

Metal ion complexation in organometallic crown ethers Structural and rate effects on the migratory insertion of carbon monoxide in indenyl and cyclopentadienyl iron (II) complexes ¹

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Abstract

The iron complexes $[\text{Fe}(\eta^5\text{-ligand})(\text{CO})_2\text{R}]$ [ligand = C_5H_5 (Cp), R = Me (**1**); ligand = C_5H_5 , R = CHMe_2 (**2**); ligand = C_9H_7 (Ind), R = Me (**3**)] react with the crown ether functionalized phosphine $[\text{Ph}_2\text{P}-\text{CH}_2\text{-(aza-15-crown-5)}]$ (L) to give the products of alkyl migratory insertion $[\text{Fe}(\eta^5\text{-ligand})(\text{COR})(\text{CO})(\text{L})]$ **4**, **5** and **6**, respectively. The cyclopentadienyl methyl complex $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Me}]$ reacts with L only in refluxing hexane. The reactions of **2** and **3**, in acetonitrile or chloroform, have been followed by FT-IR spectroscopy, or by UV-Vis. The presence of sodium or calcium salts, NaI, NaPF_6 , or CaI_2 , does not affect the reactivity of the cyclopentadienyl complex **2**, whereas it increases two to three times the rate of reaction of the indenyl complex **3**. The acetyl complexes $[\text{Fe}(\eta^5\text{-ligand})(\text{COMe})(\text{CO})(\text{L})]$, (ligand = Cp, **4**; ligand = Ind, **6**) exhibit a shift of the stretching band $\nu(\text{COMe})$ to lower frequencies, in the presence of metal salts, up to 40 cm^{-1} in the case of $\mathbf{6} \cdot \text{NaPF}_6$ in chloroform, and up to 46 cm^{-1} in the case $\mathbf{6} \cdot \text{KPF}_6$ in dichloromethane, as a result of coordination of the carbonyl oxygen to the crown ether held cation. This shift is absent or small in the more polar solvents tetrahydrofuran, acetonitrile, or dioxane, and it is not observed for the isopropyl complex **5**, suggesting that steric hindrance of the alkyl group prevents acyl coordination to the metal ion. The terminal carbonyl group of complexes **4**, **5** and **6** displays a shift of the $\nu(\text{CO})$ band to higher frequencies in most solvents, up to 27 cm^{-1} for $\mathbf{6} \cdot \text{NaPF}_6$ in acetonitrile and to 26 cm^{-1} for $\mathbf{6} \cdot \text{LiClO}_4$ in dichloromethane, arising from electronic polarization by the metal ion and indicating electronic communication between the two metal centres. © 1998 Elsevier Science S.A.

Keywords: Crown ether; Carbon monoxide; Indenyl

1. Introduction

The migratory insertion of carbon monoxide in transition metal complexes can be promoted both by donor molecules and by Lewis acids [1]. We have reported in recent years the reaction of indenyl and cyclopentadienyl carbonyl iron(II) complexes $[\text{Fe}(\eta^5\text{-ligand})(\text{CO})_2\text{R}]$ (ligand = C_9H_7 , C_5H_5 ; R = Me, *i*Pr) with phosphines to give the corresponding acyl complexes [2,3] [4,5]. The occurrence of an associative mechanism has been described, involving fast and reversible formation of equilibrium followed by a rate determining carbon-carbon coupling. The reactions with

different donor molecules have also been reported for pentamethylcyclopentadienyl complexes of rhodium and iridium $[\text{M}(\eta^5\text{-C}_5\text{Me}_5)(\text{R})(\text{CO})(\text{X})]$ (M = Rh, Ir; R = Me, aryl; X = Cl, Br, I, MeCO_2 , CF_3CO_2) [6–8], as well as comparative studies of the effect of the two different metals on rates of migratory insertion [9].

The activation of CO by strong Lewis acids has been clearly documented in the literature [10–13]. Interaction of the acidic centre with the oxygen atom and the resulting stabilizing effect in the acyl product is presumed to be the driving force, as supported by the isolation of bimetallic $\mu\text{-COR}$ complexes [10]. Rate effects of different cations have been reported for the migratory insertion process on the anionic carbonyl species $\text{M}^+[\text{Fe}(\text{CO})_4\text{R}]^-$ (M = Li, Na, Na-crown ether, $(\text{PPh}_3)_2\text{N}$), and ion pairing equilibrium constants were found to be higher in the corresponding acyl complexes $\text{M}^+[\text{Fe}(\text{CO})_4(\text{COR})]^-$, the acyl group acting as the cation binding site [14].

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¹ Dedicated to Professor Peter M. Maitlis, with gratitude, on the occasion of his 65th birthday.

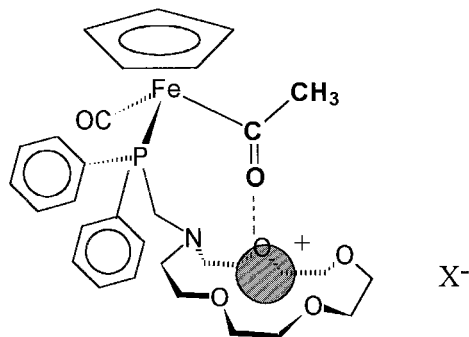


Fig. 1. Intramolecular acetyl oxygen-cation interaction in the complexation of metal salts to $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{COMe})(\text{CO})(\text{L})]$.

