Coordination Chemistry Reviews, 43 (1982) 377–384
Elsevier Scientific Publishing Company, Amsterdam—Printed in The Netherlands

NEW TYPES OF REACTIONS INVOLVING RHODIUM AND IRIDIUM COMPOUNDS

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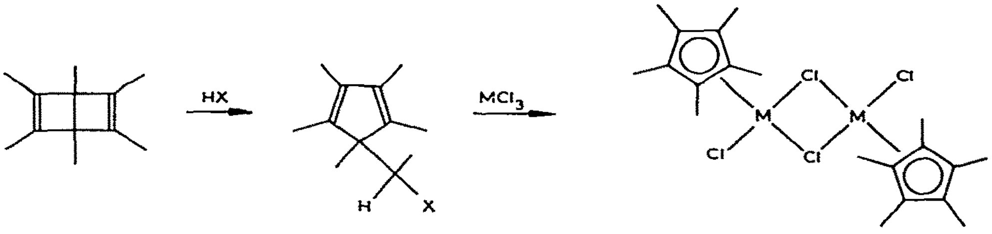
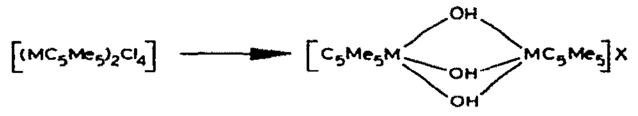
In 1967 Kang, Moseley and I made the discovery [1] that reaction of hexamethyl "Dewar" benzene (**1**) [2] with rhodium trichloride in methanol gave the dimeric pentamethylcyclopentadienylrhodium chloride complex (**3a**). The reaction proceeded via an acid-promoted ring contraction of (**1**) to the substituted cyclopentadiene (**2**) which then reacted with the rhodium chloride to give (**3a**). An analogous reaction with iridium trichloride gave (**3b**).



(1) (2) (3)

(a, M = Rh, b, M = Ir)

It immediately became clear that the complexes (**3**) had unusual stability for an organometallic half-sandwich compound so far as the ring-to-metal bond was concerned. For example, (**3a**) readily dissolved in aqueous sodium hydroxide to give large orange yellow needles of the tri-μ-hydroxo complex (**4a**, X = Cl) [3]. Analogous iridium complexes, (**4b**), have also been prepared [4]. The anions can be interchanged by standard metathesis routes and two of these complexes, the very basic $[(RhC_5Me_5)_2(OH)_3]OH \cdot 11H_2O$ and $[(IrC_5Me_5)_2(OH)_3]OAc \cdot 14H_2O$, have had their crystal structures determined [4].



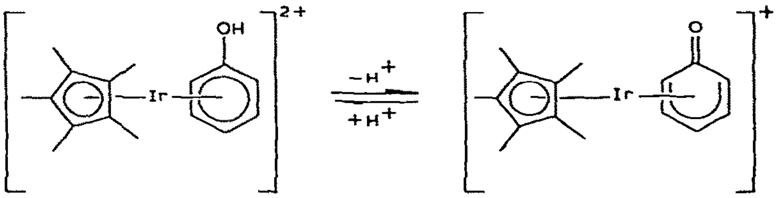
(3) (4)

The chloride complexes also undergo standard metathesis reactions to give $[(MC_5Me_5)_2X_4]$, where X = Br, I, RCO_2, N_3, NCS or NCO, etc. [5]; most of these in turn undergo bridge-splitting reactions with suitable ligands (phosphines, amines, etc.) to give mononuclear complexes, $[(MC_5Me_5)X_2L]$ [5].

