parison is the reaction of nitroaquobis(dimethylglyoximato)cobalt(III) with SCN^- and N_3^-.[23]

The second-order rate constants for N_3^- and SCN^- are respectively 5.7×10^{-4} and 5.8×10^{-4} M^{-1} sec^{-1}. These rates are about 10^6 slower than those observed for the Co(III) hematoporphyrin reactions. The geometry and charge of these complexes are similar; thus a steric reason cannot be invoked to explain the lability of the metalloporphyrins. The metal ions in metalloporphyrins are so involved in the delocalized orbitals of the porphyrin molecule that they lose their transition metal ion character.[24] Thus Co(III) complexes, which exhibit low-spin d^6 configurations that have orbitals containing these electrons that are "predominantly" metal orbitals, should be kinetically inert toward substitution reactions as are the majority of Co(III) complexes. When the Co(III) ion becomes involved in a macrocyclic that has a "delocalized" electronic structure, the complex might be kinetically labile. The lability follows the breakdown of the Co(III) oxidation-state formalism. The problem of the oxidation state of transition metals in complexes with delocalized electronic structures has been a very active one recently.[25,26]

At present there is no way to give a quantitative description of the electronic structure of cobalt complexes to be able to determine *a priori* which complexes will be labile and which inert.[27]

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Kinetics and Mechanism of Substitution Reactions of Dinitrosyldicarbonyliron(0)

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Abstract: Dinitrosyldicarbonyliron(0) undergoes carbon monoxide substitution reactions in the presence of phosphines, phosphites, and triphenylarsine to give the monosubstituted derivatives, $Fe(NO)_2(CO)L$. The preparation and spectra of several mono- and disubstituted derivatives are reported. The rates of these reactions depend on the concentration and nature of reagent. For reagents with the same donor atom, the rates of reaction increase with increasing basicity (or polarizability) of the reagents. The results obtained support a bimolecular displacement mechanism with nucleophilic attack by the entering reagent on the class b or soft iron(0). This is discussed in terms of the nature of the chemical bonding in $Fe(NO)_2(CO)_2$.

Studies of the kinetic behavior of metal carbonyls is a subject of considerable current interest.[2] Many of the metal carbonyl substrates studied are found to undergo CO substitution reactions by a first-order process. From reactions of this type one can obtain information on the factors which affect the reactivities of different substrates but not on factors that contribute to the nucleophilic strengths of various reagents toward metal carbonyls.

Since Heck[3] reported briefly that the rate of the reaction of $Co(NO)(CO)_3$ with $(C_6H_5)_3P$ was first order in both substrate and reagent concentrations, there has been a continued effort to investigate metal carbonyl systems which undergo CO substitution reactions by a second-order process. From reactions of this type, one obtains information on the factors which affect the reactivities of different substrates, but, more important, one can also obtain useful information concerning the factors which contribute to the nucleophilic strength of various reagents toward these substrates.

Recent studies on $Co(NO)(CO)_3$[4,5] and $Mn(NO)_3(CO)$[6] have shown that these two members of the pseudo-tetracarbonylnickel series undergo CO substitution reactions in part by a second-order process. This is in contrast to the CO substitution[3,7] and ^{14}CO exchange[7,8] reactions of the isoelectronic and isostructural $Ni(CO)_4$. Both of these reactions were found to be first-order in $Ni(CO)_4$ and independent of the concentration of the entering reagent.

This paper reports the kinetic data concerning the first step of CO substitution of $Fe(NO)_2(CO)_2$

$$Fe(NO)_2(CO)_2 + L \longrightarrow Fe(NO)_2(CO)L + CO \quad (1)$$

where L = phosphines, phosphites, or triphenylarsine. This is an extension of a study of the kinetic behavior of members of the pseudo-tetracarbonylnickel series. Previously it had been reported[9] that the ^{14}CO exchange

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of $Fe(NO)_2(CO)_2$ in benzene solution at 25° has a half-life of 400 hr. This is the only report in the literature of kinetic work on this substrate.

Also described in this paper are the synthesis and characterization of some of the monosubstituted derivatives of $Fe(NO)_2(CO)_2$.

