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UNIVERSITIES OF MILAN AND PADUA, ITALY

## Olefin Replacement on Cyclooctatetraeneiron Tricarbonyl by Neutral Ligands

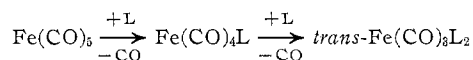
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Kinetic data are reported on reactions of cyclooctatetraeneiron tricarbonyl with tertiary phosphines (L) and 1,2-bis(diphenylphosphino)ethane (L-L) in decalin at various temperatures. The reactions involve replacement of cyclooctatetraene leading to *trans*-Fe(CO)<sub>3</sub>L<sub>2</sub> and *cis*-Fe(CO)<sub>3</sub>(L-L). Reaction rates depend on the nature and concentration of the entering ligand. Results are interpreted in terms of a mechanism consisting of a slow coordination of L on the substrate followed by fast elimination of cyclooctatetraene from the resulting labile intermediate. Activation parameters are discussed to support this mechanism.

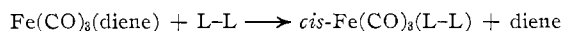
## Introduction

Derivatives of iron pentacarbonyl obtained through reaction of Fe(CO)<sub>5</sub> with neutral ligands L are mono- and disubstituted complexes



These reactions occur under drastic experimental conditions.<sup>1-4</sup>

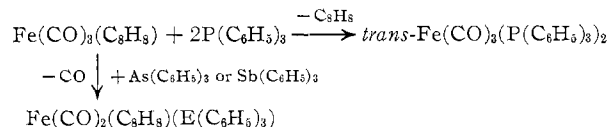
Disubstituted *cis* derivatives have been obtained by treating Fe(CO)<sub>3</sub>(diene) with bidentate ligands (L-L).<sup>5,6</sup>



With monodentate ligands, on the other hand, substitution of one carbonyl group takes place leading to Fe(CO)<sub>3</sub>(diene)L.<sup>6</sup>

The compound Fe(CO)<sub>3</sub>(C<sub>4</sub>H<sub>6</sub>) (C<sub>4</sub>H<sub>6</sub> = butadiene) reacts with tertiary phosphines to give substituted products which always contain the coordinated diolefin.<sup>6</sup>

Fe(CO)<sub>3</sub>(C<sub>8</sub>H<sub>8</sub>) (C<sub>8</sub>H<sub>8</sub> = cyclooctatetraene) is obtained from the reaction of iron pentacarbonyl and cyclooctatetraene. Rather surprising is the reaction of this compound with monodentate ligands of the type E(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub> (E = P, As, and Sb) whereby different products are obtained<sup>7</sup>



This peculiarity prompted us to undertake a kinetic investigation of the reaction of Fe(CO)<sub>3</sub>(C<sub>8</sub>H<sub>8</sub>) with some monodentate and bidentate tertiary phosphines. The present paper reports the results of such a study.

## Experimental Section

**Preparation and Purification of Materials.**—The compounds Fe(CO)<sub>3</sub>(C<sub>8</sub>H<sub>8</sub>) and Fe(CO)<sub>3</sub>(C<sub>4</sub>H<sub>6</sub>) were prepared as described in the literature.<sup>7,8</sup> Ethyldiphenylphosphine was prepared

according to Meisenheimer, *et al.*<sup>9</sup> 1,2-Bis(diphenylphosphino)ethane was prepared by the method of Chatt and Hart.<sup>10</sup> Triphenylphosphine, commercial reagent grade, was recrystallized from petroleum ether (bp 40–70°). Tributylphosphine (Fluka) was distilled before use. The solvents decalin and methylcyclohexane were distilled from sodium under nitrogen and stored under nitrogen.

