Thermodynamic and Kinetic Studies of Migratory CO Insertion in Alkyl Complexes of Iron(II)

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The reaction of *cis,trans*-$Fe(CO)_2(PMe_3)_2MeX$ with carbon monoxide to give the corresponding cis,trans- and trans,trans-acetyls has been studied in toluene for X = Cl, Br, or I at various temperatures. The formation rates and the equilibrium constants of cis,trans-acetyl with respect to cis,trans-methyl follow the order NCS $\simeq$ CN > Cl > Br > I and are determined by the withdrawing power of X, while the equilibrium constants of trans,trans-acetyl as compared to cis,trans-acetyl follow the order I > Br > Cl $\gg$ CN, Me and are influenced by the steric hindrance of the ligands. *trans,trans*-$Fe(CO)_2(PMe_3)_2MeI$ has been prepared and characterized. Its reaction rate with CO is much slower than that of the corresponding cis,trans complex and is not influenced by the carbon monoxide concentration. Other trans,trans-methyl complexes with L = $PPhMe_2$, $P(OMe)_3$, $P(n\text{-}Bu)_3$, and PPh_2Me have been prepared and characterized by ^1H NMR spectroscopy.

Introduction

The reaction mechanism of octahedral iron(II) alkyl complexes $Fe(CO)_2L_2RX$ with carbon monoxide has been extensively studied in the last ten years.[1-5] The complexes show a wide range of reactivity as a function of solvent[4,6] and nature of ligands (L)[7,8] and halides (X).[2,3] It has been observed that the reaction intermediates are dynamic and many different isomers can be formed; furthermore η^2-acyl structures have been detected and isolated.[7] Carbon monoxide insertion proceeds via the classical alkyl migratory insertion mechanism,[3,4] but in polar solvents a new mechanism is observed, involving direct substitution of the X ligand by CO, followed by an halide-promoted methyl migration.[6] Mechanistic details were confirmed by labeling studies with ^{13}CO and by stereochemical assignments on the basis of ^{13}C and ^{31}P NMR[3] chemical shifts and coupling constants.

Although the general mechanism is reasonably well characterized, there remains a paucity of kinetic and thermodynamic studies which does not allow an accurate description of the energy as a function of the reaction coordinate. Extraction of these important parameters is difficult since this system is complicated by the presence of a large number of isomers. Complexes **1c**, **2c**, and **2t** with X = I, Cl, and Br (Figure 1) have been described in the literature.[1,2,7] In this work we present the photochemical and thermal synthesis of isomer **1t** (X = I) (Figure 1), which completes the possible isomers with mutual trans phosphine ligands. Thermodynamic and kinetic studies of CO insertion reactions of both isomers in toluene have been carried out in order to delineate an energetic profile of the reaction.

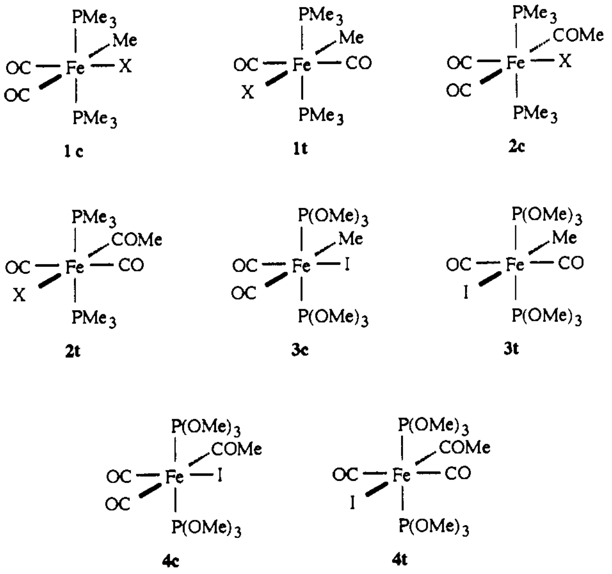

Figure 1. Structures of the complexes.

Experimental Section

Diethyl ether, *n*-hexane, and toluene were purified by standard methods.[9] Dichloromethane was distilled from P_2O_5; trimethylphosphine was prepared by following the method described by Schmidbaur.[10] $Fe(CO)_4Br_2$ was prepared by following the method described by Basolo et al.[11] *cis,trans*-$Fe(CO)_2(PMe_3)_2CH_3X$ (**1c**), *cis,trans*-$Fe(CO)_2(PMe_3)_2(COCH_3)X$ (**2c**), and *trans,trans*-$Fe(CO)_2(PMe_3)_2(COCH_3)X$ (**2t**) were prepared as described in the literature.[1,2] Other compounds were commercial products. IR spectra were recorded on a Perkin-Elmer 983 spectrophotometer. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on various spectrophotometers. The structures of the complexes examined in this study are shown in Figure 1.

