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Dehydrohalogenation of Haloalkanes promoted by Metal Halides. Hydrogen Halometalates formation and their use as Hydrohalogenating Agents

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Abstract: In the dehydrohalogenation of 1,2-dihalo-1,1-diphenylethanes, **1**, to 2-halo-1,1-diphenylethene, **2**, either at 76°C or at 50°C, promoted by catalytic amount of the anhydrous bromides of Fe(III), Ru(III) and Al(III) and Fe(III) chloride the chemical transformation of the metal halides was observed. In reactions carried out in vacuum or under nitrogen atmosphere, the hydrogen halide eliminated from the organic substrate reacted with the metal halides rendering the unstable hydrogen perhalometalates $H^+_n[MX_{3+n}]^{n-}$. We demonstrate that these compounds behave as hydrogen halide donors in the hydrohalogenation of olefins at 4°C. © 1998 Elsevier Science Ltd. All rights reserved.

INTRODUCTION

We have previously reported[1,2,3] the catalytic dehydrobromination of 1,2-dibromo-1,1-diarylethanes, **1**, to 2-bromo-1,1-diarylethenes, **2**, as shown in equation 1. Powdered transition metals and aluminum as well as their anhydrous bromides were used in catalytic amount in contact with carbon tetrachloride solutions of the substrates.

$$\underset{\mathbf{1}}{Ar_2CBr - CHRBr} \xrightarrow{MBr_n\ ,\ 76°C} \underset{\mathbf{2}}{Ar_2C = CRBr} + HBr + MBr_n \qquad (1)$$

M = Fe, Ru, Al ; n = 0-3 ; R = H, CH_3
Ar = C_6H_5 ; 4-CH_3-C_6H_4 ; 4-Cl-C_6H_4

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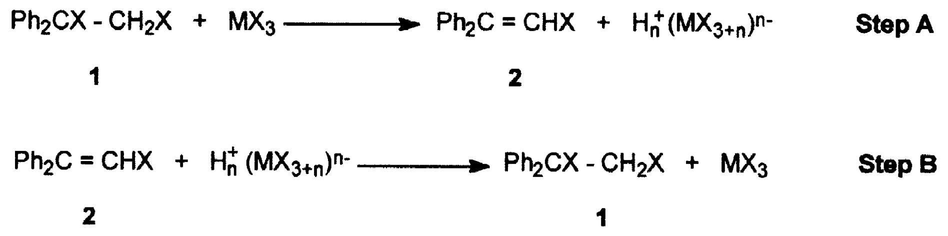
Under these conditions, in the presence of both the hydrogen and metal halide, a catalytic low temperature hydrohalogenation of the olefin **2** should be borne in mind. An interesting question was what actually happened with the metal halide in such a catalytic cycle. Formation of complexes of Fe(III) halides by introduction of hydrogen halides in an organic solution of the salt was recently reported.[4] This issue could be of significant interest from the standpoint of hydrohalogenation of olefins with the inorganic species involved. The hydrogen halides additions to alkenes have been carried out under a variety of conditions.[5] For instance, ethylene and its halogenated derivatives react with HCl in the presence of Lewis acids catalyst.[6] In addition, in the halogen exchange catalyzed by Fe(III) bromide reported by Kochi,[7] the addition of halogen bromide to the unsaturated substrate was detected as a by reaction.

Keeping all these facts into account we investigated the transformation of the metal halide in the catalytic cycle to establish the extent of the hydrohalogenation reaction in such a system. We hereby report that in the dehydrohalogenation reaction the catalysts turned into hydrogen halide donors, **M(HX)**, which promote the hydrohalogenation of compound **2** as observed when the reaction mixtures were cooled. To substantiate this assumption and to explore the so far unreported performance of such hydrohalogenating agents we have tested them with different olefins.

RESULTS AND DISCUSSION

Reversibility of the Dehydrohalgenation Reaction. Metal halide changes occurred when reactions of 1,2-dihalo-1,1-diphenylethane, **1a**, with catalytic amount of Fe(III) bromide were carried out at different temperatures, as shown in Scheme 1.

