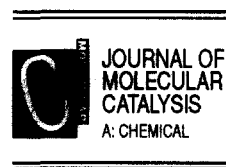




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Selective hydrogenolysis of chlorofluorocarbons by $\text{RhCl}(\text{PPh}_3)_3$

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Abstract

Factors affecting hydrogenolysis of CFC-113a (CF_3CCl_3) catalyzed by $\text{RhCl}(\text{PPh}_3)_3$ were studied to have an insight on the mechanism of the reaction. A slightly polar solvent such as THF is found to be appropriate for selective hydrogenolysis of fluorochlorocarbons. Kinetic analysis showed the reaction was first-order with respect to the concentrations of catalyst and substrate, respectively. Reaction rates were dependent on the concentration of Cl^- ions added; the reaction rate increased initially but remained constant at the higher Cl^- concentration. Striking effect of halide ions were rationalized by increased nucleophilicity of $[\text{RhX}_2(\text{PPh}_3)_2]^-$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$), a product from the initial reaction between catalysts and added halide ions, toward CFC-113a. Hydrogenolysis of CFC-113 ($\text{CF}_2\text{ClCFCl}_2$) produced HCFC-123a ($\text{CF}_2\text{ClCHClF}$) and chlorotrifluoroethene ($\text{CF}_2=\text{CFCl}$), a product from β -elimination of HCFC-123a, indicating nucleophilic attack of metal complexes to more electropositive carbons actually occurred. These results appear to support the $\text{S}_{\text{N}}2$ mechanism for the oxidative addition of CFC-113a. Added amines decreased reaction rates most probably by inhibiting the formation of more nucleophilic complexes mentioned above. Added proton induced decrease in reaction rates. Effect of added phosphines is rather complicated; reaction rates initially decline to the range where the ratio of $[\text{PPh}_3]$ to $[\text{catalyst}]$ is 6 but increase thereafter. This rate enhancement strongly indicates the existence of an independent phosphonium-containing reaction cycle. Light brownish compound was actually isolated and was spectroscopically characterized as $[\text{Ph}_3\text{P}(\text{CCl}_2\text{CF}_3)]\text{Cl}$. Plausible reaction cycles are proposed and the rate equations for this proposed mechanism are derived.

1. Introduction

Gradual reduction of ozone layer has recently attracted great interest, and long-lived species containing C–Cl bond such as Freon were blamed for depleting of this valuable layer that is indispensable for the survival of humankind [1]. Recent mandatory control of these materials by worldwide agreements such as Montreal Protocol [2] reflects this trend of environmental awareness.

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Since the ultimate ban of these materials will be expected in the near future, new production processes of possible substituents for Freon have been intensively investigated. HCFC-123 (CF_3CHCl_2), a promising substituent for CFC-11 (CFCl_3), is one of the CFC-alternatives under extensive study. Several processes for the production of HCFC-123 based on heterogeneous catalysts have been proposed [3], and related studies on heterogeneous catalytic hydrogenolysis of organic species containing C–Cl bonds are well established [4–9]. It is surprising that only a limited number of reports on the homogeneous catalytic hydrogenolysis of fluorine-containing chlorohydrocarbons have been published even though homogeneous catalytic hydrogenolysis of chloroarenes and halocyclopropane by using transition metal complexes are well documented [10–13]. In the previous paper, we have shown that highly selective production of HCFC-123 from the hydrogenolysis reaction of CFC-113a (CF_3CCl_3) can be achieved by several group VIII transition metal complexes [14]. As a continuation of our previous work, the kinetic and mechanistic studies on the homogeneous catalytic hydrogenolysis of CFC-113a by $\text{RhCl}(\text{PPh}_3)_3$ have been conducted.

2. Results and discussion

In our previous paper, we reported that several group VIII transition metal complexes, especially 16-electron, square planar complexes are active for the selective hydrogenolysis of CFC-113a to produce HCFC-123. Understanding the mechanism of this reaction would give an insight to establish an efficient process for HCFC-123 production, which includes developing new catalysts and process design. For this purpose, several factors affecting the reaction rates were investigated and a plausible mechanism was proposed.

2.1. Effect of solvent

The hydrogenolysis reactions of CFC-113a were conducted in various solvents. Either in benzene or n-hexane, no reaction was observed. The reaction proceeded rapidly in methanol, but the formations of undesirable products, dimethylether and dimethoxymethane were predominant. The same products were also obtained by the liquid-phase heterogeneous hydrogenolysis of CFC-113a in methanol, and these results could be explained by a mechanism in which MeOH played as a substrate [15]. Unlike in MeOH, HCFC-123 was produced in THF with high yield and selectivity. Only small amount of overhydrogenated product, HCFC-133a ($\text{CF}_3\text{CH}_2\text{Cl}$) was produced in addition to HCFC-123.

2.2. Effect of temperature and hydrogen pressure

Fig. 1 shows the dependence of the rate of hydrogenolysis of CFC-113a with respect to reaction temperature. The temperature was varied in the range 50–150°C. As shown in Fig. 2, the initial rate of reaction increased with hydrogen pressure up to 6.80 atm. Beyond 6.80 atm, however, the reaction rates were independent of hydrogen pressure, which might indicate the concentrations of active species reached a steady state or sufficient amount of hydrogen was dissolved at this point. The amount of an overhydrogenated product, HCFC-133a ($\text{CF}_3\text{CH}_2\text{Cl}$), was not changed significantly with the hydrogen pressure within the experimental range, which indicates a stepwise hydrogenolysis. This is supported by the fact that the formation of HCFC-133a was not observed during the initial stage in which the conversion of CFC-113a was less than 5%. Over 95% selectivity toward

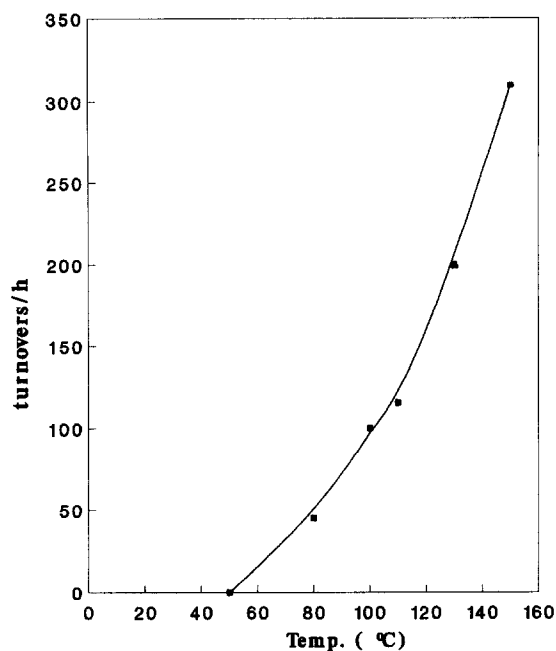


Fig. 1. Effect of temperature on the hydrogenolysis of CFC-113a catalyzed by $\text{RhCl}(\text{PPh}_3)_3$ (catalyst: 1.08×10^{-4} mole, CFC-113a: 5.30×10^{-2} mole, hydrogen pressure: 8 atm, reaction time: 5 h).