Experimental Section

Dinitrosyldicarbonyliron(0). The dinitrosyldicarbonyliron(0), $Fe(NO)_2(CO)_2$, was prepared according to the method of Hieber and Beutner[10] with some minor modifications. It was identified by its infrared spectrum.

Reagents. The reagents $(C_6H_5)_3P$ and PCl_3 were obtained commercially and used without further purification. The $(n\text{-}C_4H_9)_3P$ was obtained commercially but was distilled under nitrogen before use. The $(n\text{-}C_4H_9O)_3P$ and $(C_6H_5O)_3P$ were obtained commercially. Before use they were each dissolved in a suspension of sodium in ether, allowed to stand overnight, and then fractionally distilled under nitrogen. The $(C_6H_5)_3As$, which was obtained commercially, was recrystallized from methanol before use. The $(C_6H_{11})_3P$,[11] $(C_2H_5)_3P$,[12] $(C_2H_5)_2(C_6H_5)P$,[12] $(C_2H_5)(C_6H_5)_2P$,[12] $(p\text{-}CH_3OC_6H_4)_3P$,[12] and $P(OCH_2)_3CCH_3$[13] were prepared by methods described in the literature. The $(C_6H_5)_2PC_2H_4P(C_6H_5)_2$ was prepared by the method of Chatt and Hart[14] but was purified by chromatography on silica gel.

Solvents. All of the solvents were distilled in an atmosphere of nitrogen. Toluene and hexane were refluxed over and distilled from sodium. Dichloromethane was refluxed over and distilled from phosphorus pentoxide. Tetrahydrofuran was refluxed over and distilled from sodium and benzophenone. All of these solvents were stored under nitrogen.

Stock Solutions. Stock solutions of $Fe(NO)_2(CO)_2$ in an appropriate solvent were prepared, stored, and used in exactly the same manner as was described for $Co(NO)(CO)_3$.[4]

Preparation of Complexes. Several of the monosubstituted derivatives of $Fe(NO)_2(CO)_2$ obtained in this kinetic study had previously been prepared and reported in the literature. Therefore, when studying the kinetics of a reaction which produced one of these known products, the infrared spectrum of the final reaction mixture was compared to the published spectrum for the product. Thus the following products were not isolated in this work but have been reported elsewhere: $Fe(NO)_2(CO)[(C_6H_5)_3P]$,[15] $Fe(NO)_2(CO)[(C_6H_5O)_3P]$,[16] $Fe(NO)_2(CO)[(C_6H_5)_3As]$,[16] and $Fe(NO)_2(CO)[(C_6H_{11})_3P]$.[17]

All new complexes prepared during this work were prepared under an atmosphere of nitrogen using tetrahydrofuran as a solvent. This solvent was chosen for two reasons: (1) the high volatility which makes it easy to remove, and (2) from the kinetic studies it was found that even poor reagents react rapidly with $Fe(NO)_2(CO)_2$ in this solvent.[18] Approximately 1:1 molar ratios of $Fe(NO)_2(CO)_2$ to reagent were used in every case. All the chromatographic separations were carried out in air on silica gel.

$Fe(NO)_2(CO)[(n\text{-}C_4H_9)_3P]$. A tetrahydrofuran solution (5 ml) containing 0.26 g (1.5 mmoles) of $Fe(NO)_2(CO)_2$ and 0.37 ml (1.5 mmoles) of $(n\text{-}C_4H_9)_3P$ was allowed to stand at room temperature for *ca.* 1 hr. The volatile materials were removed under reduced pressure (*ca.* 25 mm at 25°). The residue was chromatographed on silica gel using a 1:1 mixture of dichloromethane and hexane as an eluent. Some decomposition occurred on the column. The solvent of the effluent was removed under reduced pressure (*ca.* 25 mm) at 40°. The red oil that remained was kept under high vacuum overnight (10^{-4} mm). The final product was a dark red oil.

Anal. Calcd for $Fe(NO)_2(CO)[(n\text{-}C_4H_9)_3P]$: C, 45.10; H, 7.86; N, 8.09. Found: C, 45.06; H, 7.89; N, 8.11.

