Intermolecular Complexes as Reactive Species in the Migratory CO Insertion of Indenyliron(II) Alkyl Complexes

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The reaction of indenyl complexes $(C_9H_7)Fe(CO)_2R$ (R = $CHMe_2$, Me) with phosphines in toluene (20–60 °C) gives the product of alkyl migratory insertion $(C_9H_7)Fe(CO)$(phosphine)(COR) by a mechanism involving (i) rapid formation of a molecular complex $[(\eta^5\text{-}C_9H_7)Fe(CO)_2R$, phosphine] and (ii) rate determining alkyl migration. The equilibrium constants for the preequilibrium step (K, M^{-1}) and the rate constants for C—C coupling (k_2, s^{-1}) are obtained from analysis of kinetic data for phosphines of widely different steric and electronic properties. The K values are greater for R = $CHMe_2$ than for R = Me, and increase with increasing electron withdrawing character of the para substituent of isosteric triarylphosphines $[P(p\text{-}XC_6H_4)_3]$. The effects of structural and electronic changes indicate that the molecular complex $[(\eta^5\text{-}C_9H_7)Fe(CO)_2R$, phosphine] forms through an electron donor—acceptor interaction, in which the iron complex behaves as donor and the phosphine as acceptor. Correlation of K values for triarylphosphines with the σ_{para} constants displays electronic sensitivity for precursor formation as $\varrho = 0.62$ for R = $CHMe_2$ (20 °C) and $\varrho = 0.47$ for R = Me (40 °C). This effect is temperature dependent and levels off at the isoequilibrium temperature (60 °C) for R = Me. Experiments with trialkylphosphines (PBu_3, PCy_3) show that the reaction proceedes by the same mechanism as with alkylaryl- and triarylphosphines and indicate that formation of the molecular complexes is not due to aromatic π-stacking. The alkyl migration step (k_2) for R = $CHMe_2$, which is faster than for R = Me and independent of the nature of the phosphorus donor, involves a negligible extent of Fe—P bond formation in the transition state of the isopropyl complex. Reactions do not proceed with nitrogen donors (pyridine, triethylamine) in place of phosphines, and rates are not affected by the presence of triphenylphosphine oxide.

Introduction

Because of its crucial role in the activation of carbon monoxide, the alkyl to acyl migratory insertion reaction is among the most studied processes in organometallic chemistry.[1]

The mechanism has been assessed in pioneering work on the different aspects of the process.[2] Kinetic studies have indicated a mechanism in which alkyl migration from metal to CO occurs in the first step and an unsaturated 16 electron or a solvent saturated acyl intermediate is generated. Attack of a nucleophile on the intermediate produces the final product.[3] It has now become evident that many of the alkyl to acyl migratory insertion reactions are assisted by concomitant incorporation of a nucleophilic solute or solvent. The role of the nucleophile in the first step of the reaction has been suggested in either neutral 18 electron[4] or in oxidized or reduced complexes.[5] These studies have concluded that the reaction is nucleophilically assisted.

Associative reactions between nucleophiles and the metal center are promoted in η^5-indenyl transition metal complexes.[6] We have recently reported a study of the migratory insertion reaction induced by phosphines on the $(C_9H_7)Fe(CO)_2Me$ complex.[7] In this paper we have presented clean kinetic and spectroscopic evidence that the reaction is triggered by the phosphine through rapid formation of a weak molecular complex $[(C_9H_7)Fe(CO)_2$-Me, phosphine], which precedes the rate determining alkyl migration step, according to Scheme 1 (L = phosphine; R = Me).

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Table 1. Equilibrium (K) and Rate (k_2) Constants for the Reaction of $(C_9H_7)Fe(CO)_2CHMe_2$ (1) with Different Phosphines in Toluene

T, °C	phosphine	K, M^{-1}	k_2, s^{-1}	10^4Kk_2, $M^{-1}\,s^{-1}$	pK_a	θ, deg
20.0	PBu_3	5.3(±0.1)	$(4.0 \pm 0.04) \times 10^{-4}$	21(±0.2)	8.43	136
20.0	PBu_3[a]	5.2(±0.2)	$(4.0 \pm 0.1) \times 10^{-4}$			
40.0	PMe_2Ph	23.8(±1.5)	$(3.4 \pm 0.1) \times 10^{-3}$	768(±15)	6.5	122
40.0	$PMePh_2$	9.8(±0.9)	$(3.6 \pm 0.1) \times 10^{-3}$	358(±5)	4.57	136
20.0	$PMePh_2$	8.5(±0.7)	$(5.1 + 0.2) \times 10^{-4}$	45(±2)		
0.0	$PMePh_2$	9.3(±2.3)	$(3.6 \pm 0.3) \times 10^{-5}$	3.0(±0.2)		
40.0	PPh_3	1.5(±0.2)	$(6.0 \pm 0.5) \times 10^{-3}$	91(±2)	2.73	145
25.0	PPh_3	2.7(±0.2)	$(9.6 \pm 0.4) \times 10^{-4}$	26(±0.9)		
10.0	PPh_3	5.7(±0.4)	$(1.0 \pm 0.05) \times 10^{-4}$	6.0(±0.2)		
20.0	$P(p\text{-}ClC_6H_4)_3$	7.7(±0.3)	$(4.3 \pm 0.1) \times 10^{-4}$	33(±0.6)	1.03	145
20.0	$P(p\text{-}FC_6H_4)_3$	5.6(±0.4)	$(4.7 \pm 0.2) \times 10^{-4}$	28(±1.2)	1.97	145
20.0	PPh_3	3.5(±0.4)[b]	$(4.5 \pm 0.3) \times 10^{-4}$[b]	16		
20.0	$P(p\text{-}MeC_6H_4)_3$	2.9(±0.1)	$(4.7 \pm 0.1) \times 10^{-4}$	13(±0.1)	3.84	145
20.0	$P(p\text{-}MeOC_6H_4)_3$	1.8(±0.5)	$(6.8 \pm 1) \times 10^{-4}$	12(±0.6)	4.59	145

[a] $[Ph_3PO] = 0.05$ M. [b] By interpolation from the data between 10 and 40 °C.

