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Dehalogenation of Hexachlorocyclohexanes and Simultaneous Chlorination of Triethylsilane Catalyzed by Rhodium and Ruthenium Complexes

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Complexes RhCl(PPh$_3$)$_3$ and RhH$_2$Cl(P^{i}Pr$_3$)$_2$ catalyze the dehalogenation of γ-hexachlorocyclohexane to benzene and the simultaneous chlorination of HSiEt$_3$ to ClSiEt$_3$. In the presence of RhCl(PPh$_3$)$_3$, the dehalogenation is inhibited by addition of PPh$_3$. ^{1}H and ^{31}P-{^{1}H} NMR spectroscopy studies at variable temperature, on the behavior of the complex RhCl(PPh$_3$)$_3$ in the presence of γ-hexachlorocyclohexane and/or HSiEt$_3$, indicate that the catalytic reaction involves the initial interaction of the catalyst with the silane and that chloro−hydride intermediates related to RhH$_2$Cl(PPh$_3$)$_3$ are the main species during the catalysis. The complexes RuHCl(PPh$_3$)$_3$, RuH$_2$Cl$_2$(P^{i}Pr$_3$)$_2$, and RuHCl(η^2-H$_2$)(P^{i}Pr$_3$)$_2$ also catalyze the dehalogenation of γ-hexachlorocyclohexane and the simultaneous chlorination of HSiEt$_3$ to ClSiEt$_3$. In these cases, the dehalogenation products are 6/4 cyclohexene/cyclohexane (RuHCl(PPh$_3$)$_3$) and 4/6 cyclohexene/benzene (RuH$_2$Cl$_2$(P^{i}Pr$_3$)$_2$ and RuHCl(η^2-H$_2$)(P^{i}Pr$_3$)$_2$) mixtures. The dehalogenations of α- and δ-hexachlorocyclohexane catalyzed by RhCl(PPh$_3$)$_3$, RhH$_2$Cl(P^{i}Pr$_3$)$_2$, and RuHCl(PPh$_3$)$_3$ have been also investigated. The initial rates for the formation of ClSiEt$_3$ decrease in the sequence γ- > α- > δ-hexachlorocyclohexane.

Introduction

γ-Hexachlorocyclohexane is a noxious material.[1] Its degradation has been centered on microbiological methods[2] and incineration.[3] The latter generates highly toxic fumes and hydrogen chloride.[4] Chemical procedures are scarce.[5] They achieve dehalogenation by means of metal particles or copper-activated metal particles (Mg, Fe, Al, and Zn)[6] and by palladium on alumina in hydrogen-saturated water at room temperature and ambient pressure.[7] In all of the cases benzene is formed. As far as we know, homogeneous catalysis has not been employed as a tool for the dehalogenation of γ-hexachlorocyclohexane and its isomers.

A limited number of methods for hydrogenolysis of halogenated compounds employing homogeneous metal catalysts have been reported. These methods involve the use of molecular hydrogen,[8] alcohols,[9] cyclic amines,[10] metal hydrides,[11] metal alkoxides,[12] sodium formate,[13] sodium borohydrides,[14] alkyl Grignard reagents,[15] and hydrosilanes.[16] Among them, that based on the use of silicon hydrides has the advantage of the formation of chlorosilanes, which are valuable intermediates in the silicon industry and in organic synthesis. Despite this

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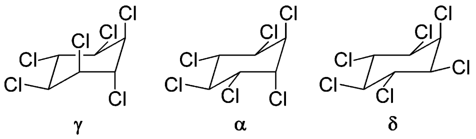
Chart 1



fact, the number of reports about the use of silicon hydrides for the dehalogenation of organic substrates is quite limited.[17]

In 1996, Chatgilialoglu and co-workers observed that the heterogeneous system formed from $PdCl_2$ and $HSiEt_3$ catalyzes the dehalogenation of a variety of organic halides.[16b] Schubert and co-workers have recently reported the dehalogenation of alkyl chlorides by $HSiMe_2Ph$ in the presence of catalytic amounts of the complex $[Ph_2PCH_2CH_2NMe_2\text{-}\kappa^2P,N]PtMeCl$ to give alkanes and $ClSiMe_2Ph$.[16d] We have shown that the homogeneous systems formed from $RhCl(PPh_3)_3$, $[Rh(\mu\text{-Cl})(COE)_2]_2/PPh_3$ (COE = cyclooctene), $RhH_2Cl(P^iPr_3)_2$, $RuHCl(PPh_3)_3$, and $HSiEt_3$ are effective in the dehalogenation of chlorobenzene and polychlorinated benzenes.[18]

We have now observed that rhodium and ruthenium complexes are also effective homogeneous catalysts for the dehalogenation of γ-hexachlorocyclohexane and its α and δ isomers (Chart 1) and the simultaneous chlorination of $HSiEt_3$. In this paper we report a mechanistic study on this catalysis, the influence of the catalyst, and the reaction conditions on the dehalogenation products and the influence of the stereochemistry of the hexachlorocyclohexane isomers on the activity of the catalysts.

