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Journal of Organometallic Chemistry 593–594 (2000) 119–126

Journal of Organometallic Chemistry

Effect of anions on the isocyanide insertion reaction in cationic alkyl complexes of iron(II): kinetic, thermodynamic and solution interionic structural studies

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Received 21 May 1999; accepted 2 August 1999

Dedicated to Professor Fausto Calderazzo.

Abstract

The equilibrium and kinetics of isocyanide insertion of complexes $[Fe(PMe_3)_2(CO)_2(CH_3)(CNR)]^+X^-$ (**1**) [CNR = *tert*-butylisocyanide; $X^- = I^-$ (**1a**), BPh_4^- (**1b**); BF_4^- (**1c**)] which afford complexes $[Fe(PMe_3)_2(CO)_2(\eta^2\text{-}C(CH_3){=}N\text{–}C(CH_3)_3)]^+X^-$ (**2**) were investigated in dichloromethane, methanol, acetone and nitromethane. The results indicate that the reaction proceeds via an associative mechanism with the preliminary formation of contact ion pairs. The structure of the contact ion pair in solution was studied by ^{1}H-NOESY and ^{19}F{^{1}H}-HOESY NMR spectroscopy. The results indicate that structure is independent of the nature of the solvent and of the counterion. In complexes **1b,c** the counterion is located between the CO and the isocyanide ligands; in complexes **2b,c** the counterion is located near the dihaptoiminoacyl ligand. The reaction rate increases with the charge density and the coordinating power of the anions. The effect of the solvent can be also explained on the basis of its coordinating power. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Anion; Ion pairs; NOESY NMR spectroscopy; Insertion

1. Introduction

Cationic organometallic complexes, in which reactivity is strongly influenced by anions, are very numerous in the literature. Examples of this behaviour concern both homogeneous catalytic processes such as the polymerisation of olefins [1], the copolymerisation of carbon monoxide and olefins [2], Diels–Alder reactions [3], etc., and fundamental processes such as carbon monoxide [4] and isocyanide [5] insertions in the metal–alkyl bonds, a reaction that has been extensively studied [6].

Isocyanide insertion in the alkyl complex $[Fe(PMe_3)_2(CO)_2(CH_3)(CNR)]^+X^-$ (**1**) (CNR = *tert*-butylisocyanide; $X^- = Cl^-, Br^-, I^-, NO_3^-, ClO_4^-, BF_4^-, BPh_4^-$) occurs according to Scheme 1 [5a].

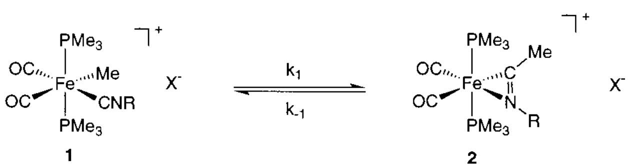
The reaction rate is strongly affected by the counterion. In dichloromethane, the reactivity follows the order:

$$Cl^- \sim Br^- > I^- > NO_3^- \gg ClO_4^-$$

No reaction was observed with $X^- = BPh_4^-$ and BF_4^-.

While the influence of the anions on the reactivity was attributed to the formation of contact ion pairs, it was difficult to explain the reactivity order basing on the anion size, in particular for the position of BF_4^-.

In recent years our research group has developed a methodology for studying the ion pair structure in solution of organometallic complexes, based on detecting interionic contacts, i.e. dipolar interactions between



R = *tert*-Butyl

$X^- = Cl^-, Br^-, I^-$(**1a**, **2a**), NO_3^-, ClO_4^-, BPh_4^-(**1b**, **2b**), BF_4^-(**1c**, **2c**)

Scheme 1.

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PII: S0022-328X(99)00468-4

Table 1
^{1}H- and ^{19}F-NMR chemical shifts (in ppm) for complexes **1** and **2** in different solvents

Complex	Solvent	δ_{Me}	δ_{PMe_3}	δ_{CMe_3}	$\delta_{counterion}$
1b	CD_2Cl_2	−0.09	1.55	1.55	7.34(H^o), 7.09(H^m), 6.94(H^p)
2b	CD_2Cl_2	2.92	1.31	1.39	7.37(H^o), 7.09(H^m), 6.94(H^p)
1b	$(CD_3)_2CO$	−0.04	1.69	1.63	7.36(H^o), 6.95(H^m), 6.80(H^p)
2b	$(CD_3)_2CO$	3.21	1.44	1.48	7.36(H^o), 6.95(H^m), 6.80(H^p)
1b	CD_3OD	−0.08	1.60	1.54	7.31(H^o), 6.98(H^m), 6.85(H^p)
2b	CD_3OD	3.10	1.37	1.43	7.31(H^o), 6.98(H^m), 6.85(H^p)
1b	CD_3NO_2	−0.06	1.63	1.56	7.36(H^o), 7.01(H^m), 6.86(H^p)
2b	CD_3NO_2	3.14	1.41	1.46	7.36(H^o), 7.01(H^m), 6.86(H^p)
1c	CD_2Cl_2	−0.08	1.62	1.57	
					−152.87 ($^{10}BF_4^-$)
					−152.93 ($^{11}BF_4^-$)
2c	CD_2Cl_2	3.11	1.39	1.44	
1c	$(CD_3)_2CO$	−0.05	1.71	1.65	
					−151.70 ($^{10}BF_4^-$)
					−151.75 ($^{11}BF_4^-$)
2c	$(CD_3)_2CO$	3.26	1.47	1.50	

