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Reactivity of cyclopentadienyl and indenyl alkylcarbonyliron(II) complexes. η^5 Species as key intermediates in the migratory insertion of carbon monoxide

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The reactions of the complexes [Fe(η^5-L)(CO)$_2$R] (L = C_5H_5 or C_9H_7, R = Me or CHMe$_2$) with PR'$_3$ (PMe$_2$Ph, PMePh$_2$ and PPh$_3$) have been studied in toluene and tetrahydrofuran (thf) by UV/VIS and IR spectroscopy. The products of alkyl migratory insertion [Fe(η^5-C_5H_5)(CO)(COR)(PR'$_3$)] are formed *via* an associative mechanism, involving (*i*) a rapid pre-equilibrium (K) between complex and phosphine and (*ii*) rate-determining alkyl migration (k_2), in analogy to the mechanism previously established for [Fe(η^5-C_9H_7)(CO)$_2$R]. In the intermediate molecular complexes {[Fe(η^5-L)(CO)$_2$R], phosphine} the compounds [Fe(η^5-C_5H_5)(CO)$_2$R] bind to phosphine less efficiently than do the indenyl analogues and react one order of magnitude more slowly. Reaction rates are similar in thf and in toluene, in agreement with the proposal that the alkyl migration is not solvent assisted.

Transition-metal complexes having different spectator ligands of the cyclopentadienyl family (L) may exhibit changes in the rate of associative reactions.[1] Remarkable effects were reported for ligand substitution in rhodium(I) complexes.[2] For instance, [Rh(η^5-C_9H_7)(CO)$_2$] (C_9H_7 = indenyl) reacts 10^8 times faster with PPh$_3$ than does [Rh(η^5-C_5H_5)(CO)$_2$]. This phenomenon has been described as the *indenyl ligand effect*, and interpreted in terms of the different stabilities of the corresponding trihapto intermediates [Rh(η^3-L)(CO)$_2$(PPh$_3$)] or transition states.[2b]

Although the migratory insertion of carbon monoxide is a reaction studied in great detail,[3] relatively little attention has been given to the effects of ancillary ligands which are not part of the migration step.[4] In particular, effects in complexes of different pentahapto ligands have been described only in a few cases. Facile carbonylation reactions have been reported for [Fe(η^5-C_9H_7)(PPh$_3$)(CO)Me] and related complexes,[5] and for [Fe(η^5-C_9H_7)(CO)$_2${CH(OSiMe$_3$)R}].[6] A kinetic study on the reaction induced by tributylphosphine and triphenyl phosphite in molybdenum complexes [Mo(η^5-L)(CO)$_3$Me] (L = C_9H_7 or C_5H_5) has shown that the indenyl system is more reactive in both an associative and a nucleophile-independent mechanism.[7]

We have studied the CO migratory insertion in alkylcarbonyl (indenyl) iron(II) complexes and shown that the reaction proceeds through an associative pathway (Scheme 1, L = C_9H_7; R = CHMe$_2$ or Me; PR'$_3$ = alkyl, aryl or mixed alkyl–aryl phosphine).[8] Although cases of assistance by solvent or by the entering ligand in the migratory insertion have been presented,[9] our studies have demonstrated that the reaction of the indenyl system is induced by the incoming phosphine, and that the key intermediate is a molecular complex of the two reactants, changing into product by carbon–carbon and iron–phosphorus couplings. This situation is in contrast with the proposed mechanism for migratory insertion, which describes the process in terms of a two-step sequence characterized by (*i*) alkyl migration forming a co-ordinatively unsaturated or solvent-saturated acyl species, and (*ii*) attack of phosphine to yield the final acyl product.[3,10] We have also proposed that the intermediates of Scheme 1 are electron-donor–acceptor complexes, in which the structural features of the interacting molecules are largely preserved, the indenyl ligand binding through an η^5 mode.[8b]

$$[\mathrm{Fe}(\eta^5\text{-L})(\mathrm{CO})_2\mathrm{R}] + \mathrm{PR'}_3 \xrightleftharpoons{K} \{[\mathrm{Fe}(\eta^5\text{-L})(\mathrm{CO})_2\mathrm{R}], \mathrm{PR'}_3\}$$

$$\{[\mathrm{Fe}(\eta^5\text{-L})(\mathrm{CO})_2\mathrm{R}], \mathrm{PR'}_3\} \xrightarrow{k_2} [\mathrm{Fe}(\eta^5\text{-L})(\mathrm{CO})(\mathrm{COR})(\mathrm{PR'}_3)]$$