Scheme 1

$$(C_9H_7)Fe(CO)_2R + L \overset{K}{\rightleftharpoons} [(C_9H_7)Fe(CO)_2R, L]$$

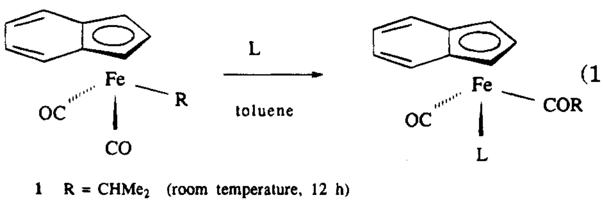
$$[(C_9H_7)Fe(CO)_2R, L] \xrightarrow{k_2} (C_9H_7)Fe(COR)(CO)(L)$$

In this intermediate, the phosphine does not perturb the molecular frame of the alkyl complex, and the indenyl ligand remains in η^5 coordination. We have found no evidence of η^3 intermediates, commonly claimed in the reactions of indenyl complexes.

Because of the peculiarity of the observed phenomenon and the possible relevance of such molecular complexes to this or other organometallic reactions, further investigations aimed at giving a better understanding of the binding forces between the iron complex and the phosphine are clearly needed. We now report systematic kinetics of the reaction of $(C_9H_7)Fe(CO)_2R$ ($R = CHMe_2$, Me) with a series of phosphorus donors of widely different steric and electronic properties. Structural changes in both the iron complex and the nucleophile shed light on the nature of the molecular complex and the effects on the reaction parameters.

Results

The complexes $(C_9H_7)Fe(CO)_2R$ ($R = CHMe_2$ (**1**), Me (**2**)) reacted with phosphorus donors (L) in toluene to form the acyl complexes $(C_9H_7)Fe(CO)(COR)(L)$ in spectroscopically quantitative yields (eq 1).



(1)

1 R = $CHMe_2$ (room temperature, 12 h)

2 R = Me (50-60 °C, 24 h)

Reaction conditions, product analyses, the kinetic method, and the crystal structure of $(C_9H_7)Fe(CO)(COCHMe_2)(PPh_3)$ have been reported in recent papers.[7,8]

Table 2. Equilibrium (K) and Rate (k_2) Constants for the Reaction of $(C_9H_7)Fe(CO)_2Me$ (2) with Different Phosphines in Toluene, at 40.0 °C

phosphine	K, M^{-1}	k_2, s^{-1}	10^5Kk_2, $M^{-1}\,s^{-1}$	pK_a
PMe_3[a]			94(±0.3)	8.65
PBu_3	0.94(±0.1)	$(7.2 \pm 0.6) \times 10^{-5}$	7.1(±0.2)	8.43
PCy_3	1.6(±0.1)	$(1.6 \pm 0.1) \times 10^{-5}$	2.5(±0.1)	9.70
PMe_2Ph[a]	1.2(±0.1)	$(6.2 \pm 0.3) \times 10^{-4}$	79(±1)	6.5
$PMePh_2$[a]	2.2(±0.1)	$(3.2 \pm 0.1) \times 10^{-5}$	7.4(±0.1)	4.57
$P(p\text{-}CF_3C_6H_4)_3$	8.0(±1)	$(1.7 \pm 0.1) \times 10^{-5}$	14(±0.9)	−1.39[b]
$P(p\text{-}ClC_6H_4)_3$	4.2(±0.6)	$(2.6 \pm 0.2) \times 10^{-5}$	11(±0.8)	1.03
$P(p\text{-}ClC_6H_4)_3$[c]	3.2(±0.5)	$(2.0 \pm 0.2) \times 10^{-4}$	65(±4)	
$P(p\text{-}FC_6H_4)_3$[c]	3.3(±0.9)	$(1.7 \pm 0.3) \times 10^{-4}$	56(±3)	
PPh_3[a]	2.8(±0.4)	$(2.0 \pm 0.2) \times 10^{-5}$	5.2(±0.3)	2.73
PPh_3[c]	3.6(±0.6)	$(1.2 \pm 0.1) \times 10^{-4}$	39(±2)	
$P(p\text{-}MeC_6H_4)_3$[c]	3.1(±0.9)	$(1.1 \pm 0.2) \times 10^{-4}$	34(±2)	3.84
$P(p\text{-}MeOC_6H_4)_3$	1.9(±0.9)	$(2.7 \pm 0.9) \times 10^{-5}$	4.8(±0.4)	4.59

[a] Reference 7. [b] pK_a', ref 15. [c] $T = 60.0$ °C.

The kinetics were carried out using an excess of phosphine and by following the increase in absorbance due to product formation in the visible region (~400 nm) and the disappearance of the carbonyl stretching bands of the alkyl complexes in the infrared. Values of observed pseudo-first-order rate constants (k_{obs}) obtained by monitoring the same reaction by UV−vis and FTIR were always in good agreement as were rate constants obtained at different wavelengths. The phosphines used in this work are indicated in Tables 1 and 2.

