Homogeneous catalytic hydrodechlorination of CFC and HCFC compounds

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Abstract

Rhodium and palladium complexes proved to be effective catalysts in hydrodechlorination of CFC and HCFC compounds in homogeneous phase. $RhCl_3(py)_3$ and in situ generated $Pd(P^iPr_3)_3$ surpassed Pd/Al_2O_3, the most active heterogeneous catalyst tested in the transformation of CF_3CHFCl to CF_3CH_2F. In the case of CF_2Cl_2, the activity and selectivity of Rh- and Pd-containing systems depended strongly on the additives.
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1. Introduction

Chlorofluorocarbon (CFC) compounds destroy the stratospheric ozone as it was recognized in the seventies and eighties. In accordance with the "Montreal Protocol on substances that deplete the ozone layer", the production of $CFCl_3$ (CFC-11), CF_2Cl_2 (CFC-12), and several other compounds was prohibited and their application was reduced gradually. Consequently, environmental friendly refrigerants like CF_3CH_2F (HFC-134a) have been developed.

The transformation of CFC-s to valuable chemicals seemed to be reasonable to avoid the costly storage of their stocks or the waste management [1]. Heterogeneous catalytic hydrodechlorination of CF_2Cl_2 and related compounds have been studied in detail [1,2]. Using palladium catalysts dechlorinated compounds were formed as main products, thus CF_2Cl_2 was transformed predominantly to CH_2F_2. In some cases, however, defluorination took place at higher temperatures as well [2b,3]. The activity and the selectivity of the catalysts varied considerably by the metals used [2]. Palladium catalyzed hydrogenolysis is a key step in the production of CF_3CH_2F through CF_3CFCl_2 (CFC-114a), or CF_3CHFCl (HCFC-124) [1,3a].

Only very few homogeneous processes were developed for hydrodechlorination till now. The hydrogenolysis of aryl chlorides was studied in the presence of Pd(0) complexes [4] and several types of Rh-containing systems [5], as well. Only the isomers of trichlorotrifluoroethane were the CFC compounds the hydrogenation of which in homogeneous phase was described [6]. $RhCl(PPh_3)_3$ was found to be the most active among the investigated transition metal complexes. In the case of this catalyst, a detailed mechanism was suggested based on kinetic measurements [6b]. Modelling of some proposed steps of the catalytic hydrodehalogenation were studied very recently [7,8].

The aim of our study was the dechlorination of CF_2Cl_2 and CF_3CHFCl in homogeneous catalytic systems. The latter compound was used as a component of a gas mixture (named R401) wich contained CHF_2Cl (HCFC-22) and CH_3CHF_2 (HFC-152a) as well. Thus, we investigated actually the co-hydrogenolysis of CHF_2Cl and CF_3CHFCl.

2. Experimental

2.1. General

All manipulations involving air-sensitive compounds were carried out by the usual Schlenk-technique using

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deoxygenated, dry solvents and gases, and oven-dried reaction vessels. Gas chromatograms were recorded on a Hewlett-Packard model 5830 A chromatograph (with FID), while GC–MS analyses were performed on a JMS 01-SG-2 JEOL spectrometer and a Hewlett-Packard 5890 Series II GC–MSD equipment using SPB1 (Supelco) and Poraplott Q (Chrompack) capillary columns (both 30 m). Infrared spectra were recorded by using a 0.06 mm CaF_2 cuvette on a Specord IR 75 (Carl Zeiss, Jena) spectrometer which was calibrated with benzene (1959.6 cm^{-1}) and polystyrene (1601.4 cm^{-1}). ^{1}H and NMR ^{19}F NMR spectra were obtained on a Varian Unity 300 spectrometer.