HCFC-123 indicates much less reactivity of HCFC-123 toward hydrogenolysis. These results stand on the same trends shown by Honor [8]. He reported that the order of reactivity toward heterogeneous catalytic hydrogenolysis is $\text{RCCl}_3 > \text{R}_2\text{CCl}_2 \gg \text{R}_3\text{CCl}$.

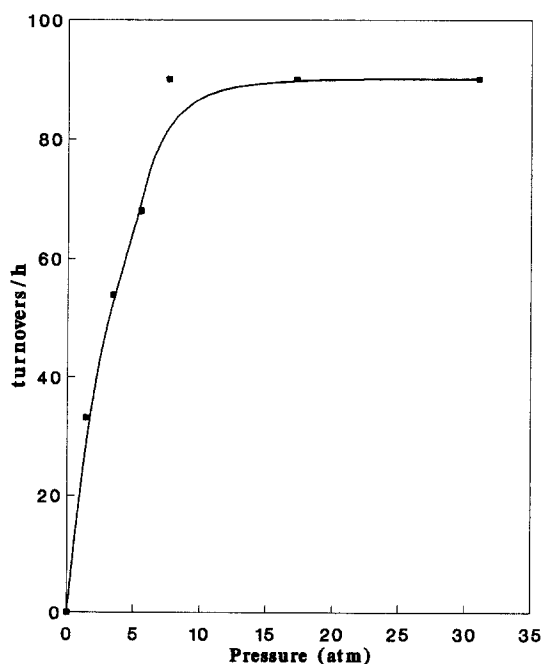


Fig. 2. Effect of H_2 Pressure on the hydrogenolysis CFC-113a catalyzed by $\text{RhCl}(\text{PPh}_3)_3$ (catalyst: 1.08×10^{-4} mole, CFC-113a: 5.30×10^{-2} mole, temperature: temperature: 100°C , reaction time: 5 h).

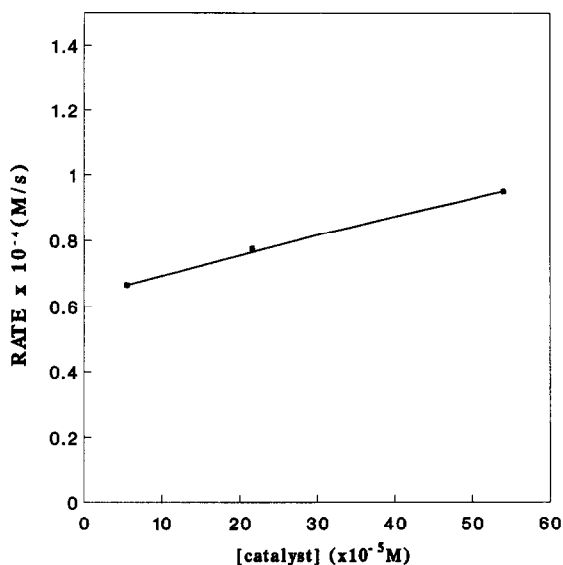


Fig. 3. Plot of rate versus [catalyst] for a series of reactions of various [catalyst] at 90°C (CFC-113a: 0.533 M, hydrogen pressure: 8 atm).

2.3. Effects of concentrations of catalysts and CFC-113a

As shown in Figs. 3 and 4, reaction rates increased with the concentrations of catalysts and CFC-113a, respectively. Linear dependence of reaction rate on the concentration of catalysts was observed in the ranges studied. However, the rate dependence on the substrate (CFC-113a) concentration was found rather complicated. The disappearance rate of the substrate is generally fast in the beginning due to a high concentration of substrate but it becomes slower with the decrease of the

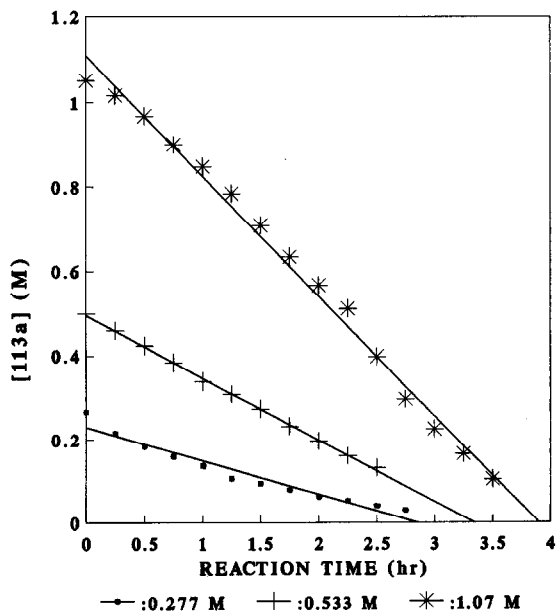


Fig. 4. Plot of [113a] versus time for a series of reactions various initial [113a] (catalyst: 2.16×10^{-4} M, hydrogen pressure: 8 atm).