The reactions were first order in the alkyl complexes. Values of k_{obs} *vs* the concentration of phosphine are given in the plot of Figure 1 for the reaction of $(C_9H_7)Fe(CO)_2(CHMe_2)$ with PMe_2Ph, $PMePh_2$, and PPh_3 at 40.0 °C. The reactions are not first order with respect to the phosphorus donors, but exhibit *saturation kinetics*, in which the reactivity tends toward a limiting value with the increasing concentration of L, as previously observed for $(C_9H_7)Fe(CO)_2(Me)$.[7] This behavior is typical of an associative mechanism, as that shown in Scheme 1 and described by eq 2.

$$k_{obs} = \frac{Kk_2[L]}{1 + K[L]} \tag{2}$$

The parameters K (M^{-1}) and k_2 (s^{-1}), optimized by a nonlinear least squares procedure to give the best fit to eq 2, are reported in Table 1 for the reactions of the isopropyl complex 1 and in Table 2 for the reactions of

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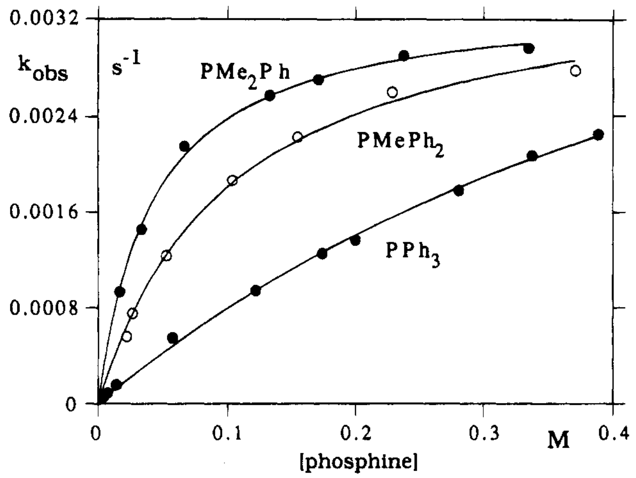

Figure 1. Plot of k_{obs} *vs* phosphine concentration for the reactions of $(C_9H_7)Fe(CO)_2CHMe_2$, in toluene at 40.0 °C.

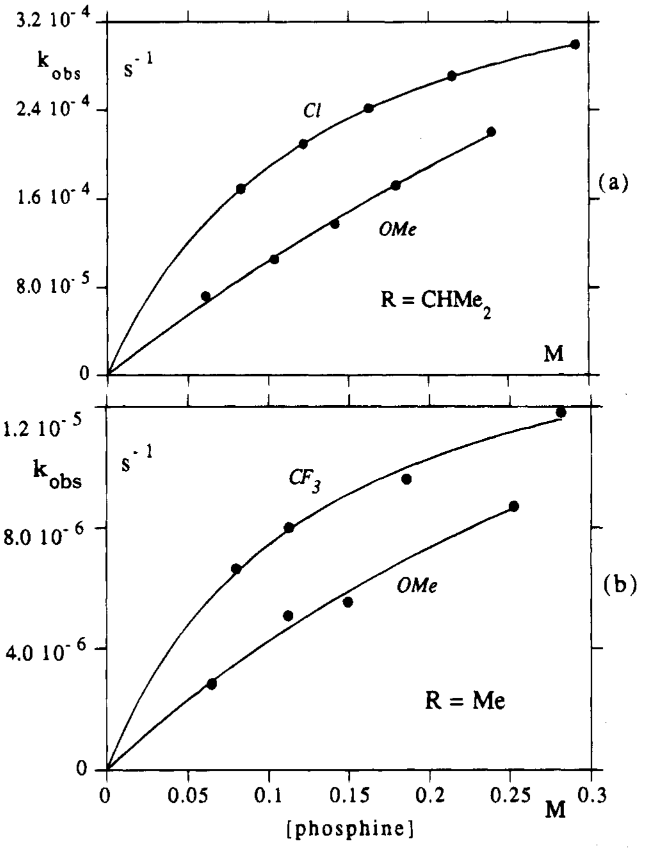

Figure 2. Plot of k_{obs} *vs* phosphine concentration for the reactions of $(C_9H_7)Fe(CO)_2CHMe_2$ with $P(p\text{-}XC_6H_4)_3$ (X = Cl, OMe; 20.0 °C) (a), and for the reactions of $(C_9H_7)Fe(CO)_2Me$ with $P(p\text{-}XC_6H_4)_3$ (X = CF_3, OMe; 40.0 °C) (b), in toluene.

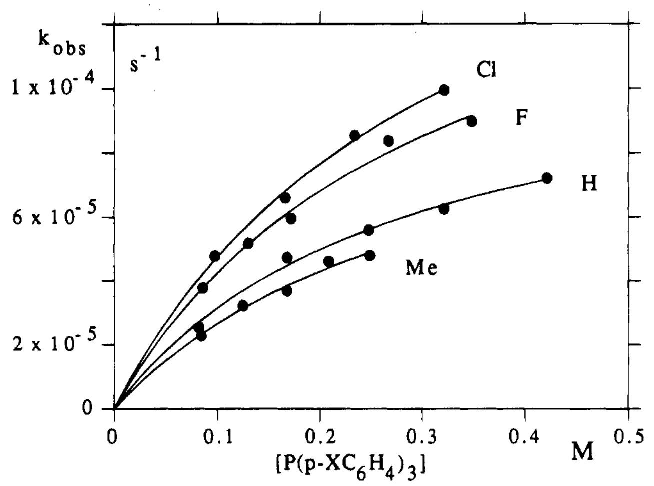

Figure 3. Plot of k_{obs} *vs* phosphine concentration for the reactions of $(C_9H_7)Fe(CO)_2Me$ with $P(p\text{-}XC_6H_4)_3$ (X = Cl, F, H, Me), in toluene at 60 °C.

