a complex with a transition metal containing ligand might be expected to raise the resonance field. This is in fact the exact opposite of the observed effect which must have a less simple explanation. The adduct $PF_2OPF_2 \cdot BH_3$ is consistent with the general observation that four-coordinate phosphorus has its resonance further upfield than three-coordinate.[18] The results for the metal carbonyl-fluorophosphine adducts suggest that more loosely bound electrons are present ($d\pi$-$d\pi$ bonding) which would cause an increase in the paramagnetic contribution to the shielding.[18] This is in agreement with the deep color of the adduct which also argues for easily excited electrons.

The infrared spectrum of $(CO)_4FePF_2OPF_2Fe(CO)_4$ in the carbonyl stretching region is like that of $(CO)_4FePF_2X$ (X = Br, SCN, Cl) but unlike that of $(CO)_4Fe\ PF_2NR_2$ in showing more absorptions than expected for either axially substituted or equatorially substituted iron alone.[2] Coupling of carbonyl stretching vibrations *via* the PF_2OPF_2 ligand would be expected to cause only a small splitting of the separate bands. The presence of six absorptions may be regarded as evidence for the existence of both axially and equatorially substituted iron. Since the two ends of the molecule are expected to have little influence on each other, an approximately statistical distribution of axial-axial, axial-equatorial, and equatorial-equatorial isomers is presumed to be present in the absence of a complete assignment of the infrared spectrum. This result is not inconsistent with the nmr finding of a single isomer.[19]

It is of interest to note that the mass spectrum of this complex did not exhibit a parent molecular ion. The highest observable peak at *m/e* 462 corresponded to the species $OP_2F_4Fe_2(CO)_7^+$. The appearance of this species in the spectrometer suggests that under the conditions employed, the parent species loses one carbon monoxide ligand and structurally rearranges to a diiron enneacarbonyl derivative in which two of the bridging carbonyl groups are replaced by the F_2POPF_2 ligand. In fact, weak peaks do occur for the species $Fe_2(CO)_x$ (x = 7.6, 4–0) and for PF_2OPF_2. Attempts to prepare the species $OP_2F_4Fe_2(CO)_7$ either from $Fe_2(CO)_9$ and F_2POPF_2 or from $OP_2F_4Fe_2(CO)_8$ by thermal or photochemical means were unsuccessful.

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Registry No. $BrPF_2Fe(CO)_4$, 42886-00-0; I, 42886-01-1.

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Kinetic Studies of Phosphine and Phosphite Exchange Reactions of Substituted Iron Tricarbonyl Carbene Complexes. A Competitive Study of Lewis Bases for the Intermediate $[Fe(CO)_3C(OC_2H_5)CH_3]$

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Kinetic and mechanistic studies of phosphorus ligand exchange reactions of *trans*-$(C_6H_5)_3PFe(CO)_3C(OC_2H_5)R$ (R = CH_3 and C_6H_5) with L′ (L′ = $P(n\text{-}C_4H_9)_3$, $P(OC_6H_5)_3$, and $P(C_6H_{11})_3$) to form *trans*-$L'Fe(CO)_3C(OC_2H_5)R$ compounds are reported. The rates of these substitution reactions are independent of the nature and concentration of the incoming ligands (L′) and proceed according to the rate expression: rate = $k_1[(C_6H_5)_3PFe(CO)_3C(OC_2H_5)R]$. These reaction rates are dependent upon the nature of the carbene ligand with $C(OC_2H_5)C_6H_5$ labilizing the *trans*-phosphine ligand more strongly than $C(OC_2H_5)CH_3$. Competitive reactions for the intermediate $[Fe(CO)_3C(OC_2H_5)CH_3]$ have been investigated for a number of ligands. The $[Fe(CO)_3C(OC_2H_5)CH_3]$ intermediate reacts with various phosphorus ligands at different rates and shows a preference for more nucleophilic reagents. Equilibrium constant measurements for the reaction $(C_6H_5)_3PFe(CO)_3C(OC_2H_5)CH_3 + L' \rightleftharpoons L'Fe(CO)_3C(OC_2H_5)CH_3 + P(C_6H_5)_3$ are also reported.

Introduction

There are numerous reports in the literature of kinetic and mechanistic studies of carbon monoxide substitution by Lewis bases in transition metal carbonyl complexes.[2] The less numerous studies involving replacement of metal-bound Lewis bases in substituted metal carbonyl complexes include the following: (1) rather detailed kinetic and mechanistic investigations of amine displacement from amine substituted group VIb metal carbonyl derivatives;[3-6] (2) carbon monoxide replacement of L (phosphines and phosphites) in $(phen)Cr(CO)_3L$ complexes;[7] (3) reactions of $(DTH)M(CO)_4$ (M = Cr and Mo; DTH = 2,5-dithiahexane) with phosphites to yield *cis*- and *trans*-$(phosphite)_2M(CO)_4$ complexes;[8] (4) kinetic studies of the substitution with α,α'-bipyridyl for phosphines and phosphites (L) in the carbonyl derivatives of

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the group VIb metals, $M(CO)_4L_2$;[9,10] (5) replacement of phosphines and phosphites (L) in $Ni(CO)_2L_2$ complexes;[11] (6) substitution reactions of $Co(CO)_2L(NO)$ complexes (L = phosphines, phosphites, and isocyanides) with phosphines (L′) to form $Co(CO)_2L'(NO)$ complexes;[12] and (7) replacement of $P(C_6H_5)_3$ in *trans*-$Rh(CO)[P(C_6H_5)_3]_2Cl$ with $(n\text{-}C_4H_9)_3P$.[13] In addition, Basolo and coworkers[14,15] have studied phosphine and phosphite substitution and exchange reactions in zerovalent tetrakis(phosphine) and -(phosphite) complexes of Ni, Pd, and Pt.