Heterogeneous hydrogenation catalysts were purchased from Fluka (Pd/Al$_2$O$_3$ (5%), Pd/C (10%)), or from Haereus (Pd/silica (5%), Rh/C (5%)). Homogeneous catalysts RhCl(PPh$_3$)$_3$ [9], [RhCl(COD)]$_2$ [10a], RhH(CO)(PPh$_3$)$_3$ [10b], RuCl(H)(CO)(P^{i}Pr$_3$)$_2$ [11], RhCl$_3$(py)$_3$ [12] and [Rh(NBD)(PPh$_3$)][BF$_4$] [13], as well as bis(diphenyphosphino)butane [14] were prepared according literature methods. Magnesium, pyridinium hydrochloride and the phosphines (PBu$_3$, P^{i}Pr$_3$ and PMePh$_2$) were purchased from Fluka and the latter were distilled freshly. Pyridine and triethylamine (Reanal) were dried on KOH pellets and distilled before use.

The gas mixture R401 and CF$_2$Cl$_2$ were gifts of the Budapest Chemical Works (Budapest). R401 contained CHF$_2$Cl (53% (w/w)), CH$_3$CHF$_2$ (13% (w/w)), CF$_3$CHFCl (34% (w/w)). CF$_2$Br$_2$, CF$_3$CH$_2$I (Aldrich) and authentic samples of CF$_3$CH$_2$F (Aldrich), as well as CH$_2$F$_2$ and CH$_3$F (Fluorchem) were commercial products.

2.2. Hydrodehalogenation reactions under pressure

Into a 20 ml stainless steel autoclave equipped with manometer and valve were added under argon the catalyst (with 0.2–1.0 mmol metal content), solvent, additive(s) and isopentane as the internal standard. The autoclave was cooled slowly to −78°C while flowing argon continuously. From a Schlenk-tube equipped with septum a measured amount of the liquid CFC or HCFC compound (20–50 mmol) was added through a stainless steel capillary by a slight argon pressure. Finally, the autoclave was closed and pressurized to 2–10 MPa with H$_2$, and shaken in a heating mantle thermostatted at the desired temperature for 6 h. After cooling to 50 °C the pressure was released slowly through a large surface trap immersed in liquid N$_2$. The content of the trap was analyzed by GC and/or GC–MS.

2.3. Atmospheric hydrodehalogenations

A thermostatted reaction vessel with magnetic stirring and a gasometric apparatus fitted with a mercury-filled burette was used. Catalyst (0.1–0.2 mmol) and additive (if any) were prehydrogenated for 1 h in tetrahydrofuran or toluene (5 ml). The reaction was started by injecting the halide (0.2–0.5 mmol of CF$_2$Br$_2$ or CF$_3$CH$_2$I) into the stirred solu-

tion. After the absorption of H$_2$ ceased, samples were taken both from the liquid and from the gas phase for GC–MS, and from the solution for IR spectroscopic analysis, respectively. The solution was transferred into a Schlenk-tube and evaporated in vacuo to dryness. The residue was analyzed by ^{19}F NMR spectroscopy in CDCl$_3$ or benzene-d_6 solution.

2.4. Hydrogenation of RhCl$_3$(py)$_3$

Into a 20 ml stainless steel autoclave equipped with manometer and valve RhCl$_3$(py)$_3$ (0.2 mmol), pyridine (0.4 mmol) and tetrahydrofurane (5 ml) were added under argon. The autoclave was pressurized to 5 MPa with H$_2$, and shaken at RT for 6 h. The pressure was released, and the content of the autoclave was transferred under argon into a Schlenk-tube. A sample was taken from the solution for IR spectroscopic analysis. The solution was evaporated in vacuo to dryness and the residue was analyzed by ^{1}H NMR spectroscopy in CDCl$_3$ solution. The IR and ^{1}H NMR spectra were identical with those of the authentic sample of pyridinium hydrochloride.

3. Results

Various homogeneous catalysts were used in hydrodehalogenation reactions and some heterogeneous ones were tested for comparison, as well. The reactions were performed at 120–180 °C and 2–10 MPa H$_2$-pressure, mostly without solvent. The products were identified by GC–MS method.