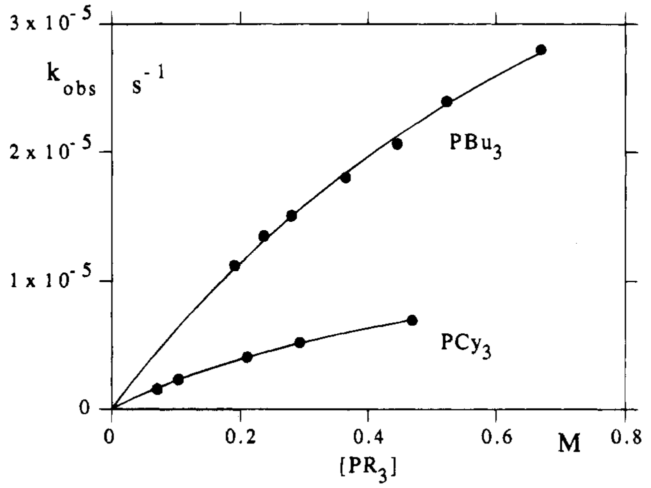

Figure 4. Plot of k_{obs} *vs* phosphine concentration for the reactions of $(C_9H_7)Fe(CO)_2Me$ with PBu_3 and PCy_3, in toluene at 40 °C.

the methyl complex **2**. The values Kk_2 (M^{-1} s^{-1}) were obtained from plots of $1/k_{obs}$ *vs* 1/[L], as the inverse of the slope.

In order to observe the dependence of the reaction rate on purely electronic effects, the kinetics were studied with a series of isosteric para-substituted triarylphosphines $P(p\text{-}XC_6H_4)_3$ (X = CF_3, Cl, F, H, Me, OMe) for both alkyl complexes. The dependence of k_{obs} on phosphine concentration is shown in Figure 2 for the reactions of complex **1** with $P(p\text{-}ClC_6H_4)_3$ and $P(p\text{-}MeOC_6H_4)_3$ (20.0 °C) and of complex **2** with $P(p\text{-}CF_3C_6H_4)_3$ and $P(p\text{-}MeOC_6H_4)_3$ (40.0 °C) and in Figure 3 for the reactions of complex **2** with $P(p\text{-}XC_6H_4)_3$ (X = Cl, F, H, Me; 60.0 °C).

The reactions were studied with the trialkylphosphines PBu_3 and PCy_3 (Cy = cyclohexyl). A reactivity profile is shown in Figure 4 for the reactions of **2** at 40 °C. The presence of 0.05 or 0.1 M Ph_3PO in the reaction of **1** with PBu_3 (20.0 °C) did not affect, beyond experimental error, either the value of k_{obs} for a single kinetic run or the reaction parameters [$K = 5.2 \pm 0.2$ M^{-1}; $k_2 = (4.0 \pm 0.1) \times 10^{-4}$ s^{-1}]. Complexes **1** and **2** did not react with the nitrogen donors pyridine or triethylamine.

Spectroscopic Studies. In order to detect spectral changes associated with the first stage of Scheme 1, UV–visible spectra of $(C_9H_7)Fe(CO)_2(CHMe_2)$ and $PMePh_2$, measured in a quartz cell with an internal septum, were recorded before and immediately after the mixing of the two solutions, in the region between 500 and 340 nm. Within this interval, the isopropyl complex shows a shoulder ($\epsilon = 780 \pm 5$ M^{-1} cm^{-1} at 400 nm) of the main ultraviolet band, which is obscured at lower wavelengths by both solvent and phosphine. The experiments were carried out at 0.0 °C in order to reduce the formation of the acyl product. A small increase of absorbance is observed after the mixing, which is dependent on the concentration of phosphine. Values

Table 3. Changes of Absorbance (ΔA)[a] of (C_9H_7)Fe(CO)$_2$CHMe$_2$ in the UV–Vis Region, before and after Rapid Mixing with Solutions of PMePh$_2$, in Toluene, at 0.0 °C

ΔA^b	[PMePh$_2$]
0.012	0.053
0.019	0.103
0.025	0.187
0.024	0.244
0.026	0.298

[a] λ = 400 nm, l = 0.874 cm. [b] [1] = 1.85 × 10^{-3} M, A = 1.262(±0.002).

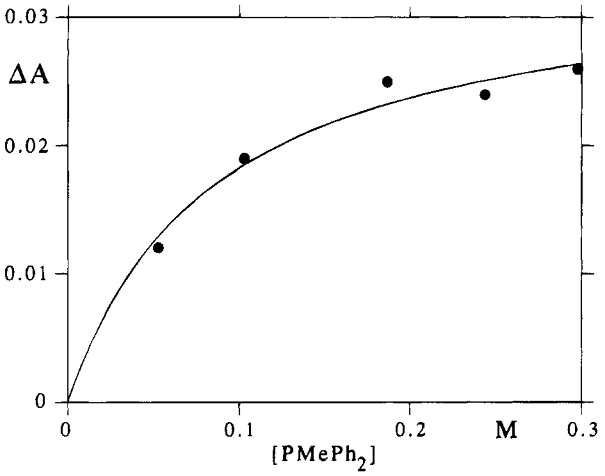

Figure 5. Changes of absorbance at λ = 400 nm upon mixing of (C_9H_7)Fe(CO)$_2$CHMe$_2$ (1.85 × 10^{-3} M) with PMePh$_2$ *vs* phosphine concentration, in toluene at 0 °C.