Recently, it was observed that the phosphorus ligands in the metal acylates, *trans*-$LFe(CO)_3C(O)R^-$, and their *carbene* derivatives are labilized and exchange with free phosphorus ligands (L′) in solution at elevated temperatures.[16] We wish to report kinetic and mechanistic studies of phosphine and phosphite exchange reactions in the *trans*-$LFe(CO)_3C(OC_2H_5)R$ complexes (L = $P(C_6H_5)_3$, $P(n\text{-}C_4H_9)_3$, $P(OC_6H_5)_3$, and $P(C_6H_{11})_3$; R = C_6H_5 and CH_3).

$$trans\text{-}LFe(CO)_3C(OC_2H_5)R + L' \rightleftharpoons trans\text{-}L'Fe(CO)_3C(OC_2H_5)R + L \qquad (1)$$

Experimental Section

Materials. Iron pentacarbonyl was purchased from Pressure Chemical Co. and was used without further purification. Triphenylphosphine and tri-*n*-butylphosphine were the generous gifts of M and T Chemical Co. Triphenyl phosphite and tricyclohexylphosphine were purchased from Aldrich and Columbia Chemicals, respectively. Tetrahydrofuran (THF) was distilled over sodium benzophenone dianion under nitrogen.

Preparation of *trans*-$LFe(CO)_3C(OC_2H_5)R$ (L = $(C_6H_5)_3P$, $(n\text{-}C_4H_9)_3P$, and $(C_6H_5O)_3P$; R = CH_3 and C_6H_5). These complexes were prepared as previously described[16] from the $LFe(CO)_4$ species and the corresponding organolithium reagent followed by alkylation with $(C_2H_5)_3O^+BF_4^-$.

Spectral and Kinetic Measurements. All spectral measurements were made in heptane or THF solvent employing a Perkin-Elmer 521 grating spectrophotometer equipped with a linear absorbance potentiometer. The instrument was calibrated in the CO stretching region with CO vapor above 2000 cm⁻¹ and with H_2O vapor below 2000 cm⁻¹. One-millimeter sodium chloride cells were used.

The exchange reactions were run under nitrogen in heptane in 25-ml erlenmeyer flasks equipped with a rubber septum cap. Studies run in THF were carried out in a thick-walled tube fitted with a Teflon stopcock and a rubber septum cap. The reaction flasks were placed in a Tamson constant-temperature bath with a constant-temperature control of ±0.05°. Samples for spectral analysis were withdrawn at regular time intervals with a hypodermic syringe. The rates of exchange of phosphorus ligands in *trans*-$LFe(CO)_3C(OC_2H_5)R$ complexes were followed by observing the decrease in the absorbance of one of the components of the split E mode in the starting materials with time. The carbonyl stretching frequencies for reactants and products are shown in Table I.

Rate constants were calculated using a linear least-squares computer program for the first-order rate plots of ln $(A_t - A_\infty)$ *vs.* time, where A_t is the absorbance at time t and A_∞ is the absorbance at infinite time. The reactions were observed to yield linear plots over several half-lives.

Table I. Infrared Spectra in the Carbonyl Stretching Region for *trans*-$LFe(CO)_3C(OC_2H_5)R$ Compounds[a]

L	R	E mode (split)	
$P(C_6H_5)_3$	C_6H_5	1913.2	1899.8
$P(OC_6H_5)_3$	C_6H_5	1929.5	1912.0
$P(C_6H_5)_3$	CH_3	1902.5	1895.6
$P(OC_6H_5)_3$	CH_3	1921.0	1909.0
$P(C_6H_{11})_3$	CH_3	1888.0	1880.0
$P(n\text{-}C_4H_9)_3$	CH_3	1891.0	1886.0

[a] Frequencies are listed in cm⁻¹ and were determined in heptane solution.

Table II. First-Order Rate Constants for the Substitution of *trans*-$LFe(CO)_3C(OC_2H_5)R$[a] Complexes in Heptane

R	L	L′	[L′]	Temp, °C	10^4k_1, sec⁻¹ [b]
C_6H_5	$P(C_6H_5)_3$	$P(OC_6H_5)_3$	0.169	44.0	1.35 ± 0.02
			0.169	50.3	3.19 ± 0.05
			0.169	57.4	8.25 ± 0.18
			0.169	62.8	15.5 ± 0.3
CH_3	$P(C_6H_5)_3$	$P(OC_6H_5)_3$	0.169	50.5	0.361 ± 0.007
			0.169	59.1	1.19 ± 0.02
			0.169	59.1	1.14 ± 0.01
			0.169	67.2	3.38 ± 0.02
			0.0443	72.9	6.82 ± 0.09
			0.169	72.9	6.67 ± 0.07
			0.329	72.9	6.91 ± 0.17
CH_3	$P(C_6H_5)_3$	$P(n\text{-}C_4H_9)_3$	0.253	59.1	1.09 ± 0.01
			0.253	72.9	6.37 ± 0.11
CH_3	$P(OC_6H_5)_3$	$P(n\text{-}C_4H_9)_3$	0.171	75.0	0.952 ± 0.030
			0.171	80.0	2.02 ± 0.04
			0.171	85.0	3.14 ± 0.12
		$P(C_6H_5)_3$	0.172	67.2	0.297 ± 0.014
CH_3	$P(n\text{-}C_4H_9)_3$	$P(C_6H_5)_3$	0.172	72.9	0.123 ± 0.009
C_6H_5[c]	$P(C_6H_5)_3$	$P(OC_6H_5)_3$	0.965	50.0	1.11 ± 0.03
			1.040	60.0	4.72 ± 0.04
			0.605	65.0	8.94 ± 0.29
			0.965	65.0	9.27 ± 0.20
			1.045	70.0	14.4 ± 0.65
			0.965	75.0	29.5 ± 1.40

