

# Simultaneous Dehalogenation of Polychloroarenes and Chlorination of HSiEt<sub>3</sub> Catalyzed by Complexes of the Groups 8 and 9

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The catalytic activity of the complexes FeCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, RuHCl(PPh<sub>3</sub>)<sub>3</sub>, RuH<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>3</sub>, RuHCl(CO)(AsPh<sub>3</sub>)<sub>3</sub>, RuHCl(CO)(P<sup>i</sup>Pr)<sub>2</sub>, OsHCl(CO)(P<sup>i</sup>Pr)<sub>2</sub>, OsH<sub>2</sub>Cl<sub>2</sub>(P<sup>i</sup>Pr)<sub>2</sub>, CoCl(PPh<sub>3</sub>)<sub>3</sub>, RhH<sub>2</sub>Cl(P<sup>i</sup>Pr)<sub>2</sub>, IrH<sub>2</sub>Cl(P<sup>i</sup>Pr)<sub>2</sub>, IrCl(PPh<sub>3</sub>)<sub>3</sub>, and IrH<sub>2</sub>(SiEt<sub>3</sub>)(COD)(PCy<sub>3</sub>) (COD = 1,5-cyclooctadiene) in the simultaneous dehalogenation of 1,2,4-trichlorobenzene and the chlorination of HSiEt<sub>3</sub> has been studied. The 3d metal complexes and the derivative IrH<sub>2</sub>(SiEt<sub>3</sub>)(COD)(PCy<sub>3</sub>) are unactive, while the 4d and 5d metal compounds simultaneously catalyze the dehalogenation of 1,2,4-trichlorobenzene and the chlorination of HSiEt<sub>3</sub>. The osmium and iridium derivatives are less effective catalysts than the derivatives of ruthenium and rhodium and undergo deactivation. Complexes RuHCl(PPh<sub>3</sub>)<sub>3</sub> and RhH<sub>2</sub>Cl(P<sup>i</sup>Pr)<sub>2</sub> also catalyze the dehalogenation of 1,2-, 1,3-, and 1,4-dichlorobenzene and chlorobenzene. The dehalogenation of 1,3- and 1,4-dichlorobenzene is favored over the dehalogenation of the 1,2-isomer. © 2000 Academic Press

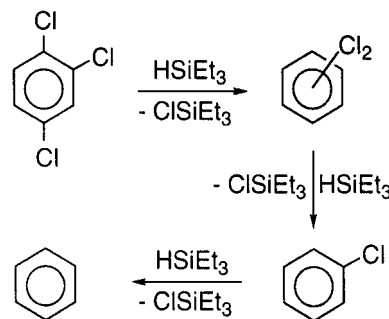
**Key Words:** homogeneous catalysis; polychloroarenes dehalogenation; HSiEt<sub>3</sub> chlorination; Rh catalyst; Ru catalyst.

## 1. INTRODUCTION

The accumulation of chloroarenes in the environment implies a serious health hazard, and their dehalogenation must be, therefore, a target with high priority. However, as result of the effort in this field (1–4), only a limited number of methods for hydrogenolysis of chloroarenes employing homogeneous metal catalysts have been reported up to now. These methods involve the use of molecular hydrogen (5–7), alcohols (8), cyclic amines (9), magnesium dihydride (10), sodium hydride (11), sodium formate (12), and alkyl Grignard reagents (13) as hydrogen source.

In 1996, Chatgililoglu and co-workers (14) found that the heterogeneous system formed from PdCl<sub>2</sub> and HSiEt<sub>3</sub> catalyzed the dehalogenation of chlorobenzene. Recently, we have observed that the homogeneous system formed from RhCl(PPh<sub>3</sub>)<sub>3</sub> or [Rh(μ-Cl)(COE)<sub>2</sub>]<sub>2</sub>/PPh<sub>3</sub> (COE = cyclooctene) and HSiEt<sub>3</sub> catalyzes not only the

dehalogenation of chlorobenzene but also the sequential hydrogenolysis of 1,2,4-trichlorobenzene, 1,2-, 1,3-, and 1,4-dichlorobenzene (15). With regard to the previously mentioned methods, the use of HSiEt<sub>3</sub> as hydrogen source has the advantage of the formation of ClSiEt<sub>3</sub> (Scheme 1), which is a valuable intermediate in the silicon industry and a useful reagent in organic synthesis.