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Preparation of *trans,trans*-Fe(CO)$_2$(PMe$_3$)$_2$MeI: Photochemical Method. Powdered crystals of *cis,trans*-Fe(CO)$_2$(PMe$_3$)$_2$MeI were irradiated in a glass vessel with a 100-W tungsten lamp under a slight flow of nitrogen for 48 h. The infrared spectrum in *n*-hexane of the crude products obtained showed an increase of the 1940-cm^{-1} band, a decrease of the 1998.5-cm^{-1} band, and the appearance of a very weak band at 2020 cm^{-1}. The NMR spectrum in CD$_2$Cl$_2$ showed that the triplet at 0.34 ppm assigned to Fe–Me in the cis,trans isomer diminished and that a new Fe–Me triplet appeared at –0.97 ppm. These results were interpreted as an incomplete isomerization of the cis,trans methyl complex to the corresponding trans,trans complex. The ratio of the cis,trans isomer to the trans,trans isomer was ca. 1:4. Further irradiation had only a slight effect; hence, a chemical separation of the two isomers was carried out.

In a first experiment CO was bubbled into a methanolic solution of a 1:4 mixture cis,trans/trans,trans containing an excess of NaBPh$_4$ for 15 min. At room temperature only the cis,trans isomer reacted to give the corresponding acetyl compound, which subsequently precipitated as [Fe(CO)$_3$(PMe$_3$)$_2$Me]BPh$_4$ leaving only the trans,trans complex in solution. Unfortunately, the trans,trans isomer could not be isolated by evaporating the solution to dryness, since the isomerization is reversible, leading again to a mixture of cis,trans and trans,trans isomers. It is possible that Na$^+$ catalyzes the isomerization.

In a second experiment the cis,trans/trans,trans mixture was dissolved in *n*-hexane, and bubbled with CO at –20 °C. The cis,trans isomer reacted with CO to form the corresponding acetyl complex which precipitated. The solution was cooled at –45 °C to complete the precipitation and then evaporated to dryness. The residue was found to be >90% trans,trans. All attempts to recrystallize trans,trans were unsuccessful; hence the complex was used as such in the kinetic experiments.

Stability Experiments. The **1t** complex (X = I) in toluene in the dark at room temperature under a nitrogen atmosphere is practically stable for at least 20 h. In CH$_2$Cl$_2$ the isomerization is faster and results in a 10% transformation into the **1c** complex (X = I) after 20 h. In methanol the isomerization rate is almost twice as fast.

Preparation of *cis,trans*-Fe(CO)$_2$(P(OMe)$_3$)$_2$MeI (3c), *trans,trans*-Fe(CO)$_2$(P(OMe)$_3$)$_2$MeI (3t), *cis,trans*-Fe(CO)$_2$(P(OMe)$_3$)$_2$(COMe)I (4c), and *trans,trans*-Fe(CO)$_2$(P(OMe)$_3$)$_2$(COMe)I (4t). *cis,trans,cis*-Fe(CO)$_2$(P(OMe$_3$)$_2$Br$_2$ (ν_{CO} = 2057 (s), 2008 (s) cm^{-1} in benzene; ^{1}H NMR (CD$_2$Cl$_2$) $\delta_{P(OMe)_3}$ = 3.23 (t, J = 5.4)), prepared by reaction of *cis*-Fe(CO)$_4$Br$_2$[11] and P(OMe)$_3$,[7] was reduced with sodium amalgam in acetonitrile (ACN) at –20 °C for 1.5 h, following the procedure of ref 7. The obtained complex, Fe(CO)$_2$(P(OMe)$_3$)$_2$(ACN), was not separated but was characterized in solution (ν_{CO} = 1897 (s), 1837 (vs) cm^{-1} in ACN).[7] The solution was filtered at –20 °C and then reacted with excess CH$_3$I for 2 h.[7] Filtration and removal of volatiles left a red oil from which yellow microcrystals precipitated upon extraction with *n*-hexane analyzed as C$_9$H$_{21}$IO$_8$P$_2$Fe. Anal. Calcd: C, 21.54; H, 4.22. Found: C, 21.7; H, 4.3. The IR and ^{1}H NMR spectra showed the presence of two isomeric methyl complexes: **3c** (ν_{CO} = 2029 (s), 1974 (s) in *n*-hexane; ^{1}H NMR (CD$_2$Cl$_2$) δ_{CH_3} = 1.01 (t, J = 8.13); $\delta_{P(OMe)_3}$ = 3.83) and **3t** (ν_{CO} = 2041 (vw), 1963 (vs) in *n*-hexane; ^{1}H NMR (CD$_2$Cl$_2$) δ_{CH_3} = –0.60 (t, J = 5.2), $\delta_{P(OMe)_3}$ = 3.80 (t, J = 5.5)). The assignments were made by analogy of the PMe$_3$ derivatives (**1c, 1t**).