[a] [*trans*-$LFe(CO)_3C(OC_2H_5)R$] ≅ 9 × 10⁻⁴ *M*. [b] Error limits for rate constant data are one standard deviation. [c] These data were determined in THF solvent.

Competition studies for the $[Fe(CO)_3C(OC_2H_5)CH_3]$ intermediate were monitored by the infrared spectral changes in the starting material *trans*-$(C_6H_5)_3PFe(CO)_3C(OC_2H_5)CH_3$. The rates of substitution of *trans*-$(C_6H_5)_3PFe(CO)_3C(OC_2H_5)CH_3$ in the presence of added $P(C_6H_5)_3$ and other added ligands were determined as described above. Plots of $1/k_{obsd}$ *vs.* $[P(C_6H_5)_3]/[L]$ were found to be linear.

Calculations. Machine calculations were performed on an IBM 7044 at the Tulane University Computer Center.

Results

The rate of substitution of *trans*-$LFe(CO)_3C(OC_2H_5)R$ complexes follows the first-order rate law, (2), which is inde-

$$\text{rate} = k_1\,[trans\text{-}LFe(CO)_3C(OC_2H_5)R] \qquad (2)$$

pendent of the concentration of the incoming phosphorus ligand. Values of the rate constants k_1, calculated from the first-order rate expression, are given in Table II for several temperatures and concentrations of the incoming ligand. Figure 1 shows the typically observed infrared traces of the disappearance of starting material ν(CO) bands with the simultaneous appearance of product ν(CO) bands, while Figure 2 illustrates the linear first-order rate plots that were obtained over the entire reaction. The activation parameters for the dissociation process (eq 3) are reported in Table III, and

$$trans\text{-}LFe(CO)_3C(OC_2H_5)R \xrightarrow[\text{slow}]{k_1} [Fe(CO)_3C(OC_2H_5)R] \xrightarrow[\text{fast}]{L'} trans\text{-}L'Fe(CO)_3C(OC_2H_5)R + L \qquad (3)$$

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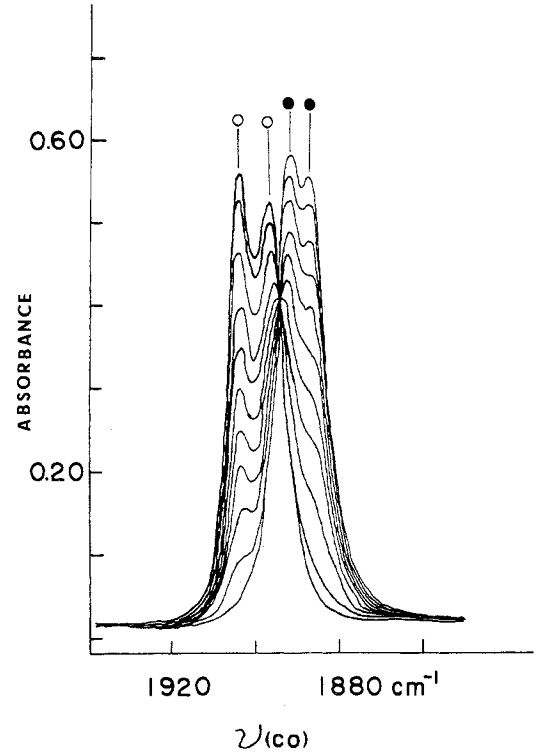

Figure 1. Representive ir spectra in the ν(CO) region in heptane of the exchange process between $(C_6H_5)_3PFe(CO)_3C(OC_2H_5)CH_3$ and $(n\text{-}C_4H_9)_3P$: (○) $(C_6H_5)_3PFe(CO)_3C(OC_2H_5)CH_3$, (●) $(n\text{-}C_4H_9)_3P\text{-}Fe(CO)_3C(OC_2H_5)CH_3$.

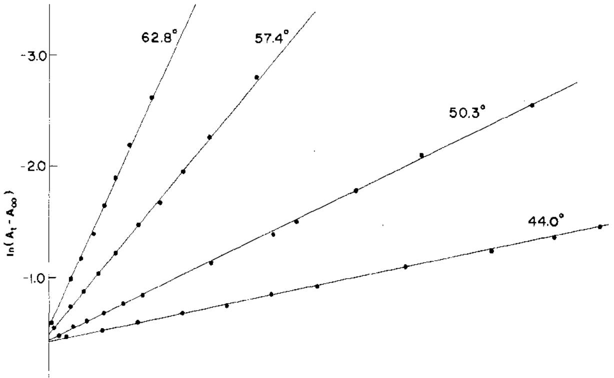

Figure 2. First-order rate plots of the exchange reaction of $(C_6H_5)_3\text{-}PFe(CO)_3C(OC_2H_5)C_6H_5$ with $P(OC_6H_5)_3$ in heptane at several temperatures.