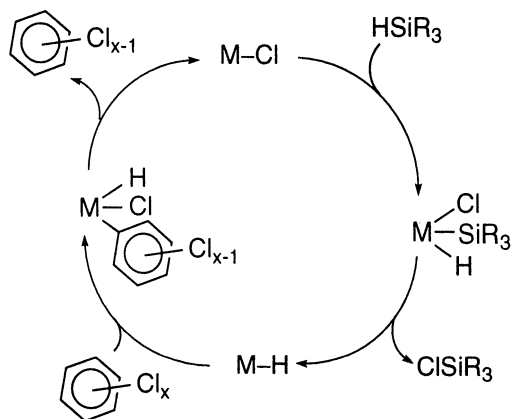


SCHEME 1

The chlorination of silicon hydrides has attracted considerable attention. Organosilicon halides have been prepared by metal-catalyzed chlorination of silicon hydrides with acid chlorides, CCl<sub>4</sub>, HCl, and alkyl halides (16–21). Kunai, Ishikawa, and co-workers (22, 23) have recently observed that the treatment of organohydrosilanes with 2 equiv of CuCl<sub>2</sub> in the presence of CuI also gives organochlorosilanes in high yield.

From the mechanistic point of view, both the hydrogenolysis of polychloroarenes with HSiEt<sub>3</sub> and the chlorination of HSiEt<sub>3</sub> with chloroarenes could be rationalized according to Scheme 2, which shows oxidative addition processes of H–Si and Cl–aryl bonds, and reductive elimination reactions of ClSiEt<sub>3</sub> and arenes on a transition metal compound. Since the above-mentioned elemental steps are common to several homogeneous catalytic processes, which are catalyzed by a variety of coordination complexes of metals of the groups 8 and 9, one should expect that the reactions shown in Scheme 1 were also catalyzed by compounds

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SCHEME 2

related to the ones used in other catalytic reactions involving elementary steps similar to those shown in Scheme 2. This prompted us to carry out the present study.

In this paper, we report the catalytic activity, in the simultaneous dehalogenation of polychloroarenes and chlorination  $\text{HSiEt}_3$ , of coordination complexes of metals of the groups 8 and 9, which are also active catalysts for the reduction and/or the hydrosilylation of unsaturated molecules (24–28).

## 2. EXPERIMENTAL

### 2.1. General Considerations

All manipulations were conducted with rigorous exclusion of air. 1,2,4-Trichlorobenzene, 1,2-dichlorobenzene, 1,3-dichlorobenzene, and chlorobenzene were dried by known procedures and distilled prior to use. Triethylsilane, *n*-octane, and 1,4-dichlorobenzene were used without further purification. The complexes  $\text{FeCl}_2(\text{PPh}_3)_2$  (29),  $\text{RuHCl}(\text{PPh}_3)_3$  (30),  $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$  (31),  $\text{RuHCl}(\text{CO})(\text{P}^i\text{Pr}_3)_2$  (32),  $\text{OsHCl}(\text{CO})(\text{P}^i\text{Pr}_3)_2$  (32),  $\text{OsH}_2\text{Cl}_2(\text{P}^i\text{Pr}_3)_2$  (33),  $\text{CoCl}(\text{PPh}_3)_3$  (34),  $\text{RhH}_2\text{Cl}(\text{P}^i\text{Pr}_3)_2$  (35),  $\text{IrH}_2\text{Cl}(\text{P}^i\text{Pr}_3)_2$  (35),  $\text{IrCl}(\text{PPh}_3)_3$  (36), and  $\text{IrH}_2(\text{SiEt}_3)(\text{COD})(\text{PCy}_3)$  (37) were prepared by published procedures. Compound  $\text{RuHCl}(\text{CO})(\text{AsPh}_3)_3$  was prepared using a procedure similar to the one described for  $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$  (31), starting from  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  (0.26 g, 1 mmol) and  $\text{AsPh}_3$  (1.827 g, 6 mmol), and giving 700 mg (65%) of a yellow solid. Anal. Calcd for  $\text{C}_{55}\text{H}_{46}\text{As}_3\text{ClORu}$ : C, 60.93; H, 4.28. Found: C, 60.70; H, 4.20. IR (Nujol,  $\text{cm}^{-1}$ ):  $\nu(\text{CO})$  1951 (s),  $\nu(\text{Ru-H})$  1915 (m).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 20°C):  $\delta$  7.60–6.90 (m, 45 H,  $\text{AsPh}_3$ ), –8.68 (s, 1H, Ru-H).

