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Reductive elimination of halogens assisted by phosphine ligands in $Fe(CO)_4X_2$ ($X = I, Br$) complexes

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Abstract

$Fe(CO)_4X_2$ complexes [$X = I$ (**1**), Br(**1′**)] react with phosphine ligands L ($L = PMe_3$, PEt_3, PMe_2Ph, $PMePh_2$, PPh_3) via a two-step mechanism: in the first step *fac*-$Fe(CO)_3LX_2$ complexes are formed; in the second step two parallel pathways, *a* and *b*, are observed; in pathway *a*, reductive elimination with formation of equimolar amounts of $Fe(CO)_3L_2$ (**5**) and phosphonium salts $[LX]^+X^-$ is observed; in pathway *b*, disubstituted dihalide complexes *cis*,*trans*,*cis*-$Fe(CO)_2L_2X_2$ are formed. The relative weights of pathways *a* and *b* depend on the basicity, steric hindrance and concentration of ligand L, on the nature of the halogen and on temperature. A radical mechanism which accounts for most of the experimental results is proposed.

Keywords: Reductive elimination; Carbonyl halide iron complexes; Phosphonium salts; Radical mechanism

1. Introduction

The reductive elimination of halogens in dihalide complexes of transition metals, shown in Scheme 1 is thermodynamically forbidden [1] since in this reaction two fairly strong metal–halogen bonds are broken and one weak halogen–halogen bond is formed. The metal–ligand bond energy, that can assist the reaction, is not sufficient to make the reaction thermodynamically allowed [2]. In order for the halide elimination to occur, it must be assisted by other reactions that can counterbalance its endothermicity. A few examples of reductive elimination of halogens are described in the literature: in particular, the reaction of $Fe(CO)_4I_2$ with PPh_3 to give $Fe(CO)_3(PPh_3)_2$ in the presence of tin(II) halides [3] and the reaction of polyhalide complexes of tungsten $W(CO)L_2I_3({=}CNEt_2)$ with PMe_3 to give $[W(CO)L_2(PMe_3)_2({=}CNEt_2)]^+I^-$ and $[PMe_3I]^+I^-$ [4].

During our previous studies [5] on the reaction of $Fe(CO)_4X_2$ with phosphine ligands to obtain *cis*,*trans*,*cis*-$FeCO)_2L_2X_2$ [$L = PPh_3$, P(*iso*-Propyl)$_3$; $X = I$, Br] the formation of small quantities of $Fe(CO)_3L_2$ was observed. The substitution reaction of $Fe(CO)_4X_2$ with phosphine ligands was studied by Basolo a long time ago [6] and in this case too, the formation of a very small quantity of $Fe(CO)_3(PPh_3)_2$ was observed.

In this paper, we report the results of our investigation on the reaction of $Fe(CO)_4X_2$ ($X = I$, Br) with phosphine ligands more basic than those studied by Basolo to highlight the reductive elimination of halogens in $Fe(CO)_4X_2$ and to shed light on its mechanism.

2. Experimental

Unless otherwise stated, all operations were carried out under nitrogen using standard Schlenk techniques. Complexes $Fe(CO)_4X_2$ ($X = I$ (**1**), Br (**1′**)) were prepared as described in [7]. $Fe(CO)_4PMe_3$ was prepared as described in [8]. Phosphine ligands (PMe_3, PMe_2Ph, $PMePh_2$, PPh_3, PEt_3) were commercial products and were used without

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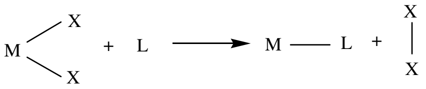


Scheme 1.

further purification. Toluene was dehydrated with Na/K alloy and distilled under nitrogen; diethylether (DE) was purified by refluxing with NaOH pellets, distilled, refluxed with Na and benzophenone and then freshly distilled under nitrogen before use; acetonitrile (ACN) was purified as described in [9]. ^{1}H and ^{31}P{H} NMR spectra were recorded on a Bruker DRX 400 spectrometer; referencing was relative to TMS (^{1}H) and 85% H_3PO_4 (^{31}P). Infrared spectra were recorded on a Perkin–Elmer 1725 X spectrophotometer. Elemental analyses were performed on a Carlo Erba 1106 elemental microanalyzer.

The structure and numbering of the complexes are given in Chart 1 in which the different ligands are distinguished by a lower case letter (a, PMe_3; b, PEt_3; c, PMe_2Ph; d, $PMePh_2$; e, PPh_3) and the halogens I and Br by an apex. The CO stretching frequencies are given in Table 1. The structure of the complexes was determined on the basis of the number and intensity of the CO stretching bands.

2.1. Preparation of $[PMe_3I]^+I^-$

Three grams of I_2 were stirred in 100 mL of toluene. An excess of PMe_3 (3 g) was added and the solution was left to react for 5 h. A yellow solid precipitated. The solid was washed and dried. Yield 72%. Anal. Calc. for $C_3H_9I_2P$: C, 10.92; H, 2.75. Found: C, 10.85; H, 2.71%.

$[PMe_3I]^+I^-$ is easily hydrolyzed by H_2O, giving $[PHMe_3]^+I^-$, which was crystallized as white crystals. ^{1}H NMR (CD_3NO_2): δ, 1.99 (dd, $^{2}J_{H-P} = 15.7$ Hz; $^{3}J_{H-H} = 5.5$ Hz, PMe_3); 6.4 (dm, $^{1}J_{H-P} = 496.4$ Hz; $^{3}J_{H-H} = 5.6$ Hz, H); ^{31}P {^{1}H} NMR (CD_3NO_2): δ, −0.44 (s, PMe_3).