The complexes (3) react with suitable solvents (solv) in the presence of silver salts of non-coordinating anions (BF_4^-, PF_6^-) to give tri-solvent complexes (5). Some of these are quite stable and can be isolated, others are very labile and reactive. These compounds are useful synthetic intermediates; for example they react with arenes to give the dicationic η^6-arene complexes (6)

$$\underset{(3)}{[(MC_5Me_5)_2Cl_4]} \xrightarrow{\text{solv., AgX}} \underset{(5)}{[C_5Me_5M(solv)_3]^{2+}} \xrightarrow{\text{arene}} \underset{(6)}{[C_5Me_5M\ \text{arene}]^{2+}}$$

While benzene and simple substituted benzenes give η^6-complexes, more complicated forms of behaviour occur when functional groups are present. For example, the complex (6, arene = phenol) can be deprotonated to give (7), a complex of the η^5-oxocyclohexadienyl ligand [6]. The η^6-indene complex (8) underwent reversible deprotonation accompanied by a shift in binding site to give the η^5-indenyl complexes (9) [7].



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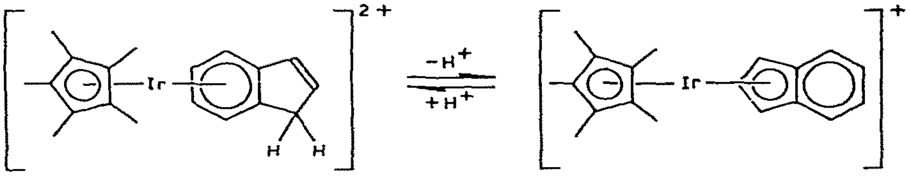
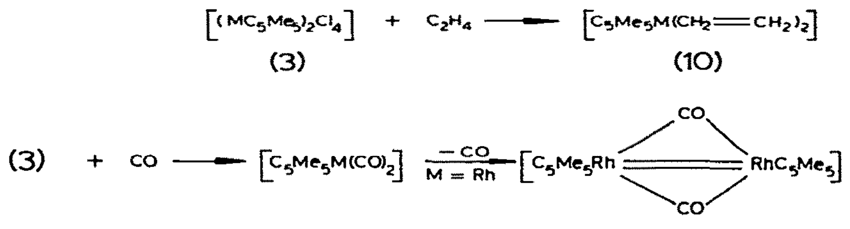


(8) (9)

In addition to this extensive chemistry where the metal is formally in the (III) oxidation state, many complexes are also known in the (I) oxidation state. For example, reaction of (3) with olefins (in the presence of ethanol and base) gives, finally, di-olefin complexes, such as (**10**) [5]. The dicarbonyls (**11**) are made similarly [5].

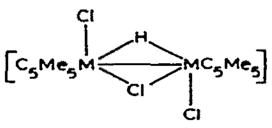
A rich chemistry of cluster complexes is also now developing; the simplest example is the highly reactive dinuclear dicarbonyl (**12**) [8] and others are mentioned below.



(3) (10) (12)

A substantial number of accurate crystal structure determinations of MC_5Me_5 complexes have now been undertaken, largely by Churchill and by Bailey. These show, first, that rhodium and iridium are essentially the same size and that their complexes are usually identical in other respects. They also show that one reason why C_5Me_5 ligands so effectively to these metals is because it can adjust itself so well to the differing electronic demands of the other ligands. Thus for example, the perpendicular distances from the ring to Rh(III) lie between 1.75 and 1.82 Å, while those to Rh(I) are substantially longer (1.85–1.91 Å) [5]. Within the former group even finer detail can be discerned, in that the metal–ring distance varies inversely with the electronegativity of the other (*trans*-) ligands. For example in the series $[(RhC_5Me_5)_2(OH)_3]OH$, $[(RhC_5Me_5)(NO_3)_2]$ and $[(RhC_5Me_5)_2X_4]$ the perpendicular ring–metal distances increase in the order, OH (1.744 Å) ~ NO_3 (1.745 Å) > Cl (1.756 Å) > Br(1.769 Å) > I(1.779 Å). Cyclopentadienyl is very much less good at stabilising Rh or Ir and present indications are that it cannot adjust itself so well to the varying demands of the metal as C_5Me_5.

The stoichiometry of the reactions of (**3**) with dienes in the presence of ethanol and base indicated the intermediacy of hydride complexes. Stable hydrides were easily prepared from (**3**) and related compounds in a variety of ways (H_2/base, isopropanol/base, borohydride, etc.) [9]. They all turned out to be dinuclear with bridging hydrides; the series included the mono-μ-hydrido-mono-μ-chloro-complexes (**13a**) and (**13b**), the iridium di-μ-hydride (**14**) and the iridium tri-μ-hydride cation (**15**). Only (**14**) has not yet been fully characterised by a crystal structure determination but the structure of another di-μ-hydride, (**16**), has been determined [10].