**Determination of Rates.**—All reactions were carried out in foil-wrapped flasks (to avoid light catalysis) under nitrogen. An oil bath was used to maintain the temperature within 0.1°. The concentration of the complex was around 10<sup>-3</sup> M; that of the nucleophile was at least 10 times greater. The rates were determined by following the disappearance of the 2050-cm<sup>-1</sup> C=O stretching absorption of Fe(CO)<sub>3</sub>(C<sub>8</sub>H<sub>8</sub>) as it reacted to form Fe(CO)<sub>3</sub>L<sub>2</sub> or Fe(CO)<sub>3</sub>(L-L). All reactions proceeded to completion and the infinite spectra were in good agreement with those of the known products prepared independently. Usually about 20 measurements were made during a period of 3 half-lives. More details about this method have been given previously.<sup>11</sup> Measurements were performed on a Perkin-Elmer Model 621 spectrophotometer.

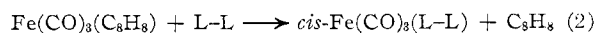
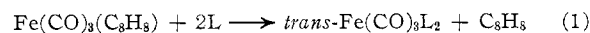
**Product Identification.**—The complex *cis*-Fe(CO)<sub>3</sub>[(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>-PC<sub>2</sub>H<sub>4</sub>P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>] was prepared as described in the literature.<sup>5</sup> The compound *trans*-Fe(CO)<sub>3</sub>[P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>]<sub>2</sub> and the new compound *trans*-Fe(CO)<sub>3</sub>[P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>]<sub>2</sub> were prepared by heating at reflux a solution of Fe(CO)<sub>3</sub>(C<sub>8</sub>H<sub>8</sub>) in *n*-butyl ether with the ligand under nitrogen. Progress of the reaction was monitored by infrared spectroscopy. After several hours, the solvent was evaporated *in vacuo* and the residual solid was recrystallized from chloroform-pentane.

*Anal.* Calcd for Fe(CO)<sub>2</sub>[P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>]<sub>2</sub>: C, 65.5; H, 5.32. Found: C, 65.2; H, 5.4. No solid product could be isolated from the reaction of Fe(CO)<sub>3</sub>(C<sub>8</sub>H<sub>8</sub>) and P(*n*-C<sub>4</sub>H<sub>9</sub>)<sub>3</sub>, but the fact that the changes in infrared spectra during the reaction were similar to those for the reaction with P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub> is strong evidence for the formation of the complex.

## Results and Discussion

We have found that treatment of Fe(CO)<sub>3</sub>(C<sub>8</sub>H<sub>8</sub>) with mono- and bidentate ligands bearing N, O, or S as donor atoms brings about decomposition.

The reactions which proved amenable to kinetic investigations are



where L = P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>, P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>(C<sub>2</sub>H<sub>5</sub>), P(*n*-C<sub>4</sub>H<sub>9</sub>)<sub>3</sub> and L-L = (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>. The analogous

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TABLE I  
 CARBONYL STRETCHING FREQUENCIES OF  
 IRON TRICARBONYL DERIVATIVES<sup>a</sup>

Compounds	$\nu$ , cm <sup>-1</sup>	Solvent
Fe(CO) <sub>3</sub> (C <sub>8</sub> H <sub>8</sub> )	2050 vs, 1990 vs, 1972 s	CCl <sub>4</sub>
<i>trans</i> -Fe(CO) <sub>3</sub> [P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ] <sub>2</sub>	1886 vs	CCl <sub>4</sub>
<i>trans</i> -Fe(CO) <sub>3</sub> [P(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (C <sub>2</sub> H <sub>5</sub> )] <sub>2</sub>	1983 sh, 1975 vs	CCl <sub>4</sub>
<i>trans</i> -Fe(CO) <sub>3</sub> [P( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub> ] <sub>2</sub>	1865 vs	Decalin
<i>cis</i> -Fe(CO) <sub>3</sub> [(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> PC <sub>2</sub> H <sub>4</sub> P(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> ]	1989 vs, 1923 s, 1902 vs	CCl <sub>4</sub>

<sup>a</sup> Abbreviations: vs, very strong; s, strong; sh, shoulder.

derivative Fe(CO)<sub>3</sub>(C<sub>7</sub>H<sub>8</sub>) (C<sub>7</sub>H<sub>8</sub> = norbornadiene) reacts with L or L-L to give *trans*-Fe(CO)<sub>3</sub>L<sub>2</sub> or *cis*-Fe(CO)<sub>3</sub>(L-L) at ca. 130°, but the reactions are too slow to follow kinetically.