In step **A**, carbon tetrachloride solutions of **1** were refluxed with the solid anhydrous metal halide under vacuum, nitrogen or air in Schlenk flasks at 76 °C or at 50 °C. At the end of this step, the remaining solid residues were kept under inert atmosphere in the Schlenk tube while ^{1}H NMR was used to evaluate the composition of the reaction mixtures in solution. The absolute percentages are obtained with adamantane as internal standard. No products other than **1** and **2** were formed under the reported conditions. Step **B** involved cooling the evacuated reaction mixtures at 4 °C after pouring the carbon tetrachloride solution back into the Schlenk flask over the solid residues. Once again, the amounts of **1** and **2** in the solutions were verified by ^{1}H NMR. For simplicity sake, step **A** plus step **B** will be referred to from now on as a reaction cycle and the solid residue from step **A** will go by the name of **M(HX)**, where M= FeX_3, RuX_3, AlX_3 and X = Br, Cl.



$$\underset{\mathbf{1}}{Ph_2CX-CH_2X} + MX_3 \longrightarrow \underset{\mathbf{2}}{Ph_2C=CHX} + H_n^+(MX_{3+n})^{n-} \qquad \textbf{Step A}$$

$$\underset{\mathbf{2}}{Ph_2C=CHX} + H_n^+(MX_{3+n})^{n-} \longrightarrow \underset{\mathbf{1}}{Ph_2CX-CH_2X} + MX_3 \qquad \textbf{Step B}$$

1a, 2a: X = Br; **1b, 2b**: X = Cl

Scheme 1

Results listed in Table 1 showed the reversibility of the complete system under vacuum, whereas hydrohalogenation of the olefinic products **2a** did not occur in air, as will be dealt with later on. However, the reversibility of the reaction was found to occur in the same way either under nitrogen or under vacuum, cycle **5**, Table 2.

Tabla 1. Reversibility of **1a** Dehydrohalogenation catalyzed by Anhydrous $FeBr_3$.[a]

Cycle N°	Substrate	Step	Atm.	Molar fraction		Difference	
				1a	**2a**	**1a**	**2a**
1	**1a**	A	air	0.10	0.70	-	-
		B	air	0.10	0.70	0[b]	0[b]
2	**1a**	A	vacuum	0.21	0.66	-	-
		B	air	0.33	0.67	+0.12	-0.1[b]
3	**1a**	A	vacuum	-	-	-	-
		B[c]	vacuum	0.67	0.23	+0.46	-0.43
4	**1a**	A	N_2	0.25	0.69	-	-
		B	N_2	0.40	0.40	+0.16	-0.22

a - Reactions carried out in CCl_4 as solvent and evaluated by ^{1}H-NMR. Steps **A** were performed at 76°C for 0.11 h, and steps **B** at 4°C for 24 h. b - Approximate values due to the error of the measurement method. c - Reaction was cooled at 4°C without opening the reaction tubes. For evaluation of step **B**, values from step **A** cycle 2 was considered.

As previously reported[1,2] in uncompleted reactions evaluated by ^{1}H NMR, the sum of molar fraction of methylenic protons from **1** and vinylic proton from **2** was lower than 1, as shown in Tables 1, 2 and 3. The observed lack of non-aromatic protons in the NMR spectra of the reaction mixtures suggested the presence of organometallic intermediates. Most likely, the difficulty and failure to direct detection of such proton signals at room temperature can be ascribed to the signal scattering arising from the dynamic proton exchange of organometallic intermediates. The presence of such organometallic intermediates was traced by several means.[1,2] Normal proton integration occurs by the end of the reaction when 1 was fully changed into product **2.**

Table 2 summarizes the data from reactions extended to other metallic salts with substrates **1a** and **1b** in vacuum. With substrate **1a** dehydrohalogenation was carried out at 76 °C and with **1b** the dehydrohalogenation was accomplished at 50 °C, since these compounds spontaneously dehalogenated at 76 °C. Results also showed that by cooling the reaction mixtures in presence of the solid residue from step A, **M(HX)**, the olefinic product **2a** was hydrohalogenated. Unlike dehydrohalogenation of **1b** which still went on at 4°C and even at lower temperatures.