of ΔA at 400 nm *vs* [PMePh$_2$], reported in Table 3 and shown graphically in Figure 5, rise toward a limiting value, in analogy to that observed in the kinetic experiments. A nonlinear least squares analysis of the dependence of ΔA on [PMePh$_2$], to give the best fit to the binding isotherm for the formation of a 1:1 molecular complex,[9,10] yields a value of equilibrium constant K of 11.1(±2.1) M^{-1} at 0.0 °C, in excellent agreement with the value of K obtained from the kinetics (K = 9.3 ± 2.3 M^{-1}). Values of apparent association constants arising from medium effects are on the order of ≤0.2 M^{-1} [11] and can be excluded in these experiments. The observed increase in absorbance is assigned to the formation of a species of molecular formula [(C_9H_7)Fe(CO)$_2$CHMe$_2$, PMePh$_2$]. The difference in extinction coefficient between complex **1** and this species is optimized by the computational method to the value $\Delta\epsilon$ = 21 ± 2 M^{-1} cm^{-1}. ^{1}H NMR and FTIR spectra of complex **1** do not show appreciable changes in the presence of phosphine. The ^{13}C NMR (CDCl$_3$) signals of (η^5-C_9H_7)Fe(CO)$_2$CHMe$_2$ at low temperature (−50 °C) did not shift upon addition of PMePh$_2$ (0.22 M).

Discussion

The saturation kinetics observed in the reaction of the isopropyl complex (C_9H_7)Fe(CO)$_2$(CHMe$_2$) with different phosphines (Figure 1) in the nonpolar solvent toluene are indicative of an associative mechanism analogous to that recently proposed for the reaction of (C_9H_7)Fe(CO)$_2$(Me) (Scheme 1).[7] The reaction parameters, K (M^{-1}), k_2 (s^{-1}), and Kk_2 (M^{-1} s^{-1}), which represent the actual reactivity within the accessible window of phosphine concentration, are reported in Table 1 for complex **1** and in Table 2 for the methyl complex **2**.

Formation of the Molecular Complex [(C_9H_7)Fe(CO)$_2$(R), phosphine]. Effect of the Alkyl Group R. The equilibrium constant (K) for the interaction between the isopropyl complex **1** and phosphine increases from PPh$_3$ (K = 1.5 M^{-1}) to PMePh$_2$ (K = 10 M^{-1}) to PMe$_2$Ph (K = 24 M^{-1}) and varies over a larger range than it does for the methyl complex **2**. In this latter case, a smaller and opposite dependence of K on the nature of the phosphine was found, the interaction increasing with substitution of methyl by phenyl groups (K = 1.2 M^{-1} for PMe$_2$Ph; K = 2.2 M^{-1} for PMePh$_2$; K = 2.8 M^{-1} for PPh$_3$). It is possible that the hindrance of the isopropyl group in **1** imposes more stringent steric requirements within the molecular complex, and interactions with phosphines of smaller cone angles become increasingly favored [PPh$_3$, K(**1**)/K(**2**) = 0.5; PMePh$_2$, K(**1**)/K(**2**) = 4.5; PMe$_2$Ph, K(**1**)/K(**2**) = 20; 40.0 °C].

A striking feature emerging from these data is that association of the crowded isopropyl complex **1** with PMePh$_2$ and PMe$_2$Ph is actually greater than that of the methyl complex **2**. Thus increasing steric hindrance of the alkyl group on the metal does not give rise to unfavorable contact with phosphine. This observed enhanced association may depend on electronic effects, in particular on changes in the metal complex electron density caused by branching of the alkyl ligand, i.e. on replacement of Me by CHMe$_2$. The electron donor ability of the two alkyl groups shows itself in the carbonyl stretching values, which are 2003.7, 1950.2 cm^{-1} (**1**, R = CHMe$_2$) and 2011.7, 1957.9 cm^{-1} (**2**, R = Me), in hexane,[8] indicative of stronger π-back-bonding from the metal to carbonyl in the isopropyl complex. The different charge density at the metal must also affect interaction with phosphine in the molecular complex. The basic information from our data is that association in [(C_9H_7)Fe(CO)$_2$R, phosphine] is favored by the increased electron density at the iron center.

The equilibrium constant for the formation of [(C_9H_7)Fe(CO)$_2$CHMe$_2$, PPh$_3$] increases with decreasing temperature, as expected for the formation of a binary complex from two separate species. A plot of ln K *vs* $1/T$ gives values of $\Delta H°$ = −7.9(±0.2) kcal mol^{-1} and $\Delta S°$ = −24.5(±0.4) eu for the standard enthalpies and entropies, respectively, in agreement with a slightly exothermic interaction between **1** and PPh$_3$ to produce a paired entity. Enthalpies of dissociation of less than 10 kcal mol^{-1} are observed in electron donor–acceptor adducts.[12] On the other hand, the effect of the temperature is negligible in the case of PMePh$_2$, a phosphine showing a larger K at 40.0 °C.

Alkyl Migration Step (k_2). Effect of the Alkyl Group R. The complex (C_9H_7)Fe(CO)$_2$(CHMe$_2$) reacts with phosphines faster than (C_9H_7)Fe(CO)$_2$(Me), as expected on the basis of the greater migratory aptitude of the isopropyl group, which was reported for the reaction of alkyl cyclopentadienyl complexes (C_5H_5)Fe-

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[9] Connors, K. A. Binding Constants. *The measurement of Molecular Complex Stability*; Wiley-Interscience: New York, 1987; p 147.

[10] ΔA = ($b\Delta\epsilon S_t K$[L])/(1 + K[L]); L = PMePh$_2$, ΔA = change in absorbance at a fixed wavelength, b = optical path length (0.874 cm), S_t = total initial concentration of complex **1**, $\Delta\epsilon$ = difference in extintion coefficient between complex **1** and [(C_9H_7)Fe(CO)$_2$CHMe$_2$, PMePh$_2$].

[11] Beck, M. T. *Chemistry of Complex Equilibria*; Van Nostrand Reinhold: London, 1970; p 86.

