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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 infleunce 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 π-allyl complexes, the widespread roles of nickel complexes in olefin coupling reactions and of rhodium in carbonylation processes, etc.

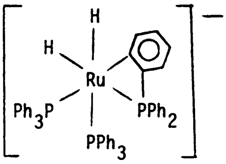
Perhaps no element better illustrates this theme than ruthenium, as reflected in the following distinctive properties that are manifested by a wide range of its complexes containing a variety of ligands.

- The propensity of ruthenium(II) for π-back-bonding (reflected, for example, in the marked stabilities of $Ru^{II}(CO)$ and $Ru^{II}(N_2)$ complexes; ref. 1).
- The tendency of ruthenium to undergo intra- and intermolecular metallation of arenes (for example the intramolecular transformation, $[Ru(C_{10}H_8)(Me_2PCH_2CH_2PMe_2)_2] \rightleftharpoons [RuH(2\text{-}C_{10}H_7)(Me_2PCH_2CH_2PMe_2)_2]$, the first example of oxidative addition of a C-H bond to a metal; ref. 2).
- The tendency to form polyhydride complexes for example, $[RuH_4(PPh_3)_3]$, $[RuH_5(PPh_3)_2]^-$, and $[RuH_3(PPh_3)_3]^-$ (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 $[RuH_2(PPh_3)_2(PPh_2C_6H_4]^-$-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).



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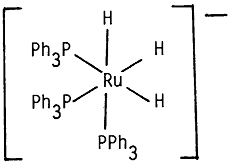

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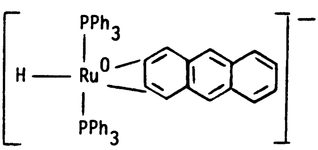

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$K[RuH_2(PPh_3)_2(PPh_2C_6H_4]$ reacts with H_2 in THF solution according to eq. 1 to form *fac*-$[RuH_3(PPh_3)_3]^-$ (2) which was isolated as the K^+ salt and which also has been synthesized independently and structurally characterized (ref. 8). 2 reacts with anthracene (eq. 2) to form a new red complex, $[RuH(PPh_3)_2(anthracene)]^-$ (3) which also has been isolated as the K^+ and $[Ph_3P{=}N{=}PPh_3]^+$ salts and identified by NMR as having the η^4-structure depicted below (ref. 4). Reaction of 1,4-diphenylbutadiene with 1 yields the analogous η^4-diene complex $[RuH(PPh_3)_2(1,4\text{-}Ph_2\text{-butadiene})]^-$. A related iridium complex, $[IrH(Pr^i_3)_2(C_4H_6)]$ (ref. 9) has been characterized crystallographically (ref. 10).

$$\underset{1}{[RuH_2(PPh_3)_2(PPh_2C_6H_4]^-} + H_2 \longrightarrow \underset{2}{fac\text{-}[RuH_3(PPh_3)_3]^-} \qquad (1)$$

$$\underset{2}{fac\text{-}[RuH_3(PPh_3)_3]^-} + 1.5\ \text{anthracene} \longrightarrow \underset{3}{[RuH(PPh_3)_2(\text{anthracene}]^-}$$

$$+\ 0.5\ (1,2,3,4\text{-tetrahydroanthracene}) + PPh_3 \qquad (2)$$

Reaction (2) was found to exhibit the same rate law as the isotopic exchange of 2 with D_2 (eq. 3), i.e., $-d[2]/dt = k_4[2]$, where $k_4 = 7.6 \times 10^{-4}\ sec^{-1}$ at 65°C, independent of the H_2 or anthracene concentration. This implies that both reactions proceed through a common first order rate-determining step, presumably the reductive elimination of H_2 to form the common intermediate $[RuH(PPh_3)_3]^-$ (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 replacment of PPh_3 by PEt_3) ruling out dissociation of PPh_3 as the rate-determining step.

$$\underline{fac}\text{-}[RuH_3(PPh_3)_3]^- \xrightarrow{D_2} [RuHD_2(PPh_3)_3]^-(\xrightarrow{D_2} [RuD_3(PPh_3)_3]^-) \tag{3}$$

$$\begin{tikzcd} & & {[RuHD_2(PPh_3)_3]^- \quad (4a)} \\ {\underline{fac}\text{-}[RuH_3(PPh_3)_3]^-} \arrow[r, "k_4", "-H_2"'] & {\underset{4}{[RuH(PPh_3)_3]^-}} \arrow[ur, "D_2"] \arrow[dr, "-PPh_3", "\text{anthracene}"'] & \\ & & {[RuH(PPh_3)_2(\text{anthracene})]^- \quad (4b)} \end{tikzcd}$$