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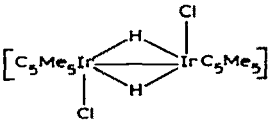

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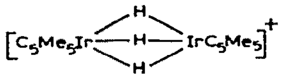

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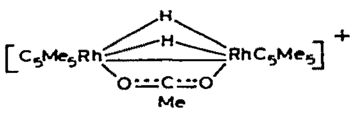

(16)

The ease of formation of the hydrides suggested that these complexes might be active in hydrogen-transfer reactions and so they proved to be. That this is to be expected comes from a consideration of the main species in the hydrogenation cycle catalysed by the Wilkinson complex $[\mathrm{Rh(PPh_3)_3Cl}]$. These are probably $[\mathrm{Rh(PPh_3)_2Cl(L)}_n]$ [11] and it will be evident that $\mathrm{RhC_5Me_5}$, with $\mathrm{C_5Me_5}$ as a tridentate, monoanionic ligand, is equivalent to the sub-unit $\mathrm{Rh(PPh_3)_2Cl}$.

In fact, $[(\mathrm{RhC_5Me_5})_2\mathrm{Cl_4}]$ is a reasonably good hydrogenation catalyst* and the kinetic behaviour (half-order in dinuclear catalyst, second order in $p(\mathrm{H_2})$) suggested a cycle the latter part of which is closely related to that proposed for $[\mathrm{Rh(PPh_3)_3Cl}]$ [12].

$$\left.\begin{array}{l} \mathrm{m_2Cl_4} \rightleftharpoons 2\,\mathrm{mCl_2} \\ \mathrm{mCl_2 + H_2 \rightleftharpoons mHCl + HCl} \\ \mathrm{mHCl + H_2 \rightleftharpoons mH_2 + HCl} \end{array}\right]\text{initiation}$$

$$\left.\begin{array}{l} \mathrm{mH_2 + olefin} \overset{\text{slow}}{\rightleftharpoons} \mathrm{mH_2\ (olefin)} \\ \mathrm{mH_2\ (olefin)} \xrightarrow{\text{fast}} \mathrm{m + alkane} \\ \mathrm{m + H_2 \rightleftharpoons mH_2} \end{array}\right]\text{propagation}$$

where $\mathrm{m = MC_5Me_5}$.

The iridium complex $[(\mathrm{IrC_5Me_5})_2\mathrm{Cl_4}]$ was more active (T/N 14.5 $\mathrm{min^{-1}}$ $[\mathrm{catalyst}]^{-1}$) and showed similar behaviour. However, the μ-hydrido complexes showed markedly poorer hydrogenation activity, i.e., $[(\mathrm{IrC_5Me_5})_2\mathrm{HCl_3}]$, $T/N = 5.0$, $[(\mathrm{IrC_5Me_5})_2\mathrm{H_2Cl_2}]$, $T/N = 1.9$, and $[(\mathrm{IrC_5Me_5})_2\mathrm{H_3}]^+$ was almost totally inactive.

We suggest that the reason for this unexpected behaviour may lie in the fact that since the catalysis is manifested by mononuclear species, the activity will depend on the ease of cleaving the dinuclear precursor. A measure of this may be found in the metal–metal separations which are 3.719 Å in $[(\mathrm{RhC_5Me_5})_2\mathrm{Cl_4}]$ and 3.769 Å in $[(\mathrm{IrC_5Me_5})_2\mathrm{Cl_4}]$, 2.90 Å in $[(\mathrm{MC_5Me_5})_2\mathrm{HCl_3}]$, (**13**), 2.681 Å in $[(\mathrm{RhC_5Me_5})_2\mathrm{H_2(OAc)}]^+$ (**16**), and 2.455 Å in $[(\mathrm{IrC_5Me_5})_2\mathrm{H_3}]^+$ (**15**). Thus the paradox that the more highly hydrided complexes are the poorer hydrogenation catalysts may be explained by (a) the decreasing metal–metal separation which, presumably, implies stronger and less easily cleaved metal–metal bonds, and (b) the high degree

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* Turnover number for cyclohexene to cyclohexane 4.4 $\mathrm{min^{-1}}$ $[\mathrm{catalyst}]^{-1}$ at 22°C, 1 atm $\mathrm{H_2}$ in isopropanol/triethylamine.

of shielding afforded by the C_5Me_5 ligands which makes bimolecular attack at the metal less likely.