Scheme 1

We have extended our studies to the cyclopentadienyl complexes in order to compare the reactivity and mechanism of indenyl- and cyclopentadienyl-iron(II) species. The reactions of iron cyclopentadienyl complexes [Fe(η^5-C_5H_5)(CO)$_2$R] (R = Me, Et or Pr^i) with phosphines in polar solvents have been previously described.[11] The alkyl to acyl migratory insertion has also been studied in cationic complexes [Fe(η^5-C_5H_5)(CO)(PR$_3$)(Me)]$^+$ and evidence has been presented that the reaction involves transient 19-electron seven-co-ordinate complexes [Fe(η^5-C_5H_5)(CO)(PR$_3$)(X)Me]$^+$ (X is the incoming ligand).[4b,12]

Experimental

The reactions and characterization of starting materials and products have been reported previously.[8,11,13,14] The phosphines were commercially available and used as received. Toluene was distilled under argon from sodium, and tetrahydrofuran from potassium, in the presence of benzophenone. The methods used for kinetic measurements and for data analysis are described in detail in ref. 8(*a*). Solutions of the iron complex and phosphine were prepared under argon, using Schlenk-line techniques, in 1 cm quartz cells for UV/VIS, or 0.5 mm CaF$_2$ cells for Fourier-transform IR measurements. Initial concentrations of iron complexes were *ca.* 10^{-4} (UV/VIS) and *ca.* 0.01 mol dm^{-3} (FTIR). Pseudo-first-order rate constants (k_{obs}) were obtained by fitting the exponential dependence of the absorbance *vs.* time data using a non-linear least-squares regression program, which also provides the absorbance after completion, A_∞, for slower reactions. Duplications of single kinetic runs were reproducible to within 6%. The uncertainties of the reaction parameters K and k_2 are reported as standard deviations, obtained from non-linear least-squares calculations. Activation parameters were obtained by an unweighted linear least-squares analysis of the dependence of $\ln(k_2/T)$ on $1/T$.

Table 1 Carbonyl stretching frequencies (±0.2 cm^{-1}, hexane) for [Fe(η^5-L)(CO)$_2$R] and [Fe(η^5-L)(CO)(COR)(PR$'_3$)] complexes

Complex	L	PR$'_3$	$\tilde{\nu}$(CO)/cm^{-1}	$\tilde{\nu}$(COR)/cm^{-1}
1	C_5H_5[a]		2014.6 1961.2	
	C_5H_5[a]	$PMePh_2$	1924.1	1607
2	C_9H_7[a,b]		2011.7 1957.9	
	C_9H_7[a,b]	$PMePh_2$	1923.7	1617
	C_9H_7[a,b]	PMe_2Ph	1920.5	1615
	C_9H_7[a,b]	PBu^n_3	1919.4	1620
3	C_5H_5[c,d]		2006.4 1952.1	
4	C_9H_7[b,c]		2003.7 1950.2	
	C_5H_5[c]	PPh_3	1921.3	1610
	C_5H_5[c]	$PMePh_2$	1921.9	1606
	C_5H_5[c]	PMe_2Ph	1917.2	1605
	C_9H_7[c]	PPh_3	1920.8	1614
	C_9H_7[c]	$PMePh_2$	1919.4	1613
	C_9H_7[c]	PMe_2Ph	1916.4	1611

[a] R = Me. [b] Ref. 8. [c] R = CHMe$_2$. [d] Ref. 14.