The existence of acyl-cation interactions in solution has been clearly demonstrated in the case of intramolecular acyl bonding to a crown ether held cation. It has been shown that alkali or alkaline-earth metal salts dissolve in dichloromethane solutions of the complex $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{COMe})(\text{CO})(\text{Ph}_2\text{P-CH}_2\text{-aza-15-crown-5})]$, producing shifts in the infrared and ^1H NMR spectra which are consistent with coordination of the acetyl oxygen atom to the metal cation in the cavity of the aza-crown ether [15] (Fig. 1).

In view of our interest in the migratory insertion reaction of carbonyl iron(II) complexes [2–9], as well as in the effect of alkali and alkaline earth cations on addition reactions to carbonyl compounds [16], we have addressed a key point underlying the study of acyl oxygen-metal ions binding, i.e., the potential effect played by such interaction on the rate of the carbon-carbon forming step. Therefore, the scope of this work is to describe whether the addition of metal ions may affect the process of migratory insertion, when the electrophilic metal centre is held in proximity of the functional group which is undergoing a change from terminal carbonyl to acyl. This possibility had been pointed out in the original communication [15] and further addressed in the literature [1], p. 372, [17]. We report here a study of the reaction of $[\text{Fe}(\eta^5\text{-ligand})(\text{CO})_2\text{R}]$ [ligand = C_5H_5 , R = Me (1); ligand = C_5H_5 , R = CHMe_2 (2); ligand = C_9H_7 , R = Me (3)]

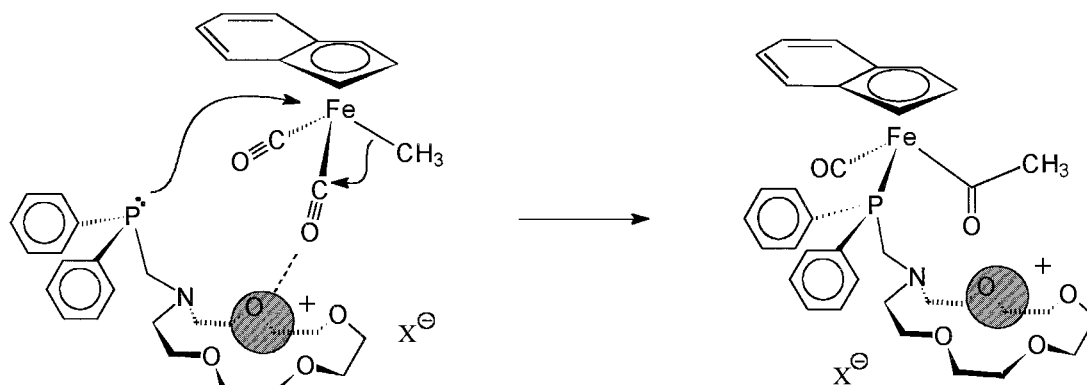
with the crown ether functionalized phosphine $[\text{Ph}_2\text{P-CH}_2\text{-(aza-15-crown-5)}]$ (L) in the presence of alkali and alkaline-earth metal salts, as depicted in Scheme 1 for complex 3.

Binding of metal ions to the cavity of L forms a heterotopic macrocyclic species, which contains a donor site at the phosphorus atom and a Lewis acid centre. Reactions of alkyl carbonyl complexes $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{R}]$ with amphoteric ligands, namely (aluminoamine)phosphines of the type $\text{Ph}_2\text{P-NR-AlR}'_2$, have been reported as very rapid [18]. Extensive work has also been described on the effect of cation binding in molybdenum and tungsten complexes of phosphorus donor crown ether ligands toward the activation of nucleophilic addition to coordinated carbon monoxide [19]. It has been reported that cobalt and rhodium complexes of the aza-crown ether L accelerate the hydroformylation of alkenes when co-complexed by Na^+ or Li^+ [20].

The field of metallomacrocycles is an area of current interest, because of different properties and applications potentially deriving from combination of metal centres in organized systems [21]. In particular, structures which combine a π -face (η^5 -ligand) for redox active transition metals and a crown ether σ -face for coordination of group I and II metal ions may display electronic interaction and attractive properties in the combination of hard and soft metal centres [22]. In this context, the effect of alkali and alkaline-earth cations and that of molecular structural changes on the infrared features of the iron(II) acyl complexes 4–6 are also described in this work.

2. Experimental

NMR spectra were recorded on a Bruker AM-300 spectrophotometer, in CDCl_3 , at 300 (^1H), or 121.7 MHz ($\{^1\text{H}\} \text{ }^{31}\text{P}$) and chemical shifts are reported with respect to Me_4Si or H_3PO_4 , respectively. Infrared spectra were taken with a FT-IR Nicolet 510 spectrophotometer, interfaced with a Nicolet 620 workstation. Low



Scheme 1.

resolution mass spectra (FAB, *m*-nitrobenzyl alcohol as matrix) have been obtained with a VG-Quattro instrument, at the Università di Tor Vergata, Roma.

All solvents were distilled under argon, tetrahydrofuran and toluene from potassium/benzophenone, hexane and pentane from sodium, and dichloromethane from calcium hydride. Acetonitrile was distilled first from calcium hydride, then from phosphorus pentoxide. Alumina (3% water) was used for the chromatographic separations. All reactions were performed under argon, using standard Schlenk line techniques.

The phosphine $\text{Ph}_2\text{P}-\text{CH}_2$ -(aza-15-crown-5), **L**, was prepared as described in the literature [23]. It is easily oxidized by air, either during preparation or in the subsequent manipulations. We have never been able to obtain samples with a purity higher than 95%, checked by ^{31}P NMR ($\delta = -28.1$ ppm), with respect to the corresponding phosphine oxide derivative ($\delta = 26.3$ ppm). Different attempts to purify it by further manipulations failed.