Results and Discussion

1. Dehalogenation of γ-Hexachlorocyclohexane Catalyzed by Rhodium Complexes. The complexes $RhCl(PPh_3)_3$ and $RhH_2Cl(P^iPr_3)_2$ catalyze the dehalogenation of γ-hexachlorocyclohexane to benzene and the simultaneous chlorination of triethylsilane (eq 1).

$$C_6H_6Cl_6 + 6HSiEt_3 \xrightarrow[70\ ^\circ C]{\text{catalyst}} C_6H_6 + 6ClSiEt_3 + 3H_2 \tag{1}$$

The reactions were carried out under an argon atmosphere in a round flask at 70 °C, using *p*-xylene as solvent and a catalyst/γ-$C_6H_6Cl_6/HSiEt_3$ molar ratio of 1/15/108. They were followed by gas chromatography. The formation of molecular hydrogen during the reaction was confirmed by an additional experiment, in which the gas formed was confined in a closed system. Once the dehalogenation was finished, the closed system was connected to a flask containing a solution of styrene and catalytic amounts of $OsHCl(CO)(P^iPr_3)_2$ in 2-propanol.[19] After 15 min at 60 °C the solution was analyzed by GC-MS, showing a peak corresponding to ethylbenzene. A control reaction in the absence of catalyst was carried out. After 24 h at 70 °C, γ-hexachlorocyclohexane and $HSiEt_3$ were recovered from the solution. In addition, to exclude a radical process, we have performed the reaction in the absence of $RhCl(PPh_3)_3$ and in the presence of catalytic amounts of benzoyl peroxide, and again, γ-hexachlorocyclohexane and $HSiEt_3$ were recovered.

The complex $RhCl(PPh_3)_3$ is a more active catalyst than $RhH_2Cl(P^iPr_3)_2$. In the presence of $RhCl(PPh_3)_3$, γ-hexachlorocyclohexane is fully dehalogenated to benzene after 31 min, while only a 29% yield of benzene is obtained after 300 min in the presence of $RhH_2Cl(P^iPr_3)_2$.

The reactions were also studied by ^1H NMR spectroscopy, using toluene-d_8 as solvent and a catalyst/γ-$C_6H_6Cl_6/HSiEt_3$ molar ratio of 1/25/150. At 70 °C, again, benzene and $ClSiEt_3$ were the products of the reactions. In addition, a peak at 4.48 ppm was observed. It can be assigned to the molecular hydrogen released in the reaction. Partially dehalogenated cyclohexanes were not detected. Under these conditions, complex $RhCl(PPh_3)_3$ is also a more active catalyst than $RhH_2Cl(P^iPr_3)_2$. Thus, in the presence of $RhCl(PPh_3)_3$, γ-hexachlorocyclohexane is fully dehalogenated to benzene after 1 h, while only a 61% yield of benzene is obtained after 51 h in the presence of $RhH_2Cl(P^iPr_3)_2$.

These results agree well with those found for the dehalogenation of 1,2,4-trichlorobenzene to 1,2-dichlorobenzene with $HSiEt_3$. While the complex $RhH_2Cl(P^iPr_3)_2$ requires 8 h to achieve an 80% yield of $ClSiEt_3$, complex $RhCl(PPh_3)_3$ reaches 90% yield after 65 min.[18]

Since the best catalytic results were obtained with the complex $RhCl(PPh_3)_3$, we have performed spectroscopic studies on the behavior of $RhCl(PPh_3)_3$ in the presence of γ-hexachlorocyclohexane and/or $HSiEt_3$, to obtain information about the mechanism of the catalysis.

The ^1H and $^{31}P\{^1H\}$ NMR spectra of the solution resulting from heating at 70 °C for 15 min a toluene-d_8 suspension of $RhCl(PPh_3)_3$ and 3 equiv of γ-hexachlorocyclohexane show only resonances due to $RhCl(PPh_3)_3$ and γ-hexachlorocyclohexane. When the NMR tube is heated for a longer time (30 min), an orange precipitate, identified as $[Rh(\mu\text{-Cl})(PPh_3)_2]_2$, is obtained. Since this compound has been prepared on heating benzene or toluene suspensions of $RhCl(PPh_3)_3$,[20] this clearly indicates that the catalytic dehalogenation does not involve the initial reaction of complex $RhCl(PPh_3)_3$ with γ-hexachlorocyclohexane.

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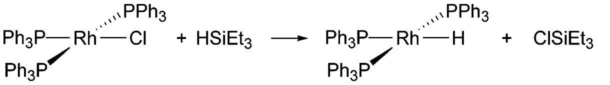
The ^1H NMR spectrum at room temperature of the orange solution resulting from heating at 70 °C for 15 min a toluene-d_8 suspension of $RhCl(PPh_3)_3$ with 2.0 equiv of $HSiEt_3$ shows a broad hydride resonance at −7.90 ppm. At −80 °C, it is converted into a double doublet of triplets by spin coupling with the rhodium ($J_{Rh-H} = 17$ Hz) and the phosphorus ($J_{P-H} = 104.7$ and 17 Hz) of the phosphine ligands. At this temperature, the $^{31}P\{^1H\}$ NMR spectrum contains a double doublet at 42.8 ppm, with P−P and P−Rh coupling constants of 24.7 and 171 Hz, and a double triplet at 37.2 ppm with a P−Rh coupling constant of 144 Hz. These data agree with those previously reported for the monohydride complex $RhH(PPh_3)_3$,[21] which is formed according to eq 2. In agreement with this, the ^1H NMR spectrum also shows peaks corresponding to $ClSiEt_3$, which was further characterized by GC-MS analysis. The formation of $ClSiR_3$ and metal−hydride complexes by reaction of chloro transition-metal compounds and silanes is a well-known elemental reaction.[22]



(2)

The reaction shown in eq 2 suggests that the first step in the dehalogenation process involves the reaction of $RhCl(PPh_3)_3$ with $HSiEt_3$ to afford the monohydride compound $RhH(PPh_3)_3$, which is an active intermediate in the catalysis. Thus, we have observed that the ^1H and $^{31}P\{^1H\}$ NMR spectra of the resulting solution from the addition at room temperature of 1.0 equiv of γ-hexachlorocyclohexane to a benzene-d_6 solution of $RhH(PPh_3)_3$ contain the characteristic resonances of $RhCl(PPh_3)_3$ and $[Rh(\mu\text{-}Cl)(PPh_3)_2]_2$. Furthermore, the GC-MS spectrum of the solution indicates the presence of $C_6H_5Cl_5$. In addition to the resonances of $RhCl(PPh_3)_3$ and $[Rh(\mu\text{-}Cl)(PPh_3)_2]_2$, the ^1H NMR spectrum shows tiny broad resonances centered at −9.38 and −16.73 ppm, whereas the $^{31}P\{^1H\}$ NMR spectrum contains a doublet at 39.4, with a P−Rh coupling constant of 115 Hz, and a broad resonance at about 20 ppm.