Results

During our study on the reaction of [Fe(η^5-C$_9$H$_7$)(CO)$_2$Me] with phosphines in toluene we observed a very slow reaction of [Fe(η^5-C$_5$H$_5$)(CO)$_2$Me] **1** with PMe$_2$Ph and PMePh$_2$ and a complicated kinetic behaviour that did not allow a meaningful comparison of rate and mechanism for indenyl and cyclopentadienyl species.[8a] We have now observed more reproducible and first-order behaviour for the reaction carried out in tetrahydrofuran (thf). The reactions of complex **1** and of [Fe(η^5-C$_9$H$_7$)(CO)$_2$Me] **2** with PMePh$_2$ and PPh$_3$ proceed to the formation of the corresponding acyl products, according to equation (1). The isopropyl complex [Fe(η^5-C$_5$H$_5$)(CO)$_2$(CHMe$_2$)] **3** also reacts smoothly with PMe$_2$Ph, PMePh$_2$ and PPh$_3$ in tetrahydrofuran or in toluene even at room temperature to give the corresponding acyl complexes [Fe(η^5-C$_5$H$_5$)(CO)(COCHMe$_2$)(PR$'_3$)] in high yields. The migratory aptitude of the isopropyl group was well suited for a kinetic study of both complex **3**[11,13] and [Fe(η^5-C$_9$H$_7$)(CO)$_2$(CHMe$_2$)] **4**.[8b,14] Infrared data for alkyl and acyl complexes are given in Table 1. The kinetics, carried out under pseudo-first-order conditions using an excess of phosphine, were studied by monitoring the product formation in the visible region (400–420 nm), or the disappearance of the carbonyl stretching bands of the alkyl complexes in the infrared. The reaction of **3** with PPh$_3$ in toluene was studied in the range 20–60 °C.

$$[\mathrm{Fe}(\eta^5\text{-L})(\mathrm{CO})_2\mathrm{Me}] + \mathrm{PR'}_3 \xrightarrow[50\,^\circ\mathrm{C}]{\mathrm{thf}} [\mathrm{Fe}(\eta^5\text{-L})(\mathrm{CO})(\mathrm{COMe})(\mathrm{PR'}_3)] \qquad (1)$$

The dependence of the rate of reaction (1) on the concentration of phosphine is shown in Fig. 1 for [Fe(η^5-C$_5$H$_5$)(CO)$_2$Me], in Fig. 2 in the reciprocal form 1/k_{obs} *vs.* 1/[phosphine], in Fig. 3 on a logarithmic scale for both complexes **1** and **2**, and in Fig. 4 for **3** and **4**. The experimental points are fitted by equation (2), which is derived from the mechanism in Scheme 1, yielding equilibrium constants K (dm^3 mol^{-1}) for adduct formation and rate constants k_2 (s^{-1}) for alkyl migration, or by equation (3) for Fig. 2. The y intercepts in the graph represent the reciprocal values of the limiting rate at [phosphine] = ∞, *i.e.* the rate constants k_2.

$$k_{obs} = \frac{Kk_2[\mathrm{L}]}{1 + K[\mathrm{L}]} \qquad (2)$$

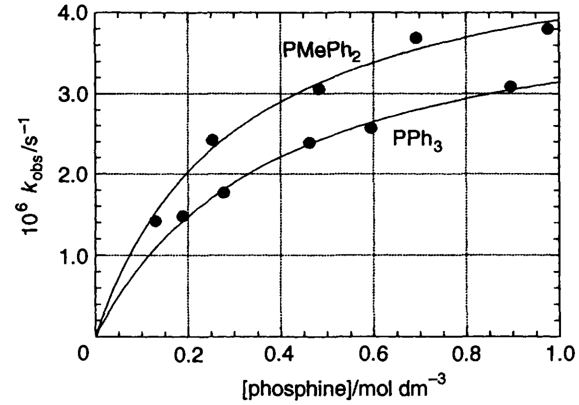


Fig. 1 Plots of k_{obs} *vs.* phosphine concentration for the reactions of [Fe(η^5-C$_5$H$_5$)(CO)$_2$Me] with PPh$_3$ and PMePh$_2$ in tetrahydrofuran at 50 °C