The C–O and N–O stretching frequencies of this compound, as well as other $Fe(NO)_2(CO)L$ and $Fe(NO)_2L_2$ compounds, are presented in Table I.

Table I. C–O and N–O Stretching Frequencies for $Fe(NO)_2(CO)L$ and $Fe(NO)_2L_2$ Compounds[a]

L	Solvent[b]	ν(C–O), cm^{-1}	ν(N–O), cm^{-1}
	$Fe(NO)_2(CO)L$		
CO	T	2090, 2040	1810, 1766
$(n\text{-}C_4H_9O)_3P$	D	2039	1779, 1727
$P(OCH_2)_3CCH_3$	D	2034	1786, 1736
$(C_6H_5O)_3P$	T	2029	1782, 1739
$(C_6H_5)_3As$	D	2019	1768, 1723
$(C_6H_5)_2PC_2H_4P(C_6H_5)_2$[c]	T	2012	1759, 1716
$(C_6H_5)_3P$	T	2010	1766, 1725
$(C_2H_5)(C_6H_5)_2P$[c]	D	2007	1758, 1714
$(p\text{-}CH_3OC_6H_4)_3P$[c]	T	2007	1757, 1714
$(C_2H_5)_2(C_6H_5)P$[c]	D	2006	1759, 1713
$(n\text{-}C_4H_9)_3P$	D	2002	1753, 1708
$(C_2H_5)_3P$[c]	T	2000	1755, 1710
$(C_6H_{11})_3P$	T	1993	1750, 1703
	$Fe(NO)_2L_2$		
$P(OCH_2)_3CCH_3$	D		1765, 1708
$(n\text{-}C_4H_9O)_3P$[c]	D		1733, 1682
$(C_6H_5)_2PC_2H_4P(C_6H_5)_2$	THF		1726, 1679
$(C_6H_5)_3As$	M		1725, 1677
$(C_6H_5)_3P$	M		1714, 1674
$(C_2H_5)(C_6H_5)_2P$[c]	D		1709, 1661

[a] All spectra were calibrated with polystyrene film using the peaks at 1946 and 1602 cm^{-1}. [b] T = toluene, D = dichloromethane, THF = tetrahydrofuran, M = methanol. [c] This $Fe(NO)_2(CO)_2$ derivative has not been isolated.

$Fe(NO)_2(CO)[(n\text{-}C_4H_9O)_3P]$. This compound was prepared and purified in a manner very similar to that used for $Fe(NO)_2(CO)[(n\text{-}C_4H_9)_3P]$. The final product was a red oil.

Anal. Calcd for $Fe(NO)_2(CO)[(n\text{-}C_4H_9O)_3P]$: C, 39.61; H, 6.90; N, 7.11. Found: C, 39.44; H, 7.17; N, 7.19.

During the chromatography a second slower moving band was observed on the column. It was eluted and the infrared spectrum was taken in the C–O and N–O stretching regions (see Table I). The compound was assumed to be $Fe(NO)_2[(n\text{-}C_4H_9O)_3P]_2$.

$Fe(NO)_2(CO)[P(OCH_2)_3CCH_3]$. This compound was prepared and purified in a manner very similar to that used for $Fe(NO)_2(CO)[(n\text{-}C_4H_9)_3P]$. The final product was an orange-red crystalline solid.

Anal. Calcd for $Fe(NO)_2(CO)[P(OCH_2)_3CCH_3]$: C, 24.68; H, 3.11; N, 9.60. Found: C, 24.80; H, 3.54; N, 8.57.

During the chromatography a second slower moving band was observed on the column. It was eluted with dichloromethane. The solvent from this effluent was removed under reduced pressure (25 mm) at 40°. The powder left was dissolved under nitrogen in a dichloromethane–hexane mixture and cooled. After sitting overnight at 0°, orange crystals precipitated. They were filtered, washed with hexane, and dried overnight in an oil pump vacuum (10^{-1} mm).

Anal. Calcd for $Fe(NO)_2[P(OCH_2)_3CCH_3]_2$: C, 29.15; H, 4.40; N, 6.80, Found: C, 29.34; H, 4.52; N, 6.21.