The ^1H NMR spectrum at room temperature of the solution resulting from heating at 70 °C for 10 min a suspension in toluene-d_8 of $RhCl(PPh_3)_3$ with 3 equiv of γ-hexachlorocyclohexane and 6 equiv of $HSiEt_3$ shows, in addition to the resonances corresponding to the substrates and products of the dehalogenation, a broad doublet centered at −9.38 ppm,with a J_{P-H} value of 152 Hz, and a broad resonance at −16.73 ppm. At −40 °C, the resonance at −9.38 ppm is converted into a complex signal with H−H and H−Rh coupling constants of 7.5 and 18.3 Hz, respectively, and H−P coupling constants of 155.4 and 12.3 Hz, while the resonance at −16.73 ppm is converted into a complex multiplet. At room temperature, the $^{31}P\{^1H\}$ NMR spectrum contains a doublet at 39.4 ppm, with a P−Rh coupling constant of 115 Hz and a broad resonance at about 20 ppm. At −40 °C, a double doublet at 39.5 ppm with P−P and P−Rh coupling constants of 19.5 and 114.8 Hz and a double triplet at 20.1 ppm with a P−Rh coupling constant of 90.8 Hz are observed. These data are similar to those previously reported for the complex $RhH_2Cl(PPh_3)_3$[23] and suggest that chloro−dihydride intermediates related to $RhH_2Cl(PPh_3)_3$ are the main species during the dehalogenation.

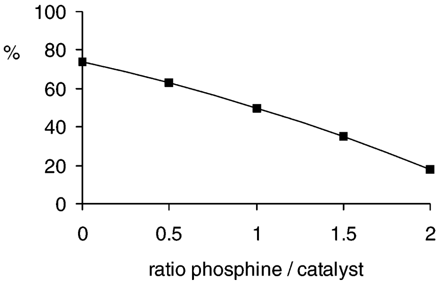
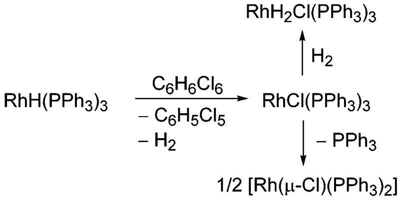


Figure 1. Influence of the phosphine added on the yield of the dehalogenation after 75 min of reaction. Conditions: 0.02 mmol of $RhCl(PPh_3)_3$; 1 mmol of γ-hexachlorocyclohexane; 7 mmol of $HSiEt_3$; 2 mL of p-xylene; 200 μL of n-octane; 60 °C.

Scheme 1



The aforementioned spectra also reveal that the reaction of $RhH(PPh_3)_3$ with γ-hexachlorocyclohexane leads, in addition to $C_6H_5Cl_5$, $RhCl(PPh_3)_3$, and $[Rh(\mu\text{-}Cl)(PPh_3)_2]_2$, to $RhH_2Cl(PPh_3)_3$. The formation of these compounds can be rationalized according to Scheme 1. Initially, complex $RhH(PPh_3)_3$ reacts with γ-hexachlorocyclohexane to give $C_6H_5Cl_5$, H_2, and $RhCl(PPh_3)_3$. The oxidative addition of molecular hydrogen to the latter affords $RhH_2Cl(PPh_3)_3$, while the dissociation of triphenylphosphine from $RhCl(PPh_3)_3$ gives rise to the dimeric species $[Rh(\mu\text{-}Cl)(PPh_3)_2]_2$.

To investigate the participation of highly unsaturated species during the catalysis, which could be generated by dissociation of phosphine, we have studied the influence of the addition of triphenylphosphine to the reaction. Figure 1 shows the yield of the dehalogenation after 75 min as a function of the phosphine/catalyst molar ratio. The extent of the reaction clearly depends on the amount of PPh_3 added. Excess phosphine has an inhibitory effect on the dehalogenation activity of $RhCl(PPh_3)_3$. This indicates that, in fact, phosphine dissociation plays an important role during the dehalogenation.

Scheme 2 shows a reaction pathway which allows us to rationalize the dehalogenation of γ−hexachlorocyclo-