nuclei belonging to different ions, in NOESY and HOESY NMR spectra [7].

In the present work we extend the application of this methodology to the study of the reaction in Scheme 1 in order to interpret the reactivity of complexes **1** and **2** on the basis of the contact ion pair structures.

Since the previously studied complexes containing NMR active nuclei in the counterions (BPh_4^- and BF_4^-) were not active in the insertion reaction in dichloromethane, we extended the kinetic study to solvents in which the reaction in Scheme 1 occurred; furthermore, we studied the kinetic and thermodynamic behaviour of I^- in these solvents in order to relate the previous results of Ref. [5a] to those obtained in this work.

2. Experimental

2.1. Physical measurements

IR spectra were recorded on a Perkin–Elmer model 1725X FT-IR spectrophotometer by using 0.1 mm NaCl cells and 10^{-2}–10^{-3} M concentrations; ^{1}H- and ^{19}F-NMR spectra were recorded on Bruker DPX 200 and DRX 400 spectrometers. Referencing is relative to TMS for ^{1}H- and CCl_3F for ^{19}F-NMR. NMR samples were prepared by dissolving 20 mg of compound in 0.5 ml of the deuterated solvent and bubbling for 5 min with dried nitrogen. ^{1}H and ^{19}F chemical shifts in the various solvents are given in Table 1. CO and CN stretching frequencies are given in Table 2. Two-dimensional ^{1}H-NOESY and $^{19}F\{^1H\}$-HOESY spectra were measured with a mixing time of 500–800 ms.

2.2. Materials

Methanol, acetone and nitromethane were purified according to the methods described in the literature [8]. Dichloromethane was dehydrated with P_2O_5; ethyl ether was dehydrated with $LiAlH_4$. $NaBPh_4$, NBu_4I, KI, $NaBF_4$, $N(CH_3)_4BF_4$, NBu_4BF_4 and *tert*-butylisocyanide were commercial products. Complexes $[Fe(PMe_3)_2(CO)_2(CH_3)(CN\text{-}tert\text{-butyl})]BPh_4$ (**1b**) and $[Fe(PMe_3)_2(CO)_2(\eta^2\text{-}C(CH_3){=}N\text{-}tert\text{-butyl})]BPh_4$ (**2b**) were prepared as described in Ref. [5a].

Table 2
CO and CN stretching frequencies (cm^{-1}) for complexes **1** and **2** in various solvents

Complex	Solvent	ν_{CO}	ν_{CN}
1a	Dichloromethane	2027, 1985	2179
2a	Dichloromethane	2015, 1951	1756
1a	Methanol	2031, 1988	2178
2a	Methanol	2014, 1951	
1a	Acetone	2027, 1985	2179
2a	Acetone	2013, 1949	
1b	Dichloromethane	2027, 1985	2180
2b	Dichloromethane	2015, 1952	1753
1b	Methanol	2029, 1987	2176
2b	Methanol	2014, 1950	
1b	Acetone	2027, 1985	2179
2b	Acetone	2013, 1949	
1b	Nitromethane	2026, 1983	
2b	Nitromethane	2012, 1948	
1c	Dichloromethane	2026, 1986	2179
2c	Dichloromethane	2013, 1947	
1c	Acetone	2026, 1984	2178
2c	Acetone	2013, 1947	

2.3. Preparation of *[Fe(PMe$_3$)$_2$(CO)$_2$(CH$_3$)(CN-tert-butyl)]BF$_4$* (**1c**)

A 0.95 g sample of $N(CH_3)_4BF_4$ (5.9×10^{-3} mol) was added to a stirred suspension of 2 g of $[Fe(PMe_3)_2(CO)_2(CH_3)(CN\text{-}tert\text{-}butyl)]BPh_4$ (**1b**) (2.9×10^{-3} mol) in methanol. During the reaction the precipitation of $N(CH_3)_4BPh_4$ was observed. The solution was stirred for 30 min to complete the exchange of anions; the solution was then filtered and dried. The solid residue was extracted with CH_2Cl_2 and the extracted solution, after filtration, was dried again. The residue was crystallised from ethyl alcohol. Yield:1.2 g (2.6×10^{-3} mol) (92%) of yellow crystals. Anal. as $C_{14}H_{30}BF_4FeNO_2P_2$: Found (Calc.): C, 37.8 (37.4); H, 6.3 (6.74); N, 3.5 (3.12)%.

