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Kinetics and Mechanism of Ligand Substitution in Iron Tricarbonyl 1,4-Dimethyltetraazabutadiene

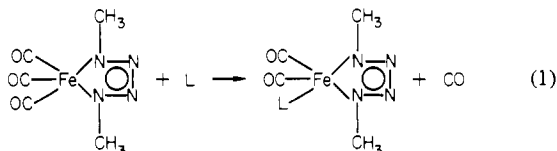
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Thermal carbon monoxide substitution in $\text{Fe}(\text{CO})_3(\text{N}_4\text{Me}_2)_2$ proceeds readily to form monosubstituted products $\text{Fe}(\text{CO})_2\text{L}(\text{N}_4\text{Me}_2)$ with $\text{L} = \text{PMe}_3, \text{PMe}_2\text{Ph}, \text{PBu}_3, \text{PEt}_2\text{Ph}, \text{P}(\text{OEt})_3, \text{P}(\text{OMe})_3, \text{PH}_2\text{Ph}, \text{P}(\text{c-Hx})_3, \text{PPh}_3, \text{AsMe}_3, \text{AsEt}_3, \text{AsMe}_2\text{Ph}, 4\text{-CNpy}$, and Me_3CNC . Bis- and trisubstituted products are also observed in the case of *tert*-butyl isocyanide. The substitution proceeds solely by a second-order process with a rate law that is first order in both $\text{Fe}(\text{CO})_3(\text{N}_4\text{Me}_2)_2$ and entering ligand. In addition, the rate is strongly dependent on the nature of the ligand, particularly its size and basicity. Activation parameters further support the associative nature of the reaction in toluene: $\text{PMe}_3, \Delta H^\ddagger = 6.9 \pm 0.2 \text{ kcal/mol}, \Delta S^\ddagger = -31.4 \pm 0.7 \text{ eu}; \text{PBu}_3, \Delta H^\ddagger = 7.3 \pm 0.3 \text{ kcal/mol}, \Delta S^\ddagger = -38.6 \pm 1.1 \text{ eu}; \text{PEt}_2\text{Ph}, \Delta H^\ddagger = 7.3 \pm 0.1 \text{ kcal/mol}, \Delta S^\ddagger = -41.1 \pm 0.2 \text{ eu}; \text{P}(\text{OMe})_3, \Delta H^\ddagger = 11.0 \pm 0.2 \text{ kcal/mol}, \Delta S^\ddagger = -35.0 \pm 0.6 \text{ eu}; \text{Me}_3\text{CNC}, \Delta H^\ddagger = 11.6 \pm 0.5 \text{ kcal/mol}, \Delta S^\ddagger = -34.9 \pm 1.4 \text{ eu}; \text{AsMe}_3, \Delta H^\ddagger = 13.3 \pm 0.3 \text{ kcal/mol}, \Delta S^\ddagger = -34.3 \pm 0.9 \text{ eu}$. Likewise in methanol: $\text{AsMe}_3, \Delta H^\ddagger = 9.8 \pm 0.1 \text{ kcal/mol}, \Delta S^\ddagger = -34.2 \pm 0.2 \text{ eu}; \text{PPh}_3, \Delta H^\ddagger = 11.9 \pm 0.8 \text{ kcal/mol}, \Delta S^\ddagger = -38.8 \pm 1.6 \text{ eu}$. The rate of reaction is increased in polar solvents and to a greater extent in alcohol solvents, which are capable of hydrogen bonding with the tetraazabutadiene nitrogens. In the presence of excess BF_3 , the rate of substitution is increased by a factor of 10^6 . Factors which facilitate nucleophilic attack in $\text{Fe}(\text{CO})_3(\text{N}_4\text{Me}_2)_2$ are discussed and contrasted with the dissociative mechanisms found for other iron carbonyls.

Introduction

Iron tricarbonyl 1,4-dimethyltetraazabutadiene readily undergoes thermal carbon monoxide substitution to form the monosubstituted derivative $\text{Fe}(\text{CO})_2\text{L}(\text{N}_4\text{Me}_2)$ (eq 1). This



is in marked contrast to that which has been observed for other pentacarbonyl iron carbonyl compounds. Thus, $\text{Fe}(\text{CO})_5$,^{3,4} and $\text{Fe}(\text{CO})_4\text{PPh}_3$ ⁵ substitute CO very slowly only at elevated temperatures by a dissociative mechanism. A half-life of more than 4 years has been estimated for exchange of CO with $\text{Fe}(\text{CO})_5$.³ Similarly $\text{Fe}(\text{CO})_3(1,3\text{-diene})$ compounds react with phosphines only under forcing conditions.⁶⁻⁸ Furthermore, compounds of the type $\text{Fe}(\text{CO})_3(1,3\text{-heterodiene})$, where heterodiene is an α, β -unsaturated aldehyde, ketone, or Schiff base, have reaction mechanisms involving partial dissociation of the heterodiene moiety.^{9,10} The enhanced reactivity of $\text{Fe}(\text{CO})_3(\text{N}_4\text{Me}_2)_2$ may be due to the great π -acceptor ability of the tetraazabutadiene ligand¹¹ which rivals that of CO and could promote nucleophilic attack on the iron. We have ex-

amined the kinetics of ligand substitution in $\text{Fe}(\text{CO})_3(\text{N}_4\text{Me}_2)_2$, and the results reported here are indeed consistent with an associative reaction mechanism.