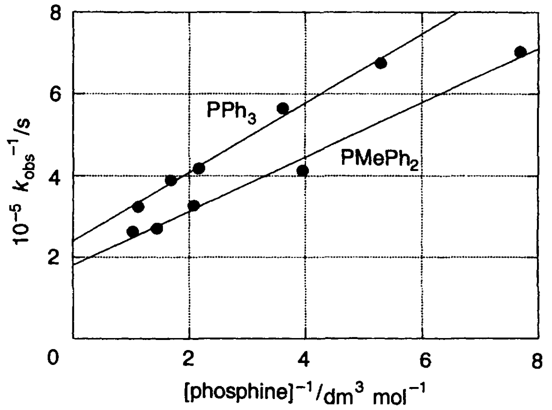


Fig. 2 Plots of 1/k_{obs} *vs.* 1/[phosphine] for the reaction of [Fe(η^5-C$_5$H$_5$)(CO)$_2$Me]

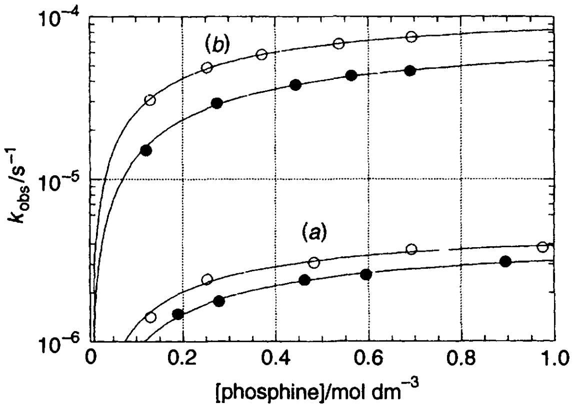


Fig. 3 Plots of k_{obs} *vs.* phosphine concentration for the reactions of (*a*) [Fe(η^5-C$_5$H$_5$)(CO)$_2$Me] and (*b*) [Fe(η^5-C$_9$H$_7$)(CO)$_2$Me] with PPh$_3$ (●) and PMePh$_2$ (○) in tetrahydrofuran at 50 °C

$$\frac{1}{k_{obs}} = \frac{1}{k_2K[\mathrm{L}]} + \frac{1}{k_2} \qquad (3)$$

The observed rate constants, k_{obs} (s^{-1}), are given in Tables 2 and 3 for the reactions in tetrahydrofuran, and in Table 4 for the reactions in toluene. Proton NMR or FTIR spectra taken during reaction of **1** or **3**, or immediately after mixing, showed only absorptions due to the starting material and product, no intermediates being detected.

Table 2 Observed rate constants, k_{obs}, for the reaction of [Fe(η^5-C_5H_5)(CO)$_2$Me] **1** and [Fe(η^5-C_9H_7)(CO)$_2$Me] **2** with PPh_3 and $PMePh_2$ in tetrahydrofuran at 50.0 °C *

1				**2**			
[PPh_3]/ mol dm^{-3}	10^6 k_{obs}/s^{-1}	[$PMePh_2$]/ mol dm^{-3}	10^6 k_{obs}/s^{-1}	[PPh_3]/ mol dm^{-3}	10^5 k_{obs}/s^{-1}	[$PMePh_2$]/ mol dm^{-3}	10^5 k_{obs}/s^{-1}
0.189	1.48	0.130	1.42	0.122	1.50	0.129	3.07
0.277	1.77	0.253	2.42	0.274	2.92	0.253	4.87
0.463	2.39	0.483	3.06	0.444	3.82	0.371	5.85
0.595	2.57	0.693	3.69	0.563	4.33	0.537	6.80
0.896	3.09	0.976	3.80	0.690	4.63	0.693	7.50

* [FeL(CO)$_2$Me] = 3×10^{-3}–8×10^{-4} mol dm^{-3}. λ = 400–425 nm.