2.1. Synthesis

2.1.1. $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{COMe})(\text{CO})(\text{Ph}_2\text{P}-\text{CH}_2\text{-aza-15-crown-5})]$ (**4**)

Complex **1** (0.78 g, 4.1 mmol) and **L** (1.35 g, 3.2 mmol) in a Schlenk tube, were stirred in hexane (10 ml) at 70°C, for 3 days. A dark brown solid precipitated out of the reaction mixture. Hexane was distilled off, the residue was recovered with dichloromethane and chromatographed. Excess starting material was eluted first with dichloromethane, then a dark band was eluted with increasing amount of tetrahydrofuran, up to a 1:6 ratio tetrahydrofuran:dichloromethane, to obtain 0.46 g (23% yield) of a thick brown oil. IR: 1923.8, 1610.7 cm^{-1} (cyclohexane). ^1H NMR: δ 7.4–7.3 (m, 10 H, phenyl), 5.28 (s, 5 H, C_5H_5), 3.7–3.3 (m, 16 H, OCH_2), 3.45 (d, 2H, $J_{\text{P-H}} = 4.4$ Hz, $\text{N}-\text{CH}_2\text{-P}$), 2.52 (tr, 4 H, $J = 5.9$ Hz, $\text{N}-(\text{CH}_2)_2$), 2.47 (s, 3 H, COMe) ppm. ^{31}P NMR: δ 73.4 ppm. Mass spectrum: m/z 608.9, 611.2 (M^+).

2.1.2. $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{COCHMe}_2)(\text{CO})(\text{Ph}_2\text{P}-\text{CH}_2\text{-aza-15-crown-5})]$ (**5**)

Complex **2** (0.56 g, 2.52 mmol) and **L** (1.03 g, 2.47 mmol) were dissolved in a Schlenk tube in toluene, and heated under stirring at 50°C, for 40 h. The crude reaction mixture was chromatographed, by elution with hexane first and then with dichloromethane, to yield 0.71 g of product (yield 45%), as a brown oil. IR: 1919.2, 1604.6 cm^{-1} (cyclohexane). ^1H NMR: δ 7.5–7.3 (m, 10 H, phenyl), 5.28 (s, 5 H, C_5H_5), 3.6–3.4 (m, 18 H, OCH_2 and $\text{N}-\text{CH}_2\text{-P}$), 2.91 (septet, 1H, $J = 3.6$ Hz, COCHMe_2), 2.56 (t, 4 H, $J = 5.8$ Hz, $\text{N}-(\text{CH}_2)_2$), 0.97–0.64 (d, 6 H, COCHMe_2) ppm.

2.1.3. $[\text{Fe}(\eta^5\text{-C}_9\text{H}_7)(\text{COMe})(\text{CO})(\text{Ph}_2\text{P}-\text{CH}_2\text{-aza-15-crown-5})]$ (**6**)

Complex **3** (0.55 g, 2.3 mmol) and **L** (1.53 g, 3.6 mmol) in a Schlenk tube, were stirred in hexane (5 ml) at 50°C, for 24 h. The dark brown solid, precipitated out of the reaction mixture, was dissolved in dichloromethane, then chromatographed with dichloromethane first, then with increasing amounts of tetrahydrofuran, up to a 1:5 ratio tetrahydrofuran:dichloromethane. Evaporation of the solvent gave complex **6** as a dark orange solid (0.85 g, yield 48%). IR: 1919.5, 1611.9 cm^{-1} (tetrahydrofuran). ^1H NMR: δ 7.6–7.1 (m, 14 H, benzo and phenyl), 5.28, 5.01, 4.78, (s, 3 H, indenyl C_2H and $\text{C}_{1,3}\text{H}$), 3.8–3.2 (m, 16 H, OCH_2), 3.41 (d, 2H, $J_{\text{P-H}} = 3.8$ Hz, $\text{N}-\text{CH}_2\text{-P}$), 2.58 (s, 3 H, COMe), 2.35 (m, 4 H, $\text{N}-(\text{CH}_2)_2$) ppm. ^{31}P NMR: δ 70.8 ppm. Mass spectrum: m/z 658.9, 661.0 (M^+).

2.2. Spectroscopic and kinetic experiments

Samples for spectroscopic and kinetic measurements were always prepared under argon. The metal salt was added in excess to a concentrated solution of acyl complex (**4–6**) and the mixture was sonicated for a few minutes. Solutions were then filtered into a 0.1 mm CaF_2 cell and analyzed by FT-IR. If water was present in the salt or solvent, a band appeared in the range 1615–1640 cm^{-1} .

In a typical experiment for UV-Vis kinetic measurements, solutions of **L** (2 ml) were mixed with solutions of complex (0.1–0.5 ml) in 1 cm quartz cells, to obtain initial concentrations of **2** or **3** of ca. 10^{-4} . For the experiments in the presence of metal salts, a weighted amount was previously added to the solution of **L** or directly into the cell (e.g., 93 mg of NaI in 2.4 ml of acetonitrile to give a clear solution 0.26 M). For more accurate comparisons of rate effects, measurements (**3–4**) were performed simultaneously in the instrument from the same batch of **L**, and grouped together in the tables. The increase in absorbance associated with product formation was followed with time, in the range 380–400 nm.