The results obtained for R401 are summarized in Table 1. CF$_3$CHFCl was hydrogenolyzed selectively to CF$_3$CH$_2$F, while CHF$_2$Cl was transformed mostly into CH$_2$F$_2$ (HFC-32). The application of phosphine-containing transition metal complexes as catalysts resulted in a slight to moderate conversion of the substrates in R401. The widely used "Wilkinsons-catalyst", RhCl(PPh$_3$)$_3$ was inactive, and only low conversion of CF$_3$CHFCl could be achieved by RhH(CO)(PPh$_3$)$_3$ and by RuCl(H)(CO)(P^{i}Pr$_3$)$_2$ (cf. reference [6]). The catalysts RhCl(P^{i}Pr$_3$)$_3$ and Pd(PR$_3$)$_n$ ($n = 3$, 4) prepared in situ behaved differently: the rhodium complex was only weakly effective, while the activity of the palladium ones depended strongly on the quality and the relative quantity of the phosphine added. Under the conditions used, P^{i}Pr$_3$ gave the best results. At least fourfold excess of the phosphine was required to prevent the decomposition to metallic Pd which is an ineffective catalyst (vide infra). Adding pyridine to the Pd(OAc)$_2$/P^{i}Pr$_3$ catalytic system to remove the formed HCl decreased the conversion of CF$_3$CHFCl.

In contrast to those above, RhCl$_3$(py)$_3$ [6,15], a complex used rarely as a hydrogenation catalyst hydrogenolyzed CF$_3$CHFCl with more than 70% conversion in the presence of an excess of pyridine (calculated on the Cl-content of the substrate, see Table 1). The conversion of CHF$_2$Cl increased from ~5 to >30% rising the temperature from 120 to 150 °C,

Table 1
Hydrodechlorination of R401[a,b]

Entry	Temperature (°C)	Catalyst	Additive	Conversion of CF_3CHClF (mol.%)	Conversion of CHF_2Cl (mol.%)	Notes
1	120	Pd/Al_2O_3 (5%)	–	15.5	–	
2	120	Rh/C (5%)	–	2.2	<1	
3	120	$RhCl(PPh_3)_3$	–	–	–	
4	120	$RhH(CO)(PPh_3)_3$	py[c]	11.0	–	
5	120	$RuCl(H)(CO)(P^iPr_3)_2$	py[d]	1.2	–	
6	120	$RhCl_3(py)_3$	py[c]	72.2	5.6	
7	120	$RhCl_3 \cdot xH_2O$	py[c]	20.6	4.5	
8	120	$[RhCl(COD)]_2$	py[c]	69.5	5.0	
9	120	$Pd(OAc)_2$	P^iPr_3 (Pd:P = 1:2)	10.7	2.7	Pd precipitation
10	120	$Pd(OAc)_2$	P^iPr_3 (Pd:P = 1:3)	8.0	2.6	Pd precipitation
11	120	$Pd(OAc)_2$	P^iPr_3 (Pd:P = 1:4.5)	44.0	14.0	
12	120	$Pd(OAc)_2$	P^iPr_3 (Pd:P = 1:7)	21.0	13.0	
13	120	$Pd(OAc)_2$	py, P^iPr_3 (Pd:P = 1:4.5)	19.0	13.0	
14	120	$Pd(OAc)_2$	$PMePh_2$ (Pd:P = 1:6)	5.0	12.0	
15	120	$Pd(OAc)_2$	Butanediphos (Pd:P = 1:4)	<1	–	
16	120	$Pd(OAc)_2$	PBu_3 (Pd:P = 1:6)	<1	–	
17	150	$[RhCl(COD)]_2$	py[c], P^iPr_3 (Rh:P = 1:4.5)	22.0	6.0	5 ml THF added
18	150	$Rh(py)_3Cl_3$[d]	py[c]	90.0	33.0	