The tri-μ-hydroxy-rhodium complexes (**4a**) also yield hydrides on treatment with either hydrogen or isopropanol. Two such complexes have been isolated, the red trinuclear $[(RhC_5Me_5)_3(H)_3O]^+$, (**17**) [10,13], and the green tetranuclear $[(RhC_5Me_5)_4(H)_4]^{2+}$, (**18**) [14]. These complexes have the common characteristic of being very rigid; the barrier, ΔG^*, to movement of the hydrides in (**17**) is at least 21 kcal mol^{-1}. This is reflected in their extremely low activity for the catalysis of hydrogenation; only under conditions where cluster breakdown occurs is there any sign of catalysis. Thus we conclude that, at least for these complexes but probably also more generally, activity for hydrogen-transfer reactions is associated with mononuclear species and that di- or poly-nuclear species are inactive until they break down.

Two unusual hydrogen-transfer reactions, also catalysed very efficiently by the C_5Me_5–Rh complexes, are (i) the formation of vinyl- and allyl-silanes from α-olefins and R_3SiH and (ii) the disproportionation of aldehydes into alcohols and carboxylic acids or carboxylates.

The first reaction takes place in preference to the 'normal' hydrosilation, which gives (**19**)

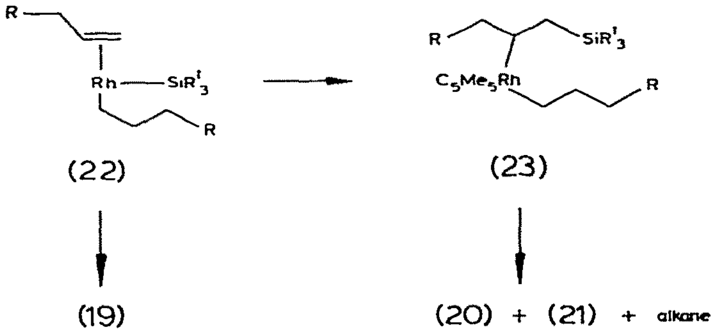
$$RCH_2CH{=}CH_2 + R^1_3SiH \rightarrow \underset{\mathbf{(19)}}{RCH_2CH_2CH_2SiR^1_3}$$

when the olefin is present in large excess compared to R^1_3SiH and at low reaction temperatures. Under favourable conditions, using $[(RhC_5Me_5)_2Cl_4]$ as catalyst precursor, 67% vinylsilane (**20**) and 21% allylsilane (**21**) can be obtained. The terminal olefin is slowly isomerised to internal olefins and alkane is formed corresponding in amount to (**20**) + (**21**) [15]. The overall reaction is therefore

$$RCH_2CH{=}CH_2 + R^1_3SiH \rightarrow \underset{\mathbf{(20)}}{RCH_2CH{=}CHSiR^1_3} + \underset{\mathbf{(21)}}{RCH{=}CHCH_2SiR^1_3} + RCH_2CH_2CH_3$$

This reaction is first order in R^1_3SiH and half-order in catalyst, again implying reaction at a mononuclear centre, and a catalytic cycle is proposed. The key intermediate is (**22**) which gives (**19**) or (**23**); the latter can then fall apart by migration of hydride giving (**20**) or (**21**) and alkane.

Other rhodium catalysts, $[Rh(PPh_3)_3Cl]$ or $[Rh(acac)_3]$, under similar conditions give similar products. However, in contrast to catalyst (**3a**) which is unaffected by small amounts of air or water, the Wilkinson catalyst needs some oxygen as a promoter. This is in order to burn off a triphenylphosphine ligand and create a vacant site.