Samples for kinetic measurements by FT-IR were prepared by addition of **L**, metal salt and complex in a 2 ml flask, to obtain an initial concentration of **2** or **3** of ca. 10^{-2} (e.g. 137 mg of **L**, 60 mg of NaPF_6 in 2 ml of acetonitrile). In chloroform, the metal salt was added to a solution of **L**, the mixture was sonicated and filtered into the reaction flask. A 0.5 mm CaF_2 cell fitted with a thermostatted jacket was filled with freshly prepared reaction mixture, under argon, sealed and placed in the sample compartment of the spectrophotometer. The reaction progress was followed by monitoring the decay of the intense $\nu(\text{CO})$ bands of the of **2** and **3**, and the growth of the carbonyl band of **5** and **6**, respectively.

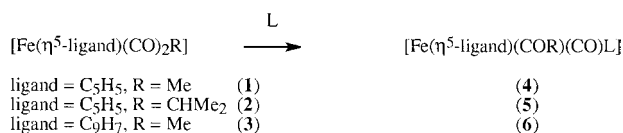
First-order rate constants, k_{obs} , were obtained by fitting the first order rate equation to the experimental data using a non linear least squares regression program. Runs were carried out under pseudo-first order conditions, using a large excess of L with respect to complex **2** or **3**. The runs were duplicated and were reproducible to within 10%. Slightly larger deviations were observed in measurements obtained from different batches of L. The actual concentration of L was corrected from the phosphine oxide by-product, determined by ^{31}P NMR. We previously checked that the presence of phosphine oxide does not affect the reactivity of the iron complexes toward phosphines [2–5].

3. Results and discussion

3.1. Reactions

Complexes **1–3** react with the aza-crown ether phosphine [$\text{Ph}_2\text{P}-\text{CH}_2-(\text{aza-15-crown-5})$] (L) to give the products of alkyl migratory insertion (Scheme 2).

The reaction of the cyclopentadienyl complex $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Me}]$ (**1**) with L was reported previously, although experimental details regarding the preparation of the acetyl product were not provided [15]. The complex is extremely reluctant toward reaction with L, under the conditions described for the reaction of **1** with phosphines and phosphites [24]. In fact, decomposition of starting materials was observed after prolonged reaction times in refluxing polar solvents. After several attempts, we found that the reaction proceeded in boiling hexane, from which the acyl product **4** separated out as a dark brown oil. Since these conditions were not suitable for a kinetic study, we have searched for structural changes which would raise the reactivity of the iron complex. This rate effect can be obtained by increasing the steric hindrance of the migrating alkyl group or by changing the nature of the pentahapto ligand. In fact, complexes **2** and **3** reacted smoothly with L in different solvents and moderate temperatures, in agreement with the higher migratory aptitude of the isopropyl group, with respect to methyl [4,25], and the higher reactivity of iron(II) indenyl complexes with respect to their cyclopentadienyl analogs [5,12]. Before studying the kinetic behaviour of the iron complexes **2** and **3**, we have checked the coordination properties of the acetyl complex **4** toward cations in different solvents, and studied those of the new complexes **5** and **6**.



Scheme 2.

Table 1

Terminal carbonyl and acyl stretching frequencies (ν , $\pm 0.2 \text{ cm}^{-1}$) of the cyclopentadienyl complexes $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{COR})(\text{CO})(\text{L})]$ (**4**, R = Me; **5**, R = CHMe_2) in the presence of metal salts

	Salt	$\nu(\text{CO})$	$\nu(\text{COR})$
<i>Complex $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{COMe})(\text{CO})(\text{L})]$ 4</i>			
Dichloromethane	none	1917.5	1596
	NaPF_6	1931.9	1565
	CaI_2	1925.9	1515
Chloroform	none	1916.8	1591
	NaPF_6	1930.6	1561
	CaI_2	1926.3	1515
1,2-dichloroethane	none	1916.9	1598
	NaPF_6	1928.2	1567
	CaI_2	1927.5	1514
Tetrahydrofuran	none	1917.7	1605
	NaPF_6	1941.3	—
<i>Complex $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{COCHMe}_2)(\text{CO})(\text{L})]$ 5</i>			
Dichloromethane	none	1910.2	1594
	NaPF_6	1926.9	1589
	CaBr_2	1910.8, 1959sh	1595
	CaI_2	1917.5, 1950sh	1603
Acetonitrile	none	1909.0	1595

3.2. Metal ion complexation

The complexation of alkali or alkaline-earth metal salts to the crown ether functionalized acyl complexes has been studied by FT-IR spectroscopy. Infrared data for the cyclopentadienyl complexes **4**, **5** and for the indenyl complex **6** are reported in Tables 1 and 2, respectively. When dichloromethane solutions of acyl

Table 2

Terminal carbonyl and acyl stretching frequencies (ν , $\pm 0.2 \text{ cm}^{-1}$) of the indenyl complex $[\text{Fe}(\eta^5\text{-C}_9\text{H}_7)(\text{COMe})(\text{CO})(\text{L})]$ (**6**) in the presence of metal salts

Solvent	Salt	$\nu(\text{CO})$	$\nu(\text{COMe})$
Dichloromethane	none	1919.3	1604
	LiClO_4	1945.8, 1932.6	1585
	LiI	1945.2, 1938.3	1589
	NaI	1924.1	1572
	NaPF_6	1924.5	1574, 1606 m
	KPF_6	1941.8	1558
	NH_4PF_6	1940.6	1604
	$\text{Mg}(\text{ClO}_4)_2$	1941.4	1570, 1528
	CaI_2	1927.3	1570
	CaI_2	1942.4	1520
	$\text{Ba}(\text{SCN})_2$	1919.6, 2066 ^a	1605
	Chloroform	none	1924.3
NaPF_6		1942.7	1559
LaCl_3		1919.2	1599
Tetrahydrofuran	none	1919.5	1612
	NaPF_6	1940.8	—
Acetonitrile	none	1917.5	1606
	NaPF_6	1944.6	1589
	KPF_6	1915.1, 1938sh	1592sh
	CaI_2	1915.2, 1927	—