$[RuH(PPh_3)_2(\text{anthracene})]^-$ reacts rapidly with H_2 in THF at 25°C, in accord with eq. 5, to yield $[RuH_5(PPh_3)_2]^-$ (5) which was isolated as the white K^+ salt (ref. 4). The NMR and IR spectral characterization of 5 are consistent with a pentagonal bipyramidal structure analogous to that of the known and structurally characterized compound $IrH_5(PPr^i_3)_2]$ (ref. 11).

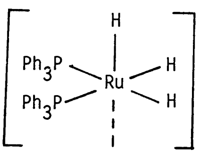
$$[RuH(PPh_3)_2(\text{anthracene})]^- + 4\ H_2 \longrightarrow \underset{5}{[RuH_5(PPh_3)_2]^-} + 1,2,3,4\text{-}H_4\text{-anthracene} \tag{5}$$

$[RuH_5(PPh_3)_2]^-$ reacts with a stoichiometric amount (1:2) of anthracene according to eq. 6 to form $[RuH(PPh_3)_2(\text{anthracene})]^-$ (3) in quantitative yield. The corresponding reaction with cyclohexadiene yields the analogous diene adduct, $[RuH(PPh_3)_2(\text{cyclohexadiene})]^-$, together with cyclohexane and cyclohexene. Reaction of 5 with 1-hexene (eq. 7) in THF results in partial dehydrogenation and formation of $[RuH_3(PPh_3)_2]^-$ (probably solvent coordinated), whose NMR spectrum is consistent with structure 6. The latter reacts readily with CO to form $[RuH_3(PPh_3)_2(CO)]^-$(7). Reaction of 5 with ethylene yields a new compound whose NMR and IR spectra reveal no evidence for a hydride ligand but are consistent with the ortho-metallated formulation $[\overline{Ru(PPh_3)(PPh_2C_6H_4})(C_2H_4)_2]^-$ (8). The latter parallels the structurally characterized compound $[\overline{Ir(PPh_3)(PPh_2C_6H_4})(C_2H_4)_2]$, formed by the corresponding reaction of C_2H_4 with $[IrH_5(PPh_3)_2]$ (ref. 9, 12).

$$\underset{6}{[RuH_5(PPh_3)_2]^-} + 2\ \text{anthracene} \longrightarrow [RuH(PPh_3)_2(\text{anthracene})]^- + 1,2,3,4\text{-}H_4\text{-anthracene} \tag{6}$$

$$[RuH_5(PPh_3)_2]^- + 1\text{-hexene} \longrightarrow \underset{6}{[RuH_3(PPh_3)_2]^-} + \text{hexane} \tag{7}$$

$$[RuH_5(PPh_3)_2]^- + 5\ C_2H_4 \longrightarrow \underset{8}{[\overline{Ru(PPh_3)(PPh_2C_6H_4})(C_2H_4)_2]^-} + 3\ C_2H_6 \tag{8}$$



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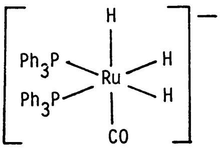

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The chemistry of hydridoruthenate complexes described above is summarized in Fig. 1 and encompasses the synthesis and characterization of several new complexes. It is noteworthy that every new anionic ruthenium complex that these studies have uncovered finds a parallel in a known (and, in most cases, structurally characterized) neutral iridium complex. Thus, $[IrH_2(PPh_3)_2(PPh_2C_6H_4)]$ (ref. 13), $\underline{fac}$-$[IrH_3(PEt_2Ph)_3]$ (ref. 14), $[IrH(PPr^i_3)_2(C_4H_6)]$ (ref. 9, 10), $[IrH_5(PPr^i_3)_2]$ (ref. 11) and $[Ir(PPh_3)(PPh_2C_6H_4)(C_2H_4)_2]$ (ref. 9, 12) are direct analogues of 1, 2, 3, 5 and 8, respectively.