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  $\times$  0.25 mm, with 0.25  $\mu\text{m}$  film thickness) and *n*-octane as the internal standard. The

oven conditions were 35°C (hold 6 min) to 110°C at 7°C/min (hold 4 min). The reaction products were identified by comparison of their retention times with those observed for pure samples.

### 2.2. Procedure

The dehalogenation reactions were carried out at constant temperature 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 sets of reaction conditions were used: (i) with the polychloroarene as solvent and (ii) with *p*-xylene as solvent.

(i) A 0.063 mmol amount of the corresponding catalyst was dissolved in 3 ml of a polychloroarene solution containing 2.4 mmol of triethylsilane and 150 mg of *n*-octane. The flask was then immersed in a bath at 98°C, and the reaction solution was magnetically stirred.

(ii) A 0.063 mmol amount of the corresponding catalyst was dissolved in 3 ml of a *p*-xylene solution containing 3.9 g of 1,4-dichlorobenzene, 2.4 mmol of triethylsilane, and 150 mg of *n*-octane. The flask was then immersed in a bath at 98°C, and the reaction solution was magnetically stirred.

*Homogeneity test.* The experimental procedure was similar to the one already described (i), but mercury (1 ml) was added to the solution at the beginning of the run.

## 3. RESULTS AND DISCUSSION

### 3.1. Screened Compounds

Table 1 shows the complexes studied in the dehalogenation of 1,2,4-trichlorobenzene with  $\text{HSiEt}_3$ , and their catalytic activities. The reactions were carried out at 98°C using the polychloroarene as solvent and a  $\text{HSiEt}_3$ /catalyst molar ratio of 38. The reaction products are dichlorobenzenes and  $\text{ClSiEt}_3$  in all cases. The formation of other products is not observed.

The iron compound  $\text{FeCl}_2(\text{PPh}_3)_2$  is prepared by reaction of anhydrous ferrous chloride with triphenylphosphine in boiling toluene (29). As far as we know, for this complex, significant catalytic properties have not been previously reported, in agreement with its null activity in the dehalogenation of 1,2,4-trichlorobenzene. In contrast to  $\text{FeCl}_2(\text{PPh}_3)_2$ , the hydride–ruthenium(II) complex  $\text{RuHCl}(\text{PPh}_3)_3$ , which is an active catalyst for the reduction of olefins, alkynes, polynuclear heteroaromatic compounds, and nitro compounds (24, 38–40), shows the highest activity of all the studied complexes.

The dihydride–carbonyl derivative  $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$  also shows a significant activity for the hydrogenolysis of 1,2,4-trichlorobenzene. Thus, 65% of  $\text{ClSiEt}_3$  is formed after 19 h. Previously, this complex has been found to be

TABLE 1  
Relationship of Compounds Screened for the Simultaneous Dehalogenation of 1,2,4-Trichlorobenzene and Chlorination of HSiEt<sub>3</sub>