Table 3 Observed rate constants, k_{obs}, for the reaction of [Fe(η^5-C_5H_5)(CO)$_2$(CHMe$_2$)] **3** with PMe_2Ph, $PMePh_2$ and PPh_3 in tetrahydrofuran at 40.0 °C *

[PPh_3]/ mol dm^{-3}	k_{obs}/s^{-1}	[$PMePh_2$]/ mol dm^{-3}	k_{obs}/s^{-1}	[PMe_2Ph]/ mol dm^{-3}	k_{obs}/s^{-1}
0.0247	1.05×10^{-5}	0.0267	2.56×10^{-5}	0.035	6.27×10^{-5}
0.0632	2.87×10^{-5}	0.040	3.31×10^{-5}	0.068	1.18×10^{-4}
0.130	6.20×10^{-5}	0.066	5.91×10^{-5}	0.254	2.33×10^{-4}
0.262	1.01×10^{-4}	0.131	9.87×10^{-5}	0.413	2.62×10^{-4}
0.343	1.31×10^{-4}	0.231	1.28×10^{-4}	0.639	2.98×10^{-4}
0.424	1.37×10^{-4}	0.304	1.66×10^{-4}		
0.512	1.68×10^{-4}				

* 420 nm.

Table 4 Observed rate constants, k_{obs}, for the reaction of [Fe(η^5-C_5H_5)(CO)$_2$(CHMe$_2$)] **3** with PMe_2Ph, $PMePh_2$ and PPh_3 *in* toluene at 40.0 °C[a]

[PPh_3]/ mol dm^{-3}	k_{obs}/s^{-1}	[PPh_3]/ mol dm^{-3}	k_{obs}/s^{-1}	[PMe_2Ph]/ mol dm^{-3}	k_{obs}/s^{-1}	[$PMePh_2$]/ mol dm^{-3}	k_{obs}/s^{-1}
0.975	3.02×10^{-4}	0.447	1.49×10^{-5} [b]	0.654	2.24×10^{-4}	0.806	2.56×10^{-4}
0.800	2.84×10^{-4}	0.378	1.37×10^{-5} [b]	0.490	2.08×10^{-4}	0.537	2.43×10^{-4}
0.654	2.42×10^{-4}	0.255	1.18×10^{-5} [b]	0.327	1.83×10^{-4}	0.376	2.09×10^{-4}
0.459	1.95×10^{-4}	0.173	1.03×10^{-5} [b]	0.163	1.32×10^{-4}	0.218	1.63×10^{-4}
0.368	1.79×10^{-4}	0.084	6.58×10^{-6} [b]	0.0654	8.72×10^{-5}	0.109	1.21×10^{-4}
0.329	1.59×10^{-4}			0.0326	6.25×10^{-5}	0.0436	6.80×10^{-5}
0.263	1.31×10^{-4}	0.378	1.17×10^{-3} [c]	0.0164	3.43×10^{-5}	0.0214	3.30×10^{-5}
0.205	1.11×10^{-4}	0.255	8.85×10^{-4} [c]			0.0109	1.60×10^{-5}
0.164	1.02×10^{-4}	0.173	6.81×10^{-4} [c]				
0.129	7.70×10^{-5}	0.084	3.71×10^{-4} [c]				

[a] λ = 360–400 nm; [**3**] = 1.5×10^{-3}–9.2×10^{-4} mol dm^{-3}. [b] At 20.0 °C. [c] At 60.0 °C.