[a] R401: CHF_2Cl (53% (w/w)), CH_3CHF_2 (13% (w/w)), CF_3CHClF (34% (w/w)) ($M = 100.8$ g/mol).
[b] Metal content of catalyst: 1.0 mmol, 40–45 mmol of R401, 120 μl of isopentane, 8–10 MPa H_2 pressure, reaction time: 6 h, unless otherwise stated.
[c] 3.0 ml of pyridine.
[d] 1.0 ml of pyridine. Metal content of catalyst: 0.3 mmol.

even at lower catalyst concentration. At this higher temperatures some hydrogenolysis of the C–F bond was observed as well: CH_3F became the main product of the hydrogenation of CHF_2Cl and traces of CH_4 were also formed. With a related catalyst system prepared in situ from $RhCl(COD)_2$ and pyridine similar conversion could be achieved as compared with $RhCl_3(py)_3$; this activity could not be reproduced by a $RhCl_3$.aq/pyridine system, however (Table 1).

Among the commonly used Pd-containing heterogeneous catalysts (cf. references [2b–3]), Pd/Al_2O_3 (5%), the only one on a basic carrier, catalyzed the hydrodehalogenation of CF_3CHFCl with a low activity at 120 °C. The other Pd catalysts were inactive. Because of the formation of HCl as a byproduct (which has a poisoning effect on the catalyst, see references [2b,3b]) the preference of a basic carrier is reasonable. We could not increase the conversion, however, by adding basic additives (MgO, CaCO₃, pyridine, NaOH/water, etc.). As a matter of fact, the conditions used generally for heterogeneous hydrodechlorination [2,3] are considerably different from our ones.

The results of CF_2Cl_2 hydrogenolysis are compiled in Tables 2 and 3. A relatively high temperature (160–180 °C) had to be used to achieve a satisfactory conversion. CHF_2Cl was the main product in most cases, but in the presence of metallic Mg and/or at 180 °C the hydrogenolysis of the C–F bond took place as well.

The complexes $RhH(CO)(PPh_3)_3$ and $[Rh(NBD)(PPh_3)]$ $[BF_4]$, as well as a heterogeneous catalyst, Pd/Al_2O_3 (5%) were only weakly active in hydrodehalogenation of CF_2Cl_2. The conversions obtained by $RhCl_3(py)_3$ changed very strongly with the additive: the activity decreased in the order $NEt_3 \gg Mg > py \gg Cl^-$. The best results were achieved

by the in situ prepared $Pd(P^iPr_3)_3$: a conversion of nearly 90% could be obtained at 170 °C when a slight excess of metallic Mg was added (calculated on the Cl^- content of the substrate). This finding is all the more interesting since the additive was in the solid phase. The effect of phosphine concentration was similar to that found in the case of R401: the rising excess slowed down the reaction but increased the selectivity of CHF_2Cl. Unidentified compounds were found mainly using the additives Mg and NEt_3 (Table 3). In these cases formation of coupling products is not to exclude (cf. references [2b–d]).

Some stoichiometric reactions were performed at room temperature and at atmospheric H_2 pressure to model the hydrodehalogenation steps. In these cases, less volatile analogs of the CFC-s (CF_2Br_2) and HCFC-s (CF_3CH_2I) were used. $RhCl_3(py)_3$ was inactive under these conditions, but the hydride complex, $RhH(CO)(PPh_3)_3$ hydrogenolyzed both of these substrates to CHF_2Br and to CF_3CH_3, respectively. The system $Pd(OAc)_2/P^iPr_3$ also reduced the substrates, but only at the ratios Pd:P ≤ 1:1. No intermediates of the hydrodehalogenation could be detected by IR or ^{19}F NMR spectroscopy in the reaction mixtures, however. IR and ^1H NMR spectra of the organic products formed from $RhCl_3(py)_3$ and two equivalents of pyridine at RT and 2 MPa H_2 pressure proved the presence of py·HCl.