Other mono- and disubstituted derivatives of $Fe(NO)_2(CO)_2$ were relatively unstable and, therefore, were not isolated. They were identified by comparing their infrared spectra with the spectra of known mono- or disubstituted derivatives (see Table I).

Analyses. Analyses were performed by Microtech Laboratories, Skokie, Ill. Miss H. Beck of Northwestern University, and Dr. A. Bernhardt of the Max Planck Institut für Kohlenforschung, Höhenweg, West Germany.

Infrared Spectra. Infrared spectra were recorded using a Perkin-Elmer Model 337 spectrophotometer equipped with an external recorder.

Kinetic Studies. The rates of the substitution reactions (reaction 1) were followed by monitoring changes in the infrared spectrum of the reaction mixture and/or by measuring the volume of CO evolved.

All kinetic studies were carried out under pseudo-first-order conditions. A preliminary study showed that $Fe(NO)_2(CO)_2$ obeyed the Beer-Lambert law in the C–O stretching region, the extinction coefficient of the 2090 cm^{-1} band being 1100 M^{-1} cm^{-1} in toluene.

Most of the data were obtained by monitoring the infrared spectra since this method proved to be much more convenient than the

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gas evolution method. The reactions were carried out under nitrogen in an aluminum-foil-wrapped vessel fitted with a serum cap. The reagent solution was prepared under nitrogen and transferred into the reaction vessel by means of a syringe. After thermostating (*ca.* 20 min), a few tenths of a milliliter of a $Fe(NO)_2(CO)_2$ stock solution was injected into the reagent solution to start the reaction. The concentration of $Fe(NO)_2(CO)_2$ had to be between 3×10^{-3} and 2×10^{-2} M depending on the path length of the cells used. At appropriate time intervals aliquots were withdrawn from the reaction vessel with a syringe and transferred into the infrared cell, and their infrared spectra were measured against a reference containing only the solvent or the reagent solution. Anywhere between 10 and 20 measurements were made during a period of three or four half-lives. Since an excess of reagent was used and since CO is liberated, all of the reactions went to completion. The disappearance of the highest energy C–O stretching band (2090 cm^{-1}) of the $Fe(NO)_2(CO)_2$ was usually monitored. The absorbance A was determined at each time interval from the equation $A = \log T_\infty/T$, where T is the transmittance of the peak being monitored at time T, and T_∞ is the transmittance of the base line. A_∞ was always zero since the $Fe(NO)_2(CO)_2$ always disappeared completely. Good linear plots were obtained from the data by plotting log $(A - A_\infty)$ *vs.* time.

A few reactions were too fast to follow by the conventional aliquot method. In such instances, the reactants were prepared, thermostated, and mixed together in the normal manner. However, as soon as they were mixed an aliquot was transferred into a thermostated infrared cell with the frequency on the instrument set at 2090 cm^{-1} (corresponding to the highest energy C–O stretching band of $Fe(NO)_2(CO)_2$), and the change in absorbance was followed continuously by means of the variable speed external recorder.

The CO evolution data were obtained using the gasometric apparatus described earlier.[19] The experimental infinite time volume was always in good agreement with the calculated volume corresponding to the release of 1 mole of CO per mole of $Fe(NO)_2(CO)_2$.

The second-order rate constants obtained by the infrared and CO evolution methods were in good agreement with each other. The pseudo-first-order rate constants obtained from duplicate runs of the same reaction were reproducible to 5% or better. The second-order rate constants obtained from reactions with the same reagent but at different reagent concentrations were reproducible to 10% or better in most cases. The values of $\Delta H^\ddagger$ are estimated to be accurate to ± 0.9 kcal/mole and $\Delta S^\ddagger$ to ± 3 eu.

Results

All rate constants were determined from the disappearance of the highest energy C–O stretching band of $Fe(NO)_2(CO)_2$ (2090 cm^{-1}) unless otherwise noted.