Entry	Compound	Products	Time (h)	% ClSiEt <sub>3</sub>
1	FeCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	—	96	0
2	RuHCl(PPh <sub>3</sub> ) <sub>3</sub>	1,2-, 1,3-, 1,4-DCB (52, 26, 22)	7	96
3	RuH <sub>2</sub> (CO)(PPh <sub>3</sub> ) <sub>3</sub>	1,2-, 1,3-, 1,4-DCB (56, 28, 16)	19	65
4	RuHCl(CO)(P <sup>i</sup> Pr <sub>3</sub> ) <sub>2</sub>	1,2-, 1,3-, 1,4-DCB (47, 23, 30)	15	13
5	RuHCl(CO)(AsPh <sub>3</sub> ) <sub>3</sub>	1,2-, 1,3-, 1,4-DCB (43, 22, 35)	22	30
6	OsHCl(CO)(P <sup>i</sup> Pr <sub>3</sub> ) <sub>2</sub>	1,2-, 1,3-, 1,4-DCB (50, 25, 25)	6.5	8
7	OsH <sub>2</sub> Cl <sub>2</sub> (P <sup>i</sup> Pr <sub>3</sub> ) <sub>2</sub>	1,2-, 1,3-, 1,4-DCB (50, 25, 25)	6.25	10
8	CoCl(PPh <sub>3</sub> ) <sub>3</sub>	1,2-, 1,3-, 1,4-DCB (80, 10, 10)	6	<2 <sup>a</sup>
9	RhH <sub>2</sub> Cl(P <sup>i</sup> Pr <sub>3</sub> ) <sub>2</sub>	1,2-DCB	8	80
10	IrH <sub>2</sub> Cl(P <sup>i</sup> Pr <sub>3</sub> ) <sub>2</sub>	1,2-, 1,3-, 1,4-DCB (25, 40, 35)	8	4
11	IrCl(PPh <sub>3</sub> ) <sub>3</sub>	1,2-, 1,3-, 1,4-DCB (40, 20, 40)	25	5 <sup>b</sup>
12	IrH <sub>2</sub> (SiEt <sub>3</sub> )(cod)(PCy <sub>3</sub> )	—	20	0

Conditions: 98°C, 3 ml of 1,2,4-trichlorobenzene, 2.4 mmol of HSiEt<sub>3</sub>, 0.063 mmol of catalyst. Percentages of each product are given in parentheses.

<sup>a</sup> After 70 h of reaction the yield of ClSiEt<sub>3</sub> is 5% (1,2-DCB, 60%; 1,3-DCB, 20%; 1,4-DCB, 20%).

<sup>b</sup> After 43 h of reaction the yield of ClSiEt<sub>3</sub> is 12% (1,2-DCB, 42%; 1,3-DCB, 16%; 1,4-DCB, 42%).

an active catalyst for C–C coupling reactions. It catalyzes the dimerization of *tert*-butylacetylene to (*Z*)-1,4-di-*tert*-butylbutatriene (41) or the C–C coupling of aromatic and heteroaromatic ketones with olefins to give the corresponding *ortho*-alkylated aromatic ketones with high regioselectivity (42). The method has been applied to the regioselective introduction of a side chain to tricyclic terpenoid (43, 44) and to the copolymerization of various terminal dienes with acetophenone (45–50). The same type of reaction with esters also gives alkylated products (51).

The monohydride–carbonyl compound RuHCl(CO)(AsPh<sub>3</sub>)<sub>3</sub> containing arsine instead of phosphine ligands is also an active catalyst. However, its activity is lower than that of RuH<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>3</sub>. The five-coordinate monohydride–carbonyl complex RuHCl(CO)(P<sup>i</sup>Pr<sub>3</sub>)<sub>2</sub> is also active for the dehalogenation of 1,2,4-trichlorobenzene.

Although the catalytic activity of RuHCl(CO)(P<sup>i</sup>Pr<sub>3</sub>)<sub>2</sub> is the lowest of the ruthenium compounds studied, this complex is a more efficient catalyst than the analogous osmium(II) derivative OsHCl(CO)(P<sup>i</sup>Pr<sub>3</sub>)<sub>2</sub>. Initially, the activity of both compounds is similar. However, the osmium complex undergoes a deactivation process as the catalytic reaction is in progress. The six-coordinate dihydride–dichloro–osmium(IV) compound OsH<sub>2</sub>Cl<sub>2</sub>(P<sup>i</sup>Pr<sub>3</sub>)<sub>2</sub> shows a behavior similar to that of OsHCl(CO)(P<sup>i</sup>Pr<sub>3</sub>)<sub>2</sub>.

