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# Selective hydrogenolysis of CFC-113a by Group VIII transition metal complexes

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## Abstract

Highly efficient and selective hydrogenolysis of CFC-113a ($CF_3CCl_3$) to produce HCFC-123 ($CF_3CHCl_2$) has been achieved through the use of Group VIII transition metal complexes. The catalytic activity observed was sensitive to solvents and to the structures of the metal complexes.

*Keywords:* Selective hydrogenolysis; CFC-113a; Group VIII transition metal complexes; Catalysis; Selectivity

## 1. Introduction

HCFC-123, $CF_3CHCl_2$, is considered the best candidate for the substitution of CFC-11 ($CFCl_3$), mainly used as a blowing agent. Several processes have been proposed for this purpose [1]. Processes involving the heterogeneous catalytic hydrogenolysis of organic species containing the C–Cl bond are well established [2–7] but there is little published work concerning results of the homogeneous hydrogenolysis of fluorocarbons in terms of yield and selectivity. However, there have been some recent reports [8] on the hydrogenolysis of chloroarenes by homogeneous catalysts.

Since the activation of the C–Cl bond seems to be a key step in the hydrogenolysis reaction of CFC-113a, we have focused on the oxidative addition reactions of alkyl halides by transition metal complexes [9], particularly square-planar, 16-electron species. In the present work, the homogeneous hydrogenolysis reaction of CFC-113a has been studied and a plausible reaction mechanism is discussed.

## 2. Experimental details

Reactions were generally carried out in a 200-ml stainless-steel high-pressure reactor. Thus $5\times10^{-2}$ mol of CFC-113a, $1.08\times10^{-4}$ mol of catalyst and 50.0 ml of THF were stirred magnetically under 8 atm of $H_2$ at 100 °C for ca. 5 h, unless otherwise specified. (In the case of $RuCl(NO)(PPh_3)_2$, half the above amounts of chemicals were used.) Samples were analyzed by gas chromatography (Gow-Mac Series 750P, flame ionization detector, OV 101 column) every hour during the reaction.

## 3. Results and discussion

As can be seen from Table 1, as expected, square planar, 16-electron complexes are most active in the hydrogenolysis reaction of $CF_3CCl_3$. However, it is surprising that a tetrahedral, coordinatively saturated 18-electron complex such as $Ru(NO)_2(PPh_3)_2$ shows such drastically reduced activity, even though it can generate a vacant site by changing the bonding mode of the NO ligand from linear to bent or by dissociating $PPh_3$. RuH(NO)(etp) [etp = bis(diphenyl phosphinoethyl)phenylphosphine] is much less active than $RuH(NO)(PPh_3)_3$ and $Ru(NO)_2(PPh_3)_2$. This can be rationalized by the fact that monophosphines can reversibly dissociate to give the vacant sites required for the activation of substrates, whereas etp has a low possibility of dissociation due to the chelate effect [10]. Hence, vacant site production and the activity of this complex should be limited. However, when we consider the flexible bonding abilities of NO ligands mentioned above, this process also appears to be limited, due probably to instability of a seven-coordinate transition state.