Phosphines, Phosphites, and Triphenylarsine. The data collected from kinetic studies of reaction 1 when L is a phosphine, phosphite, or triphenylarsine show a definite dependence of the pseudo-first-order rate constants on the concentration and type of reagent L used. Some sample data taken from reaction 1 when L = $(C_6H_5)_3P$ are shown in Table II. Figure 1 illustrates the dependence of the pseudo-first-order rate constants on the reagent concentration of various reagents in toluene. The data collected in this solvent and also in dichloromethane are in accord with the rate law given by

$$\text{rate} = k_2[Fe(NO)_2(CO)_2][L] \qquad (2)$$

The plot shown in Figure 1 has a zero intercept which is required by this rate law. Under the conditions of these experiments there is no detectable contribution of a first-order reaction path[5] to the rate of reaction. Table III summarizes the second-order rate constants k_2 for reaction 1 and also gives the relative basicities[20,21] of the reagents L involved. The activation parameters of reaction 1 are presented in Table IV.

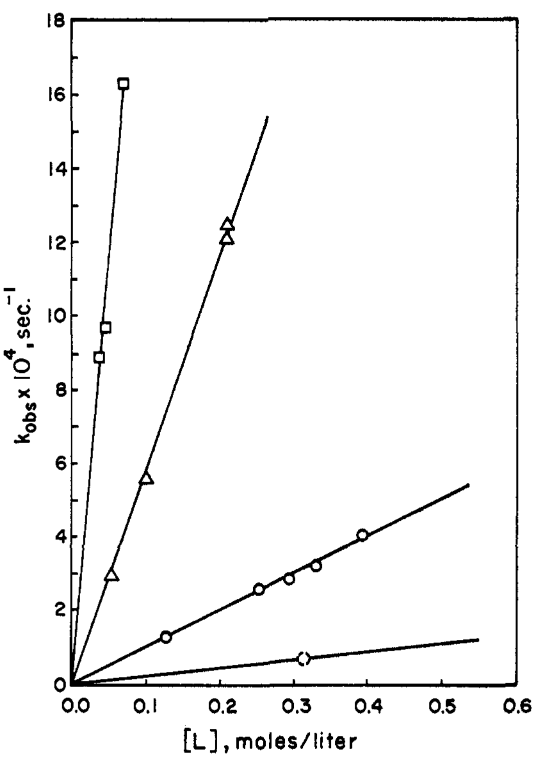

Figure 1. Plot of k_{obsd} *vs.* [L] for the reactions of $Fe(NO)_2(CO)_2$ with L in toluene at 25°: □, L = $(C_6H_{11})_3P$; △, L = $(C_2H_5)(C_6H_5)_2P$; ○, L = $(C_6H_5)_3P$; ◇, L = $P(OCH_2)_3CCH_3$.

Table II. Pseudo-First-Order Rate Constants[a] for the Reaction $Fe(NO)_2(CO)_2 + (C_6H_5)_3P \longrightarrow Fe(NO)_2(CO)[(C_6H_5)_3P] + CO$

$[(C_6H_5)_3P]$, M	Temp, °C	k_{obsd}, sec^{-1}
	In Toluene	
0.126	25	1.2×10^{-4}
0.253	25	2.6×10^{-4}
0.294	25	2.8×10^{-4} [b]
0.318	25	3.3×10^{-4}
0.393	25	4.0×10^{-4}
0.148	35	3.6×10^{-4}
0.059	45	3.3×10^{-4}
	In Dichloromethane	
0.050	25	0.55×10^{-4}
0.201	25	2.1×10^{-4}
0.618	25	6.3×10^{-4}
0.600	15	2.3×10^{-4}
0.123	35	3.1×10^{-4}

[a] All rate constants were obtained by following the disappearance of the $Fe(NO)_2(CO)_2$ in the C–O and/or N–O stretching regions of the infrared unless otherwise noted. [b] This rate constant was obtained from a gas-evolution experiment.

