Some aspects of the coordination and catalytic chemistry of ruthenium

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Abstract - Among the characteristic features of the coordination chemistry of ruthenium, which are manifested by complexes containing a considerable range of ligands, are the propensities for intra- and intermolecular metallation of arenes and for the formation of polyhydride complexes. Some aspects of this coordination chemistry are discussed, including the roles of ruthenium polyhydride complexes in catalytic hydrogenation. Distinctive features of such complexes include catalytic activity for the hydrogenation of arenes and of ketones.

INTRODUCTION

Coordination chemistry, almost by definition, is about ligands and about the influence of ligands on the chemical properties of metal atoms and ions. Indeed, it is impressive how ligands can dramatically influence the properties of a given metal, for example, by stabilizing different oxidation states, by modulating electrophilic and nucleophilic properties of the metal, etc. However, having acknowledged this, it also is striking how often certain distinctive properties of a given metallic element persist through quite drastic ligand changes; for example, the electrophilic character of palladium(II) and its propensity to form \( \pi \)-allyl complexes, the widespread roles of nickel complexes in olefin coupling reactions and of rhodium in carbonylation processes, etc.

Perhaps no element better illustrates this theme than ruthenium, as reflected in the following distinctive properties that are manifested by a wide range of its complexes containing a variety of ligands.

- The propensity of ruthenium(II) for \( \pi \)-back-bonding (reflected, for example, in the marked stabilities of \( \text{Ru}^{II}(\text{CO}) \) and \( \text{Ru}^{II}(\text{N}_2) \) complexes; ref. 1).
- The tendency of ruthenium to undergo intra- and intermolecular metallation of arenes (for example, the intramolecular transformation, \( \text{[Ru(C}_{10}\text{H}_{8})(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)_2] \rightleftharpoons \text{[RuH(2-C}_{10}\text{H}_{7})(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)_2] \), the first example of oxidative addition of a C-H bond to a metal; ref. 2).
- The tendency to form polyhydride complexes for example, \( \text{[RuH}_4(\text{PPh}_3)_3] \), \( \text{[RuH}_5(\text{PPh}_3)_2]^+ \), and \( \text{[RuH}_3(\text{PPh}_3)_3]^+ \) (ref. 3, 4).

This paper is concerned particularly with the last two themes and with our related studies on the roles of ruthenium polyhydride complexes in the catalytic hydrogenation of arenes and ketones.
COORDINATION CHEMISTRY OF HYDRIDO(PHOSPHINE)RUTHENATE COMPLEXES

The starting point of our research in this area was the synthesis by Pez, Grey and Corsi (ref. 5) of the anionic orthometallated hydridoruthenate complex (1) and their report that this complex was effective as a catalyst or catalyst precursor for the selective hydrogenation of certain arenes, for example of anthracene to 1,2,3,4-tetrahydroanthracene (ref. 6). We were interested in the origin of this selectivity, particularly in view of earlier reports of different selectivities for other homogeneous hydrogenation catalysts, for example, HCo(CO)₄, which catalyzes the hydrogenation of anthracene to 9,10-dihydroanthracene (ref. 7). As the first stage of our investigation of the [RuH₂(PPh₃)₂(PPh₂C₆H₄)]⁻-catalyzed hydrogenation of anthracene we undertook an examination of the basic coordination chemistry of 1 and related anionic ruthenium complexes and of the stoichiometric reactions of such complexes with possible relevance to their catalytic chemistry (ref. 4).

K[RuH₂(PPh₃)₂(PPh₂C₆H₄)] reacts with H₂ in THF solution according to eq. 1 to form fac-[RuH₃(PPh₃)₃]⁻ (2) which was isolated as the K⁺ salt and which also has been synthesized independently and structurally characterized (ref. 8). 2 reacts with anthracene (eq. 2) to form a new red complex, [RuH(PPh₃)₂(anthracene)]⁻ (3) which also has been isolated as the K⁺ and [Ph₃P=N=PPh₃]⁺ salts and identified by NMR as having the n⁴-structure depicted below (ref. 4). Reaction of 1,4-diphenylbutadiene with 1 yields the analogous n⁴-diene complex [RuH(PPh₃)₂(1,4-Ph₂-butadiene)]⁻. A related iridium complex, [IrH(Pr₃)₂(C₄H₆)] (ref. 9) has been characterized crystallographically (ref. 10).