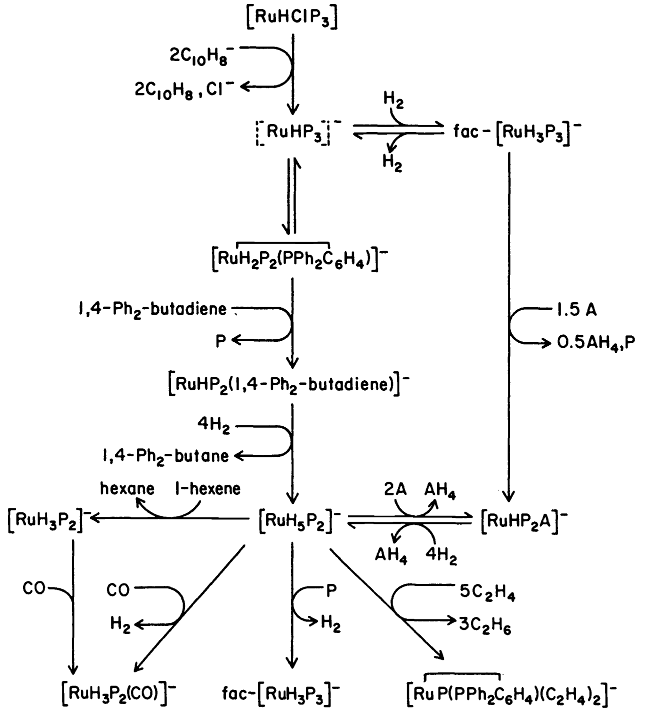


Fig. 1. Reactivity patterns of hydrido(phosphine)ruthenate complexes

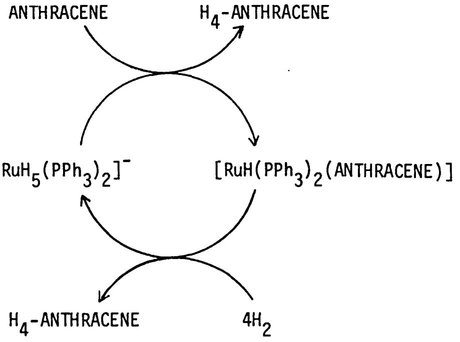


Fig. 2. Catalytic cycle for the hydrogenation of anthracene

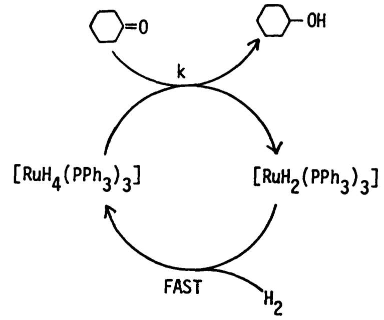


Fig. 3. Catalytic cycle for the hydrogenation of cyclohexanone

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 H_2. 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 η^4 "diene" mode (3) resulting in diene-like reactivity. It does not appear that this is related to the anionic character of these complexes since similar selectivities now have been found for neutral (ref. 15) and cationic (ref. 16) catalysts (derived from $[Rh(\eta^5\text{-}C_5Me_5)Cl]_2$ and $[Rh(DIPHOS)(MeOH)_2]^+$, respectively).

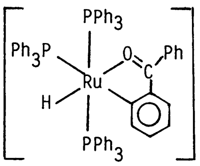
CATALYTIC HYDROGENATION OF KETONES

Grey, Pez and Wallo (ref. 17) have reported that $[\overline{RuH_2(PPh_3)_2(PPh_2C_6H_4}]^-$ (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 $[RuH_3(PPh_3)_3]^-$ or of alkoxides to solutions of $[RuH_4(PPh_3)_3]$ (9; ref. 19) leads to rapid establishment of the reversible equilibrium depicted by eq. 9 (K_9^{eq} $\sim$0.1 for cyclohexanol; $\sim$1 for diphenylmethanol; ref. 18). Accordingly, both $[RuH_3(PPh_3)_3]^-$ and $[RuH_4(PPh_3)_3]$ are present in solutions of 2 containing alcohols or of 9 containing alkoxides.

$$[RuH_3(PPh_3)_3]^- + R_2CHOH \rightleftharpoons \underset{9}{[RuH_4(PPh_3)_3]} + R_2CHO^- \qquad (9)$$

Cyclohexanone was found to react with 9 to yield cyclohexanol and $[RuH_2(PPh_3)_3]$ (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, $\Delta H^{\ddagger}_{12} = 15$ kcal/mol, $\Delta S^{\ddagger}_{12} = 16$ cal/(mol K) (ref. 18).