^a $\nu(\text{SCN})$.

complex are stirred in the presence of solid metal salts, the iron complex may extract the salt by complexation of the metal ion in the cavity of the aza-crown ether. This information is obtained by an infrared analysis of the resulting filtered solution, by comparing the values of the stretching frequencies of the terminal carbonyl $\nu(\text{CO})$ and of the acyl carbonyl $\nu(\text{COR})$ groups with those obtained in the absence of metal salt, and according to the following criteria. When the aza-crown ether coordinates the metal ion, the terminal carbonyl group exhibits a shift to higher frequencies, suggesting intramolecular electronic interaction between crown-complexed metal ions and the iron centre [22], as the result of reduced electron density on iron and hence reduced π -back bonding toward CO. The stretching of the acyl group $\nu(\text{COR})$ is either not affected by complexation or strongly shifted to lower frequencies when the acyl oxygen binds the coordinated metal ion, as depicted in Fig. 1. We have checked this interpretation by blank experiments. For instance, a dichloromethane solution of the complex $[\text{Fe}(\eta^5\text{-C}_9\text{H}_7)(\text{CO})(\text{COMe})(\text{PMePh}_2)]$ was stirred in the presence of NaI, and significant changes in the carbonyl stretching bands were not observed; the corresponding aza-crown complex $[\text{Fe}(\eta^5\text{-C}_9\text{H}_7)(\text{CO})(\text{COMe})(\text{L})]$ showed a $\nu(\text{CO})$ shift of $+4.3\text{ cm}^{-1}$ and a lower frequency $\nu(\text{COMe})$ shift of -32 cm^{-1} , after addition of NaI.

3.2.1. $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{COMe})(\text{CO})(\text{L})]$ (**4**, Table 1)

Our study was limited to sodium and calcium salts. Infrared spectra in the presence of lithium and magnesium salts as well were reported by McLain, in dichloromethane [15]. Our data are in good agreement with the reported values, except that we did not observe such a large high frequency shift of the terminal carbonyl band in the presence of CaI_2 (1952 vs. 1917 cm^{-1}) [15] but a rather smaller change (1926 vs. 1917.5 cm^{-1}). However, we do observe a consistent shoulder at higher frequency of the main band, both in dichloromethane and in chloroform, which can be attributed to the species characterized by the 1952 cm^{-1} absorbance. We have also observed the strong shift to lower frequencies of the $\nu(\text{COMe})$ band, of ca. -30 cm^{-1} for Na^+ and ca. -80 cm^{-1} for Ca^+ , indicative of intramolecular coordination of the acetyl oxygen to the crown ether held cation. These data regard chlorinated solvents. An intermediate situation is observed in tetrahydrofuran. The $\nu(\text{CO})$ band shows a large high frequency shift of $+24\text{ cm}^{-1}$ upon complexation of the sodium cation in the crown ether, whereas the absorption of the $\nu(\text{COMe})$ band appears disturbed by moisture, which probably hinders coordination of the acetyl oxygen. In the apolar solvent cyclohexane (1923.8 , 1611 cm^{-1}), the salt cannot be extracted by the acetyl complex and band shifts are not observed. In the very polar solvent 1,4 dioxane (1915.2 , 1603 cm^{-1}) metal

salts dissolve easily but band shifts are not observed as well, except for shoulders, indicating competition between solvation and complexation.

3.2.2. $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{COCHMe}_2)(\text{CO})(\text{L})]$ (**5**, Table 1)

In dichloromethane solutions, a consistent high frequency shift is observed for the $\nu(\text{CO})$ band in the presence of NaPF_6 ($+16\text{ cm}^{-1}$) and of CaI_2 ($+7\text{ cm}^{-1}$, $+40\text{ cm}^{-1}$ as a strong shoulder). On the other hand, significant changes in the frequencies of the acyl carbonyl group are not observed. It appears that complex **5** coordinates metal ions in the aza-crown ether cavity, but that intramolecular oxygen-metal ion interaction of the acetyl group does not occur. This is likely to depend on the bulkiness of the isopropyl group which hinders a suitable molecular conformation for the expected interaction.

3.2.3. $[\text{Fe}(\eta^5\text{-C}_9\text{H}_7)(\text{CO})(\text{COMe})(\text{L})]$ (**6**, Table 2)

The infrared spectra of complex **6** have been obtained in the presence of different alkali and alkaline-earth metal salts. Changes in the infrared frequencies of both terminal and acetyl carbonyl groups suggest structural arrangements similar to those of the cyclopentadienyl-complex **4** (Fig. 2).