With the aim of separating the **3t** complex from the **3c** complex in a way similar to that used for **1t** complex (vide supra), the **3c**/**3t** mixture was dissolved in *n*-hexane and bubbled with CO at –20 °C. The **3c** isomer reacted quickly with CO to form the corresponding acetyl complex (**4c**), which isomerized to **4t** and precipitated as red-yellow crystals. Complex **3t** remained in solution but isomerized to **3c** during the separation process; thus it could not be separated. The acetyl complexes were characterized by elemental analysis as C$_{10}$H$_{21}$IO$_9$P$_2$Fe. Anal. Calcd: C, 22.66; H, 3.99. Found: C, 22.8; H, 4.1. IR and ^{1}H NMR spectra are as follows. **4c**: ν_{CO} = 2028, 1983 cm^{-1} in *n*-hexane; δ_{COCH_3} (CD$_2$Cl$_2$) = 2.15 (s). **4t**: ν_{CO} (CH$_2$Cl$_2$) = 2065 (vw), 1988 (vs), ν_{COCH_3} = 1624 (s) cm^{-1}; ^{1}H NMR (CD$_2$Cl$_2$) δ_{COCH_3} = 2.33 (s), $\delta_{P(OMe)_3}$ = 3.85 (t, J = 5.3).

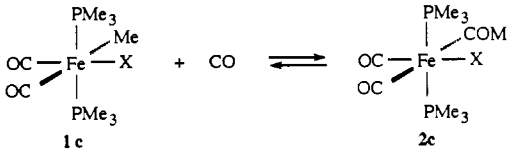
Preparation of Fe(CO)$_2$L$_2$MeI. The Fe(CO)$_2$L$_2$MeI complexes with L = PMe$_2$Ph, PMePh$_2$, or P(*n*-Bu)$_3$ were prepared as described in the literature.[7] The cis,trans complexes were in great excess as compared to the trans,trans complexes. The minor alkyl components were characterized by ^{1}H NMR spectroscopy but not isolated.

Equilibrium Constants. Equilibrium constant measurements were performed in toluene. The CO concentration at different temperatures was interpolated on the basis of the literature data[12,13] using the equation

$$\ln \alpha = \frac{0.389 \times 10^3}{T} - 2.090$$

where α is the Bunsen coefficient and T the absolute temperature. Different pressures of CO (0.01–1 atm) were obtained by dilution with nitrogen in a Mohr bottle. For reactions carried out at temperatures higher than 50 °C the partial pressure was corrected for the vapor pressure of toluene.[14] In a typical run, a solution of the complex ((1–2) × 10^{-3} M) was saturated with the gas mixture; then an aliquot (10 mL) was introduced in a thermostated reactor filled with the gas mixture. When equilibrium was reached, the IR spectrum was measured in the CO stretching region. When the reaction was very fast, the measurements were performed in less than 20 s. Complex concentrations were then measured at every temperature, using if necessary thermostated cells. The concentrations of the complexes were determined by Beer's laws, previously performed. The used bands differed by wavelength or by extinction coefficient so that the concentration of the species in equilibrium could be measured. In each experiment CO was in great excess over the complex, so that the CO concentration remained practically constant during the reaction.

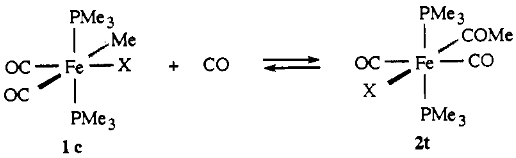
(a) Reaction 1:



(1)

Experiments were carried out in the 5–70 °C range with a CO pressure between 0.05 and 0.1 atm. Partial isomerization of complex **2c** to complex **2t** does not affect the equilibrium because its rate is much slower than that of the insertion reaction 1.