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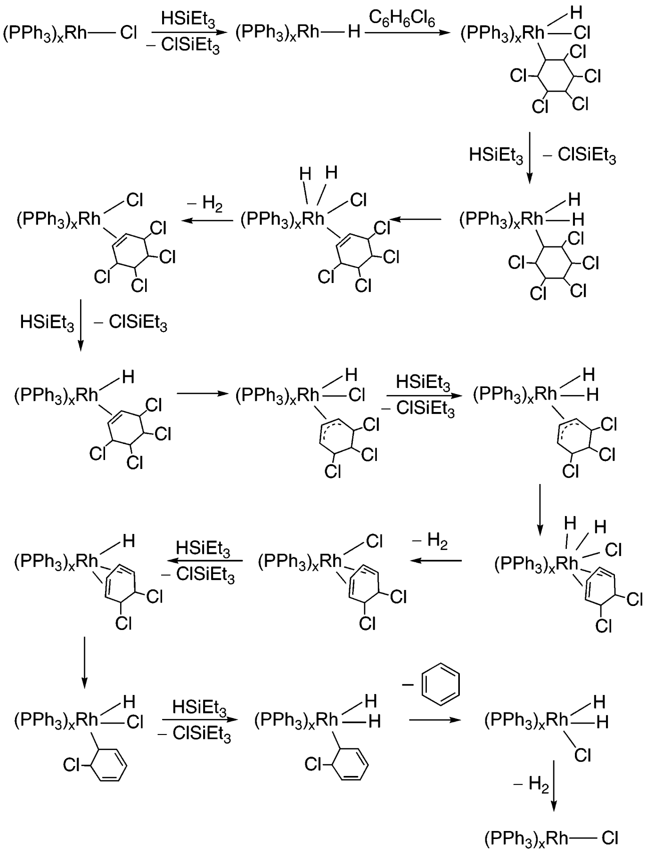
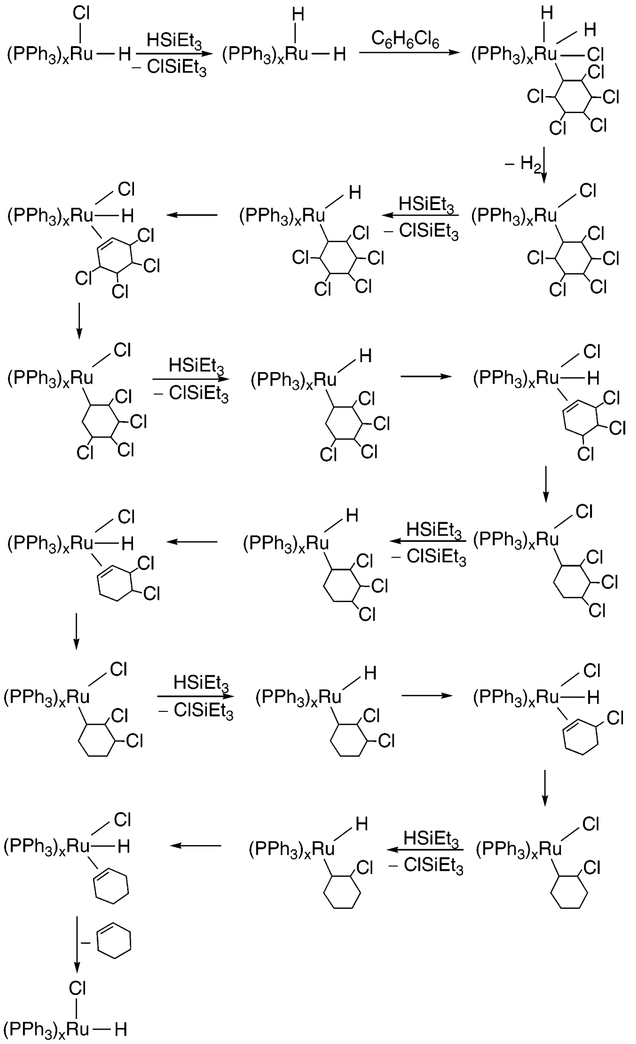
Scheme 2



Scheme 3



hexane to benzene and the simultaneous chlorination of $HSiEt_3$, as well as the previously mentioned observations. The initial reaction of $HSiEt_3$ with $RhCl(PPh_3)_3$ gives $ClSiEt_3$ and a $RhH(PPh_3)_x$ species, which by oxidative addition of one of the C−Cl bonds of γ-hexachlorocyclohexane should afford a chloro−hydride−alkyl intermediate. The oxidative addition of C−Cl bonds to unsaturated rhodium centers is a well-known process.[24] The chloro−hydride−alkyl species could generate a dihydride−alkyl intermediate upon reaction with $HSiEt_3$ and subsequent elimination of $ClSiEt_3$. Then, a β-chlorine elimination reaction should lead to a short-lived π-olefin $RhH_2Cl(\eta^2\text{-}C_6H_6Cl_4)(PPh_3)_x$ derivative, which could evolve into $RhCl(\eta^2\text{-}C_6H_6Cl_4)(PPh_3)_x$ by reductive elimination of molecular hydrogen. In this context, we note that chloride has been found to be a better leaving group than hydrogen at the β-position of palladium.[25] Successive steps involving chlorination of $HSiEt_3$, C−Cl activation, chlorination of $HSiEt_3$, C−Cl activation, and hydrogen elimination should afford a π-diolefin $RhCl(\eta^4\text{-}C_6H_6Cl_2)(PPh_3)_x$ species via allyl intermediates. Finally, a new sequence including chlorination of $HSiEt_3$, C−Cl activation, chlorination of $HSiEt_3$, and C−Cl activation should give benzene and $RhH_2Cl(PPh_3)_x$, which regenerates $RhCl(PPh_3)_x$ by reductive elimination of molecular hydrogen.

The participation of π-olefin, allyl, and π-diolefin intermediates during the catalysis is consistent with the selective formation of benzene and the absence of detectable amounts of partially chlorinated hydrocarbons. This indicates that once the molecule of γ-hexachlorocyclohexane enters in the coordination sphere of the rhodium center, it remains bonded to the metal until its complete dehalogenation. In addition, it should be noted that $RhH_2Cl(\eta^2\text{-olefin})(PPh_3)_x$ and $RhH_2Cl(\eta^4\text{-olefin})(PPh_3)_x$ species eliminate molecular hydrogen faster than they hydrogenate the bound olefins.