While a variety at least of rhodium complexes catalyse the formation of unsaturated silanes, the half-sandwich complexes appear to have a unique ability to catalyse the aldehyde disproportionation. Using acetaldehyde in water as model, two reaction regimes can be defined. Under neutral-acid conditions (pH 7–4) the reaction catalysed by RhC_5Me_5 or IrC_5Me_5 complexes gives acetic acid and ethanol in a 1 : 1 ratio [16].

$$2\,MeCHO + H_2O \rightarrow MeCO_2H + MeCH_2OH$$

However, arene–ruthenium complexes under these conditions give more acetic acid than ethanol; in addition, hydrogen is evolved briskly.

The reaction is accelerated greatly on the addition of base (NaOH), by a factor of more than 10^5 for $[(RhC_5Me_5)_2(OH)_3]Cl$, and it then becomes stoichiometric in base and all catalysts give a 1 : 1 ratio of ethanol to acetate. No hydrogen is evolved.

$$2\,MeCHO + OH^- \rightarrow MeCH_2OH + MeCO_2^-$$

This reaction is now a metal-catalysed Cannizzaro reaction; however, the Cannizzaro reaction is normally too slow to compete with the aldol condensation for acetaldehyde

$$2\,MeCHO \xrightarrow[-H_2O]{OH^-} MeCH{=}CHCHO \rightarrow$$

In the metal-catalysed reaction aldol products can be almost entirely repressed.

The neutral regime reaction is again first order in aldehyde and half-order in dinuclear catalyst, implying that the rate determining step is reaction of aldehyde with a mononuclear metal complex. Since the aldehyde is largely hydrated and since base has such an accelerating effect, the first steps may be defined as *

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* Alternatives such as oxidative addition of RCO–H to the metal centre have been ruled out.

$$H_2O + [m_2(OH)_3]OH \rightleftharpoons 2\,m(OH)_2H_2O$$

$$MeCHO + H_2O + OH^- \rightleftharpoons MeCH(OH)O^-$$

$$m(OH)_2H_2O + MeCH(OH)O^- \rightarrow m[O(CHMe)OH]OH$$

$$m[O(CHMe)OH]OH \rightarrow mH\{O{=}CMeOH\}OH \rightarrow \underset{\textbf{(24)}}{mH(O_2CMe)}$$

where $m = RhC_5Me_5$ etc.

The complexed aldehyde hydrate can then undergo a β-hydride elimination to give an acetate-hydride species (**24**); indeed $[(RhC_5Me_5)_2(H)_2OAc]^+$ and $[(RhC_5Me_5)_2(H)(OAc)_2]^+$ can be isolated from such reactions.

Another aldehyde is then coordinated to (**24**), hydride migration followed by hydrolysis yields acetic acid, ethanol, and the starting complex.

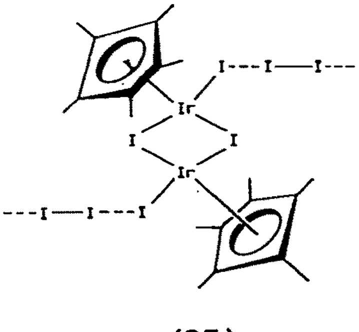
$$\underset{\textbf{(24)}}{mH(O_2CMe)} + MeCHO \rightarrow mH(O_2CMe)(MeCHO) \rightarrow m(O_2CMe)(OCH_2Me)$$

$$m(O_2CMe)(OCH_2Me) + H_2O \rightarrow m(OH)_2H_2O + MeCO_2H + MeCH_2OH$$

Very recently we have begun to develop yet another amusing facet of the chemistry of these pentamethylcyclopentadienyl complexes. We have always been puzzled by the heterolytic hydrogen activation reaction which one would expect to occur by an oxidative addition-reduction elimination sequence, e.g.

$$[(IrC_5Me_5)_2X_4] + H_2 \rightleftharpoons [(IrC_5Me_5)_2H_2X_4] \rightarrow [(IrC_5Me_5)_2HX_3] + HX$$

This suggests that higher oxidation states such as M(IV) or M(V) might have some stability. We tried the oxidative addition of halogens (X_2) to $[(IrC_5Me_5)_2X_4]$ and found that for X = I two complexes $[(IrC_5Me_5)_2I_6]$ and $[(IrC_5Me_5)_2I_8]$ could be isolated. In fact, spectroscopic and X-ray studies showed that these were not oxidative adducts but molecular iodine complexes e.g. (**25**) [17].