[12] Tamaru, K.; Ichikawa, M. *Catalysis by Electron Donor-Acceptor Complexes*; Halsted Press, John Wiley & Sons: New York, 1975; p 2.

$(CO)_2R$ with PPh_3, in DMSO.[13] The difference in reactivity varies as a function of the reacting nucleophile, the relative ratio $k_2(CHMe_2)/k_2(Me)$ changing from 300 for L = PPh_3 to 112 for L = $PMePh_2$ to 5.5 for L = PMe_2Ph, at 40.0 °C, in agreement with basic reactivity/selectivity rules.

The values of the rate constants (k_2) for the alkyl migration step have become virtually independent of the nature of the phosphorus ligands in the case of $(C_9H_7)Fe(CO)_2(CHMe_2)$, whereas the methyl complex exhibited a marked selectivity toward the different phosphines ($k_2(PMe_2Ph)/k_2(PPh_3)$ = 30).[7] The reaction rate is dominated by the tendency of the large isopropyl group to migrate and not by the properties of the activating phosphorus, the influence of which is now aspecific. This may be taken as evidence that the extent of Fe—P bond formation is negligible in the transition state for the isopropyl complex **1**.

The activation parameters for the rate determining alkyl migration step (k_2) of $(C_9H_7)Fe(CO)_2(CHMe_2)$ are $\Delta H^{\ddagger} = 23.5 \pm (0.6)$ kcal mol^{-1}, $\Delta S^{\ddagger} = 6(\pm 2)$ eu for L = PPh_3 (range 10–40 °C), and $\Delta H^{\ddagger} = 19.0(\pm 0.7)$ kcal mol^{-1}, $\Delta S^{\ddagger} = -9(\pm 2)$ eu for L = $PMePh_2$ (range 0.0–40 °C). The more positive values of activation entropy than observed in the reaction of the methyl complex **1** with PPh_3 ($\Delta S^{\ddagger} = -20 \pm 3$ eu)[7] may be indicative of a larger release of steric hindrance in the migration of the isopropyl group.

Effect of the Phosphorus Donor. Since the increase of equilibrium constant (K) from PPh_3 to PMe_2Ph for R = $CHMe_2$ follows both increasing basicity and decreasing cone angle of the phosphine,[14] it is difficult to ascertain which effect is dominating and to what extent. The reactions of **1** and **2** were studied with a series of isosteric triarylphosphines $P(p\text{-}XC_6H_4)_3$ (θ = 145°) in order to separate the net electronic effect from steric contributions on both reaction parameters. The pK_a value of the phosphines varies from −1.39 (pK_a')[15] for X = CF_3 to 4.59 for X = OMe. Both iron complexes show little dependence on the electronic properties of the phosphorus donors, the largest difference of k_{obs} falling within 1 order of magnitude. Despite this lack of selectivity, the experiments have revealed unexpected features of the reaction. The most intriguing evidence is the fact, shown in Figures 2 and 3, that increased electron withdrawing character of the para substituents on the phenyl rings enhances the overall reaction rate (Kk_2). The values (10^4) vary from Kk_2 = 33 M^{-1} s^{-1} for X = Cl to Kk_2 = 12 M^{-1} s^{-1} for X = OMe in the case of R = $CHMe_2$ (**1**) at 20.0 °C and from Kk_2 = 1.4 M^{-1} s^{-1} (CF_3) to Kk_2 = 0.5 M^{-1} s^{-1} (OMe) in the case of R = Me (**2**) at 40.0 °C. A phosphine with an electron withdrawing substituent and smaller pK_a (X = Cl or CF_3) shows a larger saturation effect, due to a greater K, than does a phosphine with an electron donating group (X = OMe), which exhibits a nearly clean second-order pattern (Figure 2). Therefore, in the low concentration range, the parameter K dominates the overall reactivity, and phosphines with lower pK_a are slightly more reactive. Association between the metal complex and phosphine is favored by the increased electron withdrawing ability of the phosphine para substituent X. Accordingly, methyldiphenylphosphine, with a lower pK_a than tributylphosphine and the same cone angle (θ = 136°), shows a larger equilibrium constant in the interaction with **1** [$K(PMePh_2)$ = 9 M^{-1}, $K(PBu_3)$ = 5 M^{-1}; 20 °C] and with **2** [$K(PMePh_2)$ = 2.2 M^{-1}, $K(PBu_3)$ = 0.9 M^{-1}; 40 °C].

Unfortunately, the very similar values of k_2 in the reactions of complexes **1** and **2** with triarylphosphines do not give information about the net electronic effect on the alkyl migration step.

Nature of the Molecular Complex. Since the equilibrium constants for formation of the molecular complexes [$(C_9H_7)Fe(CO)_2R$, phosphine] increase with increasing electron density at the metal center and decreasing basicity of isosteric phosphines, we propose that *the molecules interact through an electron donor–acceptor mechanism*, where the iron complex behaves as donor and the phosphine as acceptor. It is known that organometals become excellent electron donors by virtue of the powerful effect exerted by alkyl groups as σ-donor ligands.[16] In dialkylmercury compounds, the ionization potentials decrease with increasing alkyl substitution.[17] In ferrocene, the formation of weak intermolecular charge transfer interactions through the donor ability of the metal center toward cations or electrophilic species is well documented.[18] In the case of the strong electron donor decamethylferrocene, a full electron transfer to tetracyanoethylene occurs to produce the salt decamethylferrocenium tetracyanoethenide.[19] The interaction of phosphine with the iron complex may involve the σ^* orbital,[20] which is responsible for the π-acceptor function in metal—phosphorus bonding. This function, in agreement with the trend of K, is enhanced by electronegative substituents on phosphorus.[21] The concept of charge transfer complexes between electron acceptors and organometallic electron donors has been extensively developed.[22] This regards electron rich, generally anionic organometallic species, but the "electron donor–acceptor complex" phenomenon transcends cation/anion interactions.