\[
\text{[RuH}_2\text{(PPh}_3\text{)}_2\text{(PPh}_2\text{C}_6\text{H}_4\text{)] + H}_2 \rightarrow \text{fac-[RuH}_3\text{(PPh}_3\text{)}_3\text{]}^- \quad (1)
\]

\[
\text{fac-[RuH}_3\text{(PPh}_3\text{)}_3\text{]}^- + 1.5 \text{anthracene} \rightarrow \text{[RuH(PPh}_3\text{)}_2\text{(anthracene)]}^- \quad (2)
\]

Reaction (2) was found to exhibit the same rate law as the isotopic exchange of 2 with D₂ (eq. 3), i.e., -d[2]/dt = k₄[2], where k₄ = 7.6 x 10⁻⁴ sec⁻¹ at 55°C, independent of the H₂ or anthracene concentration. This implies that both reactions proceed through a common first order rate-determining step, presumably the reductive elimination of H₂ to form the common intermediate [RuH(PPh₃)₃]⁻ (4), an isomer of 1, in accord with eq. 4. Reactions (2) and (3) are much faster than the phosphine exchange reactions of 2, (for example, the replacement of PPh₃ by PEt₃) ruling out dissociation of PPh₃ as the rate-determining step.
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$\text{fac-}[\text{RuH}_3(\text{PPh}_3)_3]^- \xrightarrow{D_2} [\text{RuHD}_2(\text{PPh}_3)_3]^-(\xrightarrow{D_2} [\text{RuD}_3(\text{PPh}_3)_3]^-(3)

$\text{fac-}[\text{RuH}_3(\text{PPh}_3)_3]^- \xrightarrow{K_4, H_2} [\text{RuH}(\text{PPh}_3)_3]^-(4a)$

$\text{fac-}[\text{RuH}_3(\text{PPh}_3)_3]^- \xrightarrow{P\text{Ph}_3} \text{anthracene} [\text{RuH}(\text{PPh}_3)_2(\text{anthracene})]^-(4b)$

$[\text{RuH}(\text{PPh}_3)_2(\text{anthracene})]^- + 4 H_2 \xrightarrow{5} [\text{RuH}_5(\text{PPh}_3)_2]^+ + 1,2,3,4-\text{H}_4-\text{anthracene} (5)$

$[\text{RuH}_5(\text{PPh}_3)_2]^+ \text{anthracene} \xrightarrow{6} \text{RuH}_5(\text{PPh}_3)_2(\text{anthracene})]^+ + 1,2,3,4-\text{H}_4-\text{anthracene}$

$[\text{RuH}_5(\text{PPh}_3)_2]^+ + 2 \text{anthracene} \xrightarrow{6} [\text{RuH}(\text{PPh}_3)_2(\text{anthracene})]^+ + 1,2,3,4-\text{H}_4-\text{anthracene} (6)$

$[\text{RuH}_5(\text{PPh}_3)_2]^+ + 1-\text{hexene} \xrightarrow{6} [\text{RuH}_3(\text{PPh}_3)_2]^+ + \text{hexane}$

$[\text{RuH}_5(\text{PPh}_3)_2]^+ + 5 \text{C}_2\text{H}_4 \xrightarrow{8} [\text{Ru}(\text{PPh}_3)(\text{PPh}_2\text{C}_6\text{H}_4)\text{(C}_2\text{H}_4)_2]^+ + 3 \text{C}_2\text{H}_6 (8)$

6

7

The chemistry of hydridoruthenate complexes described above is summarized in Fig. 1 and encompasses the synthesis and characterization of several new complexes. It is noteworthy that every new anionic ruthenium complex that these studies have uncovered finds a parallel in a known (and, in most cases, structurally characterized) neutral iridium complex. Thus, $[\text{Ir-H}_2(\text{PPh}_3)_2(\text{PPh}_2\text{C}_6\text{H}_4)_2]$ (ref. 13), $\text{fac-[IrH}_3(\text{PET}_2\text{Ph}_3)$ (ref. 14), $[\text{IrH}(\text{PPr}_2^\text{I})\text{H}_2(\text{C}_4\text{H}_6)_2]$ (ref. 9, 10), $[\text{IrH}_5(\text{PPr}_3)_2]$ (ref. 11) and $[\text{Ir}(\text{PPh}_3)(\text{PPh}_2\text{C}_6\text{H}_4)_2]$ (ref. 9, 12) are direct analogues of 1, 2, 3, 5 and 8, respectively.
There also are significant parallels between the reactivity patterns of these corresponding pairs of complexes.