4. Discussion

Comparing our results with those of Kim and co-workers [6], significant differences can be seen. They found that $RhCl(PPh_3)_3$ was the most effective catalyst in the

Table 2
Hydrodechlorination of CF_2Cl_2[a]

Entry	Temperature (°C)	Calalyst	Additive(s)	Conversion of CF_2Cl_2 (mol.%)
1	160	$RhCl_3(py)_3$	py[b]	7.0
2	160	Pd/Al_2O_3 (5%)	–	5.0
3[c]	160	$Pd(OAc)_2$	Mg, P^iPr_3 (Pd:P = 1:4.5)	38.0
4[c]	160	$RhH(CO)(PPh_3)_3$	Mg	14.0
5[c]	170	$RhCl_3(py)_3$	Mg	21.0
6	170	$Pd(OAc)_2$	P^iPr_3 (Pd:P = 1:4.5)	24.0
7[c]	170	$Pd(OAc)_2$	Mg, P^iPr_3 (Pd:P = 1:4.5)	84.0
8[c]	170	$Pd(OAc)_2$	Mg, P^iPr_3 (Pd:P = 1:6)	41.0
9[c]	170	$Pd(OAc)_2$	Mg, P^iPr_3 (Pd:P = 1:7.5)	16.0
10	170	$RhCl_3(py)_3$	$[NEt_4]^+Cl^-$, py[b]	<1
11	170	$RhCl_3(py)_3$	py, Net_3[d]	49.5
12	170	–	Mg	<1
13	170	$[Rh(NBD)(PPh_3)_2][BF_4]$	py[b]	7.0
14	180	Pd/Al_2O_3 (5%)	–	29.0

[a] Metal content of catalyst: 1.0 mmol, 40–45 mmol of CF_2Cl_2, 120 μl of isopentane, 8–10 MPa H_2 pressure, reaction time: 6 h, unless otherwise stated.
[b] 3.0 ml of pyridine.
[c] 0.71 g of Mg, 2–4 MPa H_2 pressure.
[d] 0.5 ml of pyridine, 5.0 ml of NEt_3.

Table 3
Product composition of selected hydrodehalogenations of CF_2Cl_2[a]

Entry	Temperature (°C)	Catalyst	Additive(s)	Composition of identified products (mol%)[b]					Unidentified products (wt.%)
				CF_2Cl_2	$CHClF_2$	CH_2F_2	CH_3F	CH_4	
3	160	$Pd(OAc)_2$	Mg, P^iPr_3 (Pd:P = 1:4.5)	62.3	11.8	11.2	5.2	9.5	–
5	170	$RhCl_3(py)_3$	Mg	78.3	3.2	1.5	8.0	9.0	6.3
6	170	$Pd(OAc)_2$	P^iPr_3 (Pd:P = 1:4.5)	76.0	7.2	13.8	3.0	–	0.8
7	170	$Pd(OAc)_2$	Mg, P^iPr_3 (Pd:P = 1:4.5)	16.4	4.5	3.0	11.7	64.4	1.6
8	170	$Pd(OAc)_2$	Mg, P^iPr_3 (Pd:P = 1:6.0)	59.0	20.2	9.8	11.0	–	3.6
9	170	$Pd(OAc)_2$	Mg, P^iPr_3 (Pd:P = 1:7.5)	84.0	13.5	2.5	–	–	11.0
11	170	$RhCl_3(py)_3$	py, Et_3N	49.5	19.6	28.8	1.8	0.3	9.4
14	180	Pd/Al_2O_3 (5%)	–	71.0	6.0	3.5	11.5	8.0	2.2

[a] Conditions as in Table 2.
[b] ΣIdentified components = 100 mol%.