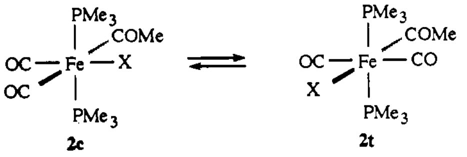
(b) Reaction 2:



(2)

This reaction was studied in the 20–50 °C range at P_{CO} = 0.10 and 0.01 atm. The reverse reaction was studied in the 50–90 °C range with P_{CO} = 0.20, 0.15, 0.10, and 0.01 atm.

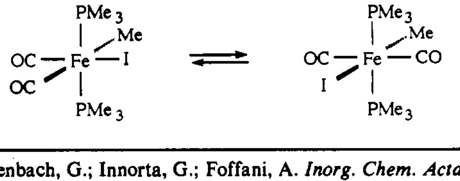
(c) Reaction 3:



(3)

Equilibrium constants were measured in the temperature range 20.6–71 °C. For X = I the concentration of complex **2t** was determined by the intensity of the higher frequency CO stretching mode of complex **2t** (ν = 2043 cm^{-1}), and that of **2c** from the intensity of the CO stretching frequency at 2018 cm^{-1}. The two peaks have similar intensities since the concentration of **2t** is higher than that of **2c**, while the extinction coefficient is higher for **2c**. The concentrations of the X = Br or Cl derivatives were measured using the intensity of the higher frequency CO mode for the **2c** complexes.

(d) Reaction 4:



(4)

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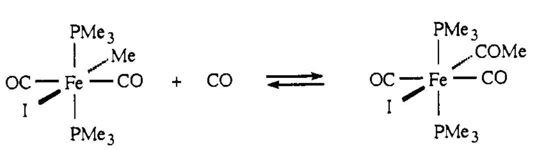
Since this reaction is very sensitive to light, all measurements were carried out in the dark. The position of equilibrium 4 lies to left, and the extinction coefficient ratio is not favorable in this case; hence, it was not possible to use the IR technique. Concentrations were therefore obtained using the ^{1}H NMR (ca. 1000 acquisitions). The measurements were carried out in the 60–80 °C range in order to allow fast equilibration. The low precision of the equilibrium constants thus obtained masked the temperature effect on K_{eq}.

Kinetic Measurements. (a) The rate of the reversible reaction 1 (X = I) in toluene was followed at 10.8 °C, keeping the CO pressure constant in every run. IR spectroscopy was used to determine the disappearance of the CO stretching mode of **1c** at 2002 cm^{-1} and the appearance of the CO stretching at ≈2018 cm^{-1} of complex **2c**. It was not possible to follow the kinetics at higher temperature since complex **2c** isomerizes to complex **2t** before equilibrium is attained. The pseudo-first-order rate constants were measured using eq 5,[15] where D_0, D_e, and D_t are the absorbances

$$\ln\frac{D_0 - D_e}{D_t - D_e} = (k_{fwd} + k_{rev})t = k_{fwd}\frac{a}{x_e}t \qquad (5)$$

of complex **1c** or **2c** at zero, equilibrium, and t times, k_{fwd} and k_{rev} are the pseudo-first-order rate constants for the forward and the reverse reaction respectively, and a and x_e are the initial and the equilibrium concentrations of **1c** and **2c**, respectively.

(b) The kinetics of reaction 6 were followed in the 35.1–55 °C range. The CO pressure was changed in the range 0.2–1 atm. Under these



(6)

experimental conditions this reaction did not behave as an equilibrium reaction. The pseudo-first-order rate constants were determined from eq 7, by following the disappearance of the CO stretching of **1t** (X = I) at 1940 cm^{-1}.

$$\ln\frac{D_0 - D_\infty}{D_t - D_\infty} = k_{fwd}t \qquad (7)$$

Results

(a) Photochemical Isomerization. The UV–vis spectra of complexes **1c** and **1t** for X = I are given in Figure 2. Complex **1c** shows a charge-transfer band at 400 nm, the irradiation of which leads to the photochemical isomerization in the solid state. The fundamental features of the photoisomerization of square planar complexes have been already delineated.[16] The photochemical isomerization of the octahedral complexes shows a variety of behaviors[17] which are ill-understood. In particular the thermal and photochemical isomerization of $M(CO)_2L_2X_2$ complexes (M = Ru,[18] Fe;[19] L = phosphine ligands; X = halides, SiR_3) has been extensively studied. When phosphine or carbon monoxide are coordinated, both the thermal and photochemical isomerizations are dissociative. The incipient unsaturated intermediate is stereolabile and rearranges to form various isomers.[17,18] The complex $Fe(CO)_2(PMe_3)_2I_2$ is unique in that isomerization occurs photochemically in the solid state.[19] In this case the mechanism was interpreted on the basis of the Fe–I ionization with formation of the ionic intermediate $[Fe(CO)_3(PMe_3)_2I]^+I^-$. We have observed a similar behavior for complex **1c** (X = I), which isomerizes to the trans,trans isomer **1t** with a 80% yield, on irradiation at 500 nm in the solid state. On the basis of the facile ionization of the Fe–I bond,[6] recently demonstrated for complex **1c** to occur also in apolar solvents,[20] it is reasonable to assume that the photochemical solid-state isomerization proceeds by ionization of the Fe–I bond according to Scheme I. In solution light decomposes complex **1c**; therefore it was not possible to obtain further evidence for mechanism 1. Another possibility is that compound **1c** isomerizes via an intramolecular rearrangement, as supposed by Stewart[21] for $Mn(CO)_4(P(OPh)_3)Ph$.