2. Dehalogenation of γ-Hexachlorocyclohexane Catalyzed by $RuHCl(PPh_3)_3$ and Related Ruthenium Complexes. The complex $RuHCl(PPh_3)_3$ also catalyzes the dehalogenation of γ-hexachlorocyclohexane and the simultaneous chlorination of $HSiEt_3$. In this case, the reactions were carried out under an argon atmosphere in a round flask at 70 °C, using toluene as solvent and a catalyst/γ-$C_6H_6Cl_6$/$HSiEt_3$ molar ratio of 1/25/150. Under these conditions, after 71 h, $ClSiEt_3$ was formed in 80% yield. In addition, it must be pointed out that, in contrast to $RhCl(PPh_3)_3$, cyclohexane and cyclohexene are obtained in a 4/6 molar ratio. As far as we know, the dehalogenation of γ-hexachlorocyclohexane to these products, which from an environmental point of view are certainly friendlier than benzene, has no precedent.

Scheme 3 shows a sequence of reactions that allows us to rationalize the dehalogenation of γ-hexachloro-

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[24] See, for example: Haarman, H. F.; Ernsting, J. M.; Kranenburg, M.; Kooijman, H.; Veldman, N.; Spek, A. L.; van Leeuwen, P. W. N. M.; Vrieze, K. *Organometallics* **1997**, *16*, 887.

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cyclohexane and the formation of cyclohexene. In a manner similar to $RhCl(PPh_3)_3$, the initial reaction of $RuHCl(PPh_3)_3$ with $HSiEt_3$ should afford a $RuH_2(PPh_3)_x$ dihydride species. Thus, the subsequent C−Cl activation of γ-hexachlorocyclohexane followed by the reductive elimination of molecular hydrogen could lead to a chloro−alkyl−ruthenium(II) intermediate, which should give $RuH(C_6H_6Cl_5)(PPh_3)_x$ by chlorination of $HSiEt_3$. The β-chlorine elimination on the alkyl ligand of this intermediate could afford the π-olefin $RuHCl(\eta^2\text{-}C_6H_6Cl_4)(PPh_3)_x$ species, which should evolve into a new chloro−alkyl−ruthenium(II) intermediate by insertion of the C−C double bond into the Ru−H bond. Three successive groups of steps, each involving one chlorination of $HSiEt_3$, β-chlorine elimination, and olefin insertion into one of the Ru−H bonds, should yield $RuCl(C_6H_{10}Cl)(PPh_3)_x$. The reaction of this intermediate with $HSiEt_3$ could afford $RuH(C_6H_{10}Cl)(PPh_3)_x$, which should give $RuHCl(\eta^2\text{-}C_6H_{10})(PPh_3)_x$, by a new chlorine β-elimination reaction. The dissociation of cyclohexene from this intermediate affords the olefin, regenerating the active catalyst.

Cyclohexane is the result of the hydrogenation of cyclohexene in the presence of $RuHCl(PPh_3)_3$. In this context, it should be noted that the complex $RuHCl(PPh_3)_3$ is an active catalyst for the hydrogenation of olefins.[26]

The higher tendency of the ruthenium complex $RuHCl(PPh_3)_3$ to yield dehalogenated saturated products, with regard to the rhodium derivative $RhCl(PPh_3)_3$, merits further comment. Both $RhCl(PPh_3)_3$ and $RuHCl(PPh_3)_3$ have been shown to be active catalysts for the hydrogenation of olefins. Kinetic studies have proved that, for the hydrogenation of cyclohexene catalyzed by the rhodium complex, the insertion of the C−C double bond of the olefin into a Rh−H bond of a $RhH_2Cl(\eta^2\text{-}C_6H_{10})(PPh_3)_x$ intermediate is the rate-determining step of the hydrogenation.[27] Theoretical calculations have also shown that the intramolecular migratory alkene insertion to give $RhH(C_2H_5)Cl(PH_3)_2$ is exothermic and is the rate-determining step for the catalytic cycle.[28] On the other hand, for the hydrogenation of olefins catalyzed by $RuHCl(PPh_3)_3$, the oxidative addition of molecular hydrogen to a $Ru(alkyl)Cl(PPh_3)_2$ intermediate is the rate-determining step of the catalysis.[26,29] The insertion of the C−C double bond of the olefin into the Ru−H bond of $RuHCl(\eta^2\text{-olefin})(PPh_3)_2$ is fast. Even at high alkene/phosphine molar ratios, $Ru(alkyl)Cl(PPh_3)_2$ intermediates are the main metallic species in the catalytic solutions.[29b]

The results from the kinetic studies on the mechanisms of the hydrogenation of olefins catalyzed by $RhCl(PPh_3)_3$ and $RuHCl(PPh_3)_3$ indicate that, for the rhodium complex, the insertion of the olefin into a Rh−H bond of $RhH_2Cl(\eta^2\text{-olefin})(PPh_3)_2$ is unfavorable with regard to the other steps, while for $RuHCl(PPh_3)_3$, the insertion of the olefin bond into the Ru−H bond of $RuHCl(\eta^2\text{-olefin})(PPh_3)_2$ is favored with regard to the other steps of the hydrogenation.

Table 1. Dehalogenation of γ-Hexachlorocyclohexane and Simultaneous Chlorination of $HSiEt_3$ Catalyzed by Ruthenium Complexes[a]

catalyst	time (h)	yield (%)[b]	products of the dehalogenation (%)		
			C_6H_{12}	C_6H_{10}	C_6H_6
$RuHCl(PPh_3)_3$	71	80	40	60	
$RuH_2Cl_2(P^iPr_3)_2$	94	77		40	60
$RuHCl(\eta^2\text{-}H_2)(P^iPr_3)_2$	175	81		36	64

[a] Conditions: 70 °C; 4 × 10^{-2} mmol of catalyst; 1 mmol of γ-$C_6H_6Cl_6$; 6 mmol of $HSiEt_3$; 4 mL of toluene. [b] Percentage of $HSiEt_3$ converted into $ClSiEt_3$.