Table 5 Equilibrium (K) and rate (k_2) constants for the reaction of [Fe(η^5-L)(CO)$_2$R] with different phosphines in tetrahydrofuran at 50.0 °C

	[Fe(η^5-C_5H_5)(CO)$_2$Me]		[Fe(η^5-C_9H_7)(CO)$_2$Me]		[Fe(η^5-C_5H_5)(CO)$_2$(CHMe$_2$)]*	
Phosphine	K/dm^3 mol^{-1}	k_2/s^{-1}	K/dm^3 mol^{-1}	k_2/s^{-1}	K/dm^3 mol^{-1}	k_2/s^{-1}
PPh_3	2.5 ± 0.3	$(4.4 \pm 0.2) \times 10^{-6}$	2.0 ± 0.2	$(8.1 \pm 0.4) \times 10^{-5}$	1.2 ± 0.3	$(4.3 \pm 0.8) \times 10^{-4}$
$PMePh_2$	3.3 ± 0.5	$(5.1 \pm 0.3) \times 10^{-6}$	3.0 ± 0.2	$(1.1 \pm 0.1) \times 10^{-4}$	3.0 ± 0.7	$(3.4 \pm 0.5) \times 10^{-4}$
PMe_2Ph					6.6 ± 0.6	$(3.6 \pm 0.1) \times 10^{-4}$

* At 40 °C.

Discussion

With regard to simple ligand effects on the ground state of the metal complexes, Table 1 shows that substitution of C_5H_5 for the indenyl ligand yields a shift of the carbonyl stretching bands (ν_{CO}) to lower frequencies due to stronger π-back bonding from iron to carbon, as the result of greater electron donation from L to iron. The same effect is observed on replacement of methyl by isopropyl in both indenyl and cyclopentadienyl complexes.[14]

The reactions of [Fe(η^5-C_5H_5)(CO)$_2$Me] in tetrahydrofuran are not first order with respect to the phosphine concentration and exhibit saturation behaviour (Fig. 1). The limiting values of reactivity for increasing concentration of $PMePh_2$ and PPh_3 appear to diverge indicating a dependence on the nature of the phosphine (Fig. 2). Although the selectivity is not as high as that previously observed for the reactions of [Fe(η^5-C_9H_7)(CO)$_2$Me] in toluene,[8a] nonetheless both the saturation behaviour and different limiting reactivities suggest that the migratory insertion reactions of the cyclopentadienyl complex [Fe(η^5-C_5H_5)(CO)$_2$Me] proceed according to the mechanism represented in Scheme 2,[15] as in the case of the corresponding indenyl complexes. The parameters are reported in Table 5 for the reactions in tetrahydrofuran and in Table 6 for the reactions in toluene. The activation parameters for the alkyl migration step (k_2) of the reaction of [Fe(η^5-C_5H_5)(CO)$_2$(CHMe$_2$)] **3** with PPh_3 in toluene are $\Delta H^‡$ = 98 ± 13 kJ mol^{-1} and $\Delta S^‡$ = 0 ± 33 J K^{-1} mol^{-1}.

Since the variations in limiting rate with phosphine are

Table 6 Equilibrium (K) and rate (k_2) constants for the reaction of [Fe(η^5-L)(CO)$_2$(CHMe$_2$)] with different phosphines in toluene at 40.0 °C

	[Fe(η^5-C$_5$H$_5$)(CO)$_2$(CHMe$_2$)]		[Fe(η^5-C$_9$H$_7$)(CO)$_2$(CHMe$_2$)][a]	
Phosphine	K/dm^3 mol^{-1}	k_2/s^{-1}	K/dm^3 mol^{-1}	k_2/s^{-1}
PMe$_2$Ph	7.4 ± 1.0	(2.6 ± 0.2) × 10^{-4}	23.8 ± 1.5	(3.4 ± 0.1) × 10^{-3}
PMePh$_2$	5.5 ± 0.5	(3.1 ± 0.1) × 10^{-4}	9.8 ± 0.9	(3.6 ± 0.1) × 10^{-3}
PPh$_3$[b]	1.6 ± 0.2	(3.0 ± 0.2) × 10^{-3}		
PPh$_3$	1.2 ± 0.1	(5.5 ± 0.2) × 10^{-4}	1.5 ± 0.2	(6.0 ± 0.5) × 10^{-3}
PPh$_3$[c]	5.6 ± 0.5	(2.0 ± 0.1) × 10^{-5}		

[a] Ref. 8(*b*). [b] At 60.0 °C. [c] At 20.0 °C.