2.4. Kinetic and equilibrium measurements

The kinetic measurements were carried out under nitrogen, in the dark, in thermostatted flasks, closed with a serum cup in the case of reactions that are complete in three days; for slower reactions and for equilibrium measurements sealed flasks were used, which were opened at various times for the solution to be analysed.

In a typical run, an excess of NBu_4X was added to a solution of **1c** (or in some cases **1b**). The solution was thermostatted in the 25–60°C range according to the solvent used and the concentration of complex **1** was measured at different times. The reaction was followed up to two half lives.

The concentrations of the complexes in solution were measured by the absorbance of the CO stretching bands on the basis of Beer's laws of complexes **1b** and **2b**, which were also used for the other complexes, since the anion does not affect the intensity of the bands.

Since the concentration of the anion X^- did not change during each kinetic run, the reaction was considered a pseudo-first-order reaction. The reaction rates were measured by following the disappearance of the CO stretching band at higher frequency of complex **1**. The kinetic relationship for the calculation of the pseudo-first-order rate constants is:

$$\ln\frac{D_0 - D_e}{D_t - D_e} = (k_{fwd} + k_{rev})t = k_{fwd}\frac{a}{x_e}t \qquad (1)$$

where D_0, D_e and D_t are zero time, equilibrium and t time absorbances of complex **1**, respectively; k_{fwd} and k_{rev} are the pseudo-first-order rate constants in the forward and reverse directions, respectively; a is the initial concentration of complex **1** and x_e is the equilibrium concentration of the dihaptoiminoacyl complex **2**. The other CO and CN stretching bands were not used because of their low intensities or their overlap with other bands.

The equilibrium of Scheme 1 does not occur with BPh_4^- and BF_4^- in dichloromethane and nitromethane; on the other hand, in these solvents the reverse reaction was observed and went to completion. The pseudo-first-order rate constant of this reaction was measured in dichloromethane in the presence of an excess of NBu_4BPh_4 (molar ratio = 50) using Eq. (2):

$$\ln\frac{D_0}{D_0 - D_t} = k_{-1}t \qquad (2)$$

in which D_0 and D_t are the initial and t time absorbances, respectively, of the band at 1951 cm^{-1} of complex **2b**; the value of the rate constant is imprecise because of slight decomposition.

3. Results

3.1. Synthesis of *[Fe(PMe$_3$)$_2$(CO)$_2$(CH$_3$)(CN-tert-butyl)]BF$_4$* (**1c**)

The method for preparing complex **1b**, described in Ref. [5a], does not give good results for complex **1c**, because, during the reaction of $Fe(CO)_2(PMe_3)_2(CH_3)I$ with *tert*-butylisocyanide in methanol, in the presence of $NaBF_4$, complex **1c**, formed in the reaction, is soluble and isomerises quickly to **2c** due to the presence of I^- in solution. Attempts to eliminate I^- by using $AgBF_4$ were unsuccessful because Ag^+ reacts with complexes **1** and **2**, which then decomposed.

Complex **1c** was obtained utilising the solubility of $N(CH_3)_4BF_4$ in methanol and its insolubility in CH_2Cl_2. By adding an excess of $N(CH_3)_4BF_4$ to a suspension of complex **1b** in methanol, complex **1c** dissolved and the salt $N(CH_3)_4BPh_4$ precipitated out. The excess $N(CH_3)_4BF_4$ was separated by dissolution in CH_2Cl_2 of the residue of the solution

3.2. Thermodynamic results

The reaction of Scheme 1 proceeds following the equilibria [5a,9] indicated in reaction (2a):

$$C^+ + X^- \overset{K_{CI}}{\rightleftharpoons} (C^+X^-) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C^{+\prime}X^- \overset{K'_{CI}}{\rightleftharpoons} C^{+\prime} + X^- \qquad (2a)$$

in which C^+ and $C^{+\prime}$ are cations **1** and **2**, respectively; K_{CI} and K'_{CI} are the formation equilibrium constants of the contact ion pairs of complex (C^+X^-) and $(C^{+\prime}X^-)$, respectively; k_1 and k_{-1} are the first-order rate constants of the insertion process in the forward and reverse directions, respectively.