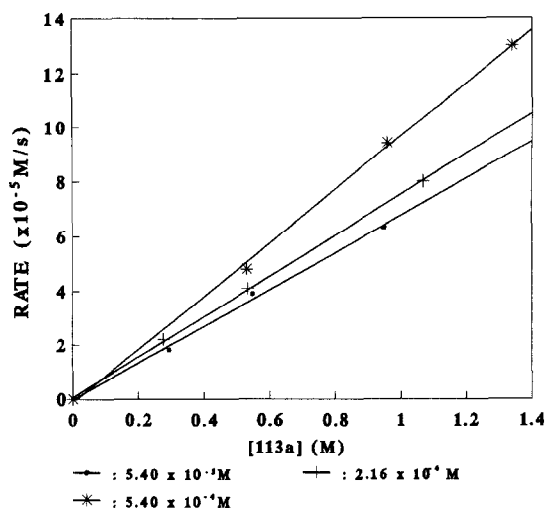


Fig. 5. Effect of initial concentration of [113a] on the rate of hydrogenolysis reactions of various [catalyst] at 90°C (hydrogen pressure: 8 atm).

concentration of substrate. However, as shown in Fig. 4, the disappearance rates of CFC-113a were found nearly constant during the reaction period. It was also found that the observed reaction rates were linearly dependent on the initial concentration of CFC-113a as shown in Fig. 5. This might indicate that at a given time total substrate concentration remains constant during the reaction by the involvement of reaction products. In other words, products, HCFC-123 or HCl is functioning to compensate the decrease of reaction rate caused by the decrease of the substrate concentration. It is observed that hydrogenolysis of CFC-113a proceeds stepwisely and the second hydrogenolysis to HCFC-133a ($\text{CF}_3\text{CH}_2\text{Cl}$) is much slower than the first hydrogenolysis reaction. The contribution of HCFC-123 to the first hydrogenolysis reaction rate is found negligible. Therefore, it can be concluded that the product, HCl is responsible for the constant reaction rate from the net reaction Eq. (1),



In order to keep the reaction rate and the reactant concentration constant during the reaction, the concentration of HCl should be included into the concentration of remaining CFC-113a,

$$[\text{CF}_3\text{CCl}_3]_{\text{initial}} = [\text{CF}_3\text{CCl}_3]_t + [\text{HCl}]_t.$$

The effect of added HCl on the reaction rate was independently studied and presented in other section of this paper. A medium polar coordinating solvent, THF was found to be an excellent solvent for the selective hydrogenolysis reactions of fluorochlorocarbons. Unlike in THF, surprisingly, no reaction was observed in nonpolar solvents such as n-hexane and benzene. This indicates that a little charge separation might occur in the reaction intermediates or transition states. Therefore, in a key C–Cl activation step, $\text{S}_{\text{N}}2$ or ionic oxidative addition mechanism might be adopted. A nucleophilic attack of the metal complex onto a more positively charged carbon of the substrate (CFC-113a) is considered as the most important step in $\text{S}_{\text{N}}2$ or ionic oxidative addition mechanism. This also explains why the reaction proceeds in a highly selective way. Substitution of a hydrogen for a chlorine reduces the partial positive charge on a carbon and the reactivity toward the hydrogenolysis of C–Cl bond. Radical mechanism can be excluded by the result obtained from the experiments using D_2 instead of H_2 . The produced HCFC-123 is d-1 compound only, not the mixture of d-1 and d-0. No reactivity in

nonpolar solvents also support this conclusion. C–F bond activation product was not obtained from the hydrogenolysis of HCFC-133a. This can be rationalized by the explanation of Kolditz [16] where low reactivity of C–F bond is attributed to the strong C–F bond due to high electronegativity of F. The same results were also reported by Gervauti [17]. However, excessive positive charge on a carbon appears to retard the reductive elimination to give hydrogenolysis products. This C–Cl bond activation step seems to be important in the reaction with other substrates such as CFC-113 ($\text{CF}_2\text{ClCFCl}_2$), HCFC-122a ($\text{CHClFCCl}_2\text{F}$) and CFC-12 (CF_2Cl_2). For example, HCFC-122a and CFC-12 showed very low reactivity toward hydrogenolysis (less than 5% conversion after 5 h) and CFC-113 gave moderately low conversion (about 20%). Hydrogenolysis of CFC-113 under similar reaction condition produced HCFC-123a ($\text{CF}_2\text{ClCHClF}$) and $\text{CF}_2=\text{CFCl}$ even though HCFC-123b ($\text{CHF}_2\text{CFCl}_2$) was expected on the basis of the degree of positive partial charge on a carbon. $\text{CF}_2=\text{CFCl}$ can be produced by β -hydrogen elimination from a M- CF_2CHClF moiety, a C–Cl bond activation product of HCFC-123a. Same type of product, $\text{CClF}=\text{CClF}$ was also obtained from the hydrogenolysis of HCFC-122a ($\text{CHClFCCl}_2\text{F}$). These results strongly indicate that the nucleophilic attack of metal species on a more positively charged carbon actually occurs to form M–C bonds. The strong M–C bonds effectively block. However, further progress of the hydrogenolysis of C–Cl bonds appears to be effectively blocked due to the strong M–C bonds. In conclusion, moderate positive charge on a carbon bearing Cl atom is important for hydrogenolysis of chlorohydrocarbons, and $\text{S}_\text{N}2$ -type oxidative addition pathway appears to be adopted in this reaction.

2.4. Effect of external bases

As shown in Eq. (1), HCl is produced as a by-product. Addition of bases is expected to accelerate the hydrogenolysis reaction by removing HCl as an ammonium salt. In order to investigate the effect of bases, several amines or phosphines were added to the reaction mixture.

2.4.1. Amines

Triethylamine, diethylamine, pyridine, aniline and *N,N*-dimethylaniline ($\text{p}K_\text{b} = 3.28, 3.20, 8.86, 9.40, 8.85$, respectively)[18] were used to test the effect of amines. As shown in Fig. 6, all the amines but pyridine showed similar effects in spite of their different electronic and steric properties. Contrary to our expectation, addition of amines did not show any significant increase in the reaction rate. In the cases of triethylamine, and *N,N*-dimethylaniline reaction rate was slow during the first 2 hour period but thereafter the reaction proceeded with the similar rate to that observed in the absence of amines. Furthermore, a slower reaction rate by about 15% was observed in the cases of diethylamine and aniline. A slower reaction rate was also monitored when pyridine was used. During the first 2 hours, there primarily occurred salt formation reactions between amines and HCl that might enhance the reaction rates. When ammonium chloride was added, any appreciable effect on the reaction rate was not observed within the experimental range. These results also indicated that the in-situ formed HCl might play an important role in this system. In NMR experiments at a room temperature, it was found that diethylamine exclusively produced *cis*- $\text{RhCl}(\text{NHEt}_2)(\text{PPh}_3)_2$ (δP in THF; 48.3(dd), $^1J_{\text{Rh-P}} = 167.1$ Hz, $^2J_{\text{pp}} = 47.5$ Hz; 55.1(dd), $^1J_{\text{Rh-P}} = 206.4$ Hz, $^2J_{\text{pp}} = 47.5$ Hz) and free phosphines while aniline and pyridine complexes showed broad peaks centered at about 50 ppm. Isolation of these amine complexes was not successful due to their instabilities. Interestingly, triethylamine and *N,N*-dimethylaniline did not give amine substituted products in the NMR tube experiment. Instead, their presences only shifted the equilibrium between $\text{RhCl}(\text{PPh}_3)_3$ and $[\text{RhCl}(\text{PPh}_3)_2]_2$ to favor monomer formation. Assignment of the product as a mono-substituted amine complex was made