hydrodechlorination of CF_3CCl_3, but this complex did not hydrogenolyze the CFC-*s* studied by us. $RhCl_3(py)_3$, however, a moderately active catalyst in hydrodechlorination of CF_3CCl_3 showed the best relative activity in our reactions. These two complexes behaved oppositely in the presence of additives: while amines decreased and chloride ion increased the conversion of CF_3CCl_3 by $RhCl(PPh_3)_3$ [6b], adding pyridine was necessary to hold $RhCl_3(py)_3$ in homogeneous phase and its hydrogenolyzing activity versus CF_2Cl_2 was reduced drastically by chloride.
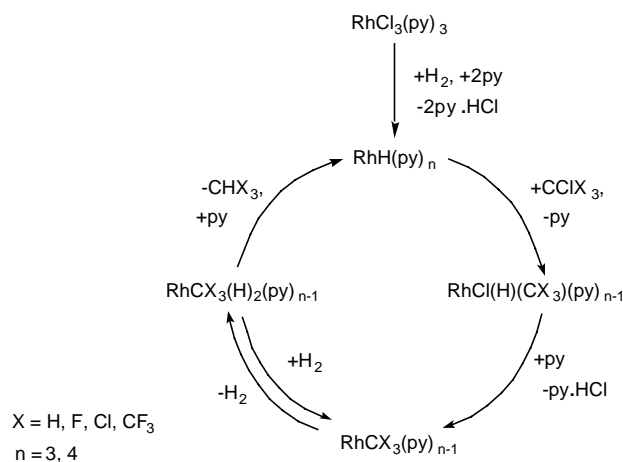
We suppose that the activation step of H_2 and/or of the substrate may be very different in the two Rh-containing catalytic systems. While the intermediacy of $RhCl(H)_2(PPh_3)_2$ in the $RhCl(PPh_3)_3$-catalyzed hydrogenations has been documented [6,9], a heterolytic activation of H_2—leading to an Rh(I) species—is much more probable in the case of $RhCl_3(py)_3$ (cf. reference [15]).

H–H········B
L_nClRh–Cl $\xrightarrow[-B \cdot HCl]{}$ L_nClRh–H $\xrightarrow[-B \cdot HCl]{+B}$ L_nRh ...
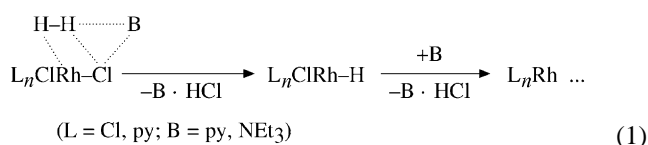
(L = Cl, py; B = py, NEt_3)   (1)

Kim and co-workers [6] suggested that $RhCl(H)_2(PPh_3)_2$ or a related species activates the substrate (CF_3CCl_3) by a nucleophilic attack. We observed, however, that relative reactivity of the CFC-*s* examined is the following: $CF_3CHFCl > CHF_2Cl > CF_2Cl_2$, i.e. the most electrophilic compound is the least reactive. This tendency contradict also the rule described for the hydrodechlorination catalyzed by heterogeneous Pd catalysts, namely, increasing the number of chlorine atoms on a carbon atom increases the reaction rate [16,17]. Consequently, even a homolytic cleavage of the C–Cl bond does not seem to be probable (cf. reference [18]). We suppose that (one of) the chlorine atom(s) of the CFC (HCFC) molecule coordinates to rhodium before the oxidative addition of the C–Cl bond [19,20]. Their coordinating ability corresponds to the above reactivity order.