Since the IR technique used for measuring the concentration of complexes **1** and **2** does not distinguish between the contact ion pairs (C^+X^-) and $(C^{+\prime}X^-)$ and the corresponding dissociated ions C^+ and $C^{+\prime}$, the experimental value of the equilibrium constants K_{sp} is given by:

Table 3
Equilibrium constant K_{sp} and thermodynamic parameters for the reaction in Scheme 1

X^-	Solvent	T (°C)	K_{sp} *	Thermodynamic parameters **
I^- (a)	Methanol	40	1.02 ± 0.05	
	Nitromethane	25	0.74 ± 0.03	$\Delta H = -6.7 \pm 0.5$ kJ mol^{-1}
		40	0.70 ± 0.03	$\Delta S = -25 \pm 3$ J K^{-1} mol^{-1}
		50	0.64 ± 0.04	
		60	0.58 ± 0.03	
	Dichloromethane [a]	25	0.75 ± 0.06	
	Acetone [a]	25	0.74 ± 0.04	
BPh_4^- (b)	Acetone	30	0.69 ± 0.02	$\Delta H = -7.9 \pm 0.5$ kJ mol^{-1}
		50	0.55 ± 0.05	$\Delta S = -29 \pm 3$ J K^{-1} mol^{-1}
		60	0.50 ± 0.05	
	Methanol	30	1.07 ± 0.02	$\Delta H = -6.6 \pm 0.5$ kJ mol^{-1}
		40	0.99 ± 0.03	$\Delta S = -21 \pm 3$ J K^{-1} mol^{-1}
		50	0.93 ± 0.04	
		60	0.85 ± 0.03	
BF_4^- (c)	Methanol	40	0.70 ± 0.04	

[a] Values published in Ref. [5a].
* The errors are given as mean deviations.
** The errors are given as the standard deviation of the linear correlation.

$$K_{sp} = \frac{[C^{+\prime}] + [C^{+\prime}X^-]}{[C^+] + [C^+X^-]} \tag{3}$$

By expressing the concentration of the dissociated ions C^+ and $C^{+\prime}$ as a function of K_{CI} and K'_{CI}, respectively, and considering the activity coefficients of the neutral species equal to one, K_{sp} becomes:

$$K_{sp} = \frac{[C^{+\prime}X^-]}{[C^+X^-]} \frac{\dfrac{1}{K'_{CI}[X^-]\gamma^-\gamma^{+\prime}} + 1}{\dfrac{1}{K_{CI}[X^-]\gamma^-\gamma^+} + 1} = K_e \frac{\dfrac{1}{K'_{CI}[X^-]\gamma^-\gamma^{+\prime}} + 1}{\dfrac{1}{K_{CI}[X^-]\gamma^-\gamma^+} + 1} \tag{4}$$

in which γ^+ and $\gamma^{+\prime}$ are the activity coefficients of C^+ and $C^{+\prime}$, respectively; γ^- is the activity coefficient of X^-; $K_e = k_1/k_{-1}$ is the true equilibrium constant of the insertion reaction.

Since C^+ and $C^{+\prime}$ have the same stucture and dimensions, we can assume that, in each run, γ^+ is also equal to $\gamma^{+\prime}$; consequently $K_{sp} = K_e$, if $K_{CI} = K'_{CI}$.

K_{CI} and K'_{CI}, calculated in dichloromethane by conductivity measurements [5a], result the same in the limits of the experimental error; it is reasonable to assume that this is also true in the other solvents.

If all the previous conditions are valid, the experimental equilibrium constant, K_{sp}, is equal to the true equilibrium constant, K_e. The values of the experimental equilibrium constants, K_{sp}, and the thermodynamic parameters in different solvents are given in Table 3.

3.3. Kinetic results

Considering that the dissociated and undissociated ions are not distinguished by the spectroscopic measurements and that the reaction proceeds via formation of contact ion pairs, the insertion rate of reaction (2a) is

$$v = -\frac{d\{[C^+] + [C^+X^-]\}}{dt} = k_1[C^+X^-] - k_{-1}[C^{+\prime}X^-] \tag{5}$$

Since $K_{CI} = K_{CI'}$ and $\gamma^+ = \gamma^{+\prime}$, as previously assumed for the equilibrium, the rate becomes:

$$v = \frac{K_{CI}[X^-]\gamma^-\gamma^+}{K_{CI}[X^-]\gamma^-\gamma^+ + 1}\{k_1([C^+] + [C^+X^-]) - k_{-1}([C^{+\prime}] + [C^{+\prime}X^-])\} \tag{6}$$