Table III. Activation Parameters for the *trans*-$LFe(CO)_3C(OC_2H_5)R$ Dissociative Process in Heptane

R	L	ΔH^*, kcal/mol^a	ΔS^*, eu^a
C_6H_5	$P(C_6H_5)_3$	27.6 ± 0.4	+10.5 ± 1.4
C_6H_5^{b}	$P(C_6H_5)_3$	29.6 ± 0.8	+15.3 ± 2.4
CH_3	$P(C_6H_5)_3$	29.0 ± 0.4	+10.7 ± 1.3
CH_3	$P(OC_6H_5)_3$	32.8 ± 2.5	+16.8 ± 7.7

^{a} Error limits for activation parameters are one standard deviation. ^{b} These data were determined in THF solvent.

a representative Arrhenius plot is shown in Figure 3. In the case of the exchange reaction between triphenyl phosphite and *trans*-$(C_6H_5)_3PFe(CO)_3C(OC_2H_5)C_6H_5$ to form *trans*-$(C_6H_5O)_3PFe(CO)_3C(OC_2H_5)C_6H_5$, activation parameters are reported in both heptane and THF solvents. The production of *trans*-$L'Fe(CO)_3C(OC_2H_5)R$ derivatives is quantitative with no side reactions occurring under the conditions of these studies.

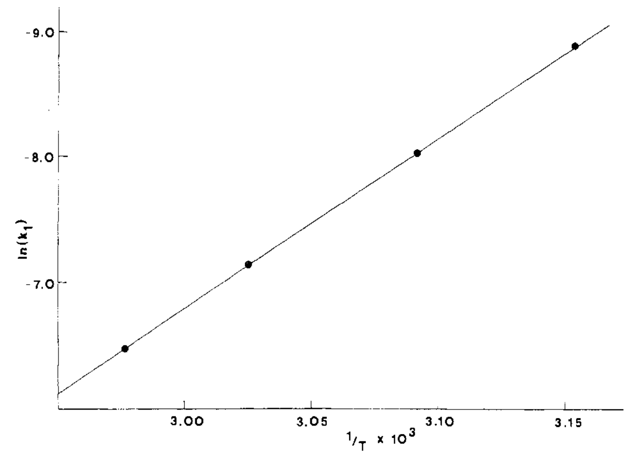

Figure 3. Arrhenius plot of $-\ln k_1$ *vs.* $1/T$ for the exchange reaction of $(C_6H_5)_3PFe(CO)_3C(OC_2H_5)C_6H_5$ with $P(OC_6H_5)_3$ in heptane solvent.

It is possible to observe competitive reactions for the intermediate species $[Fe(CO)_3C(OC_2H_5)CH_3]$ produced from *trans*-$(C_6H_5)_3PFe(CO)_3C(OC_2H_5)CH_3$ by employing simultaneously an excess of $P(C_6H_5)_3$ and other phosphorus ligands (L′). A steady-state solution to eq 4, when the reverse step of the second equilibrium is negligible, yields the rate expression 5.

$$\textit{trans}\text{-}(C_6H_5)_3PFe(CO)_3C(OC_2H_5)CH_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (C_6H_5)_3P +$$

$$[Fe(CO)_3C(OC_2H_5)CH_3] \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \textit{trans}\text{-}L'Fe(CO)_3C(OC_2H_5)CH_3 \quad (4)$$

$$\text{rate} = k_1[\textit{trans}\text{-}(C_6H_5)_3PFe(CO)_3C(OC_2H_5)CH_3] \times \frac{k_2[L']}{k_{-1}[(C_6H_5)_3P] + k_2[L']} \quad (5)$$

The pseudo-first-order rate constants (k_{obsd}) for the disappearance of the starting complex in the presence of large excesses of $(C_6H_5)_3P$ and L′ were determined as a function of $[(C_6H_5)_3P]$ and [L′].

$$k_{obsd} = \frac{k_1k_2[L']}{k_{-1}[(C_6H_5)_3P] + k_2[L']}$$

or

$$\frac{1}{k_{obsd}} = \frac{1}{k_1} + \frac{k_{-1}[(C_6H_5)_3P]}{k_1k_2[L']} \quad (6)$$

Values for k_{obsd} as a function of $[(C_6H_5)_3P]/[L']$ are listed in Table IV and are shown graphically in Figure 4. The ratio k_{-1}/k_2, as determined from the slope of the plot of $1/k_{obsd}$ *vs.* $[(C_6H_5)_3P]/[L']$ and the value of k_1, represents the competition of $(C_6H_5)_3P$ *vs.* L′ for the intermediate $[Fe(CO)_3C(OC_2H_5)CH_3]$. The values for k_{-1}/k_2 and k_1 (intercept) are listed in Table V.