There are precedents showing differences between the catalytic properties of RuHCl(CO)(P<sup>i</sup>Pr<sub>3</sub>)<sub>2</sub> and OsHCl(CO)(P<sup>i</sup>Pr<sub>3</sub>)<sub>2</sub>. For example, the RuHCl(CO)(P<sup>i</sup>Pr<sub>3</sub>)<sub>2</sub>-catalyzed hydrosilylation of phenylacetylene affords *cis*-PhCH=CHSiEt<sub>3</sub> with high regio- and stereoselectivity (52), while under the same conditions the OsHCl(CO)(P<sup>i</sup>Pr<sub>3</sub>)<sub>2</sub>-catalyzed reaction yields a mixture of *cis*- and *trans*-PhCH=CHSiEt<sub>3</sub> (53). In contrast with the hydrosilylation

of phenylacetylene, the hydrogenation reactions of phenylacetylene (54) and benzylideneacetone (55) in the presence of the osmium catalyst proceed with high selectivities toward the formation of styrene and 4-phenylbutan-2-one, respectively. The related complex OsH<sub>2</sub>Cl<sub>2</sub>(P<sup>i</sup>Pr<sub>3</sub>)<sub>2</sub> is also an active catalyst for the hydrogenation of olefins, diolefins, and  $\alpha,\beta$ -unsaturated ketones (33). However, attempts to hydrogenate phenylacetylene showed a rapid deactivation of the catalyst due to the formation of a hydride–carbyne derivative (56).

For the dehalogenation of 1,2,4-trichlorobenzene, the previously mentioned results indicate that, in the iron triad, ruthenium gives rise to better catalysts than osmium, and the latter better than iron. The data collected in Table 1 show that the group 9 metals behave in a similar fashion.

The cobalt complex CoCl(PPh<sub>3</sub>)<sub>3</sub> is a very poor catalyst. Furthermore, it undergoes deactivation as it is converted into CoCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>. The related iridium derivative IrCl(PPh<sub>3</sub>)<sub>3</sub> also undergoes deactivation, but is slightly more active than CoCl(PPh<sub>3</sub>)<sub>3</sub>. Both complexes are much less efficient than the Wilkinson's catalyst RhCl(PPh<sub>3</sub>)<sub>3</sub> (90% of Et<sub>3</sub>SiCl after 1 h) (15).

The iridium complex IrCl(PPh<sub>3</sub>)<sub>3</sub> is also practically unreactive in the hydrogenation of olefins. Although it reacts readily with molecular hydrogen to form the stable dihydride IrH<sub>2</sub>Cl(PPh<sub>3</sub>)<sub>3</sub> (57), under normal conditions phosphine is not dissociated from the dihydride and coordination of the substrate is thus impeded. The related complex IrH<sub>2</sub>Cl(P<sup>i</sup>Pr<sub>3</sub>)<sub>2</sub>, which unlike IrH<sub>2</sub>Cl(PPh<sub>3</sub>)<sub>3</sub> is coordinatively unsaturated, catalyzes the hydrogenation of benzylideneacetone to 4-phenylbutan-2-one (58). In contrast to the hydrogenation of olefins, IrCl(PPh<sub>3</sub>)<sub>3</sub> and IrH<sub>2</sub>Cl(P<sup>i</sup>Pr<sub>3</sub>)<sub>2</sub> show a similarly poor behavior in the dehalogenation of

1,2,4-trichlorobenzene. However, the rhodium counterpart of  $\text{IrH}_2\text{Cl}(\text{P}^i\text{Pr}_3)_2$ , the complex  $\text{RhH}_2\text{Cl}(\text{P}^i\text{Pr}_3)_2$  is active, showing an activity similar to that of  $\text{RuHCl}(\text{PPh}_3)_3$ . Furthermore, interestingly, it is the only one complex of the those studied that selectively affords 1,2-dichlorobenzene.

Although complex  $\text{IrH}_2(\text{SiEt}_3)(\text{COD})(\text{PCy}_3)$  ( $\text{COD}$  = 1,5-cyclooctadiene) has been found to be an active catalyst for the hydrosilylation and dehydrogenative silylation of olefins (59, 60), it is completely unactive in the dehalogenation of 1,2,4-trichlorobenzene with  $\text{HSiEt}_3$ .

The investigation of the catalytic activity in the dehalogenation of 1,2,4-trichlorobenzene with  $\text{HSiEt}_3$  of the complexes collected in Table 1 suggests that for the iron and cobalt triads, the  $3d$  and  $5d$  metals form less active catalysts than the  $4d$  metals. The inactivity of the  $3d$  metal complexes can be related to the poor nucleophilicity of the metallic center of these species, which prevents the oxidative addition of the H-Si and Cl-aryl bonds, while the lower activity of the  $5d$  metal complexes with respect to the  $4d$  metal compounds can be related to the higher stability of the M-aryl and M-silyl bonds in  $5d$  metal complexes, when they are compared with their  $4d$  counterparts.