The integration of this equation gives:

$$\ln \frac{x_e}{x_e - x} = k_{obs}t \tag{7}$$

where x_e and x are the equilibrium and t time concentrations of the sum of $C^{+\prime}$and $(C^{+\prime}X^-)$, respectively; k_{obs} is given by the following expression:

$$k_{obs} = k_{fwd} + k_{rev} = \frac{K_{CI}[X^-]\gamma^-\gamma^+}{K_{CI}[X^-]\gamma^-\gamma^+ + 1}(k_1 + k_{-1}) = \frac{K_{CI}[X^-]\gamma^-\gamma^+}{K_{CI}[X^-]\gamma^-\gamma^+ + 1} k_1 \frac{a}{x_e}$$

in which

$$k_{fwd} = \frac{K_{CI}[X^-]\gamma^-\gamma^+}{K_{CI}[X^-]\gamma^-\gamma^+ + 1} k_1 \tag{8}$$

On the basis of Eq. (8), the values of the experimental rate constant, $k_{fwd,}$ is a function of K_{CI}, of $[X^-]$ and of

Table 4
Forward pseudo-first-order rate constant (k_{fwd}) for the reaction in Scheme 1 [a] with NBu_4I in various solvents and at various temperatures

$[\mathbf{1c}] \times 10^3$ (M)	$[NBu_4I] \times 10$ (M)	$k_{fwd} \times 10^4$ (s^{-1})
Nitromethane, T = 25°C		
7.31	0	0
7.68	0.156	1.4
6.82	0.210	1.8
6.75	0.270	2.1
7.02	0.350	2.2
6.82	0.690	2.4
Nitromethane, T = 40°C		
7.31	0	0
6.88	1.39	0.55
8.95	2.68	1.02
9.06	3.84	1.36
7.57	3.68	1.49
6.57	6.63	1.65
Methanol, T = 40°C		
7.31	0	0.25
7.75	2.30	4.49
7.46	3.07	6.03
7.50	3.75	6.48
8.58	8.08	7.00

[a] The reacting complex is **1c**.

the activity coefficients γ^- and γ^+, which are not known for the various solvents.

In order to obtain the true rate constants, k_1 and k_{-1}, of the insertion process we carried out kinetic experiments at various concentrations of X^-, by adding NBu_4X. A few experimental values of k_{fwd}, obtained in these experiments, are given in Tables 4 and 5.

By plotting k_{fwd} versus $[NBu_4X]$ (Fig. 1), we obtain an asymptotic trend according to Eq. (8), since the concentration of $[X^-]$ is a function of the concentration of the salt. The asymptotic value of k_{fwd} is therefore equal to k_1, which is independent of K_{CI} and of the activity coefficient of X^-.

The values of k_1 are independent on the nature of the reacting complex; they depend only on the nature of NBu_4X and on the solvent. The k_1 values for the various anions in the different solvents are summarised in Table 6.

Table 5
Forward pseudo-first-order rate constant (k_{fwd}) for the reaction in Scheme 1 [a] with NBu_4BF_4 in methanol at 40°C

$[\mathbf{1c}] \times 10^3$ (M)	$[NBu_4I] \times 10$ (M)	$k_{fwd} \times 10^5$ (s^{-1})
7.31	0	1.85
8.71	1.75	2.18
8.75	2.62	2.45
8.69	3.49	2.49
8.04	4.21	2.48

[a] The reacting complex is **1c**.

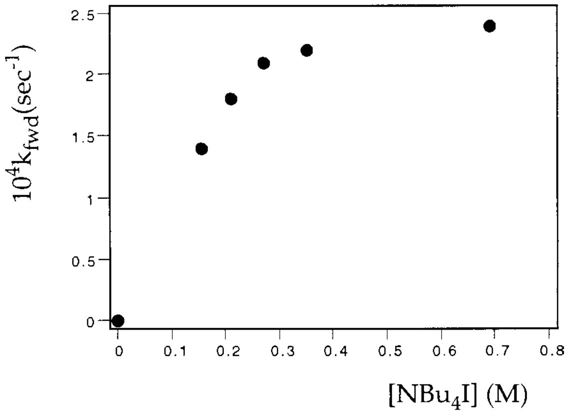

Fig. 1. k_{fwd} vs. $[NBu_4I]$ in nitromethane at 25°C for the reaction in Scheme 1; the reacting complex is $[Fe(PMe_3)_2(CO)_2(CH_3)(CN\text{-}\mathit{tert}\text{-}butyl)]BF_4$ (**1c**).

The reverse reaction of the Scheme 1 was followed only for $[Fe(PMe_3)_2(CO)_2(\eta^2\text{-}C(CH_3){=}N\text{-}\mathit{tert}\text{-}butyl)]BPh_4$ (**2b**) in dichloromethane in which the reaction goes to completion, using a strong excess of NBu_4BPh_4. The k_{-1} at 30°C is 2.4×10^{-6} s^{-1}.