Table 2. Reversibility of 1 Dehydrohalogenation with Anhydrous $FeBr_3$; $FeCl_3$; $RuBr_3$ and $AlBr_3$ as Catalysts using CCl_4 as Solvent.[a]

Cycle	Substrat	Catalyst[b]	Step	Temp	Time	Molar fraction		Difference	
N°				°C	h	**1a**	**2a**	**1a**	**2a**
5	**1a**	$FeBr_3$	**A**	76	0.11	0.21	0.66	-	-
			B	4	24	0.36	0.48	+0.15	-0.18
6	**1a**	$FeCl_3$	**A**	76	0.11	0.35	0.55	-	-
			B[c]	4	24	0.75	0.16	+0.40	-0.39
7	**1a**	$RuBr_3$	**A**	76	0.38	0.51	0.46	-	-
			B	4	40	0.60	0.35	+0.9	-0.11
8	**1a**	$AlBr_3$	**A**	76	0.75	0.39	0.56	-	-
			B	4	40	0.61	0.35	+0.22	-0.21
9	**1b**	$FeBr_3$	**A**	50	0.017	0.18	0.61	-	-
			B	4	24	0.06	0.90	-0.12	+0.19
10	**1b**	$FeCl_3$	**A**	50	0.017	0.10	0.81	-	-
			B	4	24	-	1.00	-0.10	+0.19

a - Evaluated by ^{1}H-NMR. b - The substrate:catalyst ratio was 10:1. c - Steps **B** were accomplished in presence of the remaining solid residues from steps **A**.

In order to explain these results, we may take into account three different pathways: a) direct addition of the hydrogen halide eliminated from step A to the olefinic product 2.[8] Indeed the presence of HX in the reaction mixture was observed; b) metal-catalyzed hydrohalogenation of **2** by the halogen halide free in the solution, as observed in similar systems which contained Fe(III) bromide and halogen halides;[5,6] c) change of the metal halide into active species as hydrogen halide donors, either by the coordination of halogen halide or by the formation of a complex.[7,9] A distinction among these three alternatives may be drawn from the effect of the metal species on the course of the addition reaction and from the study of the structure of the hydrohalogenating species.

Role of the Metal-Halo compounds in the Addition Reaction. We have tried to obtain further clues on the factors which rule the addition reaction of hydrogen halide by investigating the role of Fe(III) bromide and **M(HX)**, Table 3. The addition of hydrogen bromide to **2a** did not occur when the reaction, step **B** in cycle **11**, was carried out without catalyst. There was a significant transformation of **2a** into **1a** in cycle **12** where the solid formed in step **A**, **M(HX)**, was present in step **B**. Very little, if any, catalytic activity for the hydrogen bromide addition was found when the solution from step **A** was poured over fresh anhydrous Fe(III) bromide in step **B** as in cycle **13**.

Table 3. Effect of the metal center on the Reversibility of **1a** Dehydrobromination with Anhydrous $FeBr_3$.[a]

Cycle N°	Step	Catalyst	Molar fractions		Difference	
			1a	**2a**	**1a**	**2a**
11	**A**	$FeBr_3$	0.21	0.66	-	-
	B	N.C.[b]	0.21	0.64	0[c]	-0.2[c]
12	**A**	$FeBr_3$	0.21	0.66	-	-
	B	MHX	0.36	0.48	+0.15	-0.18
13	**A**	$FeBr_3$	0.21	0.66	-	-
	B	Rnwd.[d]	0.27	0.61	+0.6	-0.5

a - Reactions carried out in CCl_4 as solvent and evaluated by ^{1}H-NMR. Steps **A** were performed at 76°C for 0.11 h, and steps **B** at 4°C for 24 h. b - N.C. = Steps **B** were carried out by cooling only the CCl_4 solution from steps **A**, without the solid. c - Approximate values due to the error of the measurement method. d - Rnwd. = 10% of fresh anhydrous $FeBr_3$ was employed.