If the proper concentration ratios of $P(C_6H_5)_3$ to L′ are employed or if k_{-2} values are determined starting with the pure *trans*-$L'Fe(CO)_3C(OC_2H_5)CH_3$ complexes, it is possible to determine the overall equilibrium constant (K_{eq}) for reaction 4, K_1K_2, as a function of the substituted phosphorus

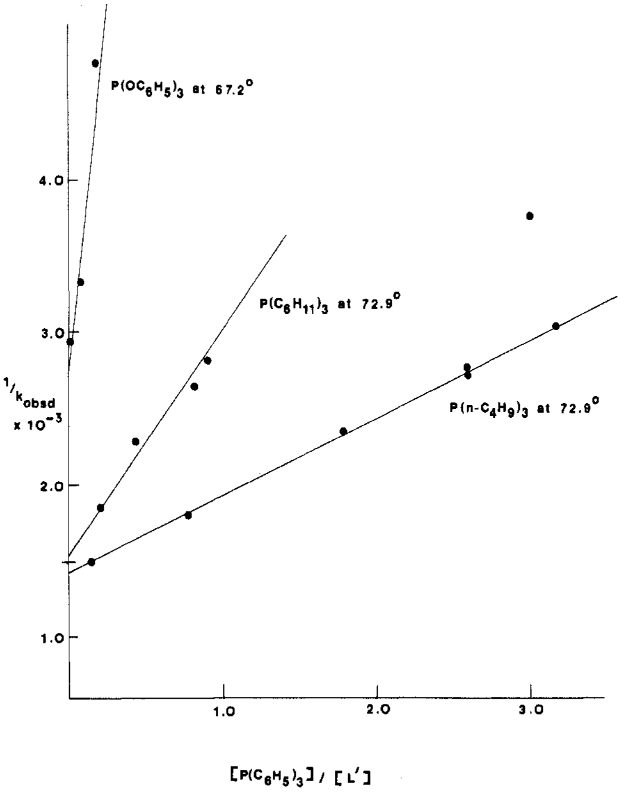

Figure 4. Plots of $1/k_{obsd}$ *vs.* $[P(C_6H_5)_3]/[L']$ for the reaction of *trans*-$(C_6H_5)_3PFe(CO)_3C(OC_2H_5)CH_3$ with $P(C_6H_5)_3$ and L′. The datum point which greatly deviates from the straight line plot in the case of $L' = P(C_6H_{11})_3$ is the result of the reaction reaching equilibrium prior to going far enough to completion.

Table IV. Competition Studies of Triphenylphosphine *vs.* Phosphorus Ligands (L′) for the Intermediate $[Fe(CO)_3C(OC_2H_5)CH_3]$ Produced from *trans*-$(C_6H_5)_3PFe(CO)_3C(OC_2H_5)CH_3$[a]

Phosphorus ligand added (L′)	[L′]	$[P(C_6H_5)_3]$	$[P(C_6H_5)_3]/[L']$	$10^4 k_{obsd}$
$P(OC_6H_5)_3$[b]	0.169	0.000	0.000	3.38
	0.169	0.0135	0.079	3.00
	0.169	0.0286	0.168	2.09
$P(n\text{-}C_4H_9)_3$[c]	0.477	0.0699	0.146	6.65
	0.111	0.0864	0.778	5.54
	0.111	0.199	1.79	4.24
	0.111	0.290	2.61	3.68
	0.111	0.291	2.61	3.60
	0.111	0.351	3.16	3.28
$P(C_6H_{11})_3$[c]	0.104	0.0207	0.200	5.41
	0.0887	0.0350	0.416	4.32
	0.104	0.0841	0.808	3.76
	0.127	0.114	0.897	3.53
	0.0356	0.107	3.00	2.65

[a] Values of k_{obsd} *vs.* $[P(C_6H_5)_3]/[L']$ in heptane. [b] 67.2°. [c] 72.9°.

Table V. *trans*-$(C_6H_5)_3PFe(CO)_3C(OC_2H_5)CH_3$ Rates of Reaction and Competition Ratios for Phosphorus Ligands in Heptane Solution

L′	$10^4 k_{intercept}$, sec^{-1}	k_{-1}/k_2	T, °C
$P(OC_6H_5)_3$	3.57[a]	3.2	67.2
$P(C_6H_{11})_3$	6.49[b]	1.0	72.9
$P(n\text{-}C_4H_9)_3$	7.04[b]	0.34	72.9

[a] The predicted value of $k_{intercept}$ for this reaction at 67.2° is 0.000338 sec^{-1}. [b] The predicted value of $k_{intercept}$ for this reaction at 72.9° is 0.000669 sec^{-1}.

ligand (L′). The values determined for K_{eq} are listed in

$$K_{eq} = \frac{k_1 k_2}{k_{-1} k_{-2}} = K_1 K_2 = \frac{[trans\text{-}L'Fe(CO)_3C(OC_2H_5)CH_3][P(C_6H_5)_3]}{[trans\text{-}(C_6H_5)_3PFe(CO)_3C(OC_2H_5)CH_3][L']} \quad (7)$$

Table VI.

Discussion

On the basis of the observed first-order rate law and the mass law retardation effect of the added triphenylphosphine, the most plausible mechanism for phosphine and phosphite exchange reactions of *trans*-$LFe(CO)_3C(OC_2H_5)R$ complexes involves a rate-determining dissociation of the phosphine or phosphite group followed by rapid addition of the substituting phosphine or phosphite ligand. The values of the activation parameters (Table III) also suggest a dissociative acitvation process. The enthalpies of activation (ΔH^*) of the exchange reactions of 27-29 kcal/mol are in good agreement with reported values for other iron triad metal-phosphorus bond breaking processes. Basolo and coworkers[14,15] found ΔH^* values of 26-28 kcal/mol for Ni-P bond rupture in $Ni(PF_3)_4$ and $Ni(P(OC_2H_5)_3)_4$. The positive entropies of activation (ΔS^*) for these phosphine exchange reactions are also consistent with a dissociative process.