Second-order rate constants and activation parameters have also been determined for reaction 1 using tetrahydrofuran as a solvent.[18] They agree with the corresponding second-order rate constants and activation parameters listed here for reaction 1 in toluene and dichloromethane. However, in tetrahydrofuran (and methanol), a large first-order rate constant is found also. This solvent effect, as well as the kinetic behavior of $Fe(NO)_2(CO)_2$ in the presence of amines, halide ions, etc., will be reported elsewhere.[18]

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Table III. Second-Order Rate Constants[a] for the Reaction $Fe(NO)_2(CO)_2 + L \longrightarrow Fe(NO)_2(CO)L + CO$

L	Solvent[b]	k_2, M^{-1} sec^{-1}	ΔHNP, mV[c]
	At 25°		
$(C_2H_5)_3P$[f]	T	Very fast	111
$(n\text{-}C_4H_9)_3P$	T	2.9×10^{-1}	131
$(C_2H_5)_2(C_6H_5)P$[f]	T	4.8×10^{-2}	300
$(C_6H_{11})_3P$	T	2.3×10^{-2}	33
$(n\text{-}C_4H_9O)_3P$	T	6.6×10^{-3}	530[d]
$(C_2H_5)(C_6H_5)_2P$[f]	T	6.0×10^{-3}	400[d]
$(p\text{-}CH_3OC_6H_4)_3P$[f]	T	5.5×10^{-3} [e]	439[d]
$(C_6H_5)_2PC_2H_4P(C_6H_5)_2$[f]	T	5.1×10^{-3}	...
$(C_6H_5)_3P$	T	1.0×10^{-3}	573
$(C_6H_5)_3P$	D	1.0×10^{-3}	573
$P(OCH_2)_3CCH_3$	T	2.3×10^{-4} [e]	665[d]
$(C_6H_5O)_3P$	T	1.3×10^{-5}	875
PCl_3	T	0	...
$(C_6H_5)_3As$	T	1.5×10^{-5}	...
$(C_6H_5)_3As$	D	2.0×10^{-5}	...
	At 15°		
$(C_6H_5)_3P$	D	3.8×10^{-4} [e]	...
	At 35°		
$(C_6H_5)_2PC_2H_4P(C_6H_5)_2$	T	1.2×10^{-2} [e]	...
$(C_6H_5)_3P$	T	2.4×10^{-3} [e]	...
$(C_6H_5)_3P$	D	2.5×10^{-3} [e]	...
$(C_6H_5)_3As$	T	6.0×10^{-5} [e]	...
$(C_6H_5O)_3P$	T	5.3×10^{-5} [e]	...
	At 45°		
$(C_6H_5)_2PC_2H_4P(C_6H_5)_2$	T	2.6×10^{-2} [e]	...
$(C_6H_5)_3P$	T	5.5×10^{-3} [e]	...
$(C_6H_5)_3As$	T	2.0×10^{-4} [e]	...
$(C_6H_5O)_3P$	T	1.5×10^{-4} [e]	...

[a] All of the second-order rate constants were determined from the slopes of plots of the pseudo-first-order rate constants *vs.* the reagent concentrations unless otherwise noted. Experimental rate constants at different conditions are available in ref 1. [b] T = toluene, D = dichloromethane, THF = tetrahydrofuran. [c] Difference in half-neutralization potential between L and N,N'-diphenylguanidine in nitromethane; the smaller ΔHNP, the more basic is L.[20] [d] From ref 4. [e] Second-order rate constant was determined by dividing the pseudo-first-order rate constant by the reagent concentration. [f] This $Fe(NO)_2(CO)L$ compound has not been isolated.

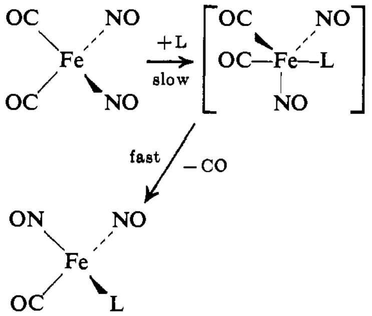
Table IV. Activation Parameters for the Reaction $Fe(NO)_2(CO)_2 + L \longrightarrow Fe(NO)_2(CO)L + CO$

Solvent	L	$\Delta H^{\ddagger}$, kcal/mole	$\Delta S^{\ddagger}$ (298°), eu
Toluene	$(C_6H_5)_2PC_2H_4P(C_6H_5)_2$[a]	15	−19
Toluene	$(C_6H_5)_3P$	16	−20
Toluene	$(C_6H_5O)_3P$	22	−7
Toluene	$(C_6H_5)_3As$	24	−1
Dichloromethane	$(C_6H_5)_3P$	16	−19

[a] This $Fe(NO)_2(CO)L$ compound has not been isolated.

