

# Rates of Substitution Reactions of Derivatives of Iron Pentacarbonyl, $\text{Fe}(\text{CO})_4\text{L}$ and $\text{Fe}(\text{CO})_3\text{L}_2$ ( $\text{L} = \text{PPh}_3, \text{AsPh}_3, \text{P}(\text{OPh})_3$ ): Application of Crystal Field Activation Energies to Organometallic Complexes

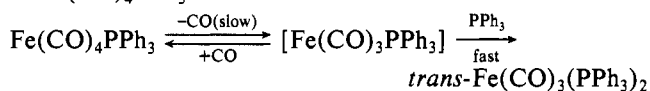
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Dissociation of ligands from  $\text{Fe}(\text{CO})_3\text{L}_2$  and  $\text{Fe}(\text{CO})_4\text{L}$  ( $\text{L} = \text{PPh}_3, \text{P}(\text{OPh})_3, \text{AsPh}_3$ ) has been investigated by reaction with carbon monoxide. These complexes are relatively inert, requiring temperatures considerably in excess of 100 °C. The relative inertness of 18-electron complexes of iron is considered. The order of ligand lability from  $\text{Fe}(\text{CO})_3\text{L}_2$  is  $\text{AsPh}_3 > \text{PPh}_3 > \text{P}(\text{OPh})_3$ , which apparently represents the general bond strength to low-valent metal centers.

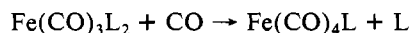
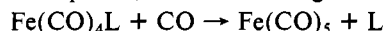
Considerable advances in understanding reactivity of organometallic complexes have been made recently, especially for substitution reactions on six-coordinate complexes.<sup>1-3</sup> A number of studies of octahedral metal carbonyl complexes have appeared, allowing general interpretations of their reactivity.<sup>4,5</sup> The reactions of  $\text{Ni}(\text{CO})_4$  and derivatives have also been investigated rather thoroughly.<sup>6,7</sup> Reactions of five-coordinate complexes such as  $\text{Fe}(\text{CO})_5$  and derivatives have not been investigated as extensively, and the reactivity is not well understood.<sup>8</sup>

Reactions of  $\text{Fe}(\text{CO})_5$  that have been reported to occur via CO dissociation at moderate conditions evidently are catalyzed by an impurity in the  $\text{Fe}(\text{CO})_5$ .<sup>8</sup> The results of a kinetic study of  $\text{Fe}(\text{CO})_4\text{PPh}_3$  for the reaction



have been reported by Siefert and Angelici.<sup>8</sup> This reaction occurs above 160 °C, probably by CO dissociation. Similar reactions of  $\text{Ru}(\text{CO})_4\text{L}$  (where  $\text{L} = \text{PPh}_3, \text{PPh}_2\text{Me}$ , or  $\text{PBu}_3$ ) with further ligand have also been investigated.<sup>9</sup> Convenient rates were obtained in the temperature range 45–70 °C, and the reaction followed pseudo-first-order kinetics. The rate constant decreased in the order  $\text{P}(\text{C}_6\text{H}_5)_3 > \text{P}(\text{C}_6\text{H}_5)_2\text{CH}_3 > \text{P}(\text{n-C}_4\text{H}_9)_3$ , which was interpreted as a steric acceleration of carbon monoxide dissociation from the complex  $\text{Ru}(\text{CO})_4\text{L}$ . Substitution on another five-coordinate complex,  $\text{Mn}(\text{CO})_4\text{NO}$ , proceeds by nucleophilic attack on the complex.<sup>10</sup>

The scarce data available suggested that five-coordinate iron carbonyl complexes react very slowly. A comparison of reactions of  $\text{Fe}(\text{CO})_4\text{PBu}_3$  and  $\text{Ru}(\text{CO})_4\text{PBu}_3$  show a very large difference in rates with comparable rates of reaction at 160 and 60 °C, respectively.<sup>8,9</sup> The magnitude of this difference in rates between the analogous first- and second-row metals is much larger than that seen for Cr and Mo complexes, where comparable rates are obtained at 120 and 90 °C, respectively.<sup>11</sup> To provide further data on the relative inertness of five-coordinate iron complexes, we have investigated the reactions



for the ligands  $\text{L} = \text{PPh}_3, \text{P}(\text{OPh})_3$ , and  $\text{AsPh}_3$ .