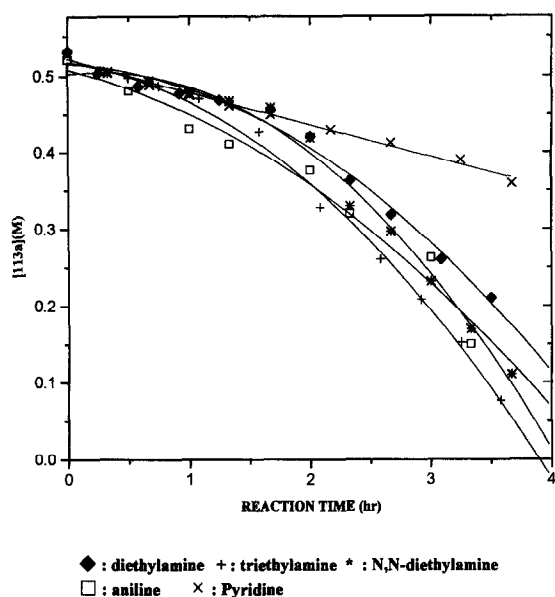


Fig. 6. Effect of various amines on the hydrogenolysis of CFC-113a at 90°C (catalyst: 2.16×10^{-4} M, hydrogen pressure: 8 atm) (amine conc.: 0.1 M).

based on the report [19]. These differences in the formation of amine complex could be explained in terms of electronic and steric effects of different amines. Slower reaction rate with diethylamine appears to be due to slower rate of dissociation of PPh_3 from $\text{cis}[\text{RhCl}(\text{NHEt}_2)(\text{PPh}_3)_2]$ to generate a vacant site. The same explanation can be adopted in the cases of aniline and pyridine. In the pyridine case, even slower dissociation of phosphines was resulted possibly due to less steric demand of a pyridine and less repulsion between a pyridine and a phosphine ligand. However, triethylamine and *N,N*-dimethylaniline appear not to strongly bind to the metal possibly due to their steric bulkiness and these amines are believed only to function as HCl scavenger by forming ammonium salts. Therefore, it is concluded that the rate depressing effects of amines are mainly attributed to the removal of chloride ions (*vide infra*) by the formation of ammonium salts. Formation of amine complexes appears to be a secondary factor.

2.4.2. Phosphines

Figs. 7 and 8 showed that the addition of PPh_3 up to 6 times to Rh reduced the reaction rate, while the presence of large excess of triphenylphosphine ($\text{PPh}_3/\text{Rh} > 6$) enhanced the rate by more than 2 times. Wilkinson's catalyst is well known to dissociate PPh_3 to form a dimer, $[\text{RhCl}(\text{PPh}_3)_2]_2$ which is active toward hydrogenation of alkenes [20]. In a ^{31}P NMR experiment, it was confirmed that there was an equilibrium between $\text{RhCl}(\text{PPh}_3)_3$ ($30.47(\text{dd}, \text{P}_1)$, $47.39(\text{td}, \text{P}_2)$, $^1J_{\text{Rh}-\text{P}_1} = 189.1$ Hz, $^1J_{\text{Rh}-\text{P}_2} = 144.7$ Hz, $^2J_{\text{P}_1-\text{P}_2} = 37.8$ Hz) and $[\text{RhCl}(\text{PPh}_3)_2]_2$ ($51.86(\text{d})$, $^1J_{\text{Rh}-\text{P}} = 195.7$ Hz) as expected. Therefore, moderate excess of free PPh_3 could hinder the dissociation of coordinated phosphines preventing the resultant formation of active species, $[\text{RhCl}(\text{PPh}_3)_2]_2$, which leads to the reduction in the reaction rates. However, enhanced reaction rates with large excess of PPh_3 strongly indicate an existence of independent pathway where PPh_3 play an important role in the formation of HCFC-123. In a separate

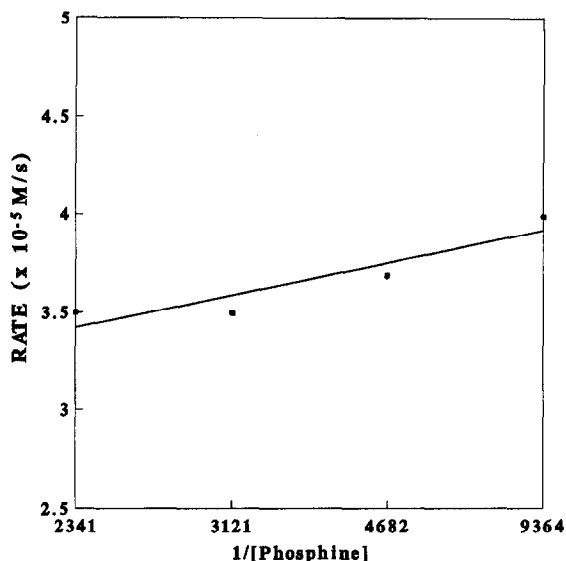


Fig. 7. Plot of rate versus $1/[\text{PPh}_3]$ for a series of reactions with various amounts of added PPh_3 at 90°C (catalyst: 2.16×10^{-4} M, CFC-113a: 0.533 M, hydrogen pressure: 8 atm).

experiment, it was found that a light brownish compound, a phosphonium salt soluble in MeOH and DMSO, was formed between PPh_3 and CFC-113a under the reaction condition,



Compound I gives a singlet at 27.33 ppm and -77.9 ppm in a $^{31}\text{P}\{^1\text{H}\}$ and a $^{19}\text{F}\{^1\text{H}\}$ NMR spectra (MeOH- d_4), respectively and a $M + 18$ (I + H_2O) (most phosphonium salt is highly hygroscopic!) peak in a FAB mass spectrum. The chemical shifts of other related phosphonium salts in ^{31}P NMR