Comparison of the rate constants of Table II shows that the rate of dissociation of $P(C_6H_5)_3$ in *trans*-$(C_6H_5)_3PFe(CO)_3C(OC_2H_5)C_6H_5$ is slower, and its activation energy is slightly higher in THF than in heptane solution. This is opposite to the solvent effect noted by Angelici and Leach[17] in substitution reactions of $Ni(CO)_4$ or by Basolo and coworkers[14,15] in substitution reactions of $Ni(PR_3)_4$, where the tricoordinate nickel transition state was found to be stabilized by interacting solvents. Evidently, the pseudo-four-coordinate $[Fe(CO)_3C(OC_2H_5)C_6H_5]$ transition state produced in these reactions is less stabilized by THF than the reactant five-coordinate complex.[18,19]

It is evident from a comparison of the rate constants and activation energies for phosphine dissociation in *trans*-$(C_6H_5)_3PFe(CO)_3C(OC_2H_5)C_6H_5$ and *trans*-$(C_6H_5)_3PFe(CO)_3C(OC_2H_5)CH_3$ complexes that the more electron-withdrawing $C(OC_2H_5)C_6H_5$ carbene ligand labilized the *trans*-triphenylphosphine group to a greater extent than the $C(OC_2H_5)CH_3$ carbene ligand.

The ability of the carbene ligand to labilize the carbon monoxide ligand has been previously observed by Werner and Rascher[20] in CO substitution reactions with phosphines in the $(CO)_5Cr(OCH_3)CH_3$ complex. In addition, we have observed that the $P(C_6H_5)_3$ ligand in *cis*-$(C_6H_5)_3PW(CO)_4C(OC_2H_5)CH_3$ exchanges with $(n\text{-}C_4H_9)_3P$ or $C_2H_5C(CH_2O)_3P$ in heptane solvent at 72.9°. The rate, however, is much slower than that observed for *trans*-phosphine ex-

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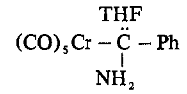
[17] R. J. Angelici and B. E. Leach, *J. Organometal. Chem.*, 11, 293 (1968).

[18] Todd and coworkers[19] have proposed interactions of the type



$$(CO)_5Cr-\overset{\overset{\textstyle THF}{\cdot\cdot}}{\underset{\underset{\textstyle NH_2}{|}}{C}}-Ph$$

based on ^{13}C nmr solvent studies. In addition, the significantly larger ΔS^* in THF solvent as compared with heptane solvent for $P(C_6H_5)_3$ dissociation in *trans*-$(C_6H_5)_3PFe(CO)_3C(OC_2H_5)C_6H_5$ is in agreement with less interaction of THF in the transition state.

[19] G. M. Bodner, S. B. Kahl, K. Bork, B. N. Storhoff, J. E. Wuller, and L. J. Todd, *Inorg. Chem.*, 12, 1071 (1973).

[20] H. Werner and H. Rascher, *Helv. Chim. Acta*, 51, 1765 (1968).

Table VI. Equilibrium Constants (K_{eq}) for the Reaction, *trans*-$(C_6H_5)_3PFe(CO)_3C(OC_2H_5)CH_3 + L' \rightleftharpoons$ *trans*-$L'Fe(CO)_3C(OC_2H_5)CH_3 + P(C_6H_5)_3$

L′	Temp, °C	K_{eq}	$\Delta G°$, kcal/mol
$P(OC_6H_5)_3$	67.2	2.8 ± 0.3^a $(2.93)^b$	−0.70
$P(n\text{-}C_4H_9)_3$	72.9	$(151)^b$	−3.47
$P(C_6H_{11})_3$	72.9	2.6 ± 0.2^c	−0.66

[a] Measured from two different $[(C_6H_5)_3P]/[P(OC_6H_5)_3]$ concentration ratios. [b] Determined kinetically by measuring k_1, k_{-1}/k_2, and k_{-2}. [c] Measured from four different $[(C_6H_5)_3P]/[(C_6H_{11})_3P]$ concentration ratios.

change in these iron carbene studies. Labilizing ligands are characteristically class a[21] or "hard"[22] bases, such as amines, nitrates, and halogens; whereas class b or "soft" bases, such as phosphines or phosphites, are generally nonlabilizing ligands. When $(C_6H_5)_3PFe(CO)_4$ and *trans*-$[(C_6H_5)_3P]_2Fe(CO)_3$ were heated in heptane with excess $(n\text{-}C_4H_9)_3P$ or $(C_6H_5O)_3P$, under the identical conditions of the observed phosphine exchange for the carbene complex, *no* phosphine exchange was observed over a prolonged reaction period (several days). Indeed, the reaction of $(C_6H_5)_3P$ with $(C_6H_5)_3PFe(CO)_4$ to form *trans*-$[(C_6H_5)_3P]_2Fe(CO)_3$ proceeds readily only at very high temperatures (>150°).[23] On the other hand, $(C_6H_5)_3PFe(CO)_3C(O)C_6H_5^-Li^+$ undergoes phosphine exchange at a considerably slower rate in THF than its carbene analog (7.55×10^{-5} sec^{-1} at 70°),[16] even though the acylate grouping is certainly a "harder" base than the ethylated acylate or carbene ligand.

