# Fluorophosphine Complexes of Ruthenium and Osmium. Part 5.[1] Alkene Hydrogenation catalysed by Ruthenium(II) Complexes †

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The effectiveness of several hydridoruthenium complexes as homogeneous hydrogenation catalysts for oct-1-ene has been studied. The activity, which decreases in the order [RuCl(H)(PPh$_3$)$_3$] ⩾ *cis*-[RuH$_2$(PPh$_3$)$_4$] > *cis*-[RuH$_2${PF$_2$(NMe$_2$)}(PPh$_3$)$_3$] > *cis*-[RuH$_2$(PF$_3$)(PPh$_3$)$_3$] > *cis*-[RuH$_2${PF$_2$(NMe$_2$)}$_2$(PPh$_3$)$_2$] > *cis*-[RuH$_2$(PF$_3$)-{PF$_2$(NMe$_2$)}(PPh$_3$)$_2$] > *cis*-[RuH$_2$(PF$_3$)$_2$(PPh$_3$)$_2$] is related to the ease of PPh$_3$ dissociation from these six-co-ordinate complexes. The monomeric complexes *cis*-[RuCl$_2$(PF$_3$)$_2$(PPh$_3$)$_2$], *cis*-[RuCl$_2${PF$_2$(NMe$_2$)}$_2$(PPh$_3$)$_2$], and *cis*-[RuCl$_2$(CO)(PF$_3$)(PPh$_3$)$_2$] do not act as catalysts for the hydrogenation of oct-1-ene, either in the presence or absence of added triethylamine. The complexes [(Ph$_3$P)$_2$(F$_3$P)RuCl$_3$RuCl(PF$_3$)(PPh$_3$)] and [(Ph$_3$P)$_2$(F$_3$P)-RuCl$_3$RuCl(PPh$_3$)$_2$] are not active catalysts, although the latter takes up H$_2$ in the presence of NEt$_3$. The hetero-bimetallic complex [(Ph$_3$P)$_2$ClRhCl$_3$RuCl(PPh$_3$)$_2$] is slightly active as a hydrogenation catalyst.

THERE is a continuing interest in the use of transition-metal complexes as homogeneous catalysts for a variety of reactions. In particular, the catalytic reduction of unsaturated organic substrates has been extensively studied [2] and is the subject of a recent comprehensive review.[3]

Wilkinson and his co-workers have reported that the complexes [RhCl(PPh$_3$)$_3$],[4] [RhH(CO)(PPh$_3$)$_3$],[5,6] and [RuCl(H)(PPh$_3$)$_3$] [7] are very efficient catalysts for the hydrogenation of terminal alkenes under mild conditions. The rate of hydrogenation of internal alkenes is slower, owing to an increase in steric hindrance around the double bond. The complex [RuCl(H)(PPh$_3$)$_3$], prepared by the sodium tetrahydroborate reduction of [RuCl$_2$(PPh$_3$)$_3$] in benzene, is the most efficient homogeneous catalyst of ruthenium yet reported. Interestingly, recent $^{31}$P n.m.r. spectroscopic studies [8] have shown no detectable phosphine dissociation of [RuCl(H)-(PPh$_3$)$_3$]. An *X*-ray crystallographic study has also been carried out on the complex.[9] Complexes of the type [RuH(O$_2$CCR$_3$)(PPh$_3$)$_3$] (R = H or F),[10] *cis*-[RuH$_2$(N$_2$)(PPh$_3$)$_3$],[11-13] and [RuH$_2$(PPh$_3$)$_4$] [14] are all olefin-hydrogenation catalysts, as are red solutions obtained by treatment of [Ru$_3$(O)(O$_2$CMe)$_6$(PPh$_3$)$_3$], [RuH(O$_2$CMe)(PPh$_3$)$_3$], or *cis*-[RuH$_2$(PPh$_3$)$_4$] with tetrafluoroboric acid.[15]