The elemental steps involved in the dehalogenation of γ-hexachlorocyclohexane to cyclohexene and cyclohexane are not significantly different from those involved in the hydrogenation of olefins, and at first glance, one should expect the same trend. Thus, the difference in behavior between $RhH_2Cl(\eta^2\text{-olefin})(PPh_3)_2$ and $RuHCl(\eta^2\text{-olefin})(PPh_3)_2$—the first of them eliminates H_2 (Scheme 2), while the second one inserts the olefin into the Ru−H bond (Scheme 3)—can explain why the dehalogenation of γ-hexachlorocyclohexane in the presence of $RhCl(PPh_3)_3$ yields benzene, while in the presence of $RuHCl(PPh_3)_3$ cyclohexene and cyclohexane are obtained.

The complexes $RuH_2Cl_2(P^iPr_3)_2$ and $RuHCl(\eta^2\text{-}H_2)(P^iPr_3)_2$ also catalyze the dehalogenation of γ-hexachorocyclohexane and the simultaneous chlorination of $HSiEt_3$. However, under the same conditions, they are less active than $RuHCl(PPh_3)_3$ (Table 1). Furthermore, the behavior of these compounds is intermediate between that of $RuHCl(PPh_3)_3$ and that of $RhCl(PPh_3)_3$. As for the rhodium complex, one of the dehalogenation products is benzene and, as for $RuHCl(PPh_3)_3$, the other product is cyclohexene. In agreement with the tendency of these ruthenium systems to catalyze the hydrogenation of olefins, when the reactions are carried out in a sealed NMR tube, cyclohexane is obtained instead of cyclohexene.

3. Dehalogenation of α- and δ-Hexachlorocyclohexane Catalyzed by $RhCl(PPh_3)_3$, $RhH_2Cl(P^iPr_3)_2$, and $RuHCl(PPh_3)_3$. The complexes $RhCl(PPh_3)_3$, $RhH_2Cl(P^iPr_3)_2$, and $RuHCl(PPh_3)_3$ catalyze not only the dehalogenation of γ-hexachlorocyclohexane but also the dehalogenation of its α and δ isomers. The catalysis was also carried out under an argon atmosphere and in a round flask. In this case the solvent employed was *p*-xylene and the catalyst/$C_6H_6Cl_6$/$HSiEt_3$ molar ratio used was 1/15/108. The reactions in the presence of $RhCl(PPh_3)_3$ and $RhH_2Cl(P^iPr_3)_2$ lead, in both cases, to benzene and $ClSiEt_3$, while those catalyzed by $RuHCl(PPh_3)_3$ afford a 6/4 cyclohexene/cyclohexane mixture and $ClSiEt_3$.

Table 2 summarizes the reaction yields. As for the dehalogenation of γ-hexachlorocyclohexane, $RhCl(PPh_3)_3$ is the most active of the three catalysts studied. Under the employed conditions, γ-hexachlorocyclohexane is dehalogenated into benzene in 100% yield after 31 min. The same yield for the dehalogenation of the α isomer is obtained after 211 min, whereas with the δ isomer as the starting material, benzene is formed

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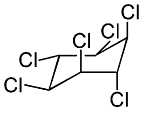
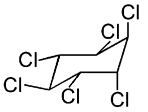
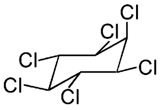
Table 2. Dehalogenation of γ-, α-, and δ-Hexachlorocyclohexane and Simultaneous Chlorination of $HSiEt_3$ Catalyzed by $RhCl(PPh_3)_3$, $RuHCl(PPh_3)_3$, and $RhH_2Cl(P^iPr_3)_2$[a]

isomer	$RhCl(PPh_3)_3$		$RuHCl(PPh_3)_3$		$RhH_2Cl(P^iPr_3)_2$	
	time (min)	% $ClSiEt_3$	time (min)	% $ClSiEt_3$	time(min)	% $ClSiEt_3$
 γ	31	100	300	40	300	29
 α	211	100	300	18	300	21
 δ	371	74	300	9	300	15

[a] Conditions: 70 °C, *p*-xylene (2 mL) as solvent, 1 mmol of $C_6H_6Cl_6$; 7 mmol of $HSiEt_3$; 7×10^{-2} mmol of catalyst; 200 μL of *n*-octane.

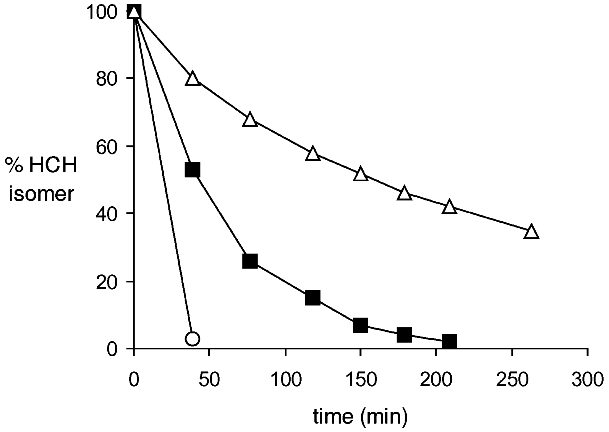


Figure 2. Dehalogenation of hexachlorocyclohexanes catalyzed by $RhCl(PPh_3)_3$ as a function of time: (○) γ isomer; (■) α isomer; (△) δ isomer.

in 74% yield after 371 min. Although the extent of the dehalogenation reactions is lower than in the presence of $RhCl(PPh_3)_3$, a similar trend is observed when $RuHCl(PPh_3)_3$ is used as catalyst. Thus, after 300 min, 40% of the γ isomer was dehalogenated, while only 18 and 9% of the α and δ isomers, respectively, were achieved. When the catalyst used is $RhH_2Cl(P^iPr_3)_2$, the sequence of the dehalogenation is the same, giving after 300 min of reaction a conversion of the hexachlorocyclohexanes to benzene of 29, 21, and 15%, respectively.