The carbene ligand is generally considered a "soft" ligand, possessing some ability to accept electron density from the metal π^* orbitals, and is normally found in complexes in which the metal is in a low oxidation state.[24,25] In other words, the carbene ligand has been regarded as being in the category of phosphine bases, *i.e.*, these ligands are good σ donors while weaker π acceptors.[20,26,27] Recently, ^{13}C nmr studies have suggested that the carbene carbon atom is electrophilic in character and that the carbene ligand may be considered similar to carbonium ions.[19,28-31] Similarly, reactivity studies on $[(\pi\text{-}C_5H_5)Fe(CO)P(C_6H_5)_3C(OC_2H_5)CH_3]BF_4$ indicate that the metal-bound carbene ligand should be considered as a metal-stabilized carboxonium rather than carbenoid complex.[32] It seems reasonable to conclude, however, that the carbene ligand, albeit not a strong π acceptor of metal d electrons, does exhibit π acceptor properties similar to phosphine bases. Yet it is a labilizing ligand unlike phosphine bases.

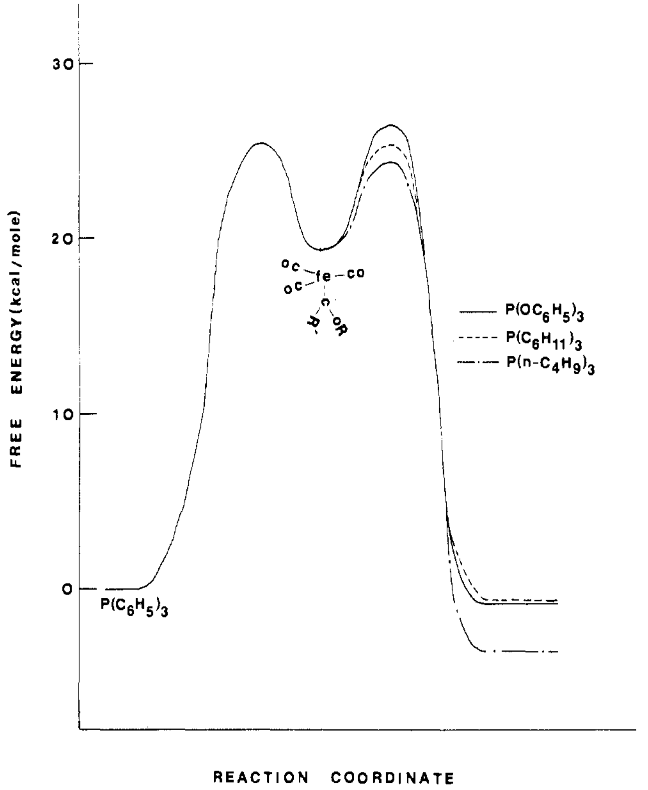


Figure 5. Plots of free energy *vs.* reaction coordinate for the exchange reaction of $(C_6H_5)_3PFe(CO)_3C(OC_2H_5)CH_3$ with L′ ligands.

The positive entropy of activation (ΔS^*) values observed would suggest that the intermediate, $[Fe(CO)_3C(OC_2H_5)R]$, resembles the transition state; therefore, the enthalpies of activation (or rate constants) for ligand dissociation should reflect Fe–P bond dissociation energies, these bond energies being less than or equal to the ΔH^* values. From the observed rates of ligand dissociation the indicated order of Fe–L bond strengths would be $P(n\text{-}C_4H_9)_3 > P(OC_6H_5)_3 > P(C_6H_{11})_3$[33] $> P(C_6H_5)_3$. This is the same order as observed for the equilibrium constants. This order is also similar to that reported for Cr–L ligand dissociation processes.[7] For L substitution in $Ni(CO)_2L_2$ complexes the rate of L dissociation decreased with $L = (C_6H_5)_3P > (n\text{-}C_4H_9)_3P \gg (C_6H_5O)_3P$.[11] However, this is the order of decreasing steric bulk, and steric factors have been shown to play a dominant role in these latter reactions.[34]

It is possible to calculate Gibbs free-energy values from the measured equilibrium constants at one temperature but not the enthalpy values, which would be measures of the changes of total bond energy. However, any changes in ΔS would be expected to be small since the reactants and products have the same numbers of bonds between the same elements. Hence it is reasonable to regard $\Delta G°$ values as adequate bases for a qualitative comparison of bond energies. The calculated values of $\Delta G°$ are reported in Table VI. $\Delta G°$ decreases in the order: $P(C_6H_5)_3 > P(C_6H_{11})_3 \approx P(OC_6H_5)_3 > P(n\text{-}C_4H_9)_3$. Figure 5 illustrates plots of free energy against the reaction coordinate for the reaction $(C_6H_5)_3PFe(CO)_3C(OC_2H_5)CH_3 + L' \rightleftharpoons L'Fe(CO)_3C(OC_2H_5)CH_3 + P(C_6H_5)_3$.

The ratios of k_{-1}/k_2 listed in Table V illustrate the dis-

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(33) The k_{-2} value at 72.9° for this ligand calculated from k_1, k_{-1}/k_2, and K_{eq} was found to be 2.57×10^{-4} sec^{-1}.