The higher energy shift of the $\nu(\text{CO})$ band is large upon complexation of Li^+ , K^+ , Mg^{2+} and Ca^{2+} (up to $+26\text{ cm}^{-1}$ for Li^+) in dichloromethane. The ammonium ion NH_4^+ yields a shift as well ($+21\text{ cm}^{-1}$), in agreement with the ability of the cation to fit into the aza-15-crown-5 ring [26]. For Na^+ , we have observed larger shifts in chloroform or tetrahydrofuran than in dichloromethane. Complexation of Ba^{2+} is observed only as a high frequency shoulder ($\sim 1940\text{ cm}^{-1}$) of the band due to uncomplexed **6** (1919.6 cm^{-1}), present as the main species. The fact that the lanthanum salt $[\text{LaCl}_3 \cdot (\text{H}_2\text{O})_x]$ did not induce any band shift may be due to the effect of the strong lattice energy of lanthanum chloride, preventing complexation by the aza-crown ether system. Shifts of the acetyl $\nu(\text{COMe})$ band are large for Na^+ , K^+ , Ca^{2+} and Mg^{2+} . The lack of acetyl shift in the presence of the ammonium salt

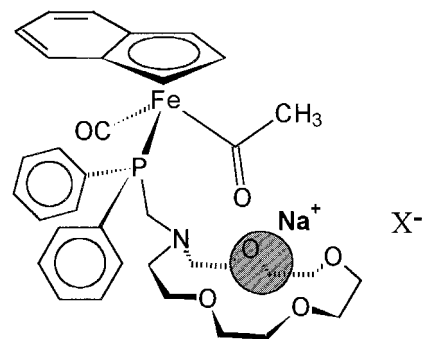


Fig. 2. Intramolecular acetyl oxygen-cation interaction in the complexation of metal salts to $[\text{Fe}(\eta^5\text{-C}_9\text{H}_7)(\text{COMe})(\text{CO})(\text{L})]$ (**6**).

represents a clean example of discrimination between aza-crown ether and acetyl oxygen complexation to the added cation. In the polar solvent acetonitrile, coordination of the metal cation in the aza-crown ring is indicated by the shift of the $\nu(\text{CO})$ band, as in the presence of NaPF_6 , although shifts of the acetyl band are small or absent. Fig. 3 shows the shift of the $\nu(\text{CO})$ band of complex **6** in the presence of NaPF_6 and KPF_6 . The existence of shoulders of the main $\nu(\text{CO})$ band or the values observed in different sample preparations (entries 9, 10 in Table 2) indicate the presence of both coordinated and uncoordinated species or different complex conformations in solution.

In summary, the changes of acetyl stretching frequencies vary up to -80 cm^{-1} for the cyclopentadienyl complex **4** and up to -84 cm^{-1} for the indenyl complex **6** in the presence of CaI_2 . The changes of the terminal carbonyl stretching frequencies vary up to $+40 \text{ cm}^{-1}$ for complex **4** upon interaction with MgI_2 in dichloromethane [15], and up to 26 cm^{-1} for complex **6** in the presence of LiClO_4 . The shifts of the CO group are indicative of effective electronic interactions between the two metal centres, and are especially significant when compared to those in other literature reports. For instance, $\text{Cr}(\text{CO})_3$ -substituted benzocrown ethers used as FT-IR-readable molecular sensors for metal ions display shifts of $\nu(\text{CO})$ up to 7 cm^{-1} after complexation of group I metal ions [27,28]. The cymantrene complex $\text{Mn}(\text{CO})_3(\eta^5\text{-2-indenyl-aza-15-crown-5})$ shows a 2 cm^{-1} shift upon complexation with LiClO_4 , and only protonation in strong acidic media of the crown ether nitrogen atom produces a desired change of $\nu(\text{CO})$ by 36 cm^{-1} to higher frequency [22].

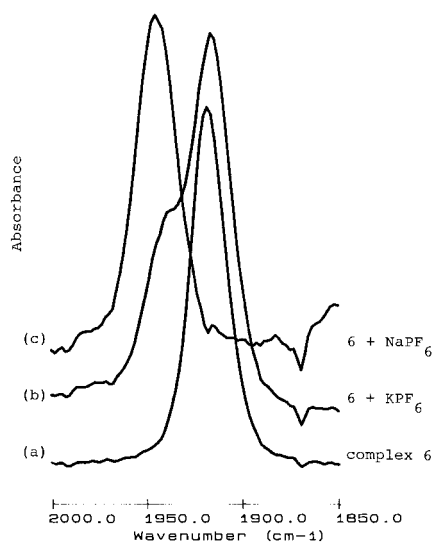


Fig. 3. Infrared spectra of complex $[\text{Fe}(\eta^5\text{-C}_9\text{H}_7)(\text{COMe})(\text{CO})(\text{L})]$ **6** (a), complex **6**· KPF_6 (b), and complex **6**· NaPF_6 (c) in acetonitrile, in the region of the terminal carbonyl stretching band $\nu(\text{CO})$.

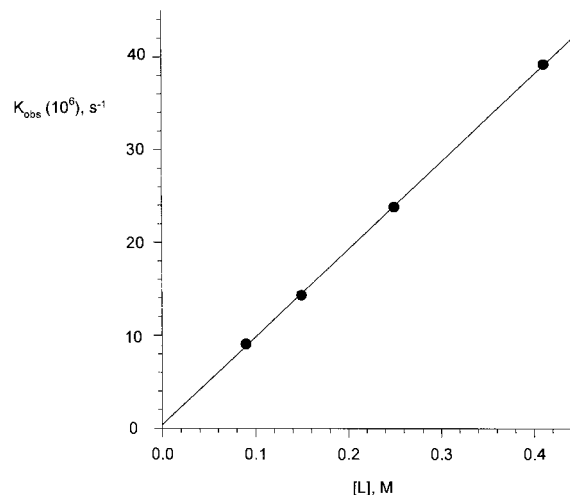


Fig. 4. Plot of k_{obs} (s^{-1}) versus concentration of $\text{Ph}_2\text{P-CH}_2\text{-(aza-15-crown-5)}$ (L) for the reaction of complex $[\text{Fe}(\eta^5\text{-C}_9\text{H}_7)(\text{CO})_2\text{Me}]$ (**3**), in acetonitrile at 40°C .