The use of strongly electron donating, bulky phosphines as ligands in homogeneous hydrodechlorination has been reported several times [4,5a,21]. However, the present report demonstrates at first that Pd(0) complexes containing such ligands hydrogenolyze CFC-*s* and HCFC-*s*. Although the effects of the electronic and steric properties, as well as of

RhCl$_3$(py)$_3$

+H$_2$, +2py
-2py .HCl

RhH(py)$_n$

-CHX$_3$,
+py

+CCIX$_3$,
-py

RhCX$_3$(H)$_2$(py)$_{n-1}$

RhCl(H)(CX$_3$)(py)$_{n-1}$

+H$_2$

-H$_2$

+py
-py.HCl

X = H, F, Cl, CF$_3$
n = 3, 4

RhCX$_3$(py)$_{n-1}$

Scheme 1.

the chelating ability of the phoshines have not been studied systematically yet, it is clear from the data in Table 1 that the above type of ligands are the most advantageous ones. It is known, that P^{i}Pr$_3$ forms easily a 14 e$^-$ Pd(0) complex [22]. The inhibiting effect of added pyridine found for Pd(P^{i}Pr$_3$)$_3$ hints also at the role of a coordinatively unsaturated species which would activate the CFC (HCFC) molecule (vide supra, cf. references [19,20,23]).

The proposed mechanisms for the hydrodehalogenations of a substrate CCIX$_3$ (X: H, F, Cl, CF$_3$) catalyzed by RhCl$_3$(py)$_3$ and Pd(P^{i}Pr$_3$)$_3$ are outlined in the Schemes 1 and 2, respectively. The intermediate RhH(py)$_n$ ($n = 3, 4$) formed by the successive reduction of the starting complex (see Eq. (1)) reacts with the substrate into an Rh(III)-alkyl. From this species, a pyridine-induced elimination of HCl takes place. The resulted Rh(I)-alkyl adds H$_2$ to form an Rh(III) intermediate and the cycle will be closed by the reductive elimination of CHX$_3$.

Pd(P^{i}Pr$_3$)$_3$ loses a ligand giving a 14 e$^-$ intermediate which activates the substrate (Scheme 2). The Pd(II)-alkyl complex formed reacts with H$_2$—presumably in more steps—producing CHX$_3$ and HCl. There are examples in the literature both for the formation of PdCl(H)L$_2$ by the hydrogenation of a Pd–C-bonded species—probably through

PdL$_3$

+L,
-HCl

-L

+L

Cl
L$_2$Pd
H

PdL$_2$

+H$_2$,
-CHX$_3$

+CCIX$_3$

Cl
L$_2$Pd
CX$_3$
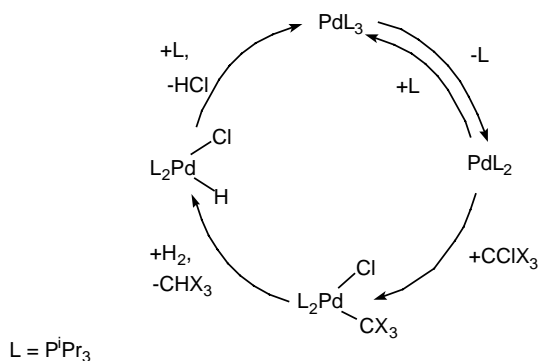
L = P^{i}Pr$_3$

Scheme 2.

a Pd(IV) intermediate—[24a,c], and for the ligand-induced reductive elimination of HCl from a PdCl(H)L$_2$ complex [24d]. It can not be excluded that our proposed intermediate, PdCl(H)(P^{i}Pr$_3$)$_2$ itself has some catalytic activity in hydrodechlorination (cf. references [24a,25]).

Adding metallic Mg to both active complex catalysts enhanced significantly the conversion of CF$_2$Cl$_2$ decreasing simultaneously the selectivity, consequently, the reaction mechanisms should be altered. We suppose that Mg induces radical pathways, e.g. by cleaving the M–Cl (M: Rh, Pd) bond. Mg can play a role as a reductant of Pd(OAc)$_2$, as well. Although Mg itself showed no hydrodechlorinating activity, it can not be excluded that Mg-alkyls appear in the reaction mixtures (cf. reference [26]).

At this stage of our work it is not possible to suggest more detailed mechanisms for the above homogeneous hydrodechlorinations. Kinetic investigations are in progress in order to provide more detailed information about the reaction pathways.

Acknowledgements

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