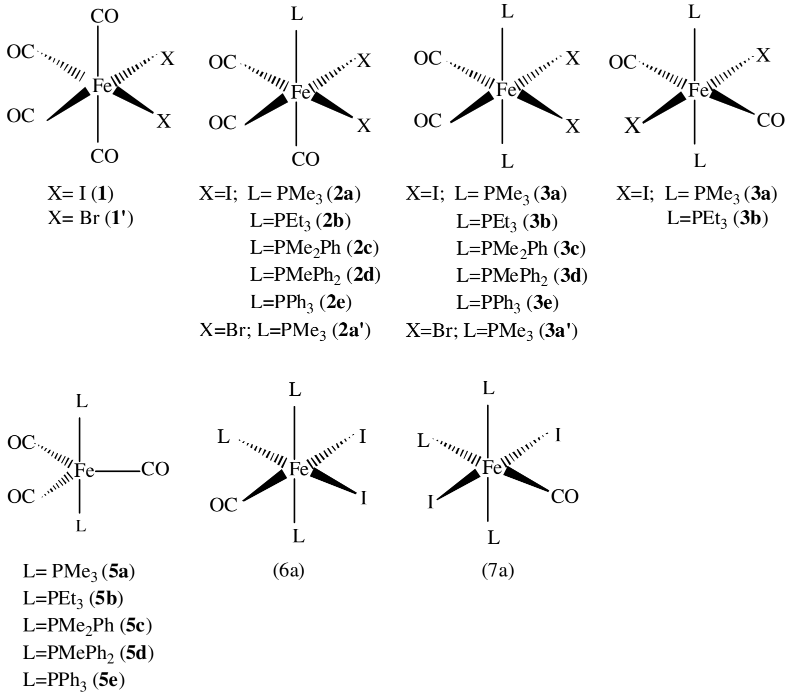


Chart 1.

Table 1
CO stretching frequencies (cm^{-1}) of the complexes *fac*-$Fe(CO)_3LX_2$, *cis,trans,cis*-$Fe(CO)_2L_2X_2$, *all trans*-$Fe(CO)_2L_2X_2$ and $Fe(CO)_3L_2$ in toluene

L	X	*fac*-$Fe(CO)_3LX_2$	*cis,trans,cis*-$Fe(CO)_2L_2X_2$	*All trans*-$Fe(CO)_2L_2X_2$	$Fe(CO)_3L_2$
PMe_3	Br	2096, 2055, 2022	2022, 1970		1868
PMe_3	I	2089, 2043, 2015	2024, 1964	1974	1868
PMe_2Ph	I	2089, 2045, 2022	2023, 1971		1874
$PMePh_2$	I	2088, 2043, 2022	2022, 1973		1876
PPh_3	I	2087, 2041, 2026			
PEt_3	I	2084, 2037, 2014	2007, 1956	1966	1865
PEt_3	Br		2016,1983		1866

2.2. Preparation of fac-$Fe(CO)_3PMe_3I_2$ (**2a**)

Three grams of $Fe(CO)_4PMe_3$ [8] were dissolved in 100 mL of DE; 3.12 g of iodine were slowly added to this stirred solution cooled to −15 °C. The reaction was complete in 15 min; the solution was filtered, concentrated up to 20 mL and crystallized at −20 °C. Complex **2a** was obtained as orange crystals. Yield 90%. Anal. Calc. for $C_6H_9FeI_2O_3P$: C, 15.33; H, 1.93. Found: C, 15.45; H, 1.98%. ν_{CO} (CH_2Cl_2, cm^{-1}): 2091, 2046, 2022.

2.3. Reaction between complex **2a** and PMe_3

(a) 0.15 g of complex **2a** were dissolved in 10 mL of toluene and introduced into a reactor thermostatted at −20 °C; 0.145 g of PMe_3 were added (molar ratio 6/1). The course of the reaction was followed by IR. The formation of complex **3a** was observed but no $Fe(CO)_3(PMe_3)_2$ was formed. After 18 h only 10% of complex **2a** had reacted. The solution was then heated up to 25 °C and the reaction was complete in 12 h.

(b) 0.15 g of complex **2a** and 0.027 g of complex $[Fe(CO)_4I_2]$ (**1**) were dissolved in 10 mL of toluene, thermostatted at −20 °C; 0.145 g of PMe_3 were added. The reaction was complete in 30 min with formation of **3a**, **5a**, and $[PMe_3I]^+I^-$.

2.4. Preparation of cis,trans,cis-$Fe(CO)_2(PMe_3)_2I_2$ (**3a**)

Five grams of $Fe(CO)_4I_2$ were dissolved in 100 mL of DE; 2.70 g of PMe_3 (molar ratio 3/1) were added under magnetic stirring at −15 °C. The reaction was complete in 30 min; the solution was filtered and dried. Complex **3a** was crystallized from CH_2Cl_2–*n*-hexane solution at −15 °C as red–brown crystals. Yield: 75%. Anal. Calc. for $C_8H_9FeI_2O_2P_2$: C, 18.89; H, 1.78. Found: C, 18.95; H, 1.81%. ν_{CO} (DE, cm^{-1}): 2021, 1971. ^1H NMR (CD_2Cl_2): $\delta = 1.89$ (t_{Harris}, $^{|2+4|}J_{H-P} = 8.4$ Hz, PMe_3); $^{31}P\{H\}$ NMR(CD_2Cl_2): $\delta = 7.39$ (s, PMe_3).