Table I. Melting Points and Microanalyses for Substituted Iron Carbonyls

compd	mp, °C	% found			% calcd		
		C	H	Fe	C	H	Fe
$\text{Fe}(\text{CO})_4\text{PPh}_3$	201 <sup>a</sup>	61.5	3.7	12.9	61.4	3.5	13.0
$\text{Fe}(\text{CO})_4\text{P}(\text{OPh})_3$	68	55.4	3.2	11.8	55.3	3.2	11.7
$\text{Fe}(\text{CO})_4\text{AsPh}_3$	178	56.0	3.4	11.6	55.7	3.2	11.8
$\text{Fe}(\text{CO})_3[\text{PPh}_3]_2$	272 <sup>a</sup>	70.1	5.1	8.3	70.5	4.6	8.4
$\text{Fe}(\text{CO})_3[\text{P}(\text{OPh})_3]_2$	114	61.4	3.8	7.6	61.6	4.0	7.4

<sup>a</sup> With decomposition.

Table II. Carbonyl Stretching Frequencies of  $\text{Fe}(\text{CO})_4\text{L}$  and  $\text{Fe}(\text{CO})_3\text{L}_2$  in Hexane

compd	CO str freq, $\text{cm}^{-1}$		
$\text{Fe}(\text{CO})_4\text{AsPh}_3$	2049 (s)	1976 (s)	1946 (vs)
$\text{Fe}(\text{CO})_4\text{PPh}_3$	2050 (m)	1970 (s)	1930 (vs)
$\text{Fe}(\text{CO})_4\text{P}(\text{OPh})_3$	2065 (m)	1996 (m)	1959 (vs)
$\text{Fe}(\text{CO})_3[(\text{AsPh}_3)_2]$		1884 (s)	
$\text{Fe}(\text{CO})_3[\text{PPh}_3]_2$		1885 (s)	
$\text{Fe}(\text{CO})_3[\text{P}(\text{OPh})_3]_2$		1925 (s)	

## Experimental Section

Melting points were determined on a Mel-Temp melting point apparatus and are uncorrected. Infrared spectra were recorded on a Beckman IR 4240 spectrophotometer. Microanalyses were performed by Schwarzkopf Microanalytical Laboratory, Inc.

**Preparation of Compounds.  $\text{Fe}(\text{CO})_4\text{PPh}_3$  and  $\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$ .** The procedure of Clifford and Mukherjee<sup>12</sup> was followed in the preparation of these compounds. The melting points were in agreement with reported melting points and are given in Table I with the microanalyses. The CO stretching frequencies are given in Table II.

**$\text{Fe}(\text{CO})_4\text{AsPh}_3$ .** The procedure of Siegel was altered for the preparation of  $\text{Fe}(\text{CO})_4\text{AsPh}_3$ .<sup>13</sup> Sodium borohydride (0.180 g, 4.5 mmol) and 3.75 g (10 mmol) of triphenylarsine were added to a mixture of 60 mL of THF and 2 mL (15 mmol) of iron pentacarbonyl. The reaction mixture was stirred under argon at room temperature for 1 h and then was heated at 75 °C for 48 h. The solution was cooled to room temperature and was filtered through an alumina column. The column was washed with methylene chloride, and the combined eluant was concentrated in vacuo. The resulting yellow-brown solid was dissolved in a minimum of methylene chloride and chromatographed over neutral alumina (activity no. 1). The column was eluted first with hexane to remove any unreacted arsine or iron pentacarbonyl and then with a 4/1 hexane/benzene mixture, which removed the monosubstituted product. The filtrate was concentrated in vacuo, and the product was purified by recrystallizing from boiling heptane. The IR spectrum in the CO stretching region gave the expected three bands as listed in Table II. The melting point is given in Table I.