Furthermore, we also looked into the conditions required for hydrogen halide addition to **2a**. In agreement with the results mentioned in Table 3,entry 11 **B**, when **2a** was disolved in carbon tetrachloride saturated with hydrogen bromide, **2a** yielded only 3% of **1a** after 24 hours at 4°C.On the other hand, only about 10% of **1a** was formed when anhydrous Fe(III) bromide was added to this solution. All these results ratified that free hydrogen bromide soluble in carbon tetrachloride practicaly could nor self add to **2a**. Even when the addition was enhanced when the metal was present, the catalytic activity of Fe(III) bromide could not account for the amount of **1a** formed in step **B**. This clearly indicates not only that another addition pathway must be involved in the adition reaction but also that in the dehydrobromination of **1a**, the metal halides were converted into active hydrogen bromide donors.

M(HX) Structure Studies. Information regarding the mechanism of the hydrogen halide addition can be accomplished by studying the nature of the solid formed in Step **A**, **M(HX)**.

Argentometric titrations of **M(HX)** from reactions of **1a** with Fe(III) bromide; Fe(III) chloride and Ru(III) bromide carried out under vacuum revealed a halogen content increase of 3 atoms/mol compared to the precursor metal halides : $FeBr_3$, 2.72 ± 0.05, **Fe(HBr)**, 5.54 ± 0.05; $FeCl_3$, 2.67 ± 0.06; **Fe(HCl)**, 5.70 ± 0.05; $RuBr_3$, 2.61± 0.06 and **Ru(HBr)**, 5.68 ± 0.06. The solid from reactions with Al(III) bromide was not titrated since it was not completely water soluble.

UV-V spectroscopic investigation on the solid **M(HX)** arising from evacuated dehydrohalogenation of **1a** with Fe(III) halides was carried out. A series of low intensity bands in the region of 285-500 nm, typical of bromine to iron electron transfer bands, was patent in the spectra recorded in diethylether, Figure 1. At room temperature, slow changes in the spectra of the solutions were found, and after five days only the well defined bands corresponding to ferric bromide were evidenced, Spectrum V, Figure 1. One of the intermediate recorded spectra, Spectrum II, Figure 1, was the same as the spectrum of the tetrabromoferrate anion, $[Fe(III)Br_4]^-$, in dichloromethane.[10] Argentometric titrations mentioned above indicate that the hexabromo and pentabromo derivatives could occur. Moreover, the spectrum resulting from the changes in time might suggest the presence of these species. It is not surprising that we could not detect the spectra of either the $[Fe(III)Br_5]^{2-}$ or $[Fe(III)Br_6]^{3-}$ anions, since they are very unstable,[11] but the initial spectra observed, Spectrum I, might correspond to the overall absorption of these species. The existence of equilibrium which involves a higher coordination number of halogen complexes has been well established, and it is clear that the $[FeX_4]^-$ anion ruled the chemistry of Fe(III), as it did in our system.[12]

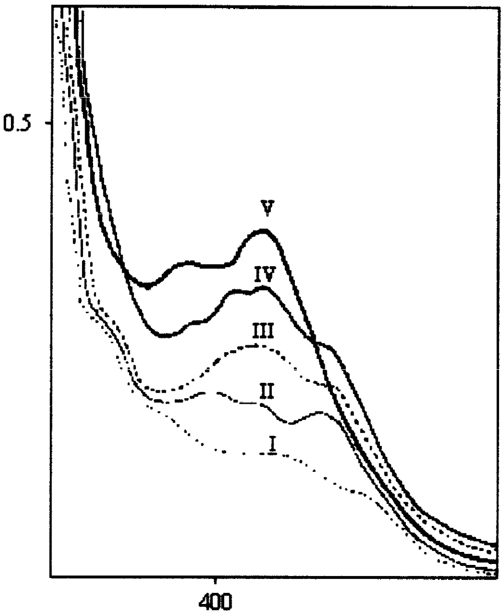


Figure 1: UV-V spectra of M(HBr) decomposition over time in dichloromethane. **I**- Initial state; **II**- $[FeBr_4^-]$; **III** y **IV**- Intermediate states; and **V**- $FeBr_3$(anhydrous).