(25)

Very recent work has shown that higher oxidation state complexes can be formed, for example, the iridium(V) tetramethyl complex (**26**) [18].

$$[(IrC_5Me_5)_2Cl_4] + Al_2Me_6 \rightarrow \underset{\mathbf{(26)}}{C_5Me_5IrMe_4}$$

REFERENCES

1 J.W. Kang and P.M. Maitlis, J. Am. Chem. Soc., 90 (1968) 3259; J.W. Kang, K. Moseley and P.M. Maitlis, J. Am. Chem. Soc., 91 (1969) 5970.
2 W. Schäfer and H. Hellmann, Angew. Chem., Int. Ed. Engl., 5 (1967) 518.
3 J.W. Kang and P.M. Maitlis, J. Organomet. Chem., 30 (1971) 127.
4 A. Nutton, P.M. Bailey and P.M. Maitlis, J. Chem. Soc. Dalton Trans., (1981) 1997.
5 P.M. Maitlis, Chem. Soc. Rev., 10 (1981) 1, and references therein.
6 C. White, S.J. Thompson and P.M. Maitlis, J. Organomet. Chem., 127 (1977) 415.
7 C. White, S.J. Thompson and P.M. Maitlis, J. Chem. Soc. Dalton Trans., (1977) 1654.
8 A. Nutton and P.M. Maitlis, J. Organomet. Chem., 166 (1979) C21.
9 C. White, A.J. Oliver and P.M. Maitlis, J. Chem. Soc. Dalton Trans., (1973) 1901. X-ray structures: M.R. Churchill and S.W.Y. Ni, J. Am. Chem. Soc., 95 (1973) 2150; M.R. Churchill, S.A. Julis and F.J. Rotella, Inorg. Chem., 16 (1977) 1137; R. Bau, W.E. Carroll, R.J. Teller and T.F. Koetzle, J. Am. Chem. Soc., 99 (1977) 3872.
10 A. Nutton, P.M. Bailey and P.M. Maitlis, J. Organomet. Chem., 213 (1981) 313.
11 J.A. Osborn, F.H. Jardine, J.F. Young and G. Wilkinson, J. Chem. Soc. A, (1966) 1711; J. Halpern and C.S. Wong, J. Chem. Soc. Chem. Commun., (1973) 629; J. Halpern, T. Okamoto and A Zakhariev, Adv. Organomet. Chem., 17 (1979) 319.
12 D.S. Gill, C. White and P.M. Maitlis, J. Chem. Soc. Dalton Trans., (1978) 617; J.E. Hamlin, K. Hirai, V.C. Gibson and P.M. Maitlis, J. Mol. Catal., in press.
13 A. Nutton, P.M. Bailey, N.C. Braund, R.J. Goodfellow, R.S. Thompson and P.M. Maitlis, J. Chem. Soc. Chem. Commun., (1980) 631.
14 P. Espinet, P.M. Bailey, P. Piraino and P.M. Maitlis, Inorg. Chem., 18 (1979) 2706.
15 A. Millan, E. Towns and P.M. Maitlis, J. Chem. Soc. Chem. Commun., (1981) 673.
16 J. Cook, J.E. Hamlin, A. Nutton and P.M. Maitlis, J. Chem. Soc. Chem. Commun., (1980) 144; J. Chem. Soc. Dalton Trans., (1981) 2342.
17 A. Millan, P.M. Bailey and P.M. Maitlis, J. Chem. Soc. Dalton Trans., (1982) 73.
18 K. Isobe, P.M. Bailey and P.M. Maitlis, J. Chem. Soc. Chem. Commun., (1981) 808.