The equilibrium constants K exhibit a good correlation with the typical electronic parameters of the isosteric phosphines, such as pK_a, χ, and the Hammett σ values. Figure 6 shows a graph of log K vs σ_{para} for both alkyl complexes and clearly indicates a slightly larger dependence on electronic effects for the isopropyl complex ($\varrho = 0.62 \pm 0.03$) than for the methyl analogue ($\varrho = 0.47 \pm 0.02$), in agreement with a greater donor ability of **1**. Of course, the small values of ϱ are indicative of poor charge separation in the molecular complex, which is

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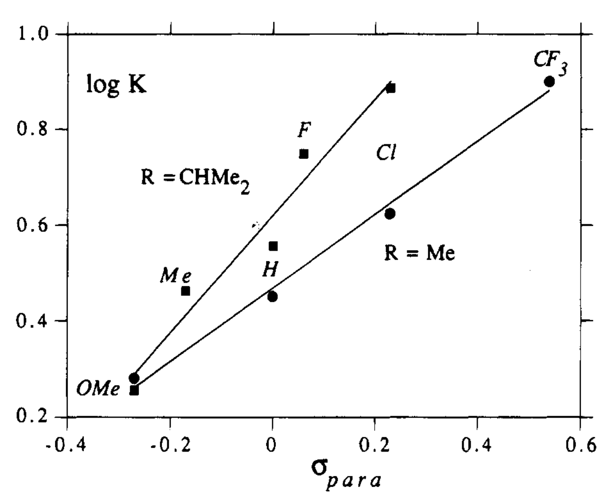

Figure 6. Plot of log K *vs* σ_p values for the reactions of $(C_9H_7)Fe(CO)_2CHMe_2$ (20 °C) and $(C_9H_7)Fe(CO)_2Me$ (40 °C) with $P(p\text{-}XC_6H_4)_3$.

however expected for a case of loose interaction between the two molecules. On the other hand, it must be pointed out that values of ϱ less than unity describe the process in the proximity of the isoequilibrium temperature and may therefore have ambiguous significance.[23] The phenomenon is in fact temperature dependent, and we have observed complete leveling off of K values in the reaction of complex **2** with the triarylphosphines at 60.0 °C. These experiments are shown graphically in Figure 3, where similar curvatures are displayed by the different triarylphosphines. The trend of overall reactivity, quantitatively expressed by the constants Kk_2, is still in the order (X = Cl > F > H > Me) previously observed for the reactions of both **1** and **2** at lower temperatures. The type of dependence (positive ϱ) on phosphine electronic effects suggests that the variation of K for the interaction of **1** with PPh_3, $PMePh_2$, and PMe_2Ph is essentially dominated by the steric requirements of the phosphorus ligands (Table 1).

The actual structure of the molecular complexes $[(C_9H_7)Fe(CO)_2R$, phosphine] and the sites and the nature of interaction are fundamental issues for this reaction. The situation varies from cases of precursor complexes which are barely detectable ($K \simeq 1$ M^{-1}) or even undefinable, as for $(C_9H_7)Fe(CO)_2(Me)$ reacting with PMe_3,[7] to cases of well sizable association, as for $(C_9H_7)Fe(CO)_2(CHMe_2)$ with PMe_2Ph ($K = 24$ M^{-1}). In order to understand whether the aromatic moieties play any role either in the formation of the molecular complexes or in the mechanism of the reaction itself, we have carried out experiments with trialkylphosphines. The reactions of the methyl complex **2** with PBu_3 and PCy_3, described graphically in Figure 4 and characterized by different k_2 values (reactivity at infinite [L]), indicate that trialkylphosphines also react by the associative mechanism of Scheme 1, as it is for triaryl- or alkylarylphosphines. Although further substitution of methyl by phenyl groups in the series PMe_nPh_{3-n} favors association with $(C_9H_7)Fe(CO)_2(Me)$, this is related to changes on the phosphorus electronic features rather than on specific forms of interaction (e.g. π stacking) between the phosphine aromatic ring and the indenyl moiety. In fact, association occurs between either complexes **1** or **2** and tributylphosphine ($K(\mathbf{1}) = 5$ M^{-1}, 20 °C; $K(\mathbf{2}) = 0.9$ M^{-1}, 40 °C) or complex **2** and cyclohexylphosphine ($K = 1.6$ M^{-1}; 40 °C).

We have previously addressed the problem that the molecular complexes $[(C_9H_7)Fe(CO)_2R$, phosphine] may be "dead end" species, which do not lie on the reaction coordinate.[7] In this case, while the significance of K is unchanged, the Kk_2 values would represent the rate constant (M^{-1} s^{-1}) for a second-order concerted attack at the metal. Such concertedness is very unlikely in a process involving two bond makings and one bond rupture. Since our experiments on cyclopentadienyl complexes show saturation kinetics and the possible existence of associative species,[24] the phenyl ring of the indenyl ligand in **1** and **2** may be excluded as the site of "not active" interaction, and only the upper side of the C_5 ring may still represent a geometric alternative to phosphine interaction at the reaction center. Even in the latter case, it is not excluded that such a contact of phosphorus on the C_5 ring may produce the electronic perturbation needed for the alkyl migration step. The fact that this association occurs between small molecules in a process involving iron–phosphorus bond formation and the overall consistency of the data reinforce our proposal that the molecular complexes $[(C_9H_7)Fe(CO)_2R$, phosphine] are on the reaction coordinate and that Scheme 1 is the most logical interpretation of the experimental data.