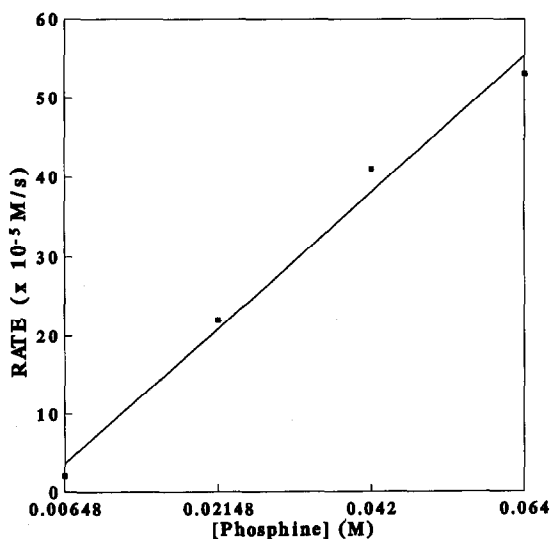
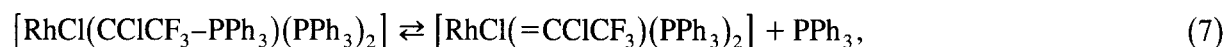
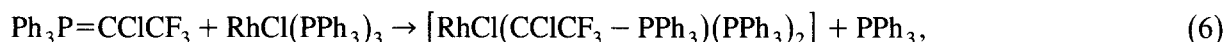


Fig. 8. Plot of rate versus $[\text{PPh}_3]$ for a series of reactions with various amounts of added PPh_3 at 90°C (catalyst: 2.16×10^{-4} M, CFC-113a: 0.533 M, hydrogen pressure: 8 atm).

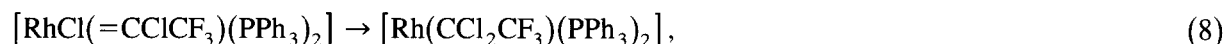
spectra are as follows [21]. $[\text{Ph}_3\text{P}(\text{CCl}_3)]\text{Cl}$, 47.5 ppm; $[\text{Ph}_3\text{P}(\text{CHCl}_2)]\text{Cl}$, 32.5 ppm; $[\text{Ph}_3\text{P}(\text{CH}_2\text{Cl})]\text{Cl}$, 23.5 ppm; $[\text{Ph}_3\text{P}(\text{CH}_3)]\text{Cl}$, 21.1 ppm. The chemical shift of compound I is different from that of $[\text{HPPh}_3]\text{Cl}$ (−41.23 ppm) which was obtained from the reaction between PPh_3 and HCl . Compound I, however, did not react with HCl at all. Compound I did not produce HCFC-123 by the reaction with H_2 unless $\text{RhCl}(\text{PPh}_3)_3$ was present. Since PPh_3 does not catalyze the hydrogenolysis of CFC-113a in the absence of Rh complexes, possible ylides pathway (Eqs. (3), (4) and (5)) can be excluded.



However, there still remains a chance that ylides can react with metal complexes to give alkyl complexes which also can be obtained by oxidative addition of CFC-113a to $\text{RhCl}(\text{PPh}_3)_3$ as follows.



Since carbenes are known to insert into $\text{M}-\text{X}$ ($\text{X} = \text{H}$, Halogen) [22], carbene complexes can give alkyl complexes as shown in Eq. (8) and then the starting complex can be regenerated by the reaction with HCl and PPh_3 (Eq. (9)).



It is believed that excess PPh_3 can assist oxidative addition of CFC-113a to the metal complexes and thus increase the reaction rates as observed. The other possibility is that the resulting product, $[\text{HPPh}_3]$ formed from the reaction of compound I with $[\text{RhH}_2\text{Cl}(\text{PPh}_3)_2]$, contributes to enhance the reaction rate. Wilkinson's catalyst, $\text{RhCl}(\text{Ph}_3)_3$ are known to react with H_2 to give $[\text{RhH}_2\text{Cl}(\text{Ph}_3)_2]$ [20]. Since the compound I actually reacts with $\text{RhCl}(\text{PPh}_3)_3$ and H_2 to give HCFC-123 in the absence of excess PPh_3 , it is believed that a direct reaction pathway is more favored even though ylides pathway cannot be completely excluded. Also in an NMR experiment at a room temperature, a mixture of compound I and $\text{RhCl}(\text{PPh}_3)_3$ in the presence of excess of PPh_3 did not show any indication of a new Rh compound formation. This is also supported by the observation that the ^1H NMR experiment with a mixture of compound I, $\text{PhCl}(\text{PPh}_3)$ and PPh_3 at a room temperature did not produce a new Rh complex formation.

2.5. Effect of external halide ions

As mentioned above, in-situ formed HCl appears to play an important role in the hydrogenolysis of CFC-113a (CF_3CCl_3). Fig. 9 shows the effect of HCl on the reaction rate; the rate increased with concentration of HCl up to about 2000 times of metal complexes but remained almost constant beyond that range. In order to determine which species (H^+ or Cl^-) are responsible for the enhancement of reaction rate, HClO_4 and LiX ($\text{X} = \text{Cl}$, Br , I) were added to the reaction mixture. Addition of HClO_4 decreased the reaction rate but LiCl showed the similar behavior as HCl as shown in Fig. 9. These results clearly indicate that chloride ions are responsible for the significant increase in the reaction rate. Reaction rate increased with the addition of LiBr or LiI up to the point where ratio of [halide] to [complex] reached 200 as expected but, surprisingly, the reaction rates decreased beyond

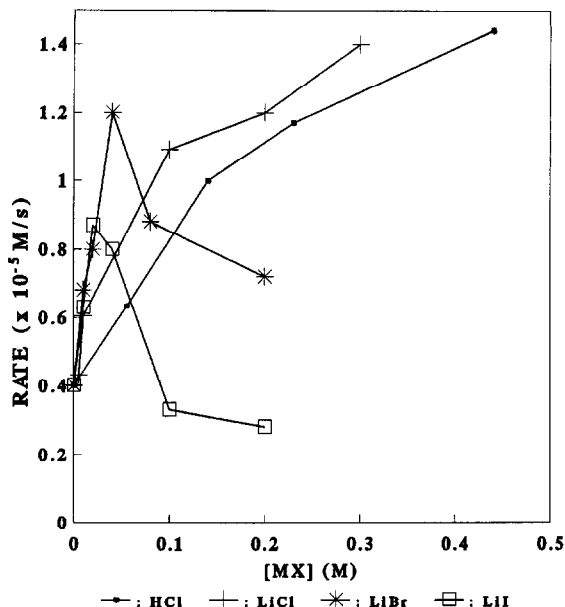


Fig. 9. Comparison of rate versus [MX] in the presence of various MXs at 90°C (catalyst: 2.16×10^{-4} M, CFC-113a: 0.533 M, hydrogen pressure: 8 atm).