In the presence of an excess of PMe_3, complex **3a** reacts slowly at room temperature in toluene forming *mer*,*cis*-$Fe(CO)L_3I_2$ (**6a**) ($\nu_{CO} = 1927\ cm^{-1}$) in 24 h. ^1H NMR (CD_2Cl_2): $d = 1.96$ (t, $^{|2+4|}J_{HP} = 8.8$ Hz, PMe_3), 1.90 (d, $^2J_{HP} = 9.2$ Hz, PMe_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): A_2B system: $\delta = -0.97$, −1.33, −3.28, −3.62, −3.67, −4.01; $\nu_A = -1.15$ ppm; $\nu_B = -3.64$ ppm, $^2J_{AB} = 58.3$ Hz.

2.5. Preparation of cis,trans,cis-$Fe(CO)_2(PEt_3)_2I_2$ (**3b**)

One gram of $Fe(CO)_4I_2$ was dissolved in 50 mL of toluene at room temperature; 0.7 g of PEt_3 (molar ratio 2.5/1) were added under stirring. The reaction was complete in 10 min. The solution was dried and complex **3b** was crystallized from CH_2Cl_2–*n*-hexane at −15 °C as red brown crystals. Yield 80%. Anal. Calc. for $C_{14}H_{30}FeI_2O_2P_2$: C, 27.93; H, 5.02. Found: C, 27.75; H, 4.95%. ν_{CO} (toluene, cm^{-1}): 2016, 1983.

2.6. Preparation of cis,trans,cis-$Fe(CO)_2(PMe_3)_2Br_2$ (**3a′**)

Five grams of $Fe(CO)_4Br_2$ were dissolved in 100 mL of DE; 3.5 g of PMe_3 (molar ratio 3/1) were added under stirring at −15 °C. The reaction was complete in 1 h. The solution was filtered and dried. Complex **3a′** was crystallized from CH_2Cl_2–*n*-hexane at −15 °C. Yield: 74%. Anal. Calc. for $C_8H_9FeBr_2O_2P_2$: C, 23.17; H, 2.19. Found: C, 23.35; H, 2.25%. ν_{CO} (toluene, cm^{-1}): 2022, 1970.

2.7. Photochemical preparation of all trans-$Fe(CO)_2(PMe_3)_2I_2$ (**4a**)

Complex **3a** (1.27 g) was dissolved in 50 mL of toluene. The solution was introduced into a photochemical reactor and irradiated with a medium pressure Hanovia lamp through a filter to block the light with $\lambda < 350$ nm. The isomerization was complete in 10 min. The solution was dried and complex **4a** was crystallized from a CH_2Cl_2–*n*-hexane solution as red crystals. Yield: 40%. ν_{CO}(toluene, cm^{-1}): 1974. In the presence of an excess of PMe_3 (molar ratio 6/1) no photochemical transformation of complex **3a** to complex **4a** was observed, but a slow reaction (≈12 h) occurred that gave complex *mer*,*trans*-$Fe(CO)L_3I_2$ (**7a**) with a CO stretching band at 1956 cm^{-1}. This last complex was characterized spectroscopically by NMR: ^1H NMR (CD_2Cl_2): δ, 1.95 (t, $^{|2+4|}J_{H-P} = 7.2$ Hz, PMe_3 *trans*), 1.85 (d, $^2J_{H-P} = 7.2$ Hz, PMe_3 *cis*). $^{31}P\ \{^1H\}$ NMR: $\delta = 42.4$ (t, $^2J_{P-P} = 55.7$ Hz, PMe_3 *trans*), 0.4 (d, $^2J_{P-P} = 55.2$ Hz, PMe_3 *cis*).

2.8. Thermal isomerization of complex **4a**

One gram of complex **4a** was dissolved in 50 mL of toluene and 0.9 g of PMe_3 were added at room temperature. Complex **4a** isomerized to complex **3a** in 10 min.

2.9. Thermal isomerization of complex **3b**

0.5 g of *cis*,*trans*,*cis*-$Fe(CO)_2(PEt_3)_2I_2$ (**3b**) were dissolved in 25 mL of toluene at 25 °C. The solution remained unchanged for 3 h; then 0.6 g of PEt_3 (molar ratio 6/1) were added. Under these conditions, complex **3b** isomerized slowly into complex **4b**. The reaction was complete in 20 h. Complex **4b** shows a CO stretching band at 1966 cm^{-1}.

2.10. Preparation of $Fe(CO)_3(PMe_3)_2$ (**5a**)

One gram of complex **3a** was dissolved in 50 mL of ACN. The solution was thermostatted at −18 °C and stirred with an excess of sodium amalgam (1.2%) (molar ratio 6/1) under bubbling of carbon monoxide. The colour of the solution initially changed from red to green and then to yellow. After 1 h the reaction was complete. The solution was filtered and dried. The solid residue crystallized from an ethyl alcohol–*n*-hexane mixture as yellow crystals and compared with a specimen prepared by $Fe_2(CO)_9$ and PMe_3 [8].

2.11. Photochemical reaction of complex **2a**

(a) 1.2 g of complex **2a** were dissolved in 50 mL of toluene and irradiated at room temperature with a medium pressure Hanovia lamp, equipped with a filter to block the ultraviolet radiation. A fast decomposition was observed with formation of complex **4a** ($\nu_{CO} = 1974\ cm^{-1}$). The formation of an intermediate, showing a CO stretching band at 2029 cm^{-1}, was also observed.