**$\text{Fe}(\text{CO})_3(\text{AsPh}_3)_2$ .** The mixture of  $\text{Fe}(\text{CO})_4\text{AsPh}_3$  and  $\text{Fe}(\text{CO})_3(\text{AsPh}_3)_2$  was prepared as previously reported<sup>13</sup> and was washed repeatedly with octane at room temperature until all the monosubstituted product was separated. The yellow solid was found to be the

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**Table III.** Extinction Coefficients of  $\text{Fe}(\text{CO})_4\text{L}$  and  $\text{Fe}(\text{CO})_3\text{L}_2$  in Hexane

compd	extinction coeff ( $\times 10^3$ ), $\text{M}^{-1} \text{cm}^{-1}$
$\text{Fe}(\text{CO})_4\text{PPh}_3$	$1.401 \pm 0.002$
$\text{Fe}(\text{CO})_4\text{P}(\text{OPh})_3$	$0.672 \pm 0.008$
$\text{Fe}(\text{CO})_4\text{AsPh}_3$	$1.312 \pm 0.002$
$\text{Fe}(\text{CO})_3[\text{PPh}_3]_2$	$0.713 \pm 0.003$
$\text{Fe}(\text{CO})_3[\text{P}(\text{OPh})_3]_2$	$0.445 \pm 0.003$
$\text{Fe}(\text{CO})_3[\text{AsPh}_3]_2$	$0.501 \pm 0.003$

disubstituted complex by IR. The CO stretching frequencies are in good agreement with previously reported values and are given in Table II. The melting point is given in Table I.

**$\text{Fe}(\text{CO})_4\text{P}(\text{OPh})_3$ .** The compound was prepared by the method of Siegel.<sup>13</sup> The crystals were purified by recrystallization from boiling heptane. The infrared spectrum is described in Table II.

**$\text{Fe}(\text{CO})_3[\text{P}(\text{OPh})_3]_2$ .** The procedure of Conder and Darensbourg<sup>14</sup> was followed to prepare this compound. The residue was placed on neutral alumina (activity no. 1) and was washed with pentane repeatedly, until a clear solution was obtained. The column was then washed with 100 mL of THF to yield a dark solution containing the disubstituted product. The solvent was removed under vacuum. The crystals were washed with boiling hexane to remove monosubstituted complex. The melting point was found to be in good agreement with previously reported values and is given in Table I. The infrared spectrum is described in Table II.

**Purification Procedure.** Reagent grade decane (Eastman) was purified by stirring with sulfuric acid for 48 h, washing with water, passing down an alumina column, and storing over sodium. Reagent grade chlorobenzene was purified by refluxing at 130 °C with calcium hydride, vacuum distilling, and storing over molecular sieves. All other reagents were used as obtained from commercial sources.

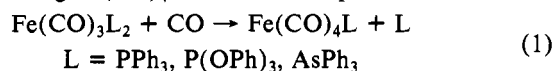
**Kinetic Measurements.** Infrared spectra were measured on a Beckman IR 4240 spectrophotometer in the absorbance mode using 1.0-mm NaCl solution cells. Beer's law plots with hexane as solvent were constructed for each mono- and disubstituted compound. These plots were linear and passed through the origin, indicating that the complexes are well-behaved and suitable for kinetic studies. The extinction coefficients are reported in Table III.

All kinetic studies were carried out in an aluminum foil wrapped, 100-mL two-necked, jacketed reaction flask equipped with a rubber septum to allow convenient sample removal via syringe. A Haake FS heater-circulator was used to maintain a constant jacket temperature to within  $\pm 0.01$  °C, and the solution was constantly stirred with a magnetic stirrer.

Typically, 25 mL of solvent and 10 mg of complex were put into the thermostated reaction flask, which was then connected to a carbon monoxide Schlenk manifold. After evacuation, the flask was filled with carbon monoxide. The reaction flasks were kept under a slight positive carbon monoxide pressure, which was monitored by using a mercury bubbler, in order to avoid the introduction of oxygen when samples were removed for infrared measurements. At appropriate time intervals, a 0.5-mL portion of the sample was removed and the IR spectrum was immediately recorded. The rates of reactions of iron-pentacarbonyl derivatives were followed by monitoring changes in the most intense carbonyl stretching frequency (E mode) in the infrared spectra of the reaction mixture. Measurements were usually made over a period of 3 half-lives. All reactions of the disubstituted complexes went to completion, giving good linear plots of  $\ln A_t$  vs.  $t$ , where  $A_t$  is the absorbance at time  $t$ .