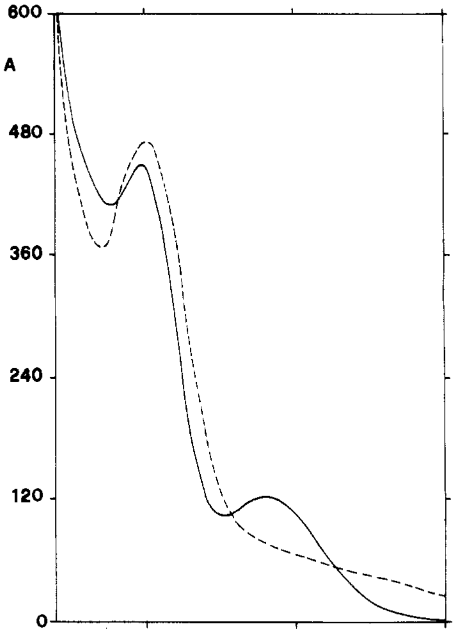
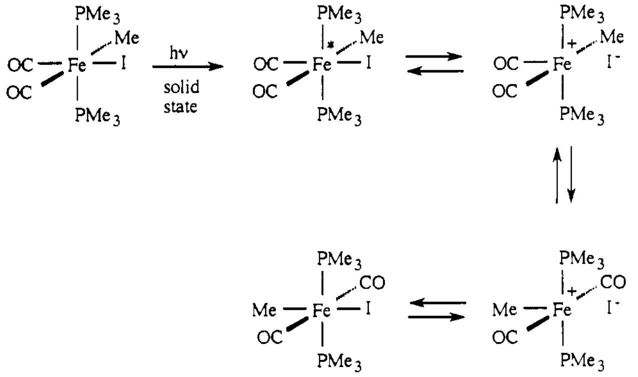


Figure 2. UV–vis spectra of the complexes **1c** (- - -) and **1t** (—) for X = I.

Scheme I



(b) Thermal Isomerization. An accurate analysis of the ^{1}H NMR spectra of the complex *cis,trans*-$Fe(CO)_2L_2MeI$ (L = $P(OMe)_3$, $P(n\text{-}Bu)_3$, $PPhMe_2$, PPh_2Me) shows the presence of small quantities of the trans,trans structure. The ^{1}H NMR characterization of these complexes is given in Table I. When L = $P(OMe)_3$, the stability of the trans,trans structure is increased. The preparation of the $P(OMe)_3$ analogs follows Scheme II.

(c) Thermodynamic Results. The equilibrium constants of reaction 1 in toluene, at various temperatures, are given in Table II for X = I, Br, Cl, CN, and CNS. The values for CN are taken

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Scheme II

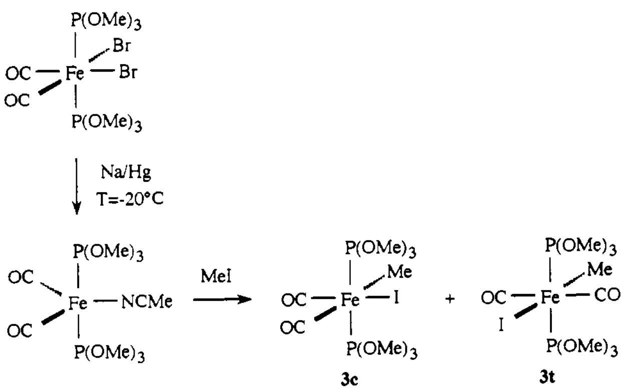


Table I. ^{1}H NMR (300 MHz) Data for Methyl Complexes $Fe(CO)_2L_2MeI$ in C_6D_6 at 303 K

L	δ_{Fe-CH_3}[a] cis,trans	δ_{Fe-CH_3}[a] trans,trans	Δ
PMe_3	0.57 (t, J = 9.5)	−0.97 (t, J = 5.9)	1.54
$PPhMe_2$	0.80 (t, J = 9.0)	−1.30 (t, J = 6.1)	2.10
$P(OMe)_3$[b]	1.50 (t, J = 8.5)	−0.06 (t, J = 5.1)	1.56
$P(n\text{-}Bu)_3$	0.67 (t, J = 7.6)	−0.82 (t, J = 5.1)	1.49
PPh_2Me		−1.13 (t, J = 5.5)	

[a] J values in Hz. [b] T = 317.7 K.