3.4. Solution interionic structures

The interionic structures of complexes **1b** and **2b** in all the solvents studied in the kinetic measurements were investigated by ^1H-NOESY NMR spectroscopy, while those for complexes **1c** and **2c** were measured by $^{19}F\{^1H\}$-HOESY NMR spectroscopy. The NOE contacts between dipolarly-coupled nuclei can only be observed if the contacts are closer than 4.5–5 Å. This means that the contact ion pairs must be the predominant species in order to observe a meaningful interionic contact. The complexes are mainly present as contact ion pair in dichloromethane (dielectric constant 8.71 at 303 K); in the other solvents (acetone, methanol and nitromethane) the complexes were partially dissociated: notwithstanding the contacts are observed in all the solvents. In some cases the spectra were recorded in the presence of an excess of counterion (up to 100 times) in order to increase the concentration of the contact ion pairs.

Sections of the ^1H-NOESY NMR spectra of complexes **1b** and **2b** in CD_2Cl_2 are given in Figs. 2 and 3, respectively; the $^{19}F\{^1H\}$-HOESY NMR spectrum of a mixture of **1c** and **2c** in acetone-d_6 are reported in Fig. 4. The NMR spectra of the complexes in nitromethane-d_3 and methanol-d_3 are similar.

In all the solvents, the spectra show strong interionic contacts between PMe_3 and *tert*-butyl protons of the cations and the NMR active nuclei of the counterions, even if the experimental observation of the isocyanide

Table 6
First-order rate constant (k_1) for the reaction in Scheme 1 in various solvents and at various temperatures [a]

X^-	T (°C)	k_1 (s^{-1})			
		Dichloromethane	Acetone	Methanol	Nitromethane
I^-	25	$(7.3 \pm 0.1) \times 10^{-4}$ [b]	Very fast	$(16.0 \pm 0.9) \times 10^{-5}$	$(2.5 \pm 0.1) \times 10^{-4}$
	40			$(75 \pm 2) \times 10^{-5}$	$(1.7 \pm 0.1) \times 10^{-3}$
BPh_4^-	30	No reaction [c]	$(1.23 \pm 0.10) \times 10^{-5}$	$(8.7 \pm 0.2) \times 10^{-6}$ [d]	No reaction
	40	No reaction		$(2.3 \pm 0.1) \times 10^{-5}$ [d]	No reaction
	50	No reaction		$(6.4 \pm 0.9) \times 10^{-5}$ [d]	No reaction
BF_4^-	40	No reaction	Very slow	$(2.5 \pm 0.1) \times 10^{-5}$	No reaction

[a] X^- refers to salts NBu_4X; with NBu_4BPh_4 the reacting complex is **1b**; with NBu_4I and NBu_4BF_4 the reacting complex is **1c**.

[b] Value published in Ref. [5a].

[c] k_{-1} at 30°C in CH_2Cl_2 is 2.4×10^{-6} s^{-1}.

[d] In these cases the salt used is $NaBPh_4$.

contacts is difficult in some solvents due to the superimposition of their resonance with those of the phosphine protons (see Table 1 and Fig. 2). The methyl group of complexes **1** show a very weak ($X^- = BPh_4^-$) or not appreciable ($X^- = BF_4^-$) contact with the counterions, while the methyl group of the dihaptoiminoacyl complexes **2** show considerable contacts with the protons and the fluorine atoms of the counterions (Figs. 3 and 4). It is interesting to note that in the case of BPh_4^-, the proximity of the counterion to certain protons can also be deduced by the shielding effect exerted by the π-electrons of the phenyl groups [10]. This is clearly shown in Table 1 where, for example, the chemical shift of the Me group for **1b** is practically independent of the solvent ($\Delta\delta = 0.05$ ppm) while in **2b** the same group substantially changes its chemical shift ($\Delta\delta = 0.29$ ppm).

The above reported results are not enough to deduce univocal interionic structures. The observation of interionic contacts between the Me and *tert*-butyl protons with the NMR active nuclei of the counterion in complexes **2** indicates that the latter is located close to the three atom ring in the η^2-complex. The problem of the specificity or non-specificity of this interaction still remains. In fact, we cannot exclude that the counterion could also go in the other side of the molecule that contains the two carbonyl ligands, since it is a 'black' side from an NMR point of view. In our previous studies, we observed a marked specificity of interionic contacts, especially when it is possible to delocalise the positive metal charge [7]. If this occurs in the η^2-complex, our hypothesised interionic structure is correct. In complex **1**, the counterion can be located between the isocyanide and the carbonyl *cis* to it. In this case, too, it is possible that the counterion is localised between the two CO ligands.