(b) 0.12 g of complex **2a** were dissolved in 50 mL of toluene. An excess of PMe_3 was added (molar ratio 8/1). The solution was irradiated as described in point a. A fast quantitative reaction of complex **2a** and its transformation into complex **3a** were observed.

2.12. Effect of the basicity and concentration of phosphine ligands on the reaction products

The reaction between $Fe(CO)_4X_2$ (X = I (**1**), Br (**1′**)) and L (PMe_3, PEt_3, PMe_2Ph, $PMePh_2$, PPh_3) were followed at various temperatures in the range −40 to +25 °C and at different concentrations of ligands in the range 1.5×10^{-1} to 10^{-2} M. In a typical experiment, 0.025 g of $Fe(CO)_4I_2$ were dissolved in 5 mL of toluene. The solution was injected in a thermostatted and blackened reactor. PMe_3 was then added and aliquots of the solution were withdrawn at various times and analyzed by IR in the range 2100–1800 cm^{-1} in order to determine their composition. The concentrations of complexes **5** and **3** and their relative ratios A (Tables 2–5) were obtained by the experimental values of the extinction coefficients. The relative ratios B of complexes **3** and **2** were measured by the ratio between the absorbance of the low frequency CO stretching of complex **3** and the absorbance of the intermediate frequency CO stretching of complex **2**, assuming the extinction coefficients were similar for the different L.

Table 2
Effect of the ligand concentration on the products of the reaction between $Fe(CO)_4I_2$ and PMe_3 at −20 °C in toluene; $[Fe(CO)_4I_2] \approx (1.35 \pm 0.15) \times 10^{-2}$ M

$10^2 \cdot [PMe_3]$ (M)	$10^3 \cdot [Fe(CO)_2(PMe_3)_2I_2]$ (**3a**) (M)	$10^3 \cdot [Fe(CO)_3(PMe_3)_2]$ (**5a**) (M)	**A**[a] = [**5a**]/[**3a**]
2.50	7.70	3.37	0.44
5.04	7.70	4.50	0.63
8.59	8.40	5.92	0.70
11.70	8.12	6.46	0.80
14.80	8.05	6.73	0.83

[a] **A** = $[Fe(CO)_3L_2]/[Fe(CO)_2L_2I_2]$.

Table 3
Effect of temperature and ligand concentration on the **A**[a] values for the reaction of $Fe(CO)_4I_2$ with PMe_3 and PEt_3

	A(PMe_3)				A(PEt_3)
$10^2 \times [L]$ (M)	−40 °C	−20 °C	0 °C	25 °C	25 °C
2.50	0.26	0.44	0.11	0.05	0.22
5.04	0.56	0.63	0.14		0.27
8.59	0.63	0.70	0.31		0.36
11.70	0.74	0.80	0.40		0.40
14.80	0.73	0.83	0.38		0.40

[a] **A** = $[Fe(CO)_3L_2]/[Fe(CO)_2L_2I_2]$.

Table 4
Effect of the ligand basicity on the **A** and **B** values at 25 °C with $[L] = 2.50 \times 10^{-2}$ M for iodide complexes

L	pK_a[a]	**A**[b]	**B**[c]
PMe_3	8.65	0.05	∞
PMe_2Ph	6.50	0.02	1.45
$PMePh_2$	4.57	0	0.11
PPh_3	2.73	0	0
Pet_3	8.69	0.22	∞

[a] Values from [10].

[b] **A** = $[Fe(CO)_3L_2]/[Fe(CO)_2L_2I_2]$.

[c] **B** = Ratio between the absorbance of the low frequency CO stretching of complex **3** and the absorbance of the intermediate frequency CO stretching of complex **2**.

Table 5
Effect of the halogen on the **A**[a] values at various temperatures ($[PMe_3] = 11.70 \times 10^{-2}$ M) in toluene

	A (PMe_3)	
T (°C)	I	Br
−40	0.74	0.08
−20	0.80	0.08
0	0.40	0.08

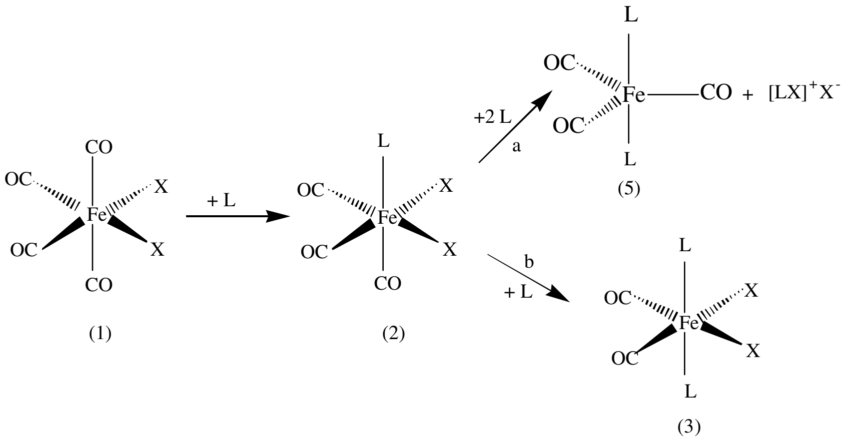
[a] **A** = $[Fe(CO)_3L_2]/[Fe(CO)_2L_2I_2]$.

The white precipitated was filtered, washed with toluene and characterized as $[PMe_3I]^+I^-$.