3.3. Kinetic measurements

Since the acetyl complex **4** formed only in refluxing hexane under heterogeneous conditions, rate measurements of the reaction of complex **1** with L were not attempted. The kinetic features of the reactions of the cyclopentadienyl isopropyl complex **2** and of the indenyl methyl complex **3** with the aza-crown ether phosphine L were first studied in the absence of metal ions (Scheme 2). The progress of the reaction was followed by UV-Vis spectroscopy, monitoring the growth of absorbance, due to product formation, around 400 nm [2–5], or by FT-IR. The phosphine, L, was used in large excess with respect to the iron complexes, in order to ensure pseudo-first order conditions. In order to determine the rate dependence on L, rate measurements for the reaction of the indenyl methyl complex $[\text{Fe}(\eta^5\text{-C}_9\text{H}_7)(\text{CO})_2\text{Me}]$ were obtained at different concentrations of L. A plot of first order observed rate constants, k_{obs} (s^{-1}), versus $[\text{L}]$ is shown in Fig. 4 and values of k_{obs} are reported in Table 3.

Table 3

Values of observed rate constants, k_{obs} , for the reaction of complex $[\text{Fe}(\eta^5\text{-C}_9\text{H}_7)(\text{CO})_2\text{Me}]$ (**3**) with the aza-crown phosphine $\text{Ph}_2\text{P-CH}_2\text{-(aza-15-crown-5)}$ (L), and with PPh_3 in acetonitrile, at 40°C , by UV-Vis^a

Salt(M)	$[\text{L}], \text{M}$	$k_{\text{obs}}, \text{sec}^{-1}$
None	0.41	3.9×10^{-5}
None	0.25	2.4×10^{-5}
None	0.15	1.4×10^{-5}
None	0.09	0.9×10^{-5}
	$[\text{PPh}_3], \text{M}$	
None	0.08	2.8×10^{-5}
NaI (0.14)	0.08	3.5×10^{-5}
CaI_2 (0.11)	0.08	2.1×10^{-5}

^aAbsorbance growth at 400 nm .

The linear dependence of rate versus phosphine concentration indicates a clean second order behaviour, which implies that the phosphine L is part of the rate limiting step. We checked whether metal salts may change the reactivity of the iron complexes by effects not related to complexation in the aza-crown ether system, and did not observe significant rate effects for the reaction of complex **3** with triphenylphosphine in acetonitrile upon addition of NaI or CaI₂ (Table 3).

Rate measurements of the reaction with L were obtained in the presence of metal salts, and carried out by FT-IR spectroscopy, in acetonitrile and in chloroform. Due to the high solubility of metal salts in acetonitrile, this solvent ensures the presence of equimolar amounts of L and of the salt, and the existence of 1:1 aggregates, due to the high affinity of monoaza-15-crown-5 for the group I and II cations [26]. On the other hand, the infrared spectra in chloroform showed shifts of both carbonyl and acyl stretching bands as the result of aggregation, and acyclic coordination, between complexes **5**, **6** and metal cations. The presence of NaPF₆ in deuterated chloroform solution of phosphine L was also observed in the ³¹P NMR spectrum, showing a septet signal due to the hexafluorophosphate counterion (δ -145 ppm, J_{PF} = 713 Hz). The experiments were carried out in the presence of sodium or calcium salts, since these metal ions exhibited the strongest band shifts and were therefore expected to display rate effects, if any.

Table 4

Values of observed rate constants, k_{obs} , for the reaction of complexes [Fe(η^5 -C₅H₅)(CO)₂CHMe₂] (**2**) and [Fe(η^5 -C₉H₇)(CO)₂Me] (**3**) with the aza-crown phosphine Ph₂P-CH₂-(aza-15-crown-5) (L)

Method	<i>T</i> , °C	Solvent	Salt (M)	[L], M	k_{obs} , sec ⁻¹
Complex 2					
FT-IR ^a	30	acetonitrile	none	0.15	5.6×10^{-5}
FT-IR ^a	30	acetonitrile	CaI ₂ (0.15)	0.11	5.2×10^{-5}
FT-IR ^a	40	acetonitrile	none	0.16	1.5×10^{-4}
FT-IR ^a	40	acetonitrile	NaPF ₆ (0.17)	0.16	1.7×10^{-4}
Complex 3					
UV-Vis ^b	40	acetonitrile	none	0.10	0.6×10^{-5}
UV-Vis ^b	40	acetonitrile	NaI (0.26)	0.10	1.6×10^{-5}
FT-IR ^c	40	acetonitrile	CaI ₂ (0.19)	0.13	1.5×10^{-5}
FT-IR ^d	40	chloroform	none	0.18	0.9×10^{-5}
FT-IR ^d	40	chloroform	NaPF ₆ ^e	0.21	1.5×10^{-5}
FT-IR ^d	40	chloroform	CaI ₂ ^e	0.24	1.6×10^{-5}

^aGrowth of the $\nu(\text{CO})$ band of **5** at 1912 cm⁻¹; ^b400 nm; ^cdecay of the $\nu(\text{CO})$ band at 2002 cm⁻¹; ^ddecay of the $\nu(\text{CO})$ band at 2005 cm⁻¹; ^esaturated solutions.