that region. When a large excess of LiI was used, an induction period was observed (Fig. 10). In case of potassium halides, reaction rates decreased in the same order of Cl, Br and I as lithium salts but the rates were slower than those with lithium salts (Fig. 11). This is probably due to lower solubilities of potassium salts in the reaction media. The positive effect of halide ions on the oxidative addition reaction was also reported by Forster [23] and Amatore et al. [24] This striking halide ion effect in the Monsanto/BP acetic acid process is due to prior coordination of an halide ion to Rh(I) complex to give a more nucleophilic complex. As in Eq. (10), halide ions might react with $[\text{RhCl}(\text{PPh}_3)_2]_2$ to

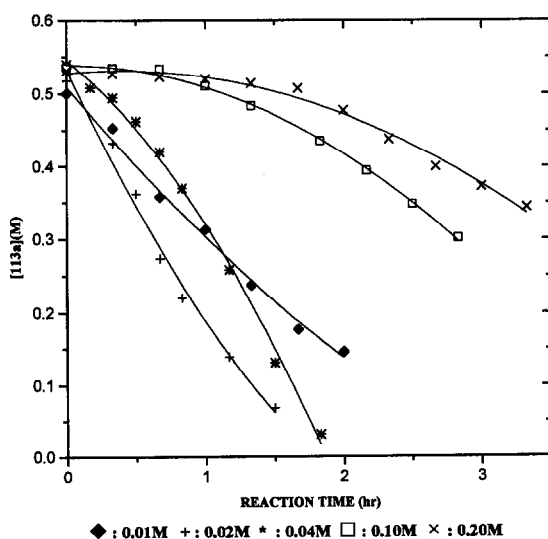


Fig. 10. Plot of [113a] versus time for a series of reactions with various [LiI] at 90°C (catalyst: 2.16×10^{-4} M, hydrogen pressure: 8 atm).

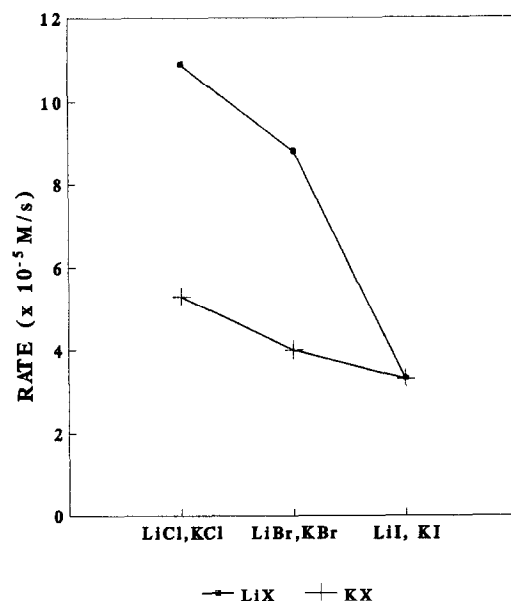
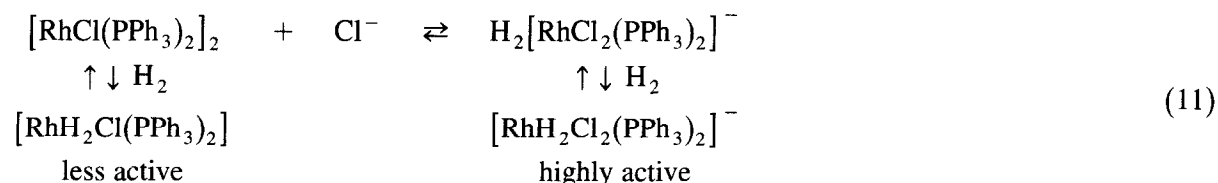


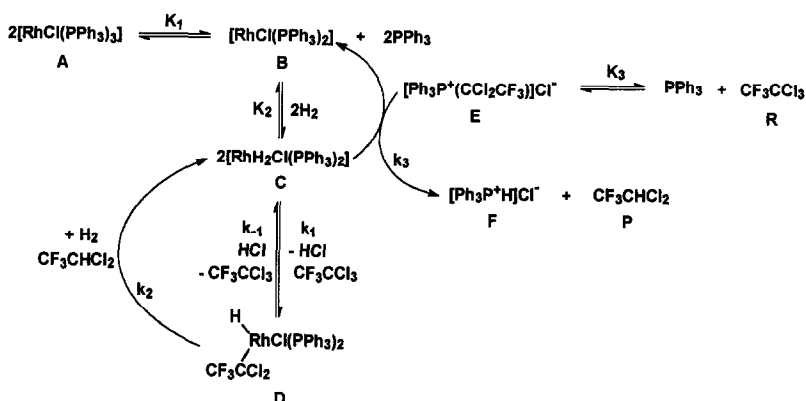
Fig. 11. Comparison of rate in the presence of various MXs at 90°C (catalyst: 2.16×10^{-4} M, CFC-113a: 0.533 M, MX: 0.10 M, hydrogen pressure: 8 atm).

form more nucleophilic complex, $[\text{RhCl}_2(\text{PPh}_3)_2]^-$ (complex II) which is believed to be a reactive species in the hydrogenolysis of CFC-113a,