3. Results

The substitution reaction of $Fe(CO)_4X_2$ [X = I (**1**); Br (**1′**)] with phosphine ligands L, having different basicity and steric hindrance (L = PMe_3, PEt_3, PMe_2Ph, $PMePh_2$, PPh_3) [10], was studied in the temperature range −40 °C to +25 °C. The reactions were complete in less of an hour at −40 °C and proceeded in two steps as shown in Scheme 2: the first step yielded the monosubstituted *fac*-$Fe(CO)_3LX_2$ (**2**) complex; the second step proceeded via two parallel pathways *a* and *b*; pathway *a* gave equimolar amounts of $Fe(CO)_3L_2$ (**5**) and phosphonium salts $[LX]^+X^-$ by reductive elimination; pathway *b* gave disubstituted dihalide *cis*,*trans*,*cis*-$Fe(CO)_2L_2X_2$ (**3**) complexes, by carbon monoxide substitution.

A quantitative study was carried out for L = PMe_3 and $Fe(CO)_4I_2$. The characterization of the phosphonium salt $[PMe_3I]^+I^-$ was achieved by elemental analysis and by comparison with a specimen prepared by PMe_3 and I_2 [11]. The NMR characterization of $[PMe_3I]^+I^-$ in solution was not possible due to its insolubility in the common organic solvents. A ^{31}P NMR spectrum is reported in the literature for the solid state (−5.3 ppm) and for $CDCl_3$ solution (80 ppm) [12]. We were not able to solubilize $[PMe_3I]^+I^-$ in either $CDCl_3$ or in other organic solvents; when the solubilization occurs the species in solution are



Scheme 2.

the products of the reaction of $[PMe_3I]^+I^-$ with the solvent (for example CH_3OD) or with H_2O contained in the solvent. In fact $[PMe_3I]^+I^-$ is very sensitive to H_2O with formation of $[PHMe_3]^+I^-$, which was isolated and completely characterized (see Section 2). Owing to the high reactivity of $[PMe_3I]^+I^-$ with H_2O, the reaction between $Fe(CO)_4I_2$ and PMe_3 was carried out in toluene dehydrated by Na/K alloy.

The concentrations of complexes **2**, **3** and **5** of Scheme 2 depend on the concentration, basicity and steric hindrance of L, on temperature and on the halogen. The effect of PMe_3 concentrations at −20 °C in toluene is given in Table 2, in which the ratios A between the concentrations of complexes **5** and **3** are reported; the **A** values represent the relative weight of the reductive elimination with respect to the substitution reaction. The **A** values increase with increasing the concentration of PMe_3 as shown in Fig. 1.

The effect of temperature on the value of **A** in the range −40° to +25 °C is given in Table 3 for various concentrations of L (L = PMe_3, PEt_3). The trend shows a maximum for the temperature of around −20°C. The values of **A** for PEt_3 are significantly greater than for PMe_3, indicating a strong effect of the steric hindrance of PEt_3, since the basicity of PMe_3 and PEt_3 is similar [10].

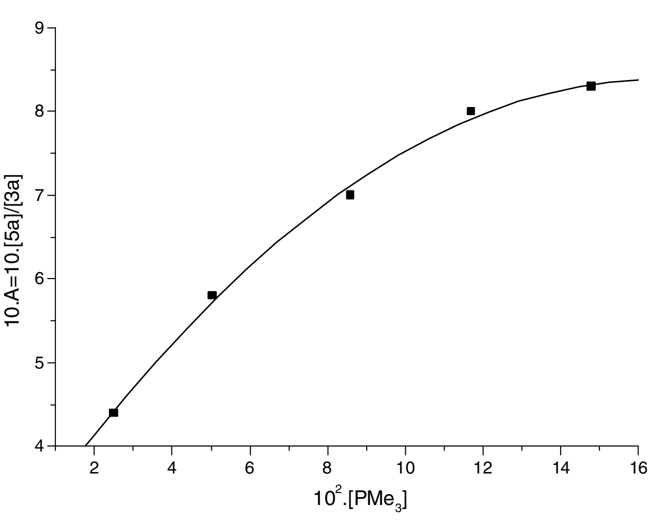


Fig. 1. Molar ratio of **5a** and **3a** complexes vs. $[PMe_3]$ for the reaction of Scheme 2 in toluene at −20 °C. $[Fe(CO)_4I_2] = (1.35 \pm 0.15) \times 10^{-2}$ M.

The effect of the basicity of the phosphine ligands on the reductive elimination is evidenced by the increase of the **A** values on increasing the pK_a of the ligands (Table 4). However the basicity of the ligands also influences the formation of *fac*-$Fe(CO)_3LI_2$. On decreasing the basicity of the ligands, the concentration of the monosubstituted complexes increases until with PPh_3 the reaction stops at the first step, as indicated by the **B** values of Table 4, which correspond to the ratio between the absorbances of *cis*,-*trans*,*cis*-$Fe(CO)_2L_2I_2$ and *fac*-$Fe(CO)_3LI_2$. The formation of *fac*-$Fe(CO)_3LI_2$ is kinetically controlled: in fact, the monosubstituted derivatives react very slowly with the phosphine ligands, forming the disubstituted dihalide derivatives **3**, by a CO dissociation mechanism, as studied by Basolo [6] for L = EPh_3 ((E = P, As, Sb). The disubstituted dihalide complexes **3** are the stable thermodynamic products of the reaction.