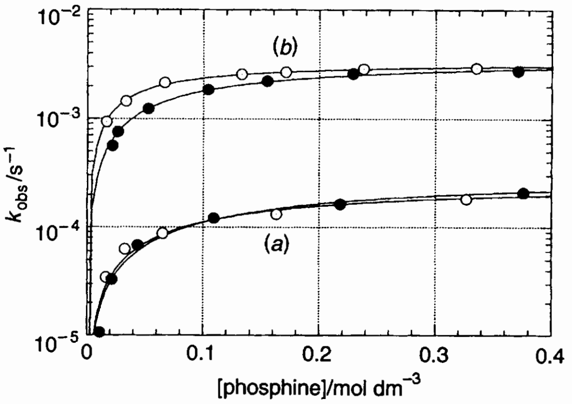
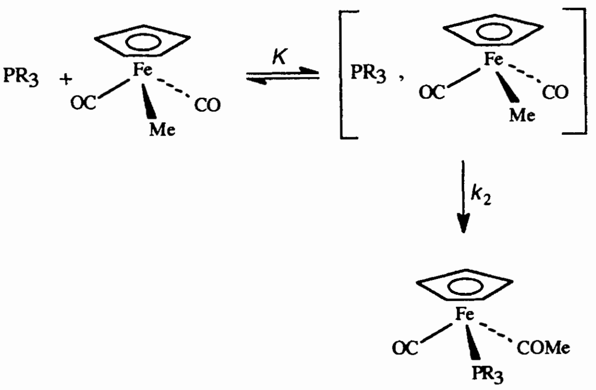


Fig. 4 Plots of k_{obs} *vs.* phosphine concentration for the reactions of (*a*) [Fe(η^5-C$_5$H$_5$)(CO)$_2$(CHMe$_2$)] and (*b*) [Fe(η^5-C$_9$H$_7$)(CO)$_2$(CHMe$_2$)] with PMe$_2$Ph (○) and PMePh$_2$ (●) in toluene at 40 °C



Scheme 2

relatively small, the alternative of a slow initial migration step coupled with competition between rapid reversal from intermediate to starting material and rapid further reaction with phosphine to give the product should not be excluded.[3,10] On the other hand, when the reactions of complex **3** are carried out in tetrahydrofuran as well as in toluene, the similar values of k_{obs} and of the reaction parameters give further support to the proposal that the process is not a solvent-assisted formation of an acyl complex, which should exhibit observable rate effects in the two solvents. The same holds for the indenyl methyl complex **2**: K = 2.0 ± 0.2 dm^3 mol^{-1}, k_2 = (8.1 ± 0.4) × 10^{-5} s^{-1} in tetrahydrofuran; K = 3.5 ± 0.8 dm^3 mol^{-1}, k_2 = (5.7 ± 0.6) × 10^{-5} s^{-1} in toluene (50 °C).[8a] The associative mechanism observed here has been also reported for the reaction of the (pentamethylcyclopentadienyl)iridium(III) complex [Ir(η^5-C$_5$Me$_5$)Cl(CO)Me].[16]

We have not found spectroscopic evidence for the adduct {[Fe(η^5-L)(CO)$_2$R], phosphine}, which is supposed to accumulate during the reaction. As previously discussed in the case of [Fe(η^5-C$_9$H$_7$)(CO)$_2$R],[8] the intermediates may be regarded as molecular complexes in which the structural features of the interacting species are essentially unperturbed with respect to the separated reactants.[17] In line with the suggestion that stronger association between the iron complex and the phosphine is favoured by higher electron density at the metal centre,[8b] we observe here that the cyclopentadienyl complexes have smaller values of K than those of the corresponding indenyl species (Tables 5 and 6). A stronger electron-donor ability of C$_9$H$_7$ *vs.* C$_5$H$_5$ toward the metal fragment has been observed by photoelectron spectroscopy in rhodium(I) complexes,[18] is shown in Table 1 by the shift of the carbonyl stretching frequencies in the infrared, and causes faster dissociation of PPh$_3$ from ruthenium(II) complexes [Ru(η^5-L)Cl(PPh$_3$)$_2$].[19] This property can therefore affect ground states, as well as intermediate and transition states, in which the spectator ligand binds the metal in a pentahapto fashion, as it does in the starting complex.