**CATALYTIC HYDROGENATION OF ANTHRACENE**

In accord with earlier reports (ref. 5), 1 was found to serve as a catalyst or catalyst precursor for the hydrogenation of anthracene to 1,2,3,4-tetrahydroanthracene (and, more slowly, for the further hydrogenation to 1,2,3,4,5,6,7,8-octahydroanthracene). Incomplete kinetic studies suggest that the kinetics are approximately first order in Ru, first order in anthracene and zero order in H₂. Compounds, 2, 3 and 5 also were found to serve as catalyst precursors for the hydrogenation of anthracene with rates that, in some cases, were initially higher than that obtained with 1 but which ultimately levelled off to approximately the same rate, suggesting that they give rise to a common catalytic mechanism. In the light of the chemistry described above it seems likely that, under conditions of the catalytic reaction, the orthometallated complex 1 is converted rapidly and irreversibly to other species (notably 3 and 5) and so is not directly involved in the catalytic mechanism. It further seems likely that the species that are involved in the catalytic cycle contain only two phosphine ligands per Ru, as do the active catalyst precursors 3 and 5.

The combination of reactions 5 and 6, as depicted by Fig. 2, corresponds to a catalytic cycle for the hydrogenation of anthracene and, thus, clearly constitutes one demonstrated mechanism for the reaction. The demonstration of
whether this is the only mechanism will require further kinetic studies on the overall catalytic reaction as well as on the several stoichiometric reactions, identified above, that may constitute component steps of the catalytic mechanism.

The distinctive selectivity of 1 or its derivatives, i.e., for the catalytic hydrogenation of anthracene to 1,2,3,4-tetrahydroanthracene, would appear to reflect the ability of these complexes to bind arenes in the \( \eta^4 \) "diene" mode \( (\mathbb{1}) \) resulting in diene-like reactivity. It does not appear that this is related to the anionic character of these complexes since similar selectivities have now been found for neutral (ref. 15) and cationic (ref. 16) catalysts (derived from \([\text{Rh}(\eta^5-C_5\text{Me}_5)\text{Cl}]_2 \) and \([\text{Rh}(\text{DIPHOS})(\text{MeOH})_2]^+ \), respectively).

**CATALYTIC HYDROGENATION OF KETONES**

Grey, Pez and Wollo (ref. 17) have reported that \([\text{RuH}_2(\text{PPh}_3)_2(\text{PPh}_2\text{C}_6\text{H}_4)]^- (\mathbb{1})\) also serves as a catalyst or catalyst precursor for the hydrogenation of ketones and of certain esters. Since the products of these reactions are alcohols and in view of the marked susceptibility of 1 and other anionic ruthenium hydride complexes to protonation, the nature of the catalyst and the mechanisms of these catalytic reactions were unclear and warranted investigation.

We have found (ref. 18) that addition of alcohols to THF solutions of \([\text{RuH}_3(\text{PPh}_3)_3]^- \) or of alkoxides to solutions of \([\text{RuH}_4(\text{PPh}_3)_3] \) (9; ref. 19) leads to rapid establishment of the reversible equilibrium depicted by eq. 9 (\( K_{eq} \approx 0.1 \) for cyclohexanol; \( \approx 1 \) for diphenylmethanol; ref. 18). Accordingly, both \([\text{RuH}_3(\text{PPh}_3)_3]^- \) and \([\text{RuH}_4(\text{PPh}_3)_3] \) are present in solutions of 2 containing alcohols or of 9 containing alkoxides.