(34) C. A. Tolman, *J. Amer. Chem. Soc.*, 92, 2956 (1970).

criminating ability of the intermediate, $[Fe(CO)_3C(OC_2H_5)CH_3]$, for triphenylphosphine *vs.* other phosphorus ligands (L′). These data also indicate that the four-coordinate species $[Fe(CO)_3C(OC_2H_5)CH_3]$ has a greater propensity for more nucleophilic ligands, the order of preference being: $(n\text{-}C_4H_9)_3P$ (2.9) > $(C_6H_{11})_3P$ (1) ≈ $(C_6H_5)_3P$ (1) > $P(OC_6H_5)_3$ (0.31). This is the usual observed order of nucleophilicity for these ligands.[2a] The fact that $(C_6H_{11})_3P$ is not more reactive toward the four-coordinate intermediate is presumably a result of the bulkiness of the cyclohexyl rings.

Therefore, the intermediate $[Fe(CO)_3C(OC_2H_5)CH_3]$ shows a significant preference (about 10:1) for the more nucleophilic ligand $(n\text{-}C_4H_9)_3P$ as compared with the more electrophilic ligand $(C_6H_5O)_3P$.[35] This is in contrast to the nature of the $[Mo(CO)_4P(C_6H_5)_3]$ intermediate produced from the corresponding amine complex which, although it is fairly nondiscriminating, shows a greater preference for electrophilic ligands: $P(OCH_2)_3CC_2H_5$ (1.62) > $P(C_6H_5)_3$ (1) > $P(n\text{-}C_4H_9)_3$ (0.68).[5]

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Registry No. $P(C_6H_5)_3Fe(CO)_3C(OC_2H_5)C_6H_5$, 42947-52-4; $P(OC_6H_5)_3Fe(CO)_3C(OC_2H_5)C_6H_5$, 42947-53-5; $P(C_6H_5)_3Fe(CO)_3C(OC_2H_5)CH_3$, 42947-54-6; $P(OC_6H_5)_3Fe(CO)_3C(OC_2H_5)CH_3$, 42947-55-7; $P(C_6H_{11})_3Fe(CO)_3C(OC_2H_5)CH_3$, 42947-56-8; $P(n\text{-}C_4H_9)_3Fe(CO)_3C(OC_2H_5)CH_3$, 42947-57-9; $P(OC_6H_5)_3$, 101-02-0; $P(n\text{-}C_4H_9)_3$, 998-40-3; $P(C_6H_5)_3$, 603-35-0; $P(C_6H_{11})_3$, 2622-14-2.

[35] G. Cardaci and V. Narciso, *J. Chem. Soc., Dalton Trans.*, 2289 (1972), have found the intermediate $[Fe(CO)_4]$ species produced *via* dissociation of $CH_2{=}CHX$ from $(CH_2{=}CHX)Fe(CO)_4$ (X = OC_2H_5, C_4H_9, C_6H_5, CO_2CH_3, and CN) complexes to be fairly nondiscriminating toward $CH_2{=}CHX$ ligands *vs.* carbon monoxide.

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Kinetics of Iron(III) Interactions with Phenol and *o*-Aminophenol

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Kinetic measurements by the stopped-flow technique are reported at 25° and $I = 0.1$ for the reaction of Fe(III) with phenol and *o*-aminophenol. For phenol, close-to-equilibrium data indicate a reaction mechanism involving the reaction of the protonated ligand with both Fe^{3+} and $FeOH^{2+}$ (second-order rate constants measured to be 25 and 720 M^{-1} sec^{-1}). The data for *o*-aminophenol on the other hand are consistent with the reaction of $FeOH^{2+}$ with the monoprotonated ligand ($k = 1.1 \times 10^5$ M^{-1} sec^{-1}). The present results are compared with previous measurements involving a wide variety of ligands in an attempt to resolve questions of "proton ambiguity."

Introduction

Of all the first-row transition metal ions, Fe(III) has been one of the most difficult to study kinetically. This has been due to the fact that the free metal ion readily hydrolyzes,[1,2] even in moderately acid solutions, to $FeOH^{2+}$, which can dimerize.[3] In addition, the complexing ligand can react with either the free ion or the $FeOH^{2+}$ species, or both.[4] If the ligand itself can exist in free and protonated forms, the number of mechanistic pathways quickly proliferates. Complexation pathways, involving the protonated and unprotonated ligands, have been found for both Fe^{3+} and $FeOH^{2+}$. Of the kinetic studies that have been carried out with Fe(III), the majority have involved "simple" ligands[4-6] such as Cl^- and Br^- which only attack in the anionic form or ligands[7,8] such as SCN^- and SO_4^{2-} which can react either in the singly protonated or in unprotonated forms. Only recently have bidentate or biprotonated ligands such as salicylic acid and analogs[9] been utilized. In many of these studies, the data could be interpreted on the basis of two or more kinetically ambiguous mechanisms, *e.g.*, by pathways involving Fe^{3+} + L or $FeOH^{2+}$ + HL. In such instances, it was necessary to choose between possible alternatives by examining the "reasonableness"[10] of the rate constants obtained. The purpose of this work was to carry out similar studies with ligands of sufficiently high pK values such that kinetic contributions from the free ligand were negligible. For this purpose we chose phenol (pK_a = 9.8) and *o*-aminophenol (pK_1 = 4.9, pK_2 ≈ 9.8).

Experimental Section

Materials. *o*-Aminophenol was added to saturation to about 100 ml of hot 95% ethanol under a nitrogen atmosphere. Activated charcoal was stirred in until the solution became colorless, after which the clear hot solution was quickly filtered and then refrigerated until all the crystals had formed. The white crystals were filtered, washed with hexane, and stored under nitrogen until used. Fisher reagent grade $Fe(NO_3)_3 \cdot 9H_2O$ and KNO_3 were used without further purification. Phenol was purified by distillation.

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