We have found no significant spectroscopic changes in the IR, ^1H NMR, or ^{13}C (−50 °C) NMR spectra of $(C_9H_7)Fe(CO)_2(CHMe_2)$ in the presence of phosphine. Only the experiments carried out in the UV–visible region, at 0.0 °C, have shown small changes which can be assigned to the formation of $[(\eta^5\text{-}C_9H_7)Fe(CO)_2(CHMe_2)$, $PMePh_2]$ and which give satisfactory quantitative agreement with the results of the kinetic analysis. The lack of spectral evidence indicates that the molecules establish a loose interaction, where alteration of the precursors is within or below the limits of conventional spectroscopy. It is in fact known that in weak charge transfer complexes the physicochemical features of the interacting molecules do not change appreciably from those of the free states.[25] Even charge transfers within cation/anion pairs, as in the case of $Co(CO)_4^-$, $Mn(CO)_5^-$, and $HFe(CO)_4^-$ anions interacting with PPh_4^+ and SPh_3^+ cations, do not show infrared evidence but only broad tailing in their visible spectra.[26]

The fact that the indenyl complexes retain their main structural features in the initial interaction with phosphines and that the "donor to acceptor" interaction appears to be in the sense "iron complex to phosphine" gives further support to our proposal that η^3 intermediates are not involved at this stage of the process.[7] In fact, an η^5 to η^3 shift of the indenyl ligand would imply a flow of electron density from phosphine to the complex. The formation of η^3 species is also very unlikely to occur during the subsequent carbon–carbon coupling, expecially in the case of the isopropyl complex **1** where the scarce dependence on the nature of phosphine suggests a negligible amount of iron–phosphorus bond formation in the transition state.

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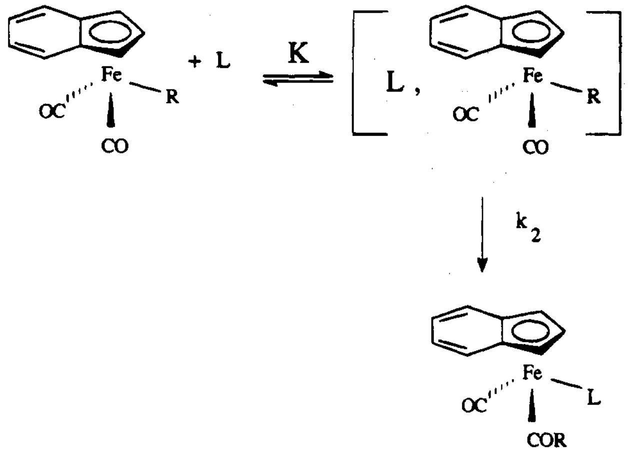
Scheme 2



We describe the reaction pathway as indicated in Scheme 2.

Conclusions

This work describes the nature of the active intermediates in the migratory insertion of carbon monoxide. An alkyliron complex and phosphine form a weak molecular complex which is favored by increased electron donation on the metal and by decreased basicity of phosphine. Species of the formula [(η^5-C_9H_7)Fe$(CO)_2$(R), phosphine] represent intermolecular complexes, in which the steric perturbation and the charge density rearrangement brought about in the iron complex activates the alkyl migration step. Especially the results shown in Figures 2 and 3 indicate that the action of the promoter cannot simply be described as "nucleophilic", as in conventional terminology for this reaction,[1,3a,4a,b,7] but it is rather more complex. Donor ability is not the only requisite for activation, as indicated by the absence of reaction with nitrogen donors, which was also observed in the original work on the cyclopentadienyl complex $(C_5H_5)Fe(CO)_2Me$.[27] Since the migration process involves conversion of an excellent back-bonding ligand (CO) into a poor one (acyl), the π-acceptor ability of the activating species may play a significant role in assisting the rearrangement of electron density during alkyl migration.

Intermolecular complexes are known to play a fundamental role in biological systems, in organic reactions, and in electron transfer processes. This paper points out to the possible role of these species in organometallic reactivity.

Experimental Section

General Data. Spectroscopic and analytical data for the iron complexes **1** and **2** and for the reaction products [(C_9H_7)Fe(CO)(COR)(phosphine)] have been previously reported.[7,8] ^{13}C NMR of $(C_9H_7)Fe(CO)_2(CHMe_2)$ ($CDCl_3$, 300 MHz, −50 °C): δ 217.7 (CO), 126.0, 124.0 (In $C_{4,7}$, $C_{5,6}$), 104.3 (In $C_{3a,7a}$), 101.8 (In C_2), 72.7 (In $C_{1,3}$), 32.6 (Me_2), 19.4 (CH). The phosphines were commercially available (Strem, Aldrich) and used as received. Values of k_{obs} obtained from distilled (sodium, under argon) and commercial PBu_3 were within experimental error. The methods used for kinetic and spectroscopic measurements and for data analysis are described in detail in ref 7. Initial concentrations of reacting complexes were in the range $(8 \times 10^{-4})-(3 \times 10^{-5})$ M in the UV−vis measurements and *ca.* 0.01 M in the FTIR runs. The UV−vis spectrophotometer was purged with argon during the experiments at 20 and 0.0 °C. Pseudo-first-order rate constants (k_{obs}) were obtained by fitting the exponential dependence of the absorbance *vs* time data using a nonlinear least squares regression program, which also provides the absorbance after completion, A_∞, for slower reactions. Duplications of single kinetic runs were reproducible to within 5%. The uncertainties of the reaction parameters K, k_2, and Kk_2 are reported as standard deviations, obtained from nonlinear least squares calculations. Activation parameters were obtained by an unweighted linear least squares analysis of the dependence of $\ln(k_2/T)$ on $1/T$.

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Supplementary Material Available: Tables of values of observed rate constants (k_{obs}) and FTIR data (4 pages). Ordering information is given on any current masthead page.

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