The spectrum of the **M(HX)** from reactions of **1a** with Fe(III) chloride also corresponded to the tetrabromoferrate anion while that of the solid from dehydrohalogenation of **1b** catalyzed by Fe(III) bromide matched the spectrum of the tetrachloroferrate anion.[10] It may be inferred that the halogen atoms originally bonded to the metal were replaced by those eliminated from the substrate.[7a,13] The spectrum of the solid from Ru(III) bromide catalyzed dehydrobromination, carried out in a 48% hydrobromic acid solution, corresponded to that of the hexabromo ruthenate anion, $[Ru(III)Br_6)]^{3-}$.[14] In a water solution the observed spectrum was that of $[Ru(III)Br_4]^-$ anion.[10]

Altogether, these observations correlate well with the notion of the transformation of the catalyst into a hydrogen halide donor species. The anhydrous halides used as catalysts in the dehydrohalogenation step were transformed into the hydrogen halometalates, $H^+_n[MX_{3+n}]^{n-}$, where n = 1-3. From these compounds the hydrogen bromide eliminated in step **A** should be transferred to **2a** in step **B**, unlike dehydrohalogenation of **1b** which prevailed even at 4°C.

Besides, taking into account the properties of the hydrogen halometalates, $H^+_n[MX_{3+n}]^n$, we could explain why the hydrohalogenation reaction of **1** did not occur in open system, Table 1. Such complexes are very hygroscopic and fuming in the moisture due hydrolysis to form HX.[15] When the complex is in contact with air the hydrogen halide is eliminated and the hydrohalogenation could not occur.

To substantiate our claim about the presence of the complex $\mathbf{H^+_n[MX_{3+n}]^n}$ and to explore the so far unreported performance of hydrogen bromoferrates as hydrobrominating agents we have tested them with different olefins.

Reaction of $HFeBr_4$ and M(HBr) with Olefins. Halometalates have been studied extensively because of their potential applications as electrolytes in high-energy batteries[16] and as counter ions in molecular conductors,[17] but they have not received attention as hydrohalogenating agents. In order to check their ability to act as hydrogen bromide donors in the hydrohalogenation reactions, the solid from reaction of **1a** with ferric bromide, **M(HBr)**, and the complex hydrogen tetrabromo ferrate-diethylether $[(Et_2O)_nH]FeBr_4$, $\mathbf{HFeBr_4}$,[15] were allowed to react with different olefins.

All the addition reactions were carried out under the same conditions as those catalyzed by the metal halides in step **B** under vacuum. The results presented in Table 4 demonstrate that the solid residue from step **A** in dehydrobromination reactions, **M(HBr)**, behaved similarly to hydrogen tetrabromoferrate in hydrobromination of olefins.

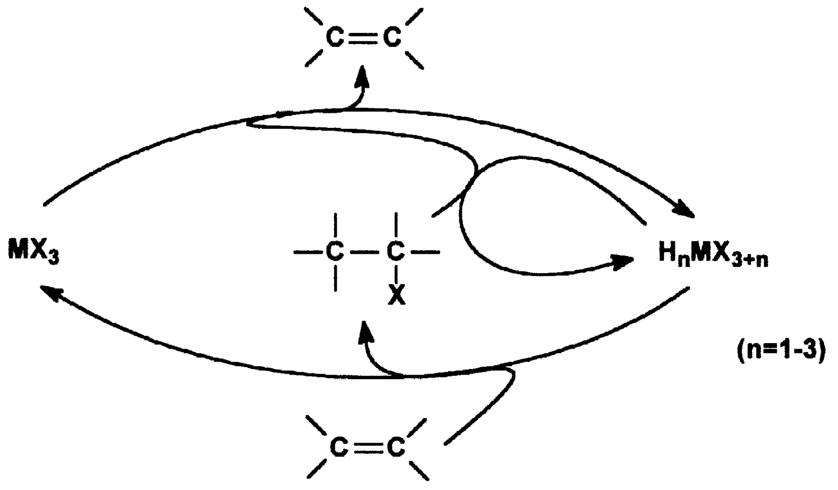
Table 4. Reactions of $\mathbf{HFeBr_4}$[a] and **MHBr**[b] with Olefins in CCl_4 Solutions at 4°C.[c]