Figure 2 shows the course of the dehalogenation reactions as a function of time when $RhCl(PPh_3)_3$ is used as catalyst. In agreement with the results collected in Table 2, the initial rates of the dehalogenation reaction decrease in the sequence γ- > α- > δ-hexachlorocyclohexane, as the number of chlorine atoms at axial positions of the most favorable conformations of the isomers decreases (γ, aaaeee; α, aaeeee; δ, aeeeee; a = axial, e = equatorial). This suggests that the chlorine atoms at axial positions of the minimum energy conformation are more easily dehalogenated than those located in equatorial positions.

In addition, it should be mentioned that the rates and extents of these reactions are unaffected by the presence of hydroquinone, suggesting that in the dehalogenation of the hexachlorocyclohexanes and in the simultaneous chlorination of $HSiEt_3$, the participation of radical-like species as catalytic intermediates is not significant.

Concluding Remarks

This study reveals that rhodium and ruthenium complexes, mainly $RhCl(PPh_3)_3$ and $RuHCl(PPh_3)_3$, catalyze the dehalogenation of γ- (lindane), α-, and δ-hexachlorocyclohexane and the simultaneous chlorination of $HSiEt_3$.

Spectroscopic studies on the behavior of the complex $RhCl(PPh_3)_3$ in the presence of γ-hexachlorocyclohexane and/or $HSiEt_3$ indicate that the catalytic reaction involves the initial interaction of the catalyst with the silane to give $RhH(PPh_3)_3$ and that chloro−hydride intermediates related to $RhH_2Cl(PPh_3)_3$ ($RuHCl(PPh_3)_3$ in the ruthenium case) are the main species during the catalysis.

The products of the dehalogenation reactions show a strong dependence on the metallic center of the catalysts. Thus, while benzene is the dehalogenation product when the complex $RhCl(PPh_3)_3$ is used as catalyst, a mixture of cyclohexene and cyclohexane is obtained in the presence of the ruthenium derivative $RuHCl(PPh_3)_3$.

The rate of the dehalogenation, which is inhibited by addition of phosphine to the catalytic solutions, depends on the metallic center of the catalyst and on the position of the chlorine atoms in the hexachlorocyclohexane isomers. Rhodium complexes are more active catalysts than the ruthenium compounds. For both rhodium and ruthenium catalysts, chlorine atoms at the axial positions of the minimum energy conformation of the hexachlorocyclohexane isomer are more easily dehalogenated than those situated in equatorial positions. Thus, the initial rate of the dehalogenation decreases in the sequence γ- > α- > δ-hexachlorocyclohexane.

Experimental Section

All manipulations were carried out with rigorous exclusion of air using standard Schlenk techniques. Solvents were dried by known procedures and distilled under argon prior to use. Triethylsilane, *n*-octane, and the hexachlorocyclohexane isomers were used without further purification. $RhCl(PPh_3)_3$,[20] $RhH_2Cl(P^iPr_3)_2$,[30] $RuHCl(PPh_3)_3$,[31] and $RuH_2Cl_2(P^iPr_3)_2$[32] were prepared by published procedures. $RuHCl(\eta^2\text{-}H_2)(P^iPr_3)_2$ was prepared using a procedure similar to that described for $RuHCl(\eta^2\text{-}H_2)(P^tBu_2Me)_2$.[33] The analysis of the products of the reactions was carried out on a Hewlett-Packard 6890 series gas chromatograph with a flame ionization detector, using a 100% cross-linked methyl silicone gum column (30 m × 0.25 mm, with 0.25 μm film thickness) and *n*-octane as the internal standard. The oven conditions used are as follows: 35 °C (hold 6 min) to 280 °C at 25 °C/min (hold 4 min). The reaction products were identified by comparison of their retention times with those observed for pure samples. GC-MS experiments were run on an Agilent 5973 mass selective detector interfaced to an Agilent 6890 series gas chromatograph system. Samples were injected into a 30 m × 250 μm HP-5MS 5% phenyl methyl siloxane column with a film thickness of 0.25 μm (Agilent). The GC oven temperature was programmed as follows: 35 °C for 6 min, 35 °C to 280 °C at 25 °C/min, 280 °C for 4 min. The carrier gas was helium at a flow of 1 mL/min. ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded either on a Varian Gemini 2000 or on a Bruker AXR 300 instrument. Chemical shifts are referenced to residual solvent peaks (^1H) or external H_3PO_4 (^{31}P).

Catalytic Dehalogenation in a Round Flask: General Procedure. The dehalogenation reactions were carried out in a two-necked flask fitted with a condenser and containing a magnetic stirring bar. The second neck was capped with a Suba seal to allow samples to be removed by syringe without opening the system. Two reaction conditions were used.

(a) A 0.07 mmol portion of catalyst was dissolved in 2 mL of a *p*-xylene solution contaning 1 mmol of hexachlorocyclohexane, 7 mmol of triethylsilane, and 200 μL of *n*-octane. The flask was then immersed in a bath at 70 °C, and the solution was magnetically stirred. The reactions were periodically checked by GC.