The reaction rates were measured in decalin and methylcyclohexane and the dependence on temperature was determined. We did not observe any significant solvent effect for reactions 1 and 2 on going from decalin to methylcyclohexane. The observed pseudo-first-order rate constants,  $k_{\text{obsd}}$  (sec<sup>-1</sup>), are reported in Table II. Data show that the  $k_{\text{obsd}}$  values depend both on the nature and on the concentration of the entering ligand and fit the rate law:  $k_{\text{obsd}} = k_2[\text{entering ligand}]$ .

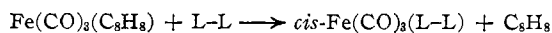
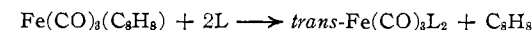
The second-order rate constants,  $k_2$  (M<sup>-1</sup> sec<sup>-1</sup>), are reported in Table III.

The activation parameters for the reaction of Fe(CO)<sub>3</sub>(C<sub>8</sub>H<sub>8</sub>) with P(*n*-C<sub>4</sub>H<sub>9</sub>)<sub>3</sub> are  $\Delta H^\ddagger = 11.41$  kcal/mol and  $\Delta S^\ddagger = -38.16$  eu. For the reaction with 1,2-bis(diphenylphosphino)ethane  $\Delta H^\ddagger$  is 14.28 kcal/mol and  $\Delta S^\ddagger$  is -30.34 eu.

Before interpreting this rate law in terms of reaction mechanism, it is worth recalling briefly the current views on the mode of bonding of the cyclooctatetraene moiety to the iron carbonyl. The complex Fe(CO)<sub>3</sub>(C<sub>8</sub>H<sub>8</sub>) has been the subject of numerous studies in order to reconcile the conflicting chemical and physical evidence for the structure of the complex. A single-crystal X-ray structural determination<sup>12</sup> combined with proton nmr,<sup>13</sup> infrared, and Raman spectra<sup>14</sup> show that in solution as well as in the solid the cyclooctatetraene ring is linked to the metal by an essentially conjugated diene system, with a chair configuration. Hence, a comparison with other dienemetal carbonyls appears most relevant from the kinetic point of view.

The displacement of 1,5-cyclooctadiene from Mo(CO)<sub>4</sub>(C<sub>8</sub>H<sub>12</sub>) by neutral ligands to give Mo(CO)<sub>4</sub>L<sub>2</sub> occurs through both S<sub>N</sub>1 and S<sub>N</sub>2 mechanisms. This latter has been described as a simple bimolecular displacement reaction of the diene.<sup>15,16</sup>