## Results

$\text{Fe}(\text{CO})_3\text{L}_2$  has been observed to react with carbon monoxide, yielding  $\text{Fe}(\text{CO})_4\text{L}$  as shown in eq 1. The reaction of



each monosubstituted complex with carbon monoxide in decane was very slow even at 150 °C, and the products were not clearly identified, whereas the reaction of all the disubstituted complexes with carbon monoxide were relatively faster with

**Table IV.** Rate Constants for the Reaction  $\text{Fe}(\text{CO})_3\text{L}_2 + \text{CO} \rightarrow \text{Fe}(\text{CO})_4\text{L} + \text{L}$  under 1 Atm of CO

ligand	temp, °C	solvent	$10^5 k_{\text{obsd}}, \text{s}^{-1}$
PPh <sub>3</sub>	125	chlorobenzene	0.985
	130	decane	1.53
	136	decane	2.64
AsPh <sub>3</sub>	90	chlorobenzene	4.57
	95	chlorobenzene	7.32
	99	chlorobenzene	11.5
P(OPh) <sub>3</sub>	135	decane	0.672
	140	decane	1.10
	145	decane	1.70

**Table V.** Activation Parameters for the Reaction  $\text{Fe}(\text{CO})_3\text{L}_2 + \text{CO} \rightarrow \text{Fe}(\text{CO})_4\text{L} + \text{L}$ 

L	$\Delta H^\ddagger$ , kcal mol <sup>-1</sup>	$\Delta S^\ddagger$ , cal mol <sup>-1</sup> deg <sup>-1</sup>
AsPh <sub>3</sub>	$27.2 \pm 3.5$	$-4.0 \pm 9.6$
PPh <sub>3</sub>	$28.2 \pm 1.0$	$-11.2 \pm 2.7$
P(OPh) <sub>3</sub>	$30.6 \pm 1.5$	$-7.7 \pm 2.6$

**Table VI.** Rate Constants for Ligand Dissociation for  $\text{Cr}(\text{CO})_4\text{L}_2$ ,  $\text{Fe}(\text{CO})_3\text{L}_2$ , and  $\text{Ni}(\text{CO})_2\text{L}_2$  at 25 °C

L	$\text{Cr}(\text{CO})_4\text{L}_2^a$	$\text{Fe}(\text{CO})_3\text{L}_2^b$	$\text{Ni}(\text{CO})_2\text{L}_2^c$
AsPh <sub>3</sub>	fast	$9.6 \times 10^{-9}$	
PPh <sub>3</sub>	$3.1 \times 10^{-6}^d$	$5.0 \times 10^{-11}$	$5.6 \times 10^{-4}$
P(OPh) <sub>3</sub>	$4.6 \times 10^{-11}$	$4.8 \times 10^{-12}$	$1.0 \times 10^{-7}$
CO	$1.9 \times 10^{-12}$		$1.2 \times 10^{-2}^e$

<sup>a</sup> Extrapolated from experimental data of ref 16. <sup>b</sup> Extrapolated from experimental data of this study. <sup>c</sup> Reference 6. <sup>d</sup> Reference 4. <sup>e</sup> Reference 7.

clear identification of the products. The reaction products were assigned solely through infrared data obtained during the kinetic studies, by comparison with the spectra of the independently prepared substituted complexes. The CO stretching frequencies are listed in Table II. The rate for each substituted complex was evaluated at three temperatures.

All pseudo-first-order rate constants,  $k_{\text{obsd}}$ , quoted are the average of rate constants obtained in at least three separate kinetic studies. The rate constants are listed in Table IV. Activation parameters for the reactions were obtained from Eyring plots of  $\ln(k_{\text{obsd}}/T)$  vs.  $1/T$ , where  $T$  is the temperature, and are reported in Table V. The slope and ordinate intercept of all the plots were determined by least-squares analysis.