The accepted mechanism for the [RuCl(H)(PPh$_3$)$_3$]-catalysed hydrogenation of alkenes involves initial co-ordination of the olefin followed by insertion into the metal–hydrogen bond to form an alkyl derivative.[7] Oxidative addition of H$_2$ followed by alkane elimination regenerates the active co-ordinatively unsaturated intermediate. The isolation of complexes containing co-ordinated ethylene,[14] styrene,[14] and pent-1-ene [16] supports this mechanism. Recently, the importance of the involvement of hydrogen atoms in *ortho* positions of the triphenylphosphine ligands has been recognised.[6,17,18]

In view of our recent report [19] of the high activity of [RhH(PF$_3$)(PPh$_3$)$_3$] as a homogeneous hydrogenation catalyst, it was of interest to study the catalytic activity of the various ruthenium(II) complexes containing fluorophosphine ligands described in the earlier papers of this series. Here we present the results of catalytic olefin-hydrogenation studies.

## RESULTS AND DISCUSSION

The dihydrido-complexes *cis*-[RuH$_2$(L)(PPh$_3$)$_3$] [L = PF$_3$ or PF$_2$(NMe$_2$)], *cis*-[RuH$_2$L$_2$(PPh$_3$)$_2$] [L = PF$_2$-(NMe$_2$)], and [RuH$_2$(PF$_3$){PF$_2$(NMe$_2$)}(PPh$_3$)$_2$] discussed earlier are found to be active homogeneous catalysts for the hydrogenation of oct-1-ene in benzene solution. The complex *cis*-[RuH$_2$(PF$_3$)$_2$(PPh$_3$)$_2$] is inactive under mild conditions. The relative rates of alkene hydrogenation catalysed by the new dihydrido-complexes are compared with that of the very active [RuCl(H)(PPh$_3$)$_3$] in the Figure. Most of the catalysts require a short induction period before alkene hydrogenation occurs, although none of the complexes studied is as active as [RuCl(H)-(PPh$_3$)$_3$]. Interestingly, there is a relation between the catalytic behaviour and the nature of the phosphine ligands co-ordinated to ruthenium for complexes of the type *cis*-[RuH$_2$L$_2$(PPh$_3$)$_2$] [L = PPh$_3$, PF$_3$, or PF$_2$-(NMe$_2$)]. The activity is greatest for *cis*-[RuH$_2$(PPh$_3$)$_4$] and decreases when fluorophosphines are substituted for triphenylphosphine ligands. Complexes containing

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the more basic (dimethylamino)difluorophosphine ligands are more catalytically active than their trifluorophosphine analogues. The complex *cis*-$[RuH_2\{PF_2(NMe_2)\}_2(PPh_3)_2]$ is more active than *cis*-$[RuH_2(PF_3)_2(PPh_3)_2]$, while *cis*-$[RuH_2(PF_3)\{PF_2(NMe_2)\}(PPh_3)_2]$ is intermediate between the two. The initial rates of dihydrogen uptake of the dihydrido-complexes are listed in the Table. The slight inconsistency in the data obtained for *cis*-$[RuH_2\{PF_2(NMe_2)\}(PPh_3)_3]$ is attributed both to the contamination of the complex with trace amounts of *cis*-$[RuH_2\{PF_2(NMe_2)\}_2(PPh_3)_2]$, and also to partial decomposition during the course of the catalytic study.

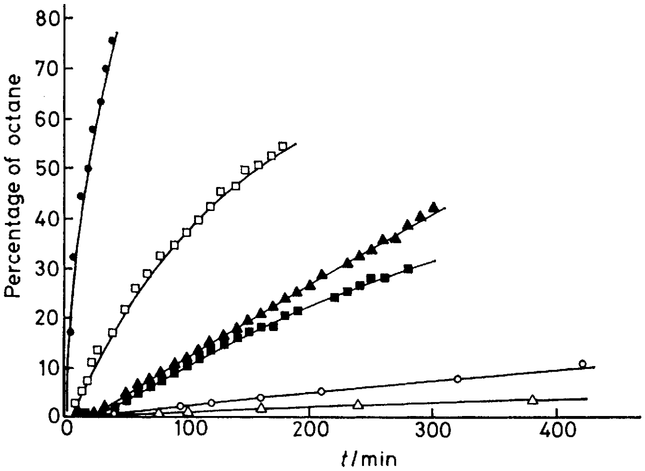

FIGURE Graph of percentage of octane against time for $[RuCl(H)(PPh_3)_3]$ (●), *cis*-$[RuH_2(PPh_3)_4]$ (□), *cis*-$[RuH_2(PF_3)(PPh_3)_3]$ (■), *cis*-$[RuH_2\{PF_2(NMe_2)\}(PPh_3)_3]$ (▲), *cis*-$[RuH_2(PF_3)\{PF_2(NMe_2)\}(PPh_3)_2]$ (△), and *cis*-$[RuH_2\{PF_2(NMe_2)\}_2(PPh_3)_2]$ (○)