Discussion

Kinetic studies on reaction 1 have shown that the rates of this reaction are dependent on the nature and concentration of the entering reagent L. This is in agreement with what has already been found for $Co(NO)(CO)_3$[4] and $Mn(NO)_3(CO)$,[6] but contrary to what was found for $Ni(CO)_4$.[3,7,8] In the solvents toluene or dichloromethane at the reagent concentrations used, the rate data conform to a simple second-order rate law given by eq 2. Figure 1 demonstrates the dependence of the pseudo-first-order rate constants on the nature and concentration of the reagent. These results suggest that substitution involves a bimolecular displacement mechanism perhaps of the type shown by eq 3.



(3)

The five-coordinated species is assumed to be an active intermediate because stable compounds of this type are known. It perhaps is a trigonal bipyramid, since there is considerable precedence for such a structure in systems containing π-bonding ligands. Compounds such as $Fe(CO)_5$,[22] $Mn(NO)(CO)_2[(C_6H_5)_3P]_2$,[23] $Rh[(C_6H_5)_3P]_3(CO)(H)$,[24] and $[Pt(SnCl_3)_5]^{3-}$,[25] all of which contain very good π-bonding ligands, are known to be trigonal bipyramidal.

The difference between NO and CO is believed to be largely responsible for the difference in kinetic behavior of the $Ni(CO)_4$, which reacts by a first-order process, and $Fe(NO)_2(CO)_2$ (as well as $Co(NO)(CO)_3$ and $Mn(NO)_3(CO)$), which reacts by a second-order process. It has been suggested[4] that although the nitric oxide is present in the ground state of these compounds as NO^+, it may be present in the transition state as NO^-. This makes available a vacant orbital of low energy on the metal which can then readily accept a pair of electrons from the entering nucleophile and facilitate a bimolecular reaction.

Since the reactions of $Fe(NO)_2(CO)_2$ are second-order, it is possible to determine the nucleophilic strengths of the various regents toward this substrate. There are three important properties that a reagent may have which determine its nucleophilic strength. These are basicity, polarizability, and π-bonding ability. The results in Table III indicate that for a series of reagents, all of which have phosphorus as their donor atom, the rates of reaction with $Fe(NO)_2(CO)_2$ increase with increasing basicity[20,21] of the reagent. This same behavior has been reported for the same reagents in reactions with $Co(NO)(CO)_3$,[4] $Mn(NO)(CO)_4$,[6] $(C_5H_5)Rh(CO)_2$,[26] *trans*-$[Pt(py)_2Cl_2]$[27], and CH_3I.[27] However, it has been suggested that, as long as the donor atom of the reagent is held constant, a measure of basicity directly parallels a measure of polarizability,[4,26] and therefore the nucleophilic strength of various reagents toward all of these substrates may be largely determined by polarizability rather than by basicity. Since the iron in $Fe(NO)_2(CO)_2$ is in a very low oxidation state, it is a class b[28] or soft[29] metal and reacts faster with the more polarizable or softer reagents.

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Figure 2 shows a linear free-energy relationship between the second-order rate constant of reaction 1 in toluene at 25° and the basicity (or polarizability) of the corresponding reagent in nitromethane solution. The relative basicities of the reagents were measured by Streuli[20] using perchloric acid in nitromethane and recording the difference in half-neutralization potentials, ΔHNP, from that of N,N′-diphenylguanidine taken as a standard. The low reactivity of $(C_6H_{11})_3P$ is believed to be due to steric effects caused by the methylene groups adjacent to phosphorus.[26]

The results also indicate that the phosphines are better reagents toward $Fe(NO)_2(CO)_2$ than are the corresponding phosphites. Since phosphites are considered to be better π bonders in these systems than are phosphines,[30] it follows that the π-bonding ability of a reagent is not a predominant factor in determining its nucleophilic strength. Also in support of this is the observation that PCl_3 which is a good π-bonding reagent does not react with $Fe(NO)_2(CO)_2$ at 25°.