## Discussion

$\text{Fe}(\text{CO})_3\text{L}_2$  reacts with CO at high temperature to yield  $\text{Fe}(\text{CO})_4\text{L}$  as shown in eq 1, where  $\text{L} = \text{AsPh}_3, \text{PPh}_3$  or  $\text{P}(\text{OPh})_3$ . The results of the kinetic studies are collected in Tables IV and V. The kinetic data indicate that the reactions obey first-order kinetics, dependent only on the concentration of the iron carbonyl complex. Consistent with earlier work on iron carbonyl complexes, we suggest that these reactions proceed by rate-determining loss of a ligand from the 18-electron complex, generating a four-coordinate 16-electron intermediate/transition state.<sup>8</sup> Analogous reactions of  $\text{Fe}(\text{C}(\text{O})_4\text{L}$  with CO did not occur at appreciable rates below 150 °C, and our apparatus did not allow investigation at higher temperatures. The order of ligand substitution by CO from  $\text{Fe}(\text{CO})_3\text{L}_2$



is very similar to that observed for ligand dissociation from  $\text{Cr}(\text{CO})_4\text{L}_2$ ,<sup>15</sup>  $\text{Cr}(\text{CO})_5\text{L}$ ,<sup>16</sup> and  $\text{Cr}(\text{CO})_4\text{LL}'$ ,<sup>4</sup> which is a

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**Table VII.** Bond Distances in the Bis(triphenylphosphine) Complexes

M	M-P, Å	atomic radius, Å	ref
Ni	2.22	1.24	18
Cr	2.42	1.27	19
Fe	2.2	1.26	20

**Table VIII.** Crystal Field Activation Energy (in  $Dq$ ) for Dissociation Mechanisms

complex	system	ground state		transition state		CFAE
		geometry	CFSE	geometry	CFSE	
Ni(CO) <sub>2</sub> L <sub>2</sub>	d <sup>10</sup>	<i>T<sub>d</sub></i>	0	trigonal planar	0	0
Cr(CO) <sub>4</sub> L <sub>2</sub>	d <sup>6</sup>	<i>O<sub>h</sub></i>	-24	TBP	-20	4
Fe(CO) <sub>3</sub> L <sub>2</sub>	d <sup>8</sup>	TBP	-14.6	<i>T<sub>d</sub></i>	-4.6	10
				SqPI	-25	-10

further indication that reactions of Fe(CO)<sub>3</sub>L<sub>2</sub> proceed by L dissociation. The slower rates of dissociation from the monosubstituted complexes are also consistent with the observations on chromium.<sup>4,15,16</sup> The activation entropies are near zero and may indicate that there is some interaction of L with Fe(CO)<sub>3</sub>L in the transition state. Activation entropies of near zero have been previously observed in dissociative processes.<sup>17</sup> The entropies are not consistent with an associative process where a gaseous CO would be coordinated; in that case the entropy of activation would be expected to be large and negative.

These iron complexes are relatively inert in comparison to their chromium and nickel analogues. Under similar conditions of temperature and pressure, the complexes show the order of lability

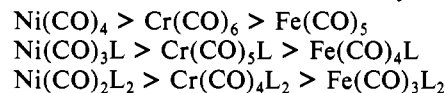


with  $\sim 10^8$  difference in rates between Ni complexes and Fe complexes as shown in Table VI. In each case the reactions proceed by first-order kinetics and have been assigned to ligand dissociation. Steric effects are often invoked for reactions of these bulky ligands, and may be important for different ligands on a specific metal center but clearly cannot be used to explain the difference between Ni, Cr, and Fe in reactivity. To assess possible ground-state properties that might lead to the observed reactivity order, we have examined M-P bond distances in disubstituted PPh<sub>3</sub> complexes. These values are shown in Table VII with the atomic radius for each metal. The rates show no correlation with the bond distances, suggesting that the rate differences are transition-state phenomena.