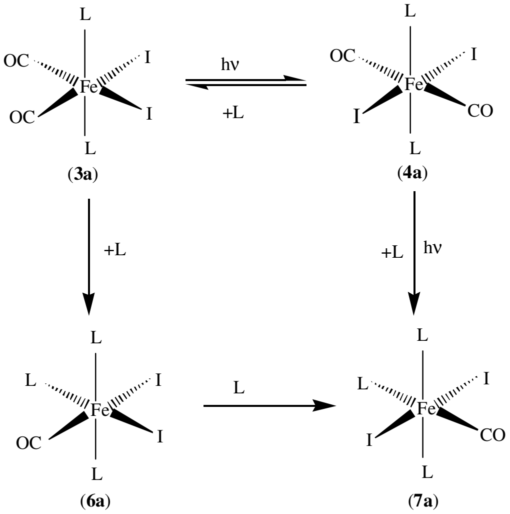
The effect of halogen is given in Table 5. The reductive elimination is much easier with iodide than with bromide as evidenced by the strong increase of the **A** values of iodide; moreover the values of **A** of iodide are influenced by temperature, while those of bromide are not influenced.

The course of the reaction of Scheme 2 shows that the reductive elimination follows the formation of the monosubstituted *fac*-$Fe(CO)_3LI_2$ complex; however, by starting from *fac*-$Fe(CO)_3LI_2$, prepared by reaction of $Fe(CO)_4PMe_3$ and iodine (see Section 2), only the formation of *cis*,*trans*,*cis*-$Fe(CO)_2L_2I_2$ via the very slow CO dissociation is observed. The addition of small amounts of $Fe(CO)_4I_2$ to the solution of *fac*-$Fe(CO)_3LI_2$ and PMe_3 increases the reaction rate and activates the elimination reaction. Then, during the first step of the reaction, intermediate species, which catalyze the second step of the reaction and promote the reductive elimination, must be formed.

In order to obtain information about these intermediates, photochemical reactions were carried out on the reaction between *fac*-$Fe(CO)_3LI_2$ and PMe_3. In the presence of stoichiometric amount of PMe_3 formation of *all trans*-$Fe(CO)_2L_2I_2$ (**4a**) complex was observed; in the presence of an excess of PMe_3, *cis*,*trans*,*cis*-$Fe(CO)_2L_2I_2$ (**3a**) was obtained. Reductive elimination was never observed. In the absence of PMe_3 *cis*,*trans*,*cis*-$Fe(CO)_2L_2I_2$ is not photochemically stable and isomerizes to *all trans*-$Fe(CO)_2L_2I_2$. This last complex in the presence of PMe_3 isomerizes to *cis*,-*trans*,*cis*-$Fe(CO)_2L_2I_2$. Complex *cis*,*trans*,*cis*-$Fe(CO)_2L_2I_2$ ($L = PEt_3$) is not thermally stable and in the presence of an excess of the ligand it slowly isomerizes to *all trans*-$Fe(CO)_2L_2I_2$.

Both *cis*,*trans*,*cis*-$Fe(CO)_2L_2I_2$ (**3a**) and *all trans*-$Fe(CO)_2L_2I_2$ (**4a**) react with PMe_3 as indicated in Scheme 3 to give trisubstituted complexes.

Complex **3a** reacts with PMe_3 to give *mer*,*cis*-$Fe(CO)L_3I_2$ (**6a**) which isomerizes thermally in the presence of L to *mer,trans*-$Fe(CO)L_3I_2$ (**7a**). Complex **7a** is formed from complex **4a** photochemically. The structures of complexes **6a** and **7a** were assigned on the basis of ^1H NMR and $^{31}P\{^1H\}$ NMR spectra. The ^1H NMR spectra show a Harris triplet and a doublet for both complexes indicating the presence of two equivalent phosphine ligands. The $^{31}P\{^1H\}$ NMR spectra are different: complex **7a** shows a triplet and a doublet corresponding to an A_2X structure, while complex **6a** shows an A_2B structure. The coupling constants $^2J_{PP}$ are $\sim$ 55 Hz for complex **7a** and 58.3 Hz for complex **6a**, in agreement with a *cis* structure between A and X and A and B, respectively [13]. The structures of trisubstituted derivatives in agreement with these spectroscopic properties are *fac,cis*-$Fe(CO)L_3I_2$, *mer*,*cis*-$Fe(CO)L_3I_2$ and *mer,trans*-$Fe(CO)L_3I_2$. While it is easy to assign the structure *mer,trans*-$Fe(CO)L_3I_2$ to complex **7a**, which is also obtained photochemically, it is difficult to choose between the *fac,cis*-$Fe(CO)L_3I_2$ and the *mer*,*cis*-$Fe(CO)L_3I_2$ structures for complex **6a**. The lower CO stretching frequency of complex **6a** suggests the structure *mer*,*cis*-$Fe(CO)L_3I_2$, in which CO is *trans* to iodide, as the most probable structure of complex **6a** with respect to the structure *fac,cis*-$Fe(CO)L_3I_2$ in which CO is *trans* to L.



Scheme 3.

Photochemical isomerization of *cis* to *trans* dihalide complexes has often been observed in iron [14] and ruthenium [15,16] complexes; similarly, *cis* to *trans* photochemical isomerizations of alkyl halide complexes of iron, ruthenium and osmium have been described previously [17]; thermal *trans* to *cis* isomerization, catalyzed by phosphine ligands have also been described in ruthenium complexes and its mechanism has been discussed [18]. Thermal *cis* to *trans* isomerization, catalyzed by phosphine ligand as the isomerization of *cis*,*trans*,*cis*-$Fe(CO)_2(PEt_3)_2I_2$ to *all trans*-$Fe(CO)_2(PEt_3)_2I_2$, is uncommon and it is due to the thermodynamic stabilization of the *trans* dihalide structure owing to the steric hindrance of the PEt_3 ligand.