Initial rates of hydrogen uptake [a]

| Complex | Rate [b]/cm³ min⁻¹ |
|---|---|
| $[RuCl(H)(PPh_3)_3]$ | 62.70 |
| *cis*-$[RuH_2(PPh_3)_4]$ | 8.07 |
| *cis*-$[RuH_2\{PF_2(NMe_2)\}(PPh_3)_3]$ | 2.43 |
| *cis*-$[RuH_2(PF_3)(PPh_3)_3]$ | 2.07 |
| *cis*-$[RuH_2\{PF_2(NMe_2)\}_2(PPh_3)_2]$ | 0.67 |
| *cis*-$[RuH_2(PF_3)\{PF_2(NMe_2)\}(PPh_3)_2]$ | 0.20 |
| *cis*-$[RuH_2(PF_3)_2(PPh_3)_2]$ | 0.00 |

[a] Recorded for hydrogenation of oct-1-ene. [b] Corrected to 25 °C and 1 atm pressure (1 atm = 101 325 Pa).

The results for these ruthenium(II) dihydrido-complexes containing fluorophosphines are interesting in relation to our studies previously carried out on $[RhH(PF_3)(PPh_3)_3]$ and $[RhH(PF_3)_2(PPh_3)_2]$.[19] The last complex is an efficient catalyst for the isomerisation of terminal alkenes to internal alkenes, but does not catalyse their hydrogenation. The present complexes do not catalyse the isomerisation reaction and only in the case of *cis*-$[RuH_2(PF_3)(PPh_3)_3]$ was *cis*-oct-2-ene (4%) detected by g.l.c. after 12 h. The difference in catalytic activity between the five-co-ordinate rhodium(I) and six-co-ordinate ruthenium(II) systems can be related to the different co-ordination number of the central metal atom.

The differences in activity of the new ruthenium(II) fluorophosphine complexes is consistent with the trend expected if phosphine dissociation is the first step in the reaction prior to co-ordination of the alkene [equation (1)]. The tendency for dissociation to occur will

$$cis\text{-}[RuH_2(PF_3)(PPh_3)_3] \rightleftharpoons [RuH_2(PF_3)(PPh_3)_2] + PPh_3 \quad (1)$$

increase as the ligands attached to ruthenium become bulkier. Hence, phosphine dissociation is expected to be greater for *cis*-$[RuH_2(PPh_3)_4]$, which contains four bulky triphenylphosphine ligands, and least for *cis*-$[RuH_2(PF_3)_2(PPh_3)_2]$. As expected, the activity of the complexes containing $PF_2(NMe_2)$ ligands is intermediate between the $PPh_3$ and $PF_3$ analogues. The ease of oxidative addition of molecular hydrogen will also change as the electronic effects of the ligands attached to the metal vary, with the $PF_3$ complexes likely to be least reactive.

The importance of the phosphine-dissociation step is established for *cis*-$[RuH_2(PF_3)(PPh_3)_3]$, since addition of $PPh_3$ to the reaction mixture decreases the rate of hydrogenation. Interestingly, the $^{31}P$ n.m.r. spectra of the new ruthenium(II) hydrido-complexes containing fluorophosphines, discussed previously, do not exhibit lines associated with unco-ordinated $PPh_3$, indicating that any active five-co-ordinate intermediates such as '$RuH_2(PF_3)(PPh_3)_2$' exist in very low concentrations. This observation is not altogether unexpected, since Hoffman and Caulton[8] recently reported no detectable phosphine dissociation for the catalytically active $[RuCl(H)(PPh_3)_3]$ and $[RuH(O_2CMe)(PPh_3)_3]$ in a careful $^{31}P$ n.m.r. study.