A reasonable explanation of the variation of the rate of substitution with the metal lies in the crystal field activation energies for the substitution reactions.<sup>21</sup> The crystal field activation energy is the difference in crystal field stabilization energies for the ground state and the transition state. Crystal field activation energies have been shown to be quite useful for interpreting the dependence of reactivity on the metal center for coordination complexes.<sup>21</sup> A primary uncertainty is the geometry of the transition state. Values of the crystal field activation energy for substitution reactions of the first-row mononuclear carbonyl complexes are shown in Table VIII for several possible geometries. Since Ni(0) is d<sup>10</sup>, there would be no CFAE. For chromium the intermediate could be either square pyramidal or trigonal bipyramidal with no difference

in the CFAE of 4*Dq*. The geometry of the transition state for loss of PPh<sub>3</sub> from Fe(CO)<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub> is not known and is very significant for the CFAE with values ranging from -10 to +10*Dq*. Allowing the geometry of Fe(CO)<sub>3</sub>PPh<sub>3</sub> to be approximated as a tetrahedron gives an excellent inverse correlation of CFAE with reactivity. The geometry suggested by matrix isolation for Fe(CO)<sub>4</sub> is a C<sub>2v</sub> distorted tetrahedron.<sup>22</sup> Replacement of one CO with a sterically demanding PPh<sub>3</sub> should favor tetrahedral geometry. The observed dependence of rates of ligand substitution on the metal (Ni(0) > Cr(0) > Fe(0)) is readily accounted for by the crystal field activation model.

Reactions of ruthenium complexes are considerably more rapid than reactions of analogous iron complexes.<sup>8,9</sup> A portion of this added reactivity can be attributed to the generally observed increase in reactivity of second-row metals over first-row metals.<sup>23,24</sup> However reactions of ruthenium carbonyl complexes are more rapid than those of analogous molybdenum complexes, a reverse of the order for the first-row complexes, and suggest added reactivity for ruthenium over iron.<sup>8,9,14,24</sup> The third-row comparison is analogous with Os(CO)<sub>5</sub> being more reactive than W(CO)<sub>6</sub>.<sup>25</sup> This reactivity of the ruthenium and osmium carbonyl complexes could result from a tendency for the four-coordinate, 16-electron transition state to be square planar with a very low CFAE as shown in Table VIII. It would not be surprising that the heavier Ru(0) and Os(0) complexes would tend more toward square planar than similar 16-electron Fe(0) complexes since the same trend is seen for the nickel group in the +2 oxidation state and the cobalt group in the +1 oxidation state. There exists very little information on the geometry of M(0) 16-electron, d<sup>8</sup> intermediates in the literature.<sup>22,27-29</sup> The reactivity relationships



pertain for the complexes, from the binary carbonyls to the disubstituted species and for dissociation of CO, P(OPh)<sub>3</sub>, and PPh<sub>3</sub>. This generality is consistent with a general phenomenon such as crystal field activation energy. The large differences in rate for different metal centers are similar to those seen for classical transition metal complexes and lend further support to the CFAE model as an explanation for the rate differences of these organometallic compounds.

In this paper we have established that the previously observed lack of reactivity toward dissociation of carbon monoxide by five-coordinate, 18-electron iron complexes extends to dissociation of group 5 donor ligands and have offered an explanation of this inertness in terms of crystal field activation energies. The effect of changing the dissociating ligand is very similar to that observed for chromium and platinum complexes, suggesting that the order represents the bond strength to low-valent metal centers.<sup>4,30</sup>

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**Registry No.** CO, 630-08-0; Fe(CO)<sub>3</sub>[AsPh<sub>3</sub>]<sub>2</sub>, 20516-72-7; Fe(CO)<sub>3</sub>[PPh<sub>3</sub>]<sub>2</sub>, 21255-52-7; Fe(CO)<sub>3</sub>[P(OPh)<sub>2</sub>]<sub>2</sub>, 20516-74-9.

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 (25) From qualitative data it is apparent that Os(CO)<sub>5</sub> reacts more rapidly than W(CO)<sub>6</sub>. Os(CO)<sub>5</sub> is converted to Os(CO)<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub> in 3 h at 130 °C.<sup>26</sup> Substitution on W(CO)<sub>6</sub> has been studied above 160 °C.<sup>24</sup>  
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