An inspection of the spectral changes occurring dur-

 TABLE II  
 PSEUDO-FIRST ORDER RATE CONSTANTS FOR THE REACTIONS<sup>a</sup>


Entering ligand	10 <sup>3</sup> [L], M	Temp, °C	10 <sup>4</sup> $k_{\text{obsd}}$ , sec <sup>-1</sup>
P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	3.23	127.2	1.00
P(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	8.36	127.2	2.43
P(C <sub>6</sub> H <sub>5</sub> )	13.49	127.2	3.85
P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	19.17	127.2	5.48
P(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	23.70	127.2	6.86
P(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (C <sub>2</sub> H <sub>5</sub> )	4.62	115	4.06
P(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (C <sub>2</sub> H <sub>5</sub> )	7.64	115	5.36
P(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (C <sub>2</sub> H <sub>5</sub> )	12.67	115	9.76
P(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (C <sub>2</sub> H <sub>5</sub> )	15.73	115	11.83
P(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (C <sub>2</sub> H <sub>5</sub> )	2.61	127.2	3.90
P(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (C <sub>2</sub> H <sub>5</sub> )	4.03	127.2	6.62
P(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (C <sub>2</sub> H <sub>5</sub> )	6.40	127.2	10.81
P(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (C <sub>2</sub> H <sub>5</sub> )	7.71	127.2	13.47
P(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (C <sub>2</sub> H <sub>5</sub> )	8.67	127.2	15.16
P( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub>	3.87	90	1.38
P( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub>	7.99	90	3.34
P( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub>	10.29	90	4.53
P( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub>	13.59	90	6.13
P( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub>	16.56	90	7.28
P( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub>	21.77	90	9.84
P( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub>	4.41	90	1.75 <sup>b</sup>
P( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub>	10.51	90	4.25 <sup>b</sup>
P( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub>	16.81	90	6.79 <sup>b</sup>
P( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub>	26.54	90	10.80 <sup>b</sup>
P( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub>	31.37	90	12.54 <sup>b</sup>
P( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub>	3.21	105	2.95
P( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub>	5.49	105	4.68
P( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub>	7.76	105	7.29
P( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub>	9.65	105	9.17
P( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub>	14.36	105	13.70
P( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub>	2.86	110	2.76
P( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub>	4.82	110	5.02
P( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub>	5.90	110	6.10
P( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub>	7.83	110	8.67
P( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub>	10.59	110	11.24
P( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub>	14.96	110	16.20
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> PC <sub>2</sub> H <sub>4</sub> P(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	1.35	110	1.28
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> PC <sub>2</sub> H <sub>4</sub> P(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	2.30	110	2.74
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> PC <sub>2</sub> H <sub>4</sub> P(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	4.64	110	5.88
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> PC <sub>2</sub> H <sub>4</sub> P(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	5.64	110	6.76
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> PC <sub>2</sub> H <sub>4</sub> P(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	6.73	110	8.51
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> PC <sub>2</sub> H <sub>4</sub> P(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	1.26	117.3	1.92
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> PC <sub>2</sub> H <sub>4</sub> P(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	1.71	117.3	2.83
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> PC <sub>2</sub> H <sub>4</sub> P(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	2.60	117.3	4.73
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> PC <sub>2</sub> H <sub>4</sub> P(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	4.32	117.3	7.71
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> PC <sub>2</sub> H <sub>4</sub> P(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	5.16	117.3	9.77
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> PC <sub>2</sub> H <sub>4</sub> P(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	7.85	117.3	15.25
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> PC <sub>2</sub> H <sub>4</sub> P(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	1.32	127.2	4.25
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> PC <sub>2</sub> H <sub>4</sub> P(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	1.93	127.2	6.37
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> PC <sub>2</sub> H <sub>4</sub> P(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	3.28	127.2	9.71
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> PC <sub>2</sub> H <sub>4</sub> P(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	4.02	127.2	12.18
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> PC <sub>2</sub> H <sub>4</sub> P(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	5.39	127.2	17.09

<sup>a</sup> In decalin at different temperatures. <sup>b</sup> Methylcyclohexane as solvent.

ing reactions 1 and 2 clearly indicates that no intermediates were present at detectable concentrations during the reactions. Based on this observation, two mechanisms can be conceived of. In the first one (A) the rate-determining step is the bimolecular attack by the entering ligand L on the substrate leading to a labile iron carbonyl intermediate containing both L and the

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TABLE III  
SECOND-ORDER RATE CONSTANTS FOR THE REACTIONS<sup>a</sup>

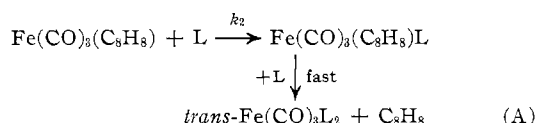
$$\text{Fe}(\text{CO})_3(\text{C}_6\text{H}_5)_2 + 2\text{L} \longrightarrow \text{trans-Fe}(\text{CO})_3\text{L}_2 + \text{C}_6\text{H}_6$$

$$\text{Fe}(\text{CO})_3(\text{C}_6\text{H}_5)_2 + \text{L-L} \longrightarrow \text{cis-Fe}(\text{CO})_3(\text{L-L}) + \text{C}_6\text{H}_6$$