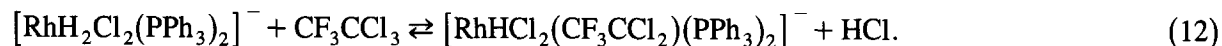
The presence of complex II was confirmed by a series of ^{31}P NMR experiments. Addition of LiCl to the THF solution of $[\text{RhCl}(\text{PPh}_3)_3]$ resulted in the appearance of a new peak (doublet, $^1J_{\text{Rh-P}} = 197.8$ Hz) centered at 52.19 ppm whose intensity increased with the concentration of LiCl. These spectroscopic parameters are very similar to those of dimer, $[\text{RhCl}(\text{PPh}_3)_2]_2$ ($^1J_{\text{Rh-P}} = 195.7$ Hz, $P = 51.86$ ppm), representing similar environment around phosphorus atoms in both complexes. Addition of excess LiBr or LiI produced similar doublets whose characteristic values are 51.38 ppm, 194.8 Hz and 48.87 ppm, 190.0 Hz, respectively. Yet, the isolation of these complexes has failed. Also, we are not able to determine whether the activation of molecular hydrogen takes place before or after the formation complex II. The correlation between activity and chloride ion concentration can be discussed on the basis of an equilibrium between a rhodium complex and the chloride ligand. Coordination of a chloride ion is indispensable for the activation of molecular hydrogen to give the highly reactive catalyst, $[\text{RhH}_2\text{Cl}_2(\text{PPh}_3)_2]^-$, and Cl^- concentration should play a key role in the formation of $[\text{RhCl}_2(\text{PPh}_3)_2]^-$, high concentration reflecting a right-shifted equilibrium in Eq. (11).



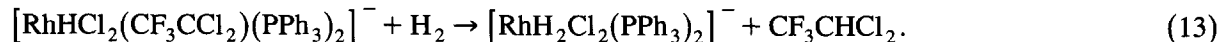


Scheme 1.

The next step for the hydrogenolysis reaction would be the interaction of $[\text{RhH}_2\text{Cl}_2(\text{PPh}_3)_2]^-$ with CF_3CCl_3 as in Eq. (12),



In Eq. (12), the addition of large excess of HCl or Cl^- would inhibit the reaction by shifting the equilibrium to the left and result in the observed behavior where the reaction rate reaches a maximum with concentrations of halide ions. This highly active species can be regenerated by the reaction with H_2 accompanying the production of HCFC-123 (Eq. (13)),



Higher reaction rates by the presence of small amounts of LiBr and LiI may represent the lower electronegativities of Br and I and consequently higher nucleophilicities of $[\text{RhH}_2\text{X}_2(\text{PPh}_3)_2]^-$ or $[\text{RhHX}(\text{PPh}_3)_2]^-$ toward CFC-113a . Reductive elimination of HX ($\text{X} = \text{Br}, \text{I}$) from $[\text{RhH}_2\text{X}_2(\text{PPh}_3)_2]^-$ could give $[\text{RhHX}(\text{PPh}_3)_2]^-$. However, in the presence of large amount of LiX , the reaction rates declined significantly (I^- showed more decreasing effect) possibly due to less tendency of dissociation of HX from initially formed $[\text{RhH}_2\text{X}_2(\text{PPh}_3)_2]^-$. It is noticeable that less tendency of dissociation of HX may reflect increasing acidity of HX in the order of $\text{Cl} < \text{Br} < \text{I}$ ($\text{p}K_a$; $\text{HI} = -10$, $\text{HBr} = -9.5$, $\text{HCl} = -7.0$) [25].

2.6. Proposed mechanism

Possible mechanisms are outlined in Schemes 1–3 based on the results discussed above. These schemes represent pathways functioning in cases of presence of moderate excess of PPh_3 , large excess of PPh_3 , and added Cl^- , respectively.

2.6.1. With moderate excess of PPh_3 ($\text{PPh}_3/\text{Rh} \leq 6$)

Preequilibria are postulated between A and B, B and C, and R and E, respectively. Preequilibrium between A and B is confirmed by a ^{31}P NMR experiment but the other two equilibria are not evident. However, considering the fact that C is easily obtained from B under a hydrogen atmosphere at a room temperature and the rate of disappearance of CFC-113a is relatively slow (about 5 h for 100% conversion), preequilibrium can be established before the activation of CFC-113a step. Since the formation of phosphonium salts is not quantitative (most of the phosphines still remains when

2.6.3. With added Cl^- ions

In the presence of added Cl^- ions, the formation of compound C has to be considered in the preequilibrium stage to explain the enhancement of reaction rates (vide supra). Without the presence of added phosphines, a phosphonium-containing cycle can be ignored as in case of Section 2.61. Therefore, a rate equation can be derived by assuming a steady-state approximation for compound E. However, in case of coexistence of phosphines and Cl^- ions, the oxidative addition of CFC-113a by compound D should be ignored or both cycles should be considered depending on the relative amounts of Cl^- and PPh_3 .

2.7. Kinetics

Considering the experimental results and proposed reaction mechanisms, three different rate equations are derived.

2.7.1. With moderate excess of PPh_3 ($\text{PPh}_3/\text{Rh} \leq 6$)

As mentioned above, a phosphonium salt containing cycle is ignored in Scheme 1. Therefore, the rate equation can be written as:

$$\frac{dP}{dt} = k_2[D]. \quad (14)$$

Assuming steady-state approximation for complex D, then [D] becomes

$$[D] = \frac{k_1}{k_2 + k_{-1}} [C][R]. \quad (15)$$

From the definitions of equilibrium constants, K_1 and K_2 , [C] can be written as follows:

$$[C] = \sqrt{K_2 K_1 \frac{[A]}{[\text{PPh}_3]} [\text{H}_2]}. \quad (16)$$

By inserting Eqs. (15) and (16) into Eq. (14), rate Eq. (17) can be obtained,

$$\frac{dP}{dt} = \sqrt{K_2 K_1 \frac{[A]}{[\text{PPh}_3]} [\text{H}_2]} [R] \left(k_2 \frac{k_1}{k_2 + k_{-1}} \right) = k' [\text{RhCl}(\text{PPh}_3)_3] [\text{CF}_3\text{CCL}] / [\text{PPh}_3] \quad (17)$$

where

$$k' = \sqrt{K_2 K_1 [\text{H}_2]} \left(k_2 \frac{k_1}{k_2 + k_{-1}} \right).$$

Fig. 8 clearly shows a linear dependence of the rate of product with respect to $1/[\text{PPh}_3]$ as expected from Eq. (17). Figs. 3 and 5 also show the linear dependence of the rates with respect to the concentrations of catalysts and CFC-113a.

2.7.2. With large excess of PPh_3 ($PPh_3/Rh > 6$)

By using the definitions of K_1 and K_2 , the rate equation can be reduced as follows:

$$\frac{dP}{dt} = k_1[B][C] = k_1K_1K_2[RhCl(PPh_3)_3][H_2][CF_3CCl_3][PPh_3] = k''[PPh_3] \quad (18)$$

where

$$k'' = k_1K_1K_2[RhCl(PPh_3)_3][H_2][CF_3CCl_3].$$

Fig. 9 shows that rate Eq. (18) can be successfully applied in this system.