\[
\begin{align*}
\text{[RuH}_3(\text{PPh}_3)_3]^- + R_2\text{CHOH} & \rightleftharpoons \text{[RuH}_4(\text{PPh}_3)_3] \rightleftharpoons [\text{RuH}_4(\text{PPh}_3)_3] \rightleftharpoons [\text{RuH}_4(\text{PPh}_3)_3] + R_2\text{CHO}^- \quad (9) \\
\end{align*}
\]

Cyclohexanone was found to react with 9 to yield cyclohexanol and \([\text{RuH}_4(\text{PPh}_3)_3] \) (10), (probably solvent- or cyclohexanone-coordinated; ref. 20), according to the stoichiometry of eq. 10 and the rate-law of eq. 11, where \( k_{11} = 2.8 \times 10^{-3} \) at 20.5°C, \( \Delta H_{12} = -16 \text{ kcal/mol} \), \( \Delta S_{12} = 16 \text{ cal/(mol K)} \) (ref. 18).

\[
\begin{align*}
[\text{RuH}_4(\text{PPh}_3)_3] + \xi\text{-C}_6\text{H}_10\text{O} & \rightarrow [\text{RuH}_2(\text{PPh}_3)_3] + \xi\text{-C}_6\text{H}_{11}\text{OH} \quad (10) \\
-\frac{d[\text{RuH}_4(\text{PPh}_3)_3]}{dt} = k_{11}[\text{RuH}_4(\text{PPh}_3)_3] \quad (11) \\
\end{align*}
\]

(10) reacts rapidly with \( H_2 \) (< 5 min at 25°C, 1 atm \( H_2 \)) to regenerate 9 according to eq. 12.

\[
\begin{align*}
[\text{RuH}_2(\text{PPh}_3)_3] + H_2 & \rightarrow [\text{RuH}_4(\text{PPh}_3)_3] \quad (12) \\
\end{align*}
\]

Eq. 10 and 12 constitute a catalytic cycle (Fig. 3) for the hydrogenation of cyclohexanone. Consistent with this, \([\text{RuH}_4(\text{PPh}_3)_3] \) was found to be an efficient catalyst for the hydrogenation of cyclohexanone (eq. 14). The kinetics of catalytic hydrogenation conform to eq. 11, confirming that this is the only catalytic mechanism and that reaction (13) is the turnover-limiting step of the cycle.

\[
\begin{align*}
\xi\text{-C}_6\text{H}_{10}\text{O} + H_2 & \rightarrow [\text{RuH}_4(\text{PPh}_3)_3] \rightarrow \xi\text{-C}_6\text{H}_{11}\text{OH} \quad (13) \\
\end{align*}
\]
The detailed mechanism of reaction (10) is unclear. Since [RuH₄(PPh₃)₃] is coordinately saturated, the direct coordination of c-C₆H₁₀O seems unlikely. Prior loss of H₂ is possible and we have confirmed that exchange of 9 with D₂ (including deuteration of the ortho positions of the PPh₃ phenyl rings) is rapid compared with reaction with c-C₆H₁₀O (ref. 18). However, such a step is not readily reconciled with the observed rate-law (eq. 11; rate independent of H₂) unless the initial inverse H₂-dependence is compensated by a subsequent H₂-dependent step (e.g., eq. 14-16). This theme warrants further examination.

\[
[RuH₄(PPh₃)₃] \rightleftharpoons [RuH₂(PPh₃)₃] + H₂ \quad (14)
\]

\[
[RuH₂(PPh₃)₃] + c-C₆H₁₀O \rightleftharpoons [RuH₂(PPh₃)₃(c-C₆H₁₀O)] \quad (15)
\]

\[
[RuH₂(PPh₃)₃(c-C₆H₁₀O)] + H₂ \rightarrow [RuH₂(PPh₃)₃] + c-C₆H₁₁O \quad (16)
\]