Entering ligand	Temp, °C	10 <sup>3</sup> k <sub>2</sub> , M <sup>-1</sup> sec <sup>-1</sup>
P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	127.2	2.85
P(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (C <sub>2</sub> H <sub>5</sub> )	115	7.42
	127.2	18.55
P( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub>	90	4.69
P( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub>	90	4.03 <sup>b</sup>
P( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub>	105	9.55
P( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub>	110	11.10
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> PC <sub>2</sub> H <sub>4</sub> P(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	110	13.10
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> PC <sub>2</sub> H <sub>4</sub> P(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	117.3	20.11
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> PC <sub>2</sub> H <sub>4</sub> P(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	127.2	30.79

<sup>a</sup> In decalin at different temperatures. <sup>b</sup> Methylcyclohexane as solvent.

polyolefin, followed by fast elimination of cyclooctatetraene



The second mechanism (B) would involve a fast pre-equilibrium step between L and the substrate, lying far over to the left, followed by slow rate-determining dissociation of cyclooctatetraene. The above mechanisms hold also for the reaction with 1,2-bis(diphenylphosphino)ethane (reaction 2) if the closure of the chelate ring is assumed to be fast in mechanism A and slow in mechanism B. If mechanism B is operating, the second-order rate constant determined experimentally will comprise both the pre-equilibrium constant and the rate constant for the release of C<sub>6</sub>H<sub>6</sub> from the intermediate. A choice between the two mechanisms may be attempted by considering the activation parameters. The highly negative values for the activation entropies suggest a type of mechanism involving a decrease of some degree of freedom during formation of the transition state. Thus, we are led to favor mechanism A, since in mechanism B the negative contribution of the pre-equilibrium stage to the over-all activation entropy should be more than compensated for by the positive contribution of the subsequent slow dissociative step. As for the nucleophilicity of the entering ligand L, it

appears to decrease with increasing substitution of phenyl groups in PR<sub>3</sub>, *i.e.*, with decreasing electron-donor ability of the phosphorus atom.

On the other hand, reaction rates depend markedly on the nature of the polyolefin bonded to iron. Thus, norbornadiene is displaced much more slowly than cyclooctatetraene by mono- and bidentate phosphines.

A cursory survey of the literature reveals that substitution mechanisms on iron carbonyl derivatives strongly depend upon the nature of the substrate. The reaction of the trigonal-bipyramidal Fe(CO)<sub>3</sub>P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub> with triphenylphosphine to form Fe(CO)<sub>3</sub>[P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>]<sub>2</sub> was reported to involve dissociation of a CO group as the rate-determining step.<sup>17</sup> The iron carbonyl halides of the type Fe(CO)<sub>4</sub>X<sub>2</sub> have been found to react with neutral ligands L having P, As, and Sb as donor atoms to give Fe(CO)<sub>2</sub>L<sub>2</sub>X<sub>2</sub>. The rate of monosubstitution of Fe(CO)<sub>4</sub>X<sub>2</sub> was also found to be independent of the nature and concentration of entering ligand and the mechanism proposed requires halogen dissociation from the carbonyl compound giving Fe(CO)<sub>4</sub> as reactive intermediate.<sup>18</sup> Such a mechanism is in agreement with that proposed for the dissociative isotopic exchange reactions of Fe(CO)<sub>4</sub>X<sub>2</sub> with the corresponding radioactive halogens in CCl<sub>4</sub>.<sup>19</sup> The CO substitution of Fe(CO)<sub>3</sub>LX<sub>2</sub> with L to give Fe(CO)<sub>2</sub>L<sub>2</sub>X<sub>2</sub> also proceeds by a dissociative path.<sup>18</sup>

On the other hand, a direct displacement process was suggested for the reaction of carbon monoxide exchange with Fe(CO)<sub>4</sub>I<sub>2</sub>, in which the rate depends upon the concentrations of both the metal carbonyl and CO.<sup>20</sup> In the case of the reaction of C<sub>5</sub>H<sub>5</sub>Fe(CO)<sub>2</sub>CH<sub>3</sub> with phosphines and phosphites (L) in tetrahydrofuran yielding C<sub>5</sub>H<sub>5</sub>Fe(CO)(COCH<sub>3</sub>)L, the rates depend upon ligand concentration, but a limiting rate is reached at higher ligand concentrations. A solvent- and/or ligand-assisted mechanism has been proposed for these reactions.<sup>21</sup>

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