(b) A 0.04 mmol portion of catalyst was dissolved in 4 mL of a toluene solution contaning 1 mmol of hexachlorocyclohexane, 6 mmol of triethylsilane, and 200 μL of *n*-octane. The flask was then immersed in a bath at 70 °C, and the solution was magnetically stirred. The reactions were periodically checked by GC and/or GC-MS.

Catalytic Dehalogenation in an NMR Tube: General Procedure. The catalyst (4×10^{-3} mmol), γ-hexachlorocyclohexane (0.1 mmol), and $HSiEt_3$ (0.6 mmol) were dissolved in toluene-d_8 (0.4 mmol), and the tube was then immersed in a bath at 70 °C. The samples were periodically checked by ^1H NMR spectroscopy. The ^1H NMR spectra show a triplet (δ 0.91, $J_{H-H} = 8$ Hz, $-CH_3$) and a quartet (δ 0.61, $J_{H-H} = 8$ Hz, $-CH_2-$), assigned to $ClSiEt_3$ by comparison with a pure sample. In addition, the ^1H NMR spectra show peaks assigned to benzene at 7.17 ppm and/or cyclohexane at 1.58 ppm.

Reaction of $RhCl(PPh_3)_3$ with $HSiEt_3$: Formation of $RhH(PPh_3)_3$. A suspension in toluene of $RhCl(PPh_3)_3$ (100 mg, 0.108 mmol) was treated with $HSiEt_3$ (43 μL, 0.27 mmol). The resulting suspension was heated at 70 °C for 15 min, giving an orange solution that was evaporated to dryness. Addition of pentane afforded an orange yellowish solid that was washed with pentane. The solid is oxygen sensitive both in solution and in the solid state. The mass spectrum of the mother liquors shows the presence of $ClSiEt_3$. ^1H NMR (300 MHz, toluene-d_8, 20 °C): δ 7.58−6.85 (m, 45H, PPh_3), −7.90 (br, 1H, Rh−H). ^1H NMR (300 MHz, toluene-d_8, −80 °C): δ 7.60−6.90 (m, 45H, PPh_3), −7.90 (ddt, $J_{Rh-H} = 17$, $J_{P(trans)-H} = 104.7$, $J_{P(cis)-H} = 17$, 1H, Rh−H). $^{31}P\{^1H\}$ NMR (121.4 MHz, toluene-d_8, 20 °C): δ 42.2 (d, $J_{Rh-P} = 156$). $^{31}P\{^1H\}$ NMR (121.4 MHz, toluene-d_8, −80 °C): δ 42.8 (dd, $J_{P-P} = 24.7$, $J_{Rh-P} = 171$), 37.2 (dt, $J_{Rh-P} = 144$, $J_{P-P} = 24.7$).

Reaction of $RhH(PPh_3)_3$ with γ-Hexachlorocyclohexane. In an NMR tube, the stoichiometric amount of γ-hexachlorocyclohexane (6.5 mg, 2.2×10^{-2} mmol) was added to a solution of $RhH(PPh_3)_3$ (20 mg, 2.2×10^{-2} mmol) in benzene-d_6 (0.4 mL). After 10 min, the ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded. The $^{31}P\{^1H\}$ NMR spectrum shows peaks corresponding to $RhCl(PPh_3)_3$, $[Rh(\mu\text{-}Cl)(PPh_3)_2]_2$, and $RhH_2Cl(PPh_3)_3$. In addition, there is an orange precipitate ($[Rh(\mu\text{-}Cl)(PPh_3)_2]_2$) at the bottom of the NMR tube. GC-MS analyses show the formation of $C_6H_5Cl_5$.

Reaction of $RhCl(PPh_3)_3$ with $HSiEt_3$ and γ-Hexachlorocyclohexane: Formation of $RhH_2Cl(PPh_3)_3$. $RhCl(PPh_3)_3$ (10 mg, 1.1×10^{-2} mmol), γ-$C_6H_6Cl_6$ (9.4 mg, 3.2×10^{-2} mmol) and $HSiEt_3$ (103 μL, 6.5×10^{-2} mmol) were mixed in an NMR tube (0.4 mL, toluene-d_8), and the resulting suspension was heated at 70 °C for 10 min, giving an orange yellowish solution. ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded after this time. ^1H NMR (300 MHz, toluene-d_8, 20 °C): δ 8.00−6.80 (m, 45H, PPh_3), −9.38 (br d, $J_{P-H} = 152$, 1H, Rh−H), −16.73 (br, 1H, Rh−H). ^1H NMR (300 MHz, toluene-d_8, −40 °C): δ 8.00−6.80 (m, 45H, PPh_3), −9.38 (dddt, $J_{P(trans)-H} = 155.4$, $J_{P(cis)-H} = 12.3$, $J_{Rh-H} = 18.3$, $J_{H-H} = 7.5$, 1H, Rh−H), −16.67 (m, 1H, Rh−H). $^{31}P\{^1H\}$ NMR (121.4 MHz, toluene-d_8, 20 °C): δ 39.4 (d, $J_{P-Rh} = 115$), 20.0 (br). $^{31}P\{^1H\}$ NMR (121.4 MHz, toluene-d_8, −40 °C): δ 39.5 (dd, $J_{P-P} = 19.5$, $J_{P-Rh} = 114.8$), 20.1 (dt, $J_{P-Rh} = 90.8$, $J_{P-P} = 19.5$). On the GC-MS of this sample, apart from $HSiEt_3$ and γ-$C_6H_6Cl_6$, peaks of C_6H_6 and $ClSiEt_3$ are observed.

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