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$$[RuH_4(PPh_3)_3] + \text{c-}C_6H_{10}O \longrightarrow \underset{10}{[RuH_2(PPh_3)_3]} + \text{c-}C_6H_{11}OH \qquad (10)$$

$$-d[RuH_4(PPh_3)_3]/dt = k_{11}[RuH_4(PPh_3)_3] \qquad (11)$$

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

$$[RuH_2(PPh_3)_3] + H_2 \longrightarrow [RuH_4(PPh_3)_3] \qquad (12)$$

Eq. 10 and 12 constitute a catalytic cycle (Fig. 3) for the hydrogenation of cyclohexanone. Consistent with this, $[RuH_4(PPh_3)_3]$ 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.

$$\text{c-}C_6H_{10}O + H_2 \xrightarrow{[RuH_4(PPh_3)_3]} \text{c-}C_6H_{11}OH \qquad (13)$$

The detailed mechanism of reaction (10) is unclear. Since $[RuH_4(PPh_3)_3]$ is coordinately saturated, the direct coordination of *c*-$C_6H_{10}O$ seems unlikely. Prior loss of H_2 is possible and we have confirmed that exchange of **9** with D_2 (including deuteration of the *ortho* positions of the PPh_3 phenyl rings) is rapid compared with reaction with *c*-$C_6H_{10}O$ (ref. 18). However, such a step is not radily reconciled with the observed rate-law (eq. 11; rate independent of H_2) unless the initial inverse H_2-dependence is compensated by a subsequent H_2-dependent step (e.g., eq. 14-16). This theme warrants further examination.

$$[RuH_4(PPh_3)_3] \rightleftharpoons [RuH_2(PPh_3)_3] + H_2 \tag{14}$$

$$[RuH_2(PPh_3)_3] + \underline{c}\text{-}C_6H_{10}O \rightleftharpoons [RuH_2(PPh_3)_3(\underline{c}\text{-}C_6H_{10}O)] \tag{15}$$

$$[RuH_2(PPh_3)_3(\underline{c}\text{-}C_6H_{10}O)] + H_2 \longrightarrow [RuH_2(PPh_3)_3] + \underline{c}\text{-}C_6H_{11}O \tag{16}$$

Surprisingly, in view of the earlier suggestion of Grey, Pez and Wallo (ref. 17), the *anionic* hydride $[RuH_3(PPh_3)_3]^-$ (i.e., the product of reaction of **1** with H_2) does not appear to be an effective catalyst for the hydrogenation of cyclohexanone. When added initially to a THF solution of *c*-$C_6H_{10}O$ under H_2, an induction period was observed, following which catalytic hydrogenation proceeded at the same rate as the corresponding $[RuH_4(PPh_3)_3]$-catalyzed reaction (Fig. 4). Presumably, $[RuH_3(PPh_3)_3]^-$ is converted to the active catalyst, $[RuH_4(PPh_3)_3]$ (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 $[RuH_4(PPh_3)_3]$ compared with that of $[RuH_3(PPh_3)_3]^-$ may well reflect the higher rate of loss of H_2 from the former. This, in turn, may be related to the recent characterization of $[RuH_4(PPh_3)_3]$ as an H_2 complex, i.e., $[RuH_2(H_2)(PPH_3)_3]$ (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).

$$Ph_2C{=}O + H_2 \longrightarrow Ph_2CHOH \tag{17}$$

Reaction of $[RuH_4(PPh_3)_3]$ with benzophenone in THF at 45°C proceeds at conveniently measureable rates in two stages (eq. 18 and 19) to yield the *ortho*-metallated complex $[\overline{RuH(PPh_3)_3(O{=}CPhC}_6H_4)]$ (**11**; ref. 22). **11** reacts rapidly with H_2 (also in two stages) to yield Ph_2CHOH and regenerate $[RuH_4(PPh_3)_3]$ 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).