4. Discussion

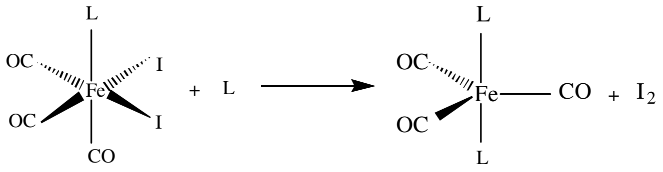
4.1. Thermodynamics

The most important aspect of the reaction studied in this work is the reductive elimination of halogens. The course of the reaction (Scheme 2) indicates that the reductive elimination occurs during the second step of the reaction. On the basis of the literature information, a few semiquantitative considerations can be made about the thermodynamics of the reductive elimination of halogens in iron complexes.

With reference to Scheme 4: and considering that the Fe–I bond strength of *fac*-$Fe(CO)_3LI_2$ is higher or equal to the Fe–I bond strength in $Fe(CO)_4I_2$, measured by Connor and coworkers [$E_{Fe–I} = 177$ kJ] [19] and using for I_2 $E_{I–I} = 156$ kJ [20], the enthalpy of the reaction of Scheme 4 (ΔH_4) is in kJ:

$$\Delta H_4 \geqslant 2E_{Fe–I} - E_{Fe–L} - E_{I–I} = 2.177 - E_{Fe–L} - 156 = 198 - E_{Fe–L}$$

The reaction of Scheme 4 is exothermic if $E_{Fe\text{-}L} > 198$ kJ. Unfortunately, $E_{Fe\text{-}L}$ are unknown in the literature; in general, however, the Metal-L bond strengths are much lower than 198 kJ [2a]. Recently, the Fe–PH_3 bond strength in $Fe(CO)_4PH_3$ was calculated as 169 kJ [21]. Since the entropic effect is negligible with respect to the enthalpic one when covalent bonds are involved [2], the ΔH_4 value confirms that the reaction of Scheme 4 is not thermodynamically allowed; it can be made thermodynamically allowed by coupling with the reaction of quaternization of L with I_2:



Scheme 4.

$$L + I_2 \rightarrow [LI]^{+}I^{-}$$

The enthalpy of the quaternization reaction is unknown; however the enthalpy of the reaction between PPh_3 and CH_3I is −137.2 kJ [22] and that of the reaction between PI_3 and I_2 to give $[PI_4]^{+}I^{-}$ was calculated to be −70 kJ [23]. Therefore it is reasonable that the quaternization reaction is exothermic enough to make the elimination reaction (pathway *a* of Scheme 2) thermodynamically allowed. To our knowledge only one example of this type of coupling is described in the literature and concerns the reaction between $W(CO)L_2I_3({=}CNEt_2)$ with PMe_3 to give $[W(CO)L_2(PMe_3)_2({=}CNEt_2)]^{+}I^{-}$ and $[PMe_3I]^{+}I^{-}$ [4].

The substitution of iodine with bromine strengthens the Fe–X bond [24] and, although the Br–Br bond is stronger than the I–I bond, the enthalpy of the reaction of Scheme 4 with bromine is less exothermic than that with iodine. This is experimentally confirmed by the **A** values for X = Br (Table 5) which are about 10 times lower than those for X = I.

5. Mechanism

Another important aspect of the elimination reaction is the mechanism of the coupling between the reaction of Scheme 4 and the quaternization reaction. It is of interest to emphasize that the first and second steps of Scheme 2 are not completely distinct. In fact, the reductive elimination does not occur by starting from *fac*-$Fe(CO)_3(PMe_3)I_2$: in this latter case only the substitution of carbon monoxide to *cis*,*trans*,*cis*-$Fe(CO)_2(PMe_3)_2I_2$ (**3a**) is observed, as described by Basolo [6]. Similarly the photochemical reaction between *fac*-$Fe(CO)_3(PMe_3)I_2$ and PMe_3 only gives complex **3a**. However the addition of a small quantity of $Fe(CO)_4I_2$ to the toluene solution of *fac*-$Fe(CO)_3(PMe_3)I_2$ and PMe_3 activates the reductive elimination reaction. This suggests that the reductive elimination occurs at the level of intermediates, which can also activate *fac*-$Fe(CO)_3(PMe_3)I_2$. This is reasonable considering that *fac*-$Fe(CO)_3(PMe_3)I_2$ is not a thermodynamic but a kinetic product of the reaction.

The Fe–I bond energy of $Fe(CO)_4I_2$ ($E_{Fe–I}$ = 177 kJ) [19] is very near to the I–I bond energy ($E_{I–I}$ = 156 kJ) [20]; so it is easy to obtain a 17-electron radical $Fe(CO)_4I$ by thermally breaking one of the Fe–I bonds. The 17-electron species can activate the steps of Scheme 5, which explain most of the experimental observations.