Table II. Equilibrium Constants[a] at Various Temperatures in Toluene for Reaction 1

T (°C)	I	Br	Cl	CN[b]	NCS
5.0				14000	
8.0				12800	
10.7	2724 ± 260				
11.9					10400 ± 200
15.0				11000	
20.1	1454 ± 85				
21.0		4285 ± 455	4954 ± 70		7100 ± 700
22.0				6700	
28.8	817 ± 45				
29.3					5275 ± 400
30.0		2230 ± 200	3276 ± 165	3300	
40.0		1113 ± 43	1987 ± 350		3600 ± 350
49.0		725 ± 35	1312 ± 180		
59.3			767 ± 25		
70.8			500 ± 20		
$\Delta H°$ (kJ/mol)[c]	−47 ± 4	−51 ± 4	−40 ± 4	−44	−28 ± 1
$\Delta S°$ (kJ/mol·K)[c] (298.15 K)	−100 ± 12	−104 ± 12	−65 ± 6	−75	−21 ± 12

[a] ± the standard deviation around the mean value. [b] Values from ref 4. [c] ± standard deviation of the linear regression.

from ref 4. Table II also gives values of $\Delta H°$ and $\Delta S°$ as a function of the substituent X.

The equilibrium constants of reaction 2 in toluene at various temperatures are given in Table III for X = I, and Br. Table III also gives $\Delta H°$ and $\Delta S°$ values; for X = Cl they are calculated on the basis of reactions 1 and 3. The equilibrium constants at various temperatures and the values of $\Delta H°$ and $\Delta S°$ in toluene for reaction 3 are reported in Table IV.

The equilibrium constants of reaction 4 for L = PMe_3 and $P(OMe)_3$ were measured in the 60–80 °C range for PMe_3 and at 25 °C for $P(OMe)_3$. The limited precision attained allows a qualitative interpretation.

(d) Kinetic Results. The forward pseudo-first-order rate constants (k_{fwd}), for reaction 1 (X = I), are given in Table V at different CO concentrations. A plot of k_{fwd} vs [CO] gives a straight line with zero intercept indicating a first-order rate law with respect to CO. The value of the second-order rate constant is 5.28 ($M^{-1}\cdot s^{-1}$) (see Figure 3). The reaction of the iodo derivative results to be almost 1 order of magnitude faster than that of the CN derivative.[4] Preliminary studies on the chloro and bromo derivatives show that these compounds react even faster.

Table III. Equilibrium Constants[a] at Various Temperatures in Toluene for Reaction 2

T (°C)	I	Br	Cl[b]
20.6	73000		
21.3		8080 ± 770	
30.3	38000	3995 ± 70	1144
40.0	19000	1802 ± 29	844
49.0		1113 ± 35	
50.0	8770		628
60.0	5100		
60.4	4980		
70.0	2310		367
80.4	1200		
89.8	690		
$\Delta H°$ (kJ/mol)[c]	−60 ± 2	−57 ± 4	−25
$\Delta S°$ (kJ/mol·K)[c] (298.15 K)	−111 ± 8	−119 ± 12	−23

[a] ± the standard deviation around the mean value. [b] Values calculated by reactions 1 and 3. [c] ± standard deviation of the linear regression.

Table IV. Equilibrium Constants[a] at Various Temperatures in Toluene for Reaction 3

T (°C)	I	Br	Cl
20.6	31 ± 2		
21.3		1.91 ± 0.02	
27.0			0.33 ± 0.02
30.0	25.8 ± 0.5	1.79 ± 0.12	
40.0	19.2	1.68 ± 0.15	0.44 ± 0.02
49.0		1.57 ± 0.10	
50.0			0.51 ± 0.02
59.5		1.25 ± 0.09	
71.0		1.02 ± 0.08	
$\Delta H°$ (kJ/mol)[b]	−18 ± 4	−10 ± 4	15 ± 4
$\Delta S°$ (kJ/mol·K)[b] (298.15 K)	−33 ± 12	−29 ± 12	42 ± 12

[a] ± the standard deviation around the mean value. [b] ± standard deviation of the linear regression.