In addition, it should be mentioned that, according to the results collected in Table 1, there do not appear to be significant differences in activity between the metals of both groups, contained in the same series.

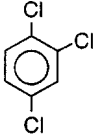





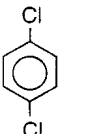



### 3.2. Dehalogenation of Polychloroarenes and Chlorination of $\text{HSiEt}_3$ Catalyzed by $\text{RuHCl}(\text{PPh}_3)_3$

This complex catalyzes not only the dehalogenation of 1,2,4-trichlorobenzene but it is also a homogeneous catalyst for the dehalogenation of 1,2-, 1,3-, and 1,4-dichlorobenzene and chlorobenzene (Table 2). Its homogeneity was proved by addition of mercury (61) to the catalytic solution, which does not produce significant changes in the catalytic activity.

The dehalogenation of 1,2,4-trichlorobenzene affords 1,2-dichlorobenzene (52%), 1,3-dichlorobenzene (26%) and 1,4-dichlorobenzene (22%), while the dehalogenation of 1,2-, 1,3- and 1,4-dichlorobenzene selectively affords chlorobenzene. The preferred formation of 1,2-dichlorobenzene during the dehalogenation of 1,2,4-trichlorobenzene suggests that, in the presence of this catalyst, the extraction of the chlorine in position 4 is favored. This agrees well with the fact that the dehalogenation of 1,2-dichlorobenzene is slower than the dehalogenation of the related 1,4-isomer (Table 2). However, the preferred formation of 1,2-dichlorobenzene is in contrast with previous studies on the oxidative addition of 1,2,4-trichlorobenzene to phosphine-nickel(0) complexes, which show that the addition of the 4-Cl-C bond is less favored than the oxidative addition of the 2-Cl-C bond (62).

The dehalogenation of 1,2-dichlorobenzene is slower not only than the dehalogenation of 1,4-dichlorobenzene but

TABLE 2  
Dehalogenation of Polychloroarenes and Chlorination of  $\text{HSiEt}_3$  Catalyzed by  $\text{RuHCl}(\text{PPh}_3)_3$

Substrate	Product (s)	Time (h)	% $\text{ClSiEt}_3$
	 (a)	7	96
		9	58
		9	91
		9	84
		9	35

Conditions: 98°C; 3 ml of polychloroarene, 2.4 mmol of  $\text{HSiEt}_3$ , 0.063 mmol of catalyst. (a) 1,2-dichlorobenzene (52%), 1,3-dichlorobenzene (26%), 1,4-dichlorobenzene (22%).

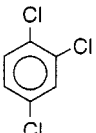






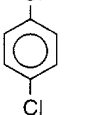



also than that of the 1,3-isomer. This, together with the preferred formation of 1,2-dichlorobenzene during the dehalogenation of 1,2,4-trichlorobenzene, indicates that the dechlorination of chloroarenes containing chlorines in adjacent positions is more difficult than the dehalogenation of those containing chlorines in nonadjacent positions. This difficulty could be related to the capacity for coordinating to the catalyst of the chlorine situated in the position adjacent to the activated chlorine. The coordination could occur before the Cl-C bond activation or/and after the cleavage of the Cl-C bond. In the first case the dihaloarene should act as a chelating *ortho*-dihalobenzene ligand, while in the second case the dichloroarene should give rise to a  $\sigma$ -bonded aryl group with an *ortho*-chlorine secondary bond.

There are precedents for both types of coordination. Complex *cis,cis,trans*- $[\text{IrH}_2(\text{Me}_2\text{CO})(\text{PPh}_3)_2]\text{BF}_4$  reacts with various *ortho*- $\text{C}_6\text{H}_4\text{X}_2$  halocarbons, which displace  $\text{Me}_2\text{CO}$  to give *cis,trans*- $[\text{IrH}_2(\kappa^2\text{-X}_2\text{C}_6\text{H}_4)(\text{PPh}_3)_2]\text{BF}_4$ , where the  $\kappa^2$ -coordination of the halocarbons has been proven by the X-ray diffraction characterization of the diiodobenzene derivative (63). The X-ray diffraction analysis of a single crystal of  $[\text{Rh}(\text{C}_6\text{Cl}_5)_4]^-$  also proves that one of the four  $\text{C}_6\text{Cl}_5$  groups coordinates to the rhodium atom through both  $\sigma$ -bonded aryl and *ortho*-chlorine secondary bond (64).