The progress of the reaction is characterized by the disappearance of the $\nu(\text{CO})$ bands of the starting complex (e.g.: 1996.5, 1938 cm⁻¹, **2** in acetonitrile) and by the growth of the terminal carbonyl band (1912 cm⁻¹) of the product. A sequence of spectra for the reaction of **2** with L in the presence of NaPF₆ is shown in Fig. 5. The disappearance of the iron complexes **2** or **3** displayed a clean first order time dependence.

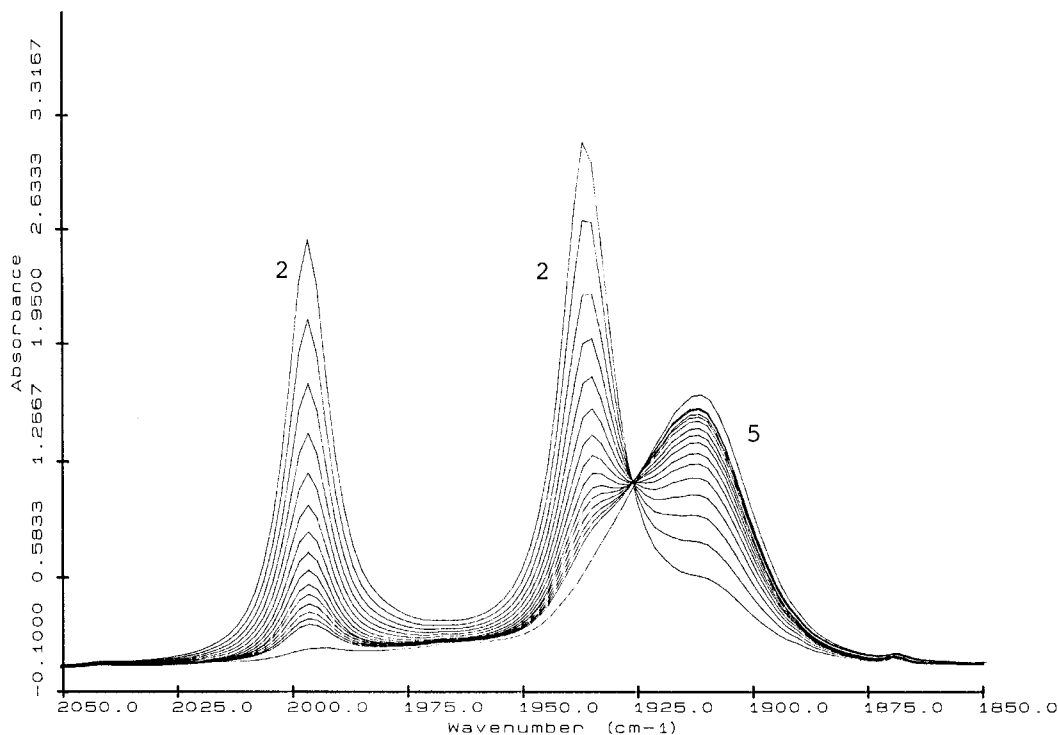


Fig. 5. A series of infrared spectra recorded during the reaction of complex [Fe(η^5 -C₅H₅)(CO)₂CHMe₂] (**2**) with L (0.16 M) in acetonitrile, at 40°C. The solution contained NaPF₆ (0.18 M). Bands are assigned to complexes **2** and **5** as indicated.

Values of k_{obs} are reported in Table 4. The indenyl complex **3** exhibits an acceleration up to three times in the presence of sodium or calcium salts, both in acetonitrile and in chloroform. In the latter solvent, where aza-crown ether complexation and acetyl oxygen coordination to the cation were observed, somewhat higher rate enhancements were expected in the case of electrophilic activation by the metal ion. These effects are rather small, although indicative of overall favorable induction by the metal ions. It is possible that when the expected oxygen-metal ion interaction is present in the transition state, it is then counterbalanced by other effects coming into play. For instance, coordination of a metal ion in the aza-crown ether cavity may reduce the donor ability of the phosphine by polarization. Furthermore, the reacting ion pair $\text{LM}^+\cdot\text{X}^-$ may introduce more stringent steric requirements as well as more extensive solvent reorganization during reaction, producing counteracting effects on reactivity. The reactivity of the isopropyl complex **2** does not appear to be affected by the presence of metal salts, in acetonitrile, which is in line with the lack of interaction between acyl oxygen and cations, as observed by FT-IR spectroscopy.

4. Conclusions

Complexation of group I and II metal ions within the cavity of the aza-15-crown-5 unity of indenyl and cyclopentadienyl acetyl complexes $[\text{Fe}(\eta^5\text{-ligand})(\text{COMe})(\text{CO})(\text{Ph}_2\text{P-CH}_2\text{-aza-15-crown-5})]$ (**4**, **6**) raises the stretching energy of the terminal carbonyl group CO, as a result of electronic polarization of the iron centre and consequent reduction of π -back bonding. Shifts to lower energy of the COMe stretching band indicate intramolecular coordination of the acetyl oxygen to the complexed cation. Such intramolecular contact is hindered by changing methyl for isopropyl in the acyl group (**5**), or in polar aprotic solvents. The reaction of the indenyl complex $[\text{Fe}(\eta^5\text{-C}_9\text{H}_7)(\text{CO})_2\text{Me}]$ with the phosphine $\text{Ph}_2\text{P-CH}_2\text{-(aza-15-crown-5)}$ is only moderately affected by the presence of metal salts in solution, whereas that of the cyclopentadienyl complex $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{CHMe}_2]$ does not show any salt dependence.

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