The activation parameters for reaction 1 are presented in Table IV. The negative entropies of activation are in accord with a bimolecular displacement process. In toluene, it might be noticed that there is a general increase in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ as the reagent is changed from 1,2-bis(diphenylphosphino)ethane to triphenylphosphine to triphenyl phosphite to triphenylarsine. Thus in the transition state involving the 1,2-bis(diphenylphosphino)ethane and $Fe(NO)_2(CO)_2$, the activation parameters indicate an appreciable amount of bond making. However, in the transition state involving triphenylarsine and $Fe(NO)_2(CO)_2$, the almost positive entropy of activation and the relatively higher enthalpy of activation indicate that bond breaking has become more important relative to the 1,2-bis(diphenylphosphino)ethane case. In other words, the reaction involving the triphenylarsine is more of a dissociation reaction than the reaction involving 1,2-bis(diphenylphosphine)ethane, which is in accord with the nucleophilic character of these two reagents.

The results in Tables II–IV show that the dielectric strength of the solvent has little or no effect on the CO substitution reactions of $Fe(NO)_2(CO)_2$. However, the coordinating ability does have a large effect. This is shown by the fact that these same reactions with $Fe(NO)_2(CO)_2$ have large first-order rate constants in tetrahydrofuran and methanol. Solvent and catalytic effects on these reactions are described in the following paper.[18]

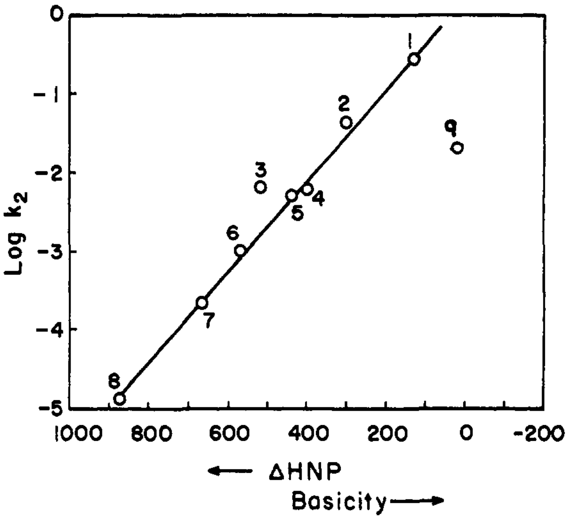

Figure 2. The linear free-energy relationship of the basicity (polarizability) of the reagent with the rate of reaction of $Fe(NO)_2(CO)_2$ in toluene at 25° with the reagents: (1) $(n\text{-}C_4H_9)_3P$; (2) $(C_2H_5)_2(C_6H_5)P$; (3) $(n\text{-}C_4H_9O)_3P$; (4) $(C_2H_5)(C_6H_5)_2P$; (5) $(p\text{-}CH_3OC_6H_4)_3P$; (6) $(C_6H_6)_3P$; (7) $P(OCH_2)_3CCH_3$; (8) $(C_6H_5O)_3P$; (9) $(C_6H_{11})_3P$.

The infrared spectra of compounds of the type $Fe(NO)_2(CO)L$ and $Fe(NO)_2L_2$ are summarized in Table I. The N–O stretching bands of both types of compounds are in the region where nitric oxide is considered to be bonding as NO^+.[31] The shifts of both the C–O and N–O stretching bands are to lower energy or smaller wave numbers as one goes from $Fe(NO)_2(CO)_2$ to $Fe(NO)_2(CO)L$ to $Fe(NO)_2L_2$. This is in accord with L being a better σ donor and poorer π acceptor than CO. Both of these effects put more electron density on the metal in the substituted compounds which is then delocalized into the antibonding orbitals of the remaining CO and NO groups. This in turn lowers their bond orders which shows up in the infrared as lower C–O and N–O stretching frequencies. The phosphines which are poorer π bonders than phosphites[30] show larger shifts to lower energy than the phosphites.

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