The dehalogenations of 1,2,4-trichlorobenzene and 1,2-, 1,3-, and 1,4-dichlorobenzene involve the selective

TABLE 3

Dehalogenation of Polychloroarenes and Chlorination of H<sub>2</sub>SiEt<sub>3</sub> Catalyzed by RhH<sub>2</sub>Cl(P<sup>i</sup>Pr<sub>3</sub>)<sub>2</sub>

Substrate	Product (s)	Time (h)	% ClSiEt <sub>3</sub>
		9	82
	 +  (a)	9	75
		9	70
		9	63
		9	67

Conditions: 98°C; 3 ml of polychloroarene, 2.4 mmol of H<sub>2</sub>SiEt<sub>3</sub>, 0.07 mmol of catalyst. (a) Chlorobenzene (84%), benzene (16%).

extraction of a chloride from the aromatic ring. Since the dehalogenation of 1,2,4-trichlorobenzene is faster than those of the dichlorobenzenes, and the extraction of a chloride from the last substrates is in the three cases faster than the dehalogenation of chlorobenzene, the selective formation of the C<sub>6</sub>H<sub>7-x</sub>Cl<sub>x-1</sub> products appears to be kinetic in origin, and for that reason the rate of dehalogenation decreases with the decrease in the number of the chlorine atoms on the aromatic ring.

### 3.3. Dehalogenation of Polychloroarenes and Chlorination of H<sub>2</sub>SiEt<sub>3</sub> Catalyzed by RhH<sub>2</sub>Cl(P<sup>i</sup>Pr<sub>3</sub>)<sub>2</sub>

Like the previous ruthenium derivative RuHCl(PPh<sub>3</sub>)<sub>3</sub>, the rhodium(III) complex RhH<sub>2</sub>Cl(P<sup>i</sup>Pr<sub>3</sub>)<sub>2</sub> catalyzes, in addition to the dehalogenation of 1,2,4-trichlorobenzene, the hydrogenolysis of 1,2-, 1,3-, and 1,4-dichlorobenzene and chlorobenzene (Table 3).

Although the behavior of both unsaturated species, RhH<sub>2</sub>Cl(P<sup>i</sup>Pr<sub>3</sub>)<sub>2</sub> and RuHCl(PPh<sub>3</sub>)<sub>3</sub>, is similar, some fine-tuning should be done. In the presence of the rhodium catalyst, the formation of 1,2-dichlorobenzene is not only preferred but also selective. Furthermore, in contrast to RuHCl(PPh<sub>3</sub>)<sub>3</sub> the dehalogenation of 1,2-dichlorobenzene affords benzene, in addition to chlorobenzene, the hydrogenolysis of chlorobenzene being faster than the dehalogenation of 1,2-dichlorobenzene.

## 4. CONCLUSION

This study has revealed that in the iron and cobalt triads, ruthenium and rhodium give rise to active catalysts for the simultaneous dehalogenation of polychloroarenes and the chlorination of H<sub>2</sub>SiEt<sub>3</sub>. The hydrogenolysis is sequential and selective according to the sequence 1,2,4-trichlorobenzene–dichlorobenzene–chlorobenzene–benzene. Although osmium and iridium also afford active systems, they are less active and undergo deactivation.

The dehalogenation of dichlorobenzenes is highly dependent on the position of the chlorine at the aromatic ring. Thus, in the presence of the unsaturated phosphine complexes RuHCl(PPh<sub>3</sub>)<sub>3</sub> and RhH<sub>2</sub>Cl(P<sup>i</sup>Pr<sub>3</sub>)<sub>2</sub>, the hydrogenolysis of chlorines in nonadjacent positions is favored over those situated in adjacent position.

In summary, in this paper, we report new catalysts for both the dehalogenation of polychloroarenes and the chlorination of silicon hydrides. In addition, we show that the chlorination of silicon hydrides can be carried out not only with alkyl halides but also with aryl halides when complexes of ruthenium and rhodium are used as homogeneous catalysts.

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