Surprisingly, in view of the earlier suggestion of Grey, Pez and Wallo (ref. 17), the anionic hydride \([RuH₃(PPh₃)₃]^-\) (i.e., the product of reaction of 1 with H₂) does not appear to be an effective catalyst for the hydrogenation of cyclohexanone. When added initially to a THF solution of c-C₆H₁₀O under H₂, an induction period was observed, following which catalytic hydrogenation proceeded at the same rate as the corresponding [RuH₄(PPh₃)₃]-catalyzed reaction (Fig. 4). Presumably, [RuH₃(PPh₃)₃]⁻ is converted to the active catalyst, [RuH₄(PPh₃)₃] (eq. 9), by cyclohexanol whose formation is initially slow and autocatalytic. This behavior would seem to contradict the original rationale (ref. 17) concerning the importance of the anionic character of ruthenium hydrides in the catalytic hydrogenation of polar compounds such as ketones. The higher catalytic activity of [RuH₄(PPh₃)₃] compared with that of [RuH₃(PPh₃)₃]⁻ may well reflect the higher rate of loss of H₂ from the former. This, in turn, may be related to the recent characterization of [RuH₂(PPh₃)₃] as an H₂ complex, i.e., [RuH₂(H₂)(PPh₃)₂] (ref. 21).

The reactions of benzophenone with these ruthenium hydrides and its catalytic hydrogenation to diphenylmethanol (eq. 17) follow a different, and more complex, pattern in which anionic as well as neutral species play a role (ref. 18).

\[
Ph₂C=O + H₂ \rightarrow Ph₂CHOH \quad (17)
\]

Reaction of [RuH₄(PPh₃)₃] with benzophenone in THF at 45°C proceeds at conveniently measureable rates in two stages (eq. 18 and 19) to yield the orthometallated complex [RuH(PPh₃)₃(O=CPPhC₆H₄)] (11; ref. 22). 11 reacts rapidly with H₂ (also in two stages) to yield Ph₂CHOH and regenerate [RuH₄(PPh₃)₃] according to eq. 20 and 21. The combination of eq. 18 and 21, and also of eq. 19 and 20, each constitutes a catalytic cycle for the hydrogenation of benzophenone (eq. 17, ref. 18).

\[
[RuH₄(PPh₃)₃] + Ph₂C=O \rightarrow [RuH₂(PPh₃)₃] + Ph₂CHOH \quad (18)
\]

\[
[RuH₂(PPh₃)₃] + 2 Ph₂C=O \rightarrow [RuH₂(PPh₃)₃(O=CPPhC₆H₄)] + Ph₂CHOH \quad (19)
\]

\[
[RuH(PPh₃)₃(O=CPPhC₆H₄)] + 2H₂ \rightarrow [RuH₂(PPh₃)₃] + Ph₂CHOH \quad (20)
\]

\[
[RuH₂(PPh₃)₃] + H₂ \rightarrow [RuH₄(PPh₃)₃] \quad (21)
\]
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Ph2CHO + RuH4(PPh3)3 \rightarrow Ph2CHOH + [RuH3(PPh3)3F]

Thus, the hydrogenation of benzophenone also is effected through a catalytic cycle initiated by the anionic complex, [RuH3(PPh3)3]− (eq. 22, in combination with reactions 21 and 23; ref. 18).

[RuH3(PPh3)3]− + Ph2C=O \rightarrow [RuH2(PPh3)3] + Ph2CHO−

Ph2CHO− + RuH4(PPh3)3 \rightarrow Ph2CHOH + [RuH3(PPh3)3]−

CONCLUDING REMARKS

Polyhydride ruthenium phosphine complexes have been found to exhibit distinctive coordination chemistry and to serve as efficient catalysts for the hydrogenation of a variety of substrates, including arenes and ketones, that are not hydrogenated readily with most other homogeneous hydrogenation catalysts. Two distinctive features of such ruthenium complexes play clearly identifiable roles in the mechanisms of these catalytic reactions, namely: (1) the ability of polyhydride complexes to serve as "hydrogen reservoirs" which lose or transfer hydrogen readily to yield vacant coordination sites
for substrate binding, and (2) the propensity for ortho-metallation of substrate or ligand phenyl rings. Contrary to an earlier suggestion (ref. 17) anionic character does not appear to be a significant contributor to catalytic activity and, indeed, neutral ruthenium hydride complexes appear to be more effective catalysts for the hydrogenation of ketones than their anionic counterparts. While we have not examined their kinetics in comparable detail, preliminary observations suggest that this also is the case for the hydrogenation of arenes (ref. 18). The study of the coordination and catalytic chemistry of the polyhydride complexes of ruthenium and other transition metals would appear to afford impressive opportunities for further novel and important discoveries.

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