The 17-electron radicals, which gave the end products *fac*-$Fe(CO)_3LI_2$, *cis*,*trans*,*cis*-$Fe(CO)_2L_2I_2$ and $Fe(CO)_3L_2$ by reactions 5g, 5h and 5i are $Fe(CO)_3LI$, $Fe(CO)_2L_2I$ and $[Fe(CO)_3L_2]^{+}$, respectively. These three species are correlated by equilibria 5d, 5e and 5f and the concentrations of the end products depend on the values of these equilibrium constants. Radical $Fe(CO)_4I$ may be responsible for the activation of *fac*-$Fe(CO)_3LI_2$ via Fe–I–Fe bridge that is easily formed in transition metal halides [25].

$$Fe(CO)_4I_2 \rightleftharpoons Fe(CO)_4I^{\bullet} + I^{\bullet} \quad (a)$$

$$Fe(CO)_4I^{\bullet} + L \rightleftharpoons Fe(CO)_4LI^{\bullet} \quad (b)$$

$$Fe(CO)_4LI^{\bullet} \rightleftharpoons Fe(CO)_3LI^{\bullet} + CO \quad (c)$$

$$Fe(CO)_3LI^{\bullet} + L \rightleftharpoons Fe(CO)_3L_2I^{\bullet} \quad (d)$$

$$Fe(CO)_3L_2I^{\bullet} \rightleftharpoons Fe(CO)_2L_2I^{\bullet} + CO \quad (e)$$

$$Fe(CO)_3L_2I^{\bullet} \rightleftharpoons [Fe(CO)_3L_2]^{\bullet +} + I^{-} \quad (f)$$

$$Fe(CO)_3LI^{\bullet} + I^{\bullet} \longrightarrow Fe(CO)_3LI_2 \quad (g)$$

$$Fe(CO)_2L_2I^{\bullet} + I^{\bullet} \longrightarrow Fe(CO)_2L_2I_2 \quad (h)$$

$$Fe(CO)_3L_2]^{\bullet +} + LI^{\bullet} \longrightarrow Fe(CO)_3L_2 + [LI]^{+} \quad (i)$$

Scheme 5.

Some steps suggested in Scheme 5 have already been proposed in the literature: equilibrium 5f was observed by Connelly and co-workers [26] in the oxidative elimination of $Fe(CO)_3(PPh_3)_2$ by I_2; radical species $[Fe(CO)_3L_2]^{+}$ were isolated [27] and their reactivity with nucleophiles and radicals [28] have been widely described; radicals $Fe(CO)_2L_2X$ (X = Br, I) were recently isolated as intermediates in the monoelectron reduction of $Fe(CO)_2L_2X_2$ [29,30]; they are very stable in the absence of monoelectron-reducing species or radicals. The reaction between 17-electron radicals and nucleophiles to give 19-electron radicals is well documented in the literature for a few metals and, in particular, for iron [27] supporting equilibria 5b, 5c, 5d and 5e.

Scheme 5 qualitatively explains most of our experimental observations: in fact, the L basicity acts on the position of equilibria 5*b* and 5*d*, influencing the relative concentrations of *fac*-$Fe(CO)_3LI_2$ and *cis*,*trans*,*cis*-$Fe(CO)_2L_2I_2$.

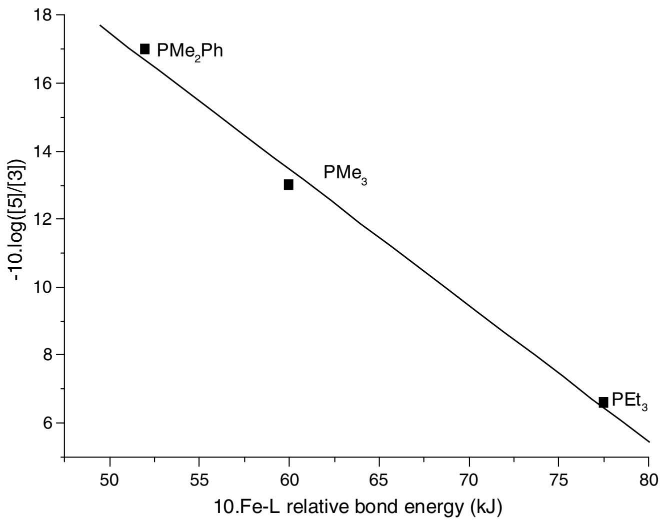


Fig. 2. $-\log \mathbf{A} = -\log[\mathbf{5}]/[\mathbf{3}]$ at 25 °C in toluene vs. relative Fe–L bond energy of $Fe(CO)_3L_2$, assuming the energy of Fe–PPh_3 bond to be zero. Relative Fe–L bond energies from [31].

With the most basic ligands PMe_3 and PEt_3 the ionization of the Fe–I bond is easier and the elimination reaction 5f is activated; then the ratio **A** between *a* and *b* reaction pathways of Scheme 2 depends prevalently on the L basicity. The higher value of **A** of PEt_3 can be explained by its higher steric hindrance, which influences the Fe–L bond energy and favours the ionization of step 5f. Fe–L bond energies are unknown; however their relative values were measured by Nolan and co-workers for the $Fe(CO)_3L_2$ complexes [31]. The plot of log **A** vs. Fe–L bond energies for L = PMe_2Ph, PMe_3, PEt_3, obtained by assuming Fe–PPh_3 equal zero, is shown in Fig. 2. It is clearly linear and suggests that the higher value of *A* for PEt_3 is due to a higher Fe–PEt_3 bond energy.

Reaction 5i requires the presence of LI radicals in solution. There is no experimental evidence of the presence of this radical in solution. LX radicals were proposed in the literature to explain the chain reaction of PPh_3 and bromoform [32] and PPh_3Me radical was hypothesized in the photochemical reaction of PPh_3 and $CpW(CO)_2Me$ [33]. R_3PX (X = halides) radicals were identified by ESR spectroscopy [34]. Although no evidence of the presence of PR_3I in solution was obtained, it is reasonable to propose their role to explain the formation of the cation $[PR_3I]^+$ through the reaction of PR_3I radical and $[Fe(CO)_3L_2]^+$ (reaction 5i).

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