrogenation at 1 atm, but on increasing the hydrogen pressure satisfactory reduction could be achieved; the functional groups were, in general, not reduced under these conditions.

Under similar conditions, the rhodium dichloride complex **1a** is about twice as active (per rhodium atom) toward cyclohexene as the Wilkinson complex, and the iridium dichloride complex **1b** is about a factor of three more active still. However, whereas [RhCl(PPh₃)₃] catalyzes the reduction of cyclohexene fifty times faster than 1-methylcyclohexene, the corresponding factor is only about 3 for **1a** and 7 for **1b**. This probably reflects a greater steric constraint in [RhCl(PPh₃)₃] than in [Rh(C₅Me₅)Cl₂]₂.

A measure of the steric factors involved may be obtained from the cone angle, θ.[31] For C₅Me₅–Rh it is calculated to be 185° while for Ph₃P θ = 145° and for the grouping *fac*-{(Ph₃P)₂Cl}Rh θ is estimated as 230°. Clearly we may therefore anticipate the C₅Me₅–M catalysts to be sterically rather less demanding than [Rh(Ph₃P)₃Cl].

Arene Hydrogenation Catalysts

While the homogeneous catalysis of olefin hydrogenation has now become almost a commonplace reaction, the hydrogenation of benzene and substituted benzenes is difficult even with heterogeneous catalysts.[32] A few homogeneous catalysts have been reported to reduce benzenes to cyclohexanes[33] but they mostly appear to be rapidly deactivated or to have a limited range.

It is therefore of especial interest that Russell recently demonstrated that (pentamethylcyclopentadienyl)-rhodium complexes such as **1a** show reasonable activity for the reduction of benzene and substituted benzenes to cyclohexanes (Table I) at 50 °C and 50 atm of hydrogen.[34] Again, base was a necessary cocatalyst and

2-propanol was the solvent of choice; this indicates, as is to be expected, the importance of a heterolytic hydrogen activation step in the reaction mechanism. No detectable amounts of metal were formed under these conditions, and turnover numbers of over 400 equiv of benzene to cyclohexane per rhodium have been obtained; in general, cyclohexenes and cyclohexadienes were not detected in the products. By contrast, the iridium complex **1b** showed only 28% of the activity of **1a**; this may correlate with the greater stability of the Ir^{III}–arene by comparison with the Rh^{III}–arene complexes previously noted, and it is interesting that **1a** reduces most easily those alkylated benzenes that form the least stable complexes in **8**. [Rh(Ph₃P)₃Cl] only showed 3% of the activity of **1a**, and [Co(C₅Me₅)I₂]₂ decomposed to metal under the same conditions.

Analysis of the products formed by **1a**-catalyzed reduction of the *o*-, *m*-, and *p*-xylenes showed a high stereoselectivity for the formation of the *cis*-dimethylcyclohexanes [*cis:trans* = 6.2:1 (*o*-xylene), 3.8:1 (*m*-xylene), and 2:1 (*p*-xylene)]. Our preliminary results also show that the catalyst can tolerate at least some functional groups on the arene, for example, –CO₂R, –COR, –NMe₂, OMe.

Activity as hydrogenation catalysts certainly only represents one aspect of the chemistry of these very versatile complexes, and more applications will undoubtedly be found. The recent syntheses of alkyl-substituted tetramethylcyclopentadienes makes the formation of [M(C₅Me₄R)X₂]₂ complexes possible, and it should also be possible to attach (C₅Me₄R)–RhX₂ onto polymers to give supported catalysts.

(31) C. A. Tolman, *Chem. Rev.*, **77**, 313 (1977).

(32) P. N. Rylander, "Catalytic Hydrogenation over Platinum Metals", Academic Press, New York, N.Y., 1967, p 309 et seq.

(33) See, for example, P. Abley, I. Jardine, and F. J. McQuillin, *J. Chem. Soc. C*, 140 (1970); P. D. Taylor and M. Orchin, *J. Org. Chem.*, **37**, 3913 (1972); M. C. Rakowski, F. J. Hirsekorn, L. S. Stuhl, and E. L. Muetterties, *Inorg. Chem.*, **15**, 2379 (1976), and references therein.

(34) M. J. H. Russell, C. White, and P. M. Maitlis, *J. Chem. Soc., Chem. Commun.*, 427 (1977).

The Prenyl Transfer Reaction. Enzymatic and Mechanistic Studies of the 1'–4 Coupling Reaction in the Terpene Biosynthetic Pathway

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The terpene biosynthetic pathway is used to synthesize a wide variety of small molecules which are often

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Hans Rilling, Professor of Biochemistry at the University of Utah, was born in Cleveland, Ohio, in 1933, and received his B.A. degree from Oberlin College. His Ph.D. thesis research at Harvard University was directed by K. Bloch, who introduced him to terpene biosynthesis. After postdoctoral work at the University of Michigan, Dr. Rilling moved to the University of Utah, where he has continued research on various aspects of terpene biosynthesis.

lipophilic and fulfill a multiplicity of functions. Important examples are sterols (structural components of eukaryotic membranes), carotenes (photoreceptors in visual and photosynthetic systems), and phosphorylated polyprenols (membrane-soluble carriers of sugars in the biosynthesis of bacterial cell wall polysaccharides and eukaryotic glycoproteins). In other systems the hydrophobic polyisoprenoid chain is used to anchor respiratory coenzymes (ubiquinone, porphyrin a) or chlorophyll to membranes. Terpenes are also involved in communication between organs (hormones) and organisms (pheromones). In addition to these few