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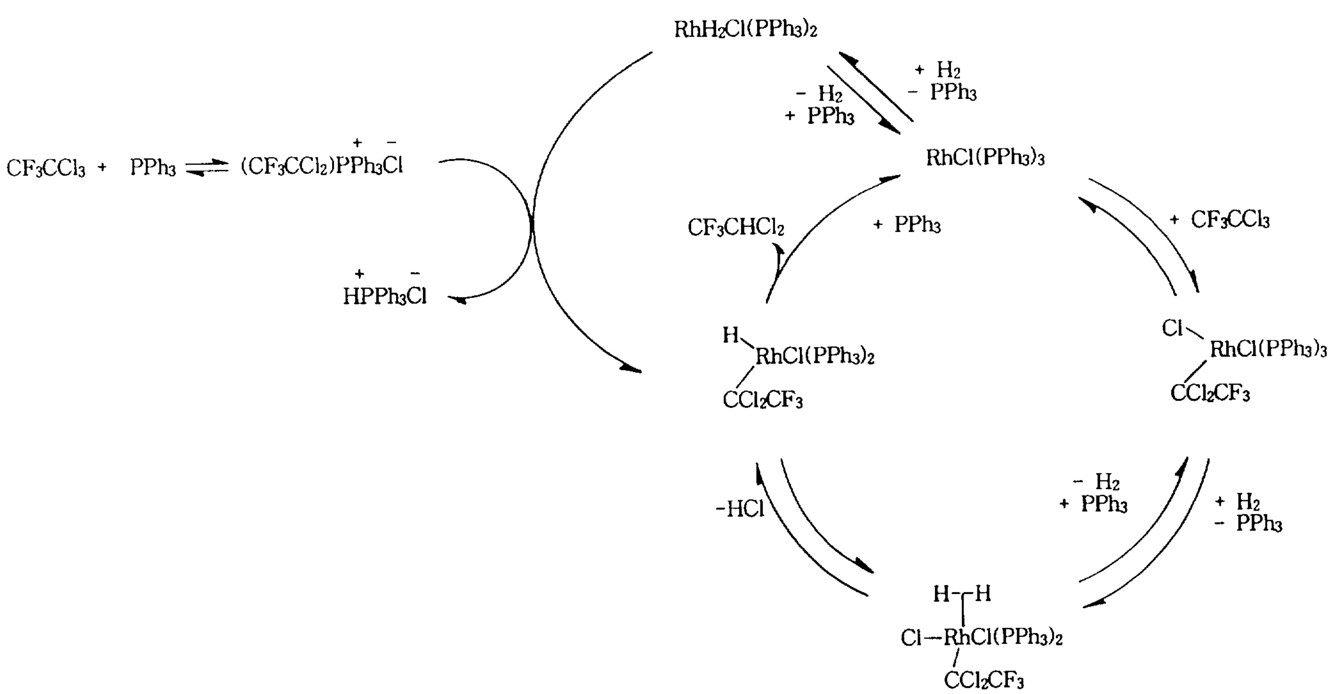

Fig. 1. Proposed mechanism for the production of HCFC-123 by $RhCl(PPh_3)_3$.

Table 1
Conversion and selectivities of various catalytic systems [a]

| Catalyst employed | Composition of products (%) | | | Conversion (%) | Selectivity | |
|---|---|---|---|---|---|---|
| | 113a | 123 | 133a | | 133a | 123 |
| $RhCl(PPh_3)_3$ | 1.9 | 94.6 | 3.5 | 98.1 | 3.6 | 96.4 |
| $RhH(PPh_3)_4$ | 24.2 | 73.8 | 2.0 | 75.8 | 2.6 | 97.4 |
| $RhCl_3(pyridine)_3$ | 31.1 | 68.1 | 0.8 | 68.9 | 1.2 | 98.8 |
| $RuCl_2(PPh_3)_3$ | 37.8 | 59.2 | 3.0 | 62.2 | 4.8 | 95.2 |
| $RuH(NO)(PPh_3)_3$ | 42.0 | 56.8 | 1.2 | 58.0 | 2.0 | 98.0 |
| RuH(NO)(etp) | 88.8 | 10.9 | 0.3 | 11.2 | 2.7 | 97.3 |
| $Ru(NO)_2(PPh_3)_2$ | 49.3 | 49.8 | 0.9 | 50.7 | 1.8 | 98.2 |
| $RuCl(NO)(PPh_3)_2$ [b] | 0.8 | 96.1 | 3.1 | 99.2 | 3.1 | 96.9 |
| $PdCl_2(PPh_3)_2$ | 9.6 | 88.8 | 1.6 | 90.4 | 1.8 | 98.2 |

[a] Conditions employed: catalyst, $108 \times 10^{-4}$ mol; CFC-113a, $5.30 \times 10^{-2}$ mol; THF, 50.0 ml; temperature, 100 °C; pressure, 8 atm; time, 5 h.

[b] 4.5 h, half-scale.

The most important feature of this work is that homogeneous catalysts are highly selective in the hydrogenolysis reaction of $CF_3CCl_3$ to give $CF_3CHCl_2$. It seems that further oxidative addition reaction of $CF_3CHCl_2$ with metal complexes which leads to the production of overhydrogenated products, e.g. $CF_3CH_2Cl$ and $CF_3CH_3$, is limited due to the reduced electrophilicity of the carbon centre in $CF_3CHCl_2$. From this, it is believed that oxidative addition of the C–Cl bond may proceed via an $S_N2$ mechanisms [11–13]. However, in view of the bulkiness of the substituents associated with CFC-113a, an outer-sphere, electron-transfer mechanism [9] cannot be excluded. THF, which is slightly polar and weakly coordinating, is found to be a good solvent. Low conversion in benzene or methanol excludes the possibilities of radical and ionic mechanisms. Coordination of THF to 16e complexes appears to stabilize these complexes pending activation of the C–Cl bond, and this, in turn, helps to increase the activities of these complexes.