Reaction N°	Substrate	Catalyst	Product	**% HBr addition**[d]
1	**2a**	$HFeBr_4$	1a	17
2	**2a**	MHBr	1a	20
3	**1-pentene**	$HFeBr_4$	2-bromopentane	97
4	**1-pentene**	MHBr	2- and 3-bromopentane	79[e]
5	**cyclohexene**	$HFeBr_4$	bromocyclohexane	99
6	**cyclohexene**	MHBr	bromocyclohexane	76
7	**1,1-diphenylethene**	$HFeBr_4$	2-bromo-1,1-diphenylethane	98
8	**1,1-diphenylethene**	MHBr	2-bromo-1,1-diphenylethane	72[f]

a - $\mathbf{HFeBr_4}$ = hydrogen tetrabromoferrate. b - **MHBr** = solid from step **A** of the reaction of **1a** with Fe(III) bromide. c - Reactions assessed by ^{1}H-NMR. d- Porcentage of the bromide hydrogen adition taking as100% the maximun amount of that the corresponding catalyst can add. e - 2-bromopentane: 3-bromopentane ratio 74:26. f - 16% 3-methyl-1,1,3-triphenylindane.

The lower yields in the addition of hydrogen bromide showed by **M(HBr)**, should be explained since they are a mixture of different species, **$H^+_n[MX_{3+n}]^{n-}$**, where n = 1-3 and we assumed for the calculation n = 3. In agreement with the commonly accepted notion of an ionic mechanism for the hydrohalogenation reaction in the presence of Lewis acids, the behavior of the studied reaction should be adequately described by a polar mechanism, with the formation of a catalyst-olefin complex, which prevented rearrangement. As an example, the different selectivity found with **$HFeBr_4$** and **M(HBr)** in reactions with 1-pentene could be explained taking this and the lability of the pentabromoferrates and hexabromoferrates into account. In this reaction, free hydrogen bromide formed by decomposition of these metalates would add to the olefin by a cationic mechanism without the selectivity of the metal-controlled hydrobromination. Furthermore, a higher reaction stabilization of the ion pair due to solvation with diethylether[4, 18] may be the reason for the better results of hydrohalogenation with **$HFeBr_4$**, whereas in the solid **M(HBr)** the formation of clusters with involvement of the product **2** and traces of water could be expected.

Dehydrohalogenation-Hydrohalogenation Catalytic Cycle. For the overall transformation asociated with the dehydrohalogenation-hydrohalogenation reactions we could present a catalytic cycle, Scheme 2.



Scheme 2

Since the hydrogen tetrabromoferrate must be an intermediate in both reactions of the catalytic cycle, Scheme 2, it was also used as catalyst for the dehydrohalogenation of **1a**, yielding 77% of **2a**.

At the end of a reaction cycle, the remaining solid was analyzed by UV-Visible spectroscopy. Results demostrated that the solid consisted of Fe(III) bromide. Moreover, when the dehydrohalogenation reaction was carried out in air, at the end of the reaction the remaining solid was still the Fe(III) bromide, since **$H^+_n[MX_{3+n}]^n$** was hydrolyzed.

CONCLUSIONS

In catalytic dehydrohalogenations of haloalkanes catalyzed by M(III), with M = Fe, Ru, Al, under vacuum, the hydrogen halide eliminated reacted with the catalyst salts yielding the hydrogen halometallates $H^{+}_{n}[MX_{3+n}]^{n-}$, where M = Fe, Ru, Al; X = Br, Cl and n = 3. The structural types of the perhalometalates are well known and identified, but for the first time the possibility of carrying out an efficient and selective halogen halide addition with hydrogen tetrahaloferrates is shown. Thus, the behavior of the reaction can be well understood by learning more about the catalyst transformation.