Table V. Pseudo-First-Order Rate Constants (k_{fwd})[a] in Toluene at 10.7 °C, for Reaction 1 (X = I)

10^4[CO] (M)	10^3k_{fwd} (s^{-1})	10^4[CO] (M)	10^3k_{fwd} (s^{-1})
11.9	6.5 ± 0.3	5.9	3.6 ± 0.1
7.9	5.1 ± 0.1	4.0	2.3 ± 0.15

[a] ± standard deviation of the linear regression.

Table VI. Pseudo-First-Order Rate Constants (k_{obs}), in Toluene, for Reaction 6 at Various Temperatures (X = I)

T (°C)	P_{CO} (atm)	10^6k_{obs} (s^{-1})[a]
35.1	0.30	2.13
	0.50	2.02
	0.75	2.05
	1.00	2.40
45.0	0.30	7.80
	0.50	7.78
	1.00	7.61
55.0	0.30	27.6
	0.70	32.2
	1.00	33.6

[a] $\Delta H^{\ddagger}_f$ = 110 ± 4 (kJ/mol); $\Delta S^{\ddagger}_f$ = 4 ± 12 (J/mol·K) (± standard deviation of the linear regression).

The pseudo-first-order rate constants (k_{obs}) for reaction 6 are independent of the concentration of CO at 35.1, 45.0, and 55.0 °C.

Discussion

(a) Structure of *trans,trans* Methyl Complexes. The chemical shifts and the coupling constant ($^3J_{Me-P}$) of the methyl complexes are given in Table I. The chemical shifts of trans,trans

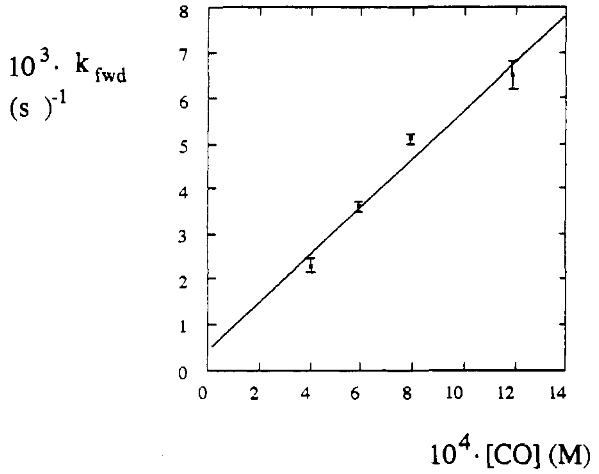


Figure 3. Trend of k_{fwd} vs [CO] for reaction 1 (X = I).

complexes are at higher field than those of the corresponding cis,trans complexes. The difference is relatively constant for all the phosphine ligands (≈1.5 ppm) except for PMe_2Ph (≈2.1 ppm). This is due to the different donor power of iodide trans to the methyl group in trans,trans complexes, compared to the ligand CO in cis,trans complexes. The consequence is a larger charge density and a stronger Fe–Me bond in the trans,trans methyl complexes.[22,18b]

The easily measured coupling constant $^3J_{Me-P}$ is a good structural indicator: in cis,trans complexes $^3J_{Me-P}$ is in the 7.6–9.5-Hz range (Table I), while in the trans,trans complexes it falls in the 5.1–6.1-Hz range. The difference can be explained on the basis of the trans effect of the ligand trans to the methyl. Ligands with a higher trans effect (CO in complexes cis,trans, compared to I in complexes trans,trans) show a larger $^3J_{Me-P}$ coupling constant.[6,23]

The chemical shift in cis,trans complexes follows the order of L basicity:[24,25]

$$PMe_3\ (0.58) \cong P(n\text{-}Bu)_3\ (0.67) > PMe_2Ph\ (0.80) > P(OMe)_3\ (1.50)$$

More basic ligands increase the charge on the metal and concomitantly shield the protons of the methyl group. The chemical shifts in trans,trans complexes are less clear-cut. However, the order is

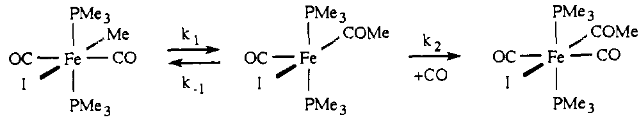
$$PMe_2Ph\ (-1.3) > PMePh_2\ (-1.13) > PMe_3\ (-0.97) \cong P(n\text{-}Bu)_3\ (-0.82) > P(OMe)_3\ (-0.06)$$

Also steric effects[24] appear to have some influence.