4. Discussion

The equilibrium and kinetic studies were carried out in dichloromethane, acetone, methanol and nitromethane in order to cover a wide range of dielectric constants and coordinative capabilities [11].

In all the solvents, the equilibrium constants decreased with increasing temperature. The Δ*H* values are therefore negative (Table 3) and are slightly influenced by the nature of the anions and of the solvent. Δ*S* values are negative and indicate a stronger solvation of complexes **2** than complexes **1**. In most solvents, the entropic and enthalpic effects compensated and the equilibrium constants were close to unity. In contrast, in dichloromethane and nitromethane with $X^- = BPh_4^-$ and BF_4^- the equilibrium shifted toward complexes **1** and insertion was not observed; on the other hand, starting from $[Fe(PMe_3)_2(CO)_2(\eta^2\text{-}C(CH_3){=}N\text{-}tert\text{-butyl})]BPh_4$ (**2b**) the reverse reaction was observed and the k_{-1} value at 30°C in dichloromethane is 2.4×10^{-6} s^{-1}. This

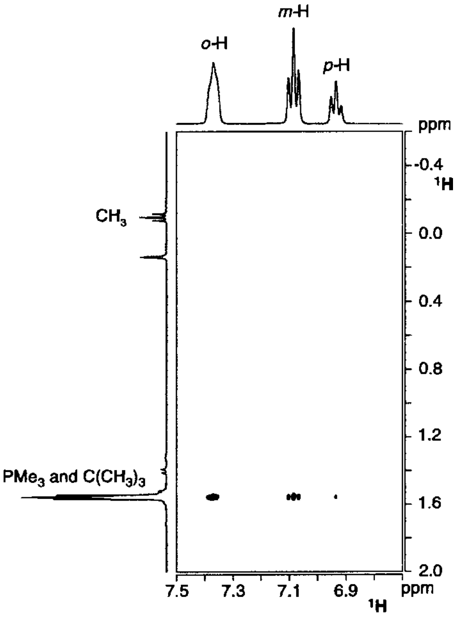

Fig. 2. A section of the ^1H-NOESY NMR spectrum of complex **1b** recorded at 400.13 MHz in CD_2Cl_2 showing the interionic interactions of the aromatic protons with PMe_3 and $C(CH_3)_3$ protons.

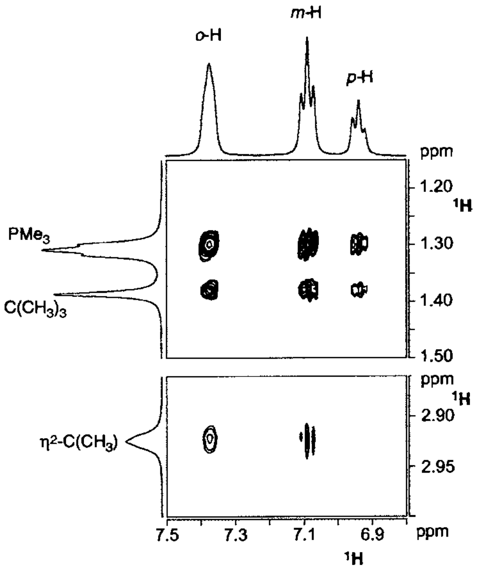

Fig. 3. Two sections of the ^{1}H-NOESY NMR spectrum of complex **2b** recorded at 400.13 MHz in CD_2Cl_2 showing the interionic interactions of the aromatic protons with PMe_3, $C(CH_3)_3$ and η^2-$C(CH_3)$ protons.

indicates that the equilibrium constant in dichloromethane is < 0.05, making complexes **1b** much more stable than complexes **2b**.

The effect of solvent on the equilibrium constants with the anions BPh_4^- and BF_4^- follows the trend:

methanol > acetone ≫ dichloromethane, nitromethane

With the anion I^- the effect is smaller and follows the order:

methanol > acetone, nitromethane, dichloromethane

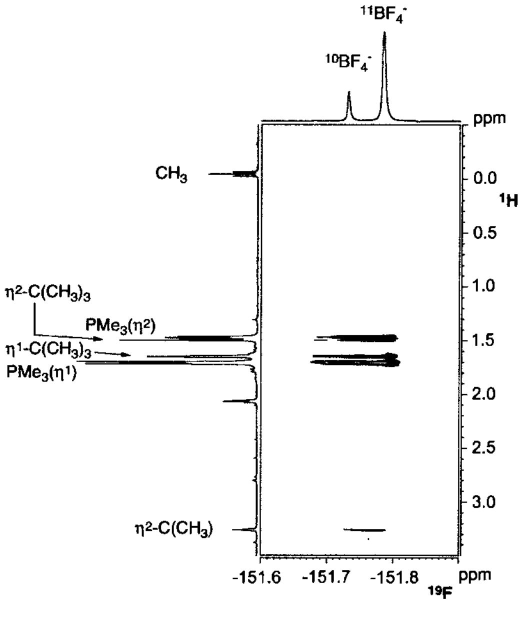

Fig. 4. $^{19}F\{^1H\}$-HOESY NMR spectrum of a mixture of complexes **1c** and **2c** recorded at 376 MHz in CD_2Cl_2 showing the interionic interactions of BF_4^- with all the protons with the exception of those of CH_3.