Table 2 shows the effects of bases on the catalytic activity. Addition of amines causes a decrease in activity, even though favoured production of HCFC-123 is expected by the formation of an amine salt with evolved HCl. This is probably due to low facilitation of reductive elimination caused by the fact that amines exhibit a low tendency to stabilize complexes of low oxidation state [14]. Another explanation is that the amine complex formed in situ, a product from the reaction of the starting phosphine complex and added amines, has little tendency to generate a vacant site. A small excess of free phosphines results in a decrease in conversion, which may be due to suppression of the dissociation of coordinated phosphines. However, a large excess of free phosphines makes the catalytic system more efficient. This phenomenon might be explained by assuming the existence of an independent pathway in which phosphines play an important role. One such possibility is the initial formation of a phosphonium salt by reaction between triphenylphosphine and CFC-113a, followed by the production of HCFC-123 by hydrogen with help of metal complexes as has been demonstrated by an independent experiment followed by $^{31}P\{^1H\}$ NMR spectroscopy. The green solid, formed by the reaction between $PPh_3$ and CFC-113a shows a

Table 2
Effects of extra base on the catalytic activity

| Mole ratio | Time (h) | Composition of products (%) | | | Conversion (%) | Selectivity | |
|---|---|---|---|---|---|---|---|
| | | 113a | 123 | 133a | | 133a | 123 |
| $RhCl(PPh_3)_3/PPh_3$ | | | | | | | |
| 1: 0 | 5 | 1.9 | 94.6 | 3.5 | 98.1 | 3.6 | 96.4 |
| : 2 | 5 | 18.8 | 78.7 | 2.5 | 81.8 | 3.1 | 96.9 |
| : 4 | 5 | 41.2 | 57.2 | 1.6 | 58.8 | 2.7 | 97.3 |
| : 6 | 5 | 29.8 | 68.9 | 1.3 | 70.2 | 1.9 | 98.1 |
| : 10 | 4.5 | 0.5 | 95.7 | 3.8 | 99.5 | 3.8 | 96.2 |
| : 30 | 4 | 2.3 | 96.4 | 1.3 | 97.6 | 1.3 | 98.7 |
| :300 | 2.5 | 0.0 | 99.8 | 0.2 | 100.0 | 0.2 | 99.8 |
| $RhCl(PPh_3)_3$/*N*,*N*-dimethylaniline | | | | | | | |
| 1: 20 | 5 | 9.4 | 88.5 | 2.1 | 90.6 | 2.3 | 97.9 |
| : 50 | 5 | 65.9 | 33.8 | 0.3 | 34.1 | 0.9 | 99.1 |
| :500 | 5 | 86.4 | 13.6 | 0.0 | 13.6 | 0.0 | 100.0 |
| $RuCl(NO)(PPh_3)_2/PPh_3$ | | | | | | | |
| 1: 0 | 4.5 | 0.8 | 96.1 | 3.1 | 99.2 | 3.1 | 96.9 |
| : 2 | 5 | 0.7 | 95.4 | 3.9 | 99.3 | 3.9 | 96.1 |
| : 4 | 5 | 33.4 | 63.5 | 3.1 | 66.6 | 4.7 | 95.3 |
| : 6 | 5 | 40.8 | 57.1 | 2.1 | 59.2 | 3.5 | 96.5 |
| : 10 | 5 | 75.4 | 24.6 | 0.0 | 24.6 | 0.0 | 100.0 |
| : 20 | 5 | 73.2 | 26.6 | 0.2 | 26.8 | 0.7 | 99.3 |
| : 30 | 5 | 55.3 | 44.9 | 0.8 | 45.7 | 1.8 | 98.2 |
| :100 | 5 | 14.7 | 82.6 | 2.7 | 85.3 | 3.2 | 96.8 |
| $RuCl(NO)(PPh_3)_2$/*N*,*N*-dimethylaniline | | | | | | | |
| 1: 20 | 5 | 26.3 | 70.4 | 3.3 | 73.7 | 4.5 | 95.5 |
| : 50 | 5 | 6.9 | 3.1 | 0.0 | 3.1 | 0.0 | 100.0 |
| :500 | 5 | 100.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |

singlet resonance in this spectrum at 13.57 ppm in $D_2O$. In the absence of a metal complex, this solid does not catalyze the formation of HCFC-123. On the basis of these results, the following mechanism (Fig. 1) is proposed for the production of HCFC-123 by $RhCl(PPh_3)_3$.

Further study is in progress to verify this mechanism and to elucidate the effects of ligands, bases and solvents on the activities of catalysts.

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