2.7.3. With added Cl^- ions

As derived in the above cases, the rate law can be formulated by using preequilibrium and steady-state approximations.

$$\begin{aligned} \frac{dP}{dt} &= K_3 \sqrt{K_1K_2 \frac{[RhCl(PPh_3)_3][Cl^-]}{[PPh_3]} [H_2][CF_3CCl_3] \left(k_2 \frac{k_1}{k_2 + k_{-1}[HCl]} \right)} \\ &= K'''[Cl^-] \left(\frac{1}{k_2 + k_{-1}[HCl]} \right) \end{aligned} \quad (19)$$

where

$$K''' = k_1k_2K_3 \sqrt{K_1K_2 \frac{[RhCl(PPh_3)_3]}{[PPh_3]} [H_2][CF_3CCl_3]}.$$

Fig. 9 can be rationalized by Eq. (19) if $[Cl^-]$ replaces $[HCl]$ or vice versa.

3. Conclusions

In this study, we investigated several factors affecting hydrogenolysis of CFC-113a (CF_3CCl_3) catalyzed by $RhCl(PPh_3)_3$ and proposed the plausible reaction mechanism. The mechanism consists of two independent cycles, one of which involves oxidative addition of CFC-113a to the Rh complex and the other comprises a participation of in-situ formed phosphonium salt. The oxidative addition of CF_3CCl_3 to Rh complex appears to proceed via S_N2 mechanism on the basis of solvent effect, kinetic analysis, halide ion effect, and product analysis of the hydrogenolysis reaction of CFC-113. Radical pathway was excluded by product analysis of an experiment using D_2 . Effect of halide ions were rather surprising and the rate enhancing effect could be rationalized by increased nucleophilicity of $[RhX_2(PPh_3)_2]^-$ ($X = Cl, Br, I$), a product from the reaction between the catalyst and the added halide ions, toward CFC-113a. Amines were expected to increase reaction rate by removing HCl formed but decrease in the reaction rate actually observed. Amines are considered to depress the reaction rate most probably by inhibiting the formation of active species. Added phosphines showed an expected behavior initially but this trend deviated in the presence of large excess of phosphines; reaction rates initially declined to the limit where the ratio of $[PPh_3]$ to $[catalyst]$ is 6 but increased thereafter. The rate enhancement by the presence of large amount of triphenylphosphine suggests the existence of an independent phosphonium-containing cycle. $[Ph_3P(CCl_2CF_3)]Cl$, a possible intermediate responsible for the rate enhancement, was isolated and spectroscopically characterized. Further studies to identify and to isolate the reaction intermediates are in progress.

4. Experimental section

4.1. Reagents

Solvents were all reagent grade and were distilled from appropriate drying agents under a nitrogen atmosphere prior to use. HCl was introduced by using 1.0 M solution in diethylether (Aldrich). Other reagent grade chemicals were purchased from Junsei and used without further purification. $\text{RhCl}(\text{PPh}_3)_3$ was purchased from Strem CFC-113a, obtained from the rearrangement reaction of CFC-113 (Ashahi) with AlCl_3 [28], was distilled under nitrogen before use.

4.2. Instrumentation.

$^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded on a Bruker AM-250 spectrometer operating at 101.256 Mhz. These spectra were referenced to external triphenylphosphine (-5.3 ppm relative to 85% H_3PO_4). ^{19}F NMR spectra were recorded on a Bruker AM-300 spectrometer operating at 282.231 MHz. The chemical shift was recorded in ppm from the CFCl_3 , internal standard. Gas chromatographic analyses were made on a Young-In 680D gas chromatography equipped with a flame ionization detector and a 6 ft long stainless steel column packed with liquid methyl silicon on chrom-W. Mass spectral analyses were carried out employing a HP 5890A GC/HP 5917A MS detector equipped with a 30 m long capillary column packed with liquid methyl silicon.

4.3. Kinetic study

Generally, in a 200 ml stainless-steel high pressure reactor, 2.16×10^{-5} mole of $\text{RhCl}(\text{PPh}_3)_3$, 5.33×10^{-2} mole of CFC-113a, 1 g of n-hexane, and 100 ml of THF were magnetically stirred under 8 atm of H_2 at 90°C . Small amount (~ 1 ml) of samples were taken from a sampling port every 30 min and analyzed by gas chromatography. The observed rate constants were determined by plotting the concentration of CFC-113a versus time and the products were analyzed by GC with the internal standard, n-hexane. Plots of the kinetic data were fitted by using conventional linear regression program.

4.4. NMR experiments

4.4.1. Reactions between $\text{RhCl}(\text{PPh}_3)_3$ and amines

Inside a glove box, a stock solution (1.74 M) was prepared by dissolving 50 mg of $\text{RhCl}(\text{PPh}_3)_3$ with 30 ml of benzene and 1 ml of benzene- d_6 . Appropriate amines (17.4 mmol) were added to 1 ml of this stock solution in a 5 mm NMR tube at the room temperature. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were taken with these samples.

4.4.2. Reactions between $\text{RhCl}(\text{PPh}_3)_3$ and halide ions

Inside a glove box, a stock solution (1.06 M) was prepared by dissolving 30 mg of $\text{RhCl}(\text{PPh}_3)_3$ with 30 ml of THF and 0.5 ml of THF- d_8 . Ten molar excess of lithium halides were added to 1 ml of this stock solution and remaining solid was removed by filtration. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were taken with these samples.

4.5. Synthesis of $[PPh_3(CF_3CCl_2)]Cl$

In a o.d. 2 cm × 20 cm, thick-wall (1 mm) pyrex tube reactor equipped with a Teflon plug valve (Furon, PV2-24), 1.25 g (6.67 mmol) of CFC-113a and 17.5 g (66.7 mmol) of PPh_3 was dissolved in 20 ml of benzene. This reactor was set in a oil bath maintained at 90°C and magnetically stirred for 4.5 h. In less than 5 min, fine solid was formed and the solution turned light yellow. The color of the solution became darker with time and finally was dark brown. The suspended white solid was filtered, washed with 15 ml of THF and acetone three times, respectively and dried under reduced pressure. Yield: 0.30 g (19%), m.p.: 270°C (decomp.)

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