The coordinative capability of the solvent appears to affect predominantly equilibrium; the dielectric constant is less important, as indicated by the same behaviour of nitromethane and dichloromethane.

The increase of the pseudo-first-order rate constant, k_{fwd}, with an increased concentration of NBu_4X (Tables 4 and 5), up to an asymptotic value (Fig. 1), as expected from Eq. (8), confirms the previous conclusion [5a] that an ion pair is the reacting species in the insertion reaction. NBu_4X increases the concentration of ion pairs (C^+X^-). k_{fwd} increases until all C^+ cations are transformed into (C^+X^-); when this limit is reached, the k_{fwd} value remains constant and this value corresponds to the insertion rate constant, k_1.

Consequently, the formation of the ion pairs precedes the insertion reaction; the electrostatic and chemical interactions in the ion pair are responsible for the reaction [12]. On the other hand, the NMR structural studies indicate that the ion pair structure is not influenced by the solvents and by the anions (Figs. 2–4); the kinetic effects therefore would not be due to a change in the solution structure of the ion pairs.

The effect of the anions and solvents can be analysed on the basis of the k_1 values in Table 6. For the same solvent the anion effect is:

$I^- \gg BPh_4^- \sim BF_4^-$

Combining this trend with previous results [5a], the following anion order is obtained:

$Cl^- \sim Br^- > I^- > NO_3^- \gg ClO_4^- > BF_4^- \sim BPh_4^-$

This reactivity order can be explained on the basis of the size of the anions [13]: smaller anions interact more strongly with the cation of the ion pairs [11] and increase the insertion rate. Based on this, the behaviour of BF_4^- is anomalous: it is much smaller [14] than BPh_4^-, yet shows a similar reactivity, and, although it is smaller than I^-, it reacts much more slowly. This anomalous behaviour can be explained by the coordinating power of the anions which is responsible for the stronger effect exerted by the monoatomic anions; ClO_4^-, BF_4^- and BPh_4^- are weakly coordinating anions but their coordinative powers follow the order observed in this work [15].

No coordinative interaction was observed in complexes **1** and **2**, since the anions do not affect the CO stretching frequencies (Table 2) or ^{1}H chemical shifts (Table 1). The coordinative power could therefore act on the stabilisation of the η^1 unsaturated intermediate $[Fe(PMe_3)_2(CO)_2(\eta^1\text{-}C(CH_3){=}NR)]^+X^-$, formed during the reaction [5b].

The solvent effect changes with the nature of the anions. With BPh_4^- and BF_4^-, the reactivity order is the same as that observed for the equilibrium constants and can be explained on the basis of the stabilisation of (C^+X^-) and ($C^{+'}X^-$) by the coordinative capability of the solvents, which is very high for methanol and acetone and is very low for dichloromethane and nitromethane [11,15].

With I^-, the reactivity order is:

$$\text{acetone} \gg \text{dichloromethane} > \text{nitromethane} > \text{methanol}$$

In this order the position of the methanol is inverted. In methanol, I^- can be strongly solvated with the formation of a solvent-separated ion pair [11,16]. In this type of ion pair, the interaction with the cation is reduced and the effect on the insertion reaction decreases.

In conclusion, the reaction studied in this work is one of the few associative reactions where the anion effect is relevant. Based on the influence of anions and solvent, it seems that size and coordinative capabilities are the most important factors affecting reactivity. The literature [17] contains a lot of information about the influence of anions on reactivity. It is generally accepted that in order to enhance chemical reactivity the anion has to be large and weakly coordinating. In these reactions, the mechanism is dissociative as is clearly shown in the copolymerisation of carbon monoxide and olefins by palladium complexes [18]. In the reaction in Scheme 1 therefore, which proceeds via an associative mechanism, it is reasonable that the effect of anions is inverted.

Acknowledgements

The authors thank the Ministero dell'Università e della Ricerca Scientifica e Tecnologica (MURST, Roma), Programmi di Ricerca Scientifica di Rilevante Interesse Nazionale, Cofinanziamento 1998–1999 for financial support and Dr A. Magistrato and Dr C. Boninti for part of the experimental work.

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