Addition of tetrafluoroboric acid to solutions of the new ruthenium(II) dihydrido-complexes results in a decrease in catalytic activity. The complex $[Ru(BF_4)H(PF_3)_2(PPh_3)_2]$ (see Part 2) also shows no catalytic properties. This is unexpected, since Wilkinson and his co-workers report that treatment of *cis*-$[RuH_2(PPh_3)_4]$ with $HBF_4$ affords an active red species. The latter is reported to react with carbon monoxide to form an inactive yellow complex. The complexes $[RuCl(H)(PF_3)_2(PPh_3)_2]$ and $[RuH(O_2CCF_3)(PF_3)_2(PPh_3)_2]$ are also catalytically inactive, presumably owing to the apparently stable arrangement of both the two trifluorophosphine and triphenylphosphine ligands attached to ruthenium.

*Catalytic Behaviour of Mono- and Bi-nuclear Ruthenium*(II) *Dichloro-complexes*.—The dichloro-complexes *cis*-$[RuCl_2(PF_3)_2(PPh_3)_2]$, $[RuCl_2\{PF_2(NMe_2)\}_2(PPh_3)_2]$, and *cis*-$[RuCl_2(CO)(PF_3)(PPh_3)_2]$ do not catalyse the hydrogenation of oct-1-ene. Addition of a base such as triethylamine does not enhance their activity, in contrast to the behaviour of $[RuCl_2(PPh_3)_3]$ which affords the active complex $[RuCl(H)(PPh_3)_3]$.[7] The trichloro-bridged complexes $[(Ph_3P)_2(F_3P)RuCl_3RuCl(PF_3)(PPh_3)_2]$ and $[(Ph_3P)_2(F_3P)RuCl_3RuCl(PPh_3)_2]$ are not active catalysts, although solutions of the latter containing $NEt_3$ take up dihydrogen at an initial rate of 0.25 cm³

$\text{min}^{-1}$. In contrast, the heterobimetallic complex $[(Ph_3P)_2ClRhCl_3RuCl(PPh_3)_2]$ is slightly active and gives rise to an initial dihydrogen uptake of 0.40 $cm^3$ $\text{min}^{-1}$.

## EXPERIMENTAL

All the experiments were carried out under similar conditions, using an Engelhard hydrogenation-control unit to maintain a constant dihydrogen gas pressure of 1 atm in the reaction vessel and to record gas uptake on a chart recorder. The unit has a calibrated reservoir of 1.12 l capacity at s.t.p., equivalent to 50 mmol of dihydrogen. Reactions were carried out in a glass vessel (250-$cm^3$ capacity) surrounded by a constant-temperature water jacket. The reaction vessel was fitted with a removable spoon having a ground-glass seal which was used to introduce the complex under investigation into the system. During the reactions, samples of the solution were removed with a syringe *via* a rubber serum cap located in the spoon. The solutions were examined by g.l.c. on an Areograph Autoprep chromatograph equipped with a column (10 ft × 0.125 in) packed with 5% oxydiproprionitrile–Chromasorb G. The g.l.c. system was periodically calibrated using standard solutions of oct-1-ene, *cis*- and *trans*-oct-2-ene, and octane. The solvent, generally benzene, and oct-1-ene were both distilled over sodium under a dry dinitrogen atmosphere prior to use.

In a typical reaction, the reaction vessel was charged with benzene (42 $cm^3$) and oct-1-ene (10 $cm^3$) and the catalyst (*ca.* 0.050 g) was introduced into the system above the solvent *via* the spoon. The reaction chamber was evacuated and flushed three times with pure dihydrogen gas and finally excess of gas was released to the atmosphere. The catalyst was then introduced to the solution by inverting the spoon and the mixture mechanically stirred. The solution was *ca.* $5 \times 10^{-4}$ mol $dm^{-3}$ in catalyst. The dihydrogen uptake was automatically recorded by the control unit and periodic g.l.c. analyses of reaction solutions were used to confirm the amount of octane produced and to check for possible isomerisation. The results obtained from the unit and g.l.c. system were in good agreement. Addition of further reagents such as tetrafluoroboric acid solution or triethylamine was made by syringe *via* the serum cap located in the spoon.

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