$$[RuH_4(PPh_3)_3] + Ph_2C{=}O \longrightarrow [RuH_2(PPh_3)_3] + Ph_2CHOH \tag{18}$$

$$[RuH_2(PPh_3)_3] + 2\ Ph_2C{=}O \longrightarrow [\overline{RuH(PPh_3)_3(O{=}CPhC}_6H_4] + Ph_2CHOH \tag{19}$$

$$[\overline{RuH(PPh_3)_3(O{=}CPhC}_6H_4] + 2H_2 \longrightarrow [RuH_2(PPh_3)_3] + Ph_2CHOH \tag{20}$$

$$[RuH_2(PPh_3)_3] + H_2 \longrightarrow [RuH_4(PPh_3)_3] \tag{21}$$

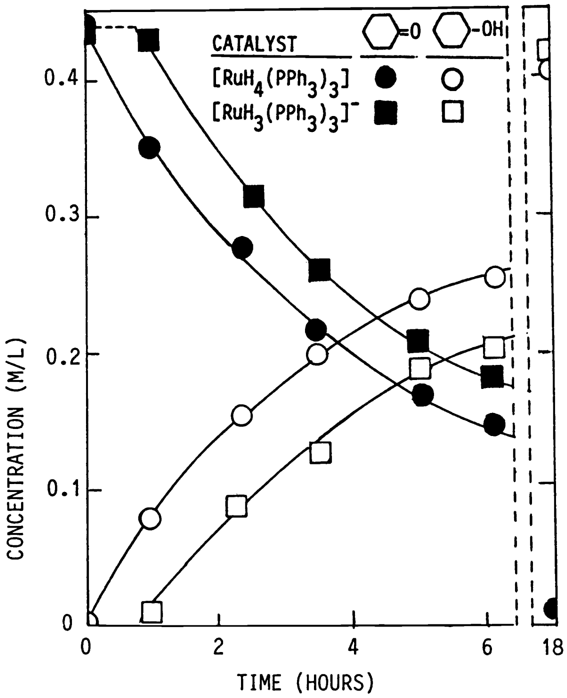

Fig. 4. Catalysis of the hydrogenation of cyclohexene by $[RuH_4(PPh_3)_3]$ and $[RuH_3(PPh_3)_3]^-$. (5.4×10^{-4} M Ru; 4 atm H_2; 45°C)

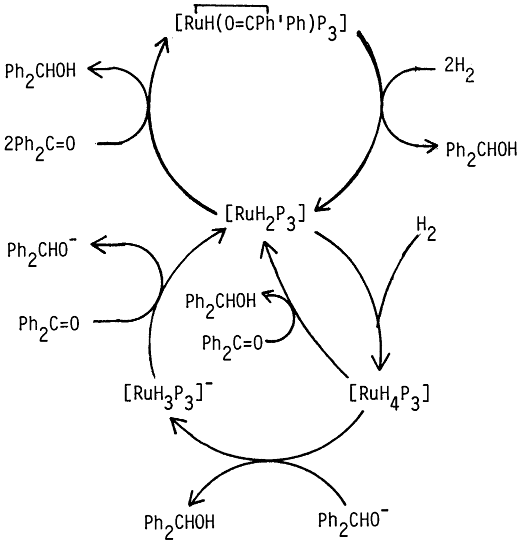

Fig. 5. Catalytic cycles for the hydrogenation of benzophenone ($P = PPh_3$).

Hydrogenation of benzophenone also is effected through a catalytic cycle initiated by the anionic complex, $[RuH_3(PPh_3)_3]^-$ (eq. 22, in combination with reactions 21 and 23; ref. 18).

$$[RuH_3(PPh_3)_3]^- + Ph_2C{=}O \longrightarrow [RuH_2(PPh_3)_3] + Ph_2CHO^- \qquad (22)$$

$$Ph_2CHO^- + RuH_4(PPh_3)_3 \longrightarrow Ph_2CHOH + [RuH_3(PPh_3)_3]^- \qquad (23)$$

Thus, the hydrogenation of benzophenone in solutions containing $[RuH_3(PPh_3)_3]^-$ and $[RuH_4(PPh_3)_3]$ appears to proceed through three interconnected catalytic cycles (Fig. 5), two involving only neutral species and the other, a combination of neutral and anionic species. All three cycles are connected through the common catalytic intermediate, $[RuH_2(PPh_3)_3]$. The relative contributions of these cycles to the overall catalytic rate remain to be established by detailed kinetic studies of the various component steps but presumably will be dictated by the ratio of Ph_2CHOH to Ph_2CHO^- (i.e., by the position of the equilibrium of eq. 9). This ratio will increase as the reaction proceeds and more Ph_2CHOH is produced.

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.

Acknowledgements

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