EXPERIMENTAL SECTION

All work involving air- or moisture-sensitive compounds was carried out under vacuum or nitrogen atmosphere, using standard Schlenk or glovebag techniques. ^{1}H-NMR spectra were recorded in a Bruker 200 FT Spectrometer with carbon tetrachloride as solvent and a capillary tube containing acetone-d_6 fixed into the NMR tube for locking purposes and as a standard reference. Argentometric titrations were performed with a Seibold equipment model GTE attached with a halogen selective electrode. Electron absorption spectra were performed in a Shimadzu 260 spectrometer. Reactions at 76°C or 50°C were carried out in a Lauda Ultra-Thermostat, temperature accuracy ±1°C and those at 4°C by keeping the samples in the fridge. Carbon tetrachloride used in the reactions was Merck Uvasol and it was employed after dried over 4Å molecular sieves. Bromine was Merck P.A. less than $1x10^{-4}$ % in heavy metals. Anhydrous $FeBr_3$, $FeCl_3$ and $AlBr_3$ were purchased from Strem Chemicals and $RuBr_3$ was supplied from Johnson Matthey Corp.. Solutions for argentometric titrations were prepared with a standard volumetric solution of silver nitrate from Carlo Erba and checked with a solution of NaBr spectroscopic grade from Merck. Silica gel for column chromatography was Kieselgel Merck 60, and for flash chromatography Kieselgel Merck 60 H was used. 1,1-Diphenylethane (Merck) was flash chromatographed on silica gel with n-hexane before use. 1,2-Dibromo-1,1-diphenylethane, **1a**, was prepared as previously described[2] and 1,2-Dicloro-1,1-diphenylethane, **1b**, by addition of chlorine to 1,1-diphenylethane at -78°C.[19] 1-pentene and cyclohexene were purchased from Merck and distilled prior to use. Hydrogen bromide was obtained from the benzene bromination[20] under anhydrous conditions and collected in traps immersed in a liquid air bath. From these traps the hydrogen bromide was distilled. The complex of hydrogen tetrabromoferrate with diethylether was prepared as reported by Gallinos et al.,[15] the solvent was removed under vacuum and the residue was treated with a nitrogen stream for 24 hours in order to remove the excess of hydrogen bromide from the solution.

General Procedure. To perform dehydrohalogenation or step **A**, reactions in air atmosphere were accomplished in reaction tubes provided with a condenser with a water trap on top and reactions under vacuum or under nitrogen atmosphere were carried out in Schlenk tubes. A solution of the substrate,1 mmol in 2 ml of carbon tetrachloride was added over 0.1 mmol of the metal halide. In general, the substrate:catalyst ratio was 10:1. To carry out the evacuated reactions, three freeze-pump-thaw cycles were run. After the appropriate procedure, the reaction mixtures were immersed in a bath at 76 °C or 50 °C. For evaluation, the reactions were halted before completion and filtered at the appropriate time in a glovebag. The carbon tetrachloride solutions were checked by ^{1}H NMR while the solid was kept in the reaction tubes avoiding contact with air.

The ^{1}H NMR spectra of uncompleted reactions showed a deficit of non-aromatic protons, that is, the sum of molar fraction of methylenic protons from **1** and the vinylic proton from **2** was lower than 1, Tables 1, 2 and 3. In previous reports,[1,2,3] the "undetected" protons in the NMR spectra of the reaction mixtures were assigned to the organometallic intermediates. The difficulty and failure to direct detection of such proton signals at room temperature may be due to the signal scattering arising from the dynamic proton exchanged of organometallic intermediates. However, normal proton integration results at the end of the reaction when **1** was fully chaiged into product **2**. The absolute percentages are obtained with adamantane as internal standard and no product other than **1** and **2** were formed under these experimental conditions.

In order to carry out hydrohalogenation of the olefins or step **B**, the carbon tetrachloride solutions from step **A** were put back into the reaction tubes containing either the solid from step **A**, or fresh anhydrous $FeBr_3$ (cycle **13**), or without catalyst (cycle **11**). After the appropriate procedure, samples were maintained in the fridge at 4 °C during 24 hours in the case of reactions catalyzed by ferric halides and during 40 hours for $RuBr_3$ and $AlBr_3$. Henceforth, the reaction mixtures were filtered and the solutions were checked again by ^{1}H-NMR.

Reactions with HFeBr$_4$ and M(HBr). Reactions of dehydrohalogenation with $[(Et_2O)_nH]FeBr_4$ and **1a** as substrate were carried out under the same experimental conditions as step **A** for the anhydrous metal halides under vacuum. Reactions of **2a**, 1-pentene, cyclohexene and 1,1-diphenyl-ethene with $[(Et_2O)_nH]FeBr_4$ as well as with the solid from **1a** dehydrobromination, **M(HBr)**, were performed under the conditions of step **B** as described in the general procedure. The reported yields were calculated on the bases of theoretical molar content of HBr in the haloferrates.

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