(b) Thermodynamic Measurements. (1) Methyl Complexes. The stability of complexes trans,trans with respect to complexes cis,trans was semiquantitatively estimated in the case of ligands $P(OMe)_3$ ([trans,trans]/[cis,trans] ≈ 0.8) and PMe_3 ([trans,trans]/[cis,trans] ≈ 4×10^{-3}). These values indicate that the stability of trans,trans is strongly increased by π and σ electron-withdrawing substituents: in fact $P(OMe)_3$ is a stronger π acceptor and a weaker σ donor[25] than PMe_3. The reason for this effect on the relative stability is not clear.

(2) Acetyl Complexes. The thermodynamic data of Tables II and III indicate that, like other d^6-MD_6 examples,[13b,26-29] CO insertion promoted by carbon monoxide is exothermic. Due to the large loss of rotational and translational entropy for CO(g) on insertion,[27] the entropy for reactions 1 and 2 is unfavorable and the position of the equilibrium depends critically on small structural perturbations.

Scheme III



The relative stability of complexes **2c** with respect to complexes **1c** (Table II) follows the order

$$CN \cong NCS > Cl > Br > I$$

The electron-withdrawing power of X appears to be the controlling factor in the stabilization of complexes **2c**.[30] This effect is due to both enthalpic and entropic effects. In fact both $\Delta H°$ and $\Delta S°$ of reaction 1 increase with increasing withdrawing power of X. Steric effects exert a minimal influence, as can be deduced from the constant values of $\Delta H°$ and $\Delta S°$ for I and Br.

The relative stability of complexes **2t** with respect to complexes **1c** (Table III) is in the order

$$I > Br > Cl \gg CN, Me, NCS$$

For CN, Me, NCS derivatives the trans form is not formed. This trend is determined by the steric hindrance.[24] The increase of the equilibrium constants is accompanied by a decrease of both $\Delta H°$ and $\Delta S°$.

Since COMe is a π withdrawing group, complexes **2t** can be stabilized by a trans σ ligand, especially when the latter is an electron donor like iodide.

The relative stability of complexes **2t** with respect to complexes **2c** (Table IV) follows the order

$$I > Br > Cl \gg CN, CNS, Me$$

The thermodynamic parameters indicate the effect is mainly enthalpic. While $\Delta S°$ is constant (−33/−42 J/(mole·K)), $\Delta H°$ increases along the series from −18.4 to +15.5 kJ/mol with contributions from both steric and trans ligand effects.

(c) Mechanism of Insertion. The mechanism of reaction 6 can be interpreted on the basis of the conventional migratory insertion of Scheme III.[31] The pseudo-first-order rate constant is

$$k_{fwd} = \frac{k_1 k_2 [CO]}{k_{-1} + k_2[CO]} \tag{8}$$

which, in the case $k_2[CO] \gg k_{-1}$, gives

$$k_{fwd} = k_1 \tag{9}$$

When $k_2[CO] \ll k_{-1}$, we obtain

$$k_{fwd} = \frac{k_1 k_2}{k_{-1}}[CO] \tag{10}$$

which is a second-order process.

Since for reaction 1 recent information[6,20] suggests a mechanism involving direct substitution of the iodide ligand by CO with formation of an ionic intermediate, a similar mechanism could

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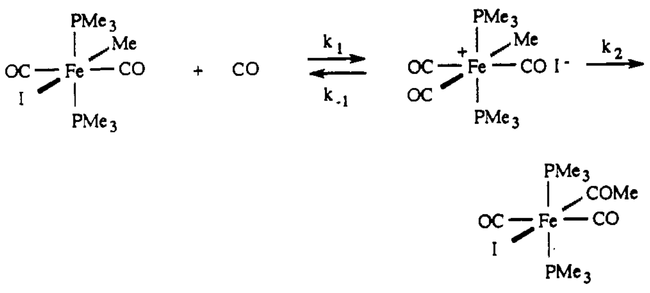
Scheme IV



be hypothized for reaction 6 according to Scheme IV. This is consistent with a second-order kinetic law if the first step is an equilibrium process.

In both hypotheses the decrease of the insertion rate of the trans complex, as compared to the cis, can be interpreted on the basis of the reciprocal influence of the methyl and iodide trans groups. In fact, in one case the iodide group is assumed to raise the activation energy for the methyl migration,[22,32] and in the other, the methyl group is expected to hinder the ionization.

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