The effect of the pentahapto ligands on the rate is shown in Fig. 3 for the reactions of the methyl complexes **1** and **2** in tetrahydrofuran at 50 °C, and in Fig. 4 for the reactions of the isopropyl complexes **3** and **4** in toluene at 40 °C. In the region of saturation, the less-reactive methyl complexes and the more reactive isopropyl complexes display a rate difference, C$_9$H$_7$ *vs.* C$_5$H$_5$, of about twenty and ten times respectively. This difference is, for the migratory insertion of alkyliron(II) complexes about the same as that displayed by molybdenum complexes [Mo(η^5-L)(CO)$_3$Me], in the same reaction with phosphorus donors, in hexane or tetrahydrofuran.[7] The effect is small when compared to that of several orders of magnitude observed for carbonyl-substitution reactions of rhodium(I),[2] but also of iron(II)[20] or molybdenum(II).[21] At the moment, a consistent 'indenyl effect' for migratory insertion has not been observed and, therefore, analogies regarding the mechanism and reaction intermediates (*e.g.* η^3 species in associative processes) for carbonyl substitution and migratory insertion should not be drawn.

In the chemistry of iron(II) several reactions of indenyl and cyclopentadienyl complexes are available for consideration. Shorter reaction times and lower temperatures have been used for carbonylation of [Fe(η^5-L)(PPh$_3$)(CO)Me] when L = C$_9$H$_7$.[5] About a 10–20 fold rate difference has been reported in the epimerization of chiral indenyl and cyclopentadienyl methyl complexes, which proceeds through a dissociative mechanism.[22] The rates of insertion of SO$_2$ in [Fe(η^5-L)(CO)$_2$(CH$_2$Ph)] complexes are the same for L = C$_9$H$_7$ and C$_5$H$_5$ in a reaction which proceeds *via* an electrophilic attack on the benzylic carbon atom by SO$_2$.[23] In studies concerning ethylene rotation it was found that replacement of C$_5$H$_5$ by C$_9$H$_7$ in [Fe(η^5-C$_5$H$_5$)(CO)$_2$(C$_2$H$_4$)]$^+$ or [Fe(η^5-C$_5$H$_5$)(CO)(C$_2$H$_4$)(SnR$_3$)] (R = Me or Ph) has an almost negligible effect.[24] Carbonyl substitution, by rate-determining dissociation, in [Fe(η^5-L)(CO)$_2$X] occurs 600 times faster for L = C$_9$H$_7$ than for L = C$_5$H$_5$.[20] Instead, substitution by P- and As-donor nucleophiles in 19-electron radicals occurs by dissociation of CO which is 10^3 times faster in $[Fe(\eta^5-C_5H_5)(CO)_3]^+$ than in the indenyl complex (*inverse* indenyl effect).[25] Among such a variety of mechanisms and ligand effects, the only case in which indenyl complexes react much faster than C_5H_5 analogues is the thermal carbonyl-substitution reaction, which proceeds through a dissociative mechanism.[20] This analysis of the literature suggests that η^3 species of indenyliron(II) complexes may not play a significant role as intermediates. If it were so, rate effects would be expected to be of several orders of magnitude in associative reactions, due to the different stability of η^3-C_9H_7 and -C_5H_5 structures, or to be small in dissociative or other processes, which is not the case. Complexes of iron(II) containing η^3-L have been isolated and structurally characterized,[26] or observed spectroscopically.[27] Therefore, it is our opinion that ring-slipped species may be sufficiently stable to exist as complexes or to form in sideways equilibria, but are not necessarily reaction intermediates in the transformation of iron(II) complexes.

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