Experimental Section

Reagents. The substrate $\text{Fe}(\text{CO})_3(\text{N}_4\text{Me}_2)_2$ was prepared as previously described.¹² Ligands were obtained from Strem or Aldrich and used as received, except as noted below. (Dimethylphenyl)phosphine was obtained from ROC/RIC. Tri-*n*-butylphosphine, trimethyl phosphite, and triethyl phosphite were distilled from sodium under nitrogen. Triphenylphosphine was recrystallized from absolute ethanol and dried under vacuum. 4-Cyanopyridine was purified by sublimation. All solvents were distilled from appropriate drying agents under nitrogen and purged with nitrogen prior to use. Methanol-*d*₁ (Aldrich) was used as received. Boron trifluoride (Linde) was purified by trap-to-trap distillation, and the vapor pressure agreed with the literature value.¹³

Spectral Studies. All manipulations were carried out under an atmosphere of prepurified nitrogen with the use of standard inert-atmosphere techniques. In addition, room light was carefully excluded to avoid any photochemical reactions. Although these compounds are known to be photosensitive,¹⁴ no appreciable photochemical substitution was observed when a toluene solution containing $2.5 \times 10^{-3} \text{ M PPh}_3$ and $2.5 \times 10^{-4} \text{ M Fe}(\text{CO})_3(\text{N}_4\text{Me}_2)_2$ was exposed to the spectrometer's light beam for 6 h with the slit wide open.

The substitution products $\text{Fe}(\text{CO})_2\text{L}(\text{N}_4\text{Me}_2)$ were characterized by their IR and electronic spectra which are completely analogous to those reported for $\text{L} = \text{PPh}_3, \text{PMe}_3, \text{and P}(\text{OMe})_3$.¹⁴ Only monosubstitution products were observed except for $\text{L} = \text{Me}_3\text{CNC}$ when $\text{Fe}(\text{CO})(\text{Me}_3\text{CNC})_2(\text{N}_4\text{Me}_2)$ is formed. The tris(isocyanide) derivative is also slowly produced thermally. $\text{Fe}(\text{Me}_3\text{CNC})_3(\text{N}_4\text{Me}_2)$ was prepared by heating $\text{Fe}(\text{CO})_3(\text{N}_4\text{Me}_2)_2$ with a stoichiometric amount of Me_3CNC for 3 days at 70 °C in heptane. The IR spectrum showed peaks at 2115 and 2020 cm^{-1} , and the mass spectrum exhibited a parent ion at m/e 391.

Infrared spectra were recorded on a Perkin-Elmer 283 spectrometer using 0.5-mm NaCl cells. Visible spectra were recorded on a Cary 14 spectrophotometer using 1.00-cm quartz cells modified for work with air-sensitive compounds.

An adduct presumed to be $\text{Fe}(\text{CO})_3(\text{N}_4\text{Me}_2)_2 \cdot 2\text{BF}_3$ is formed when an excess of BF_3 is added to a solution of $\text{Fe}(\text{CO})_3(\text{N}_4\text{Me}_2)_2$. The

- (1) (a) Nankai University, Tianjin, People's Republic of China. (b) Northwestern University.
- (2) Abbreviations: (N_4Me_2), 1,4-dimethyltetraazabutadiene; L, ligand; Me, methyl; Et, ethyl; Bu, *n*-butyl; c-Hx, cyclohexyl; Ph, phenyl; 4-CNpy, 4-cyanopyridine; DAB, 1,4-diphenyl-2,3-dimethyl-1,4-diazabuta-1,3-diene.
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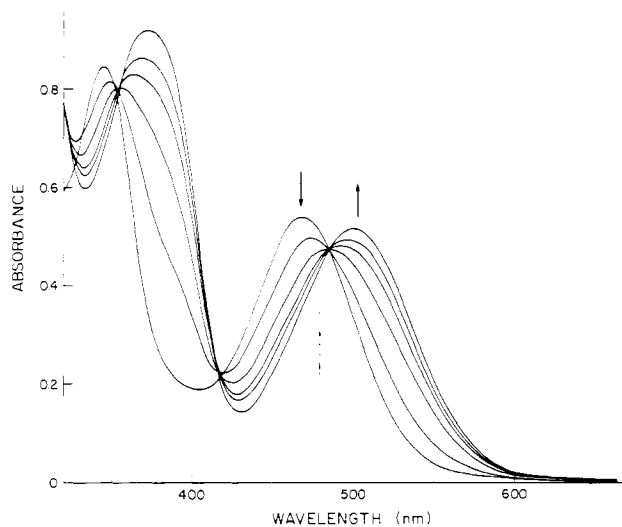


Figure 1. Visible spectral changes during the reaction between 2.03×10^{-4} M $\text{Fe}(\text{CO})_3(\text{N}_4\text{Me}_2)$ and 3.92×10^{-2} M PET_2Ph in toluene solution at 296 K.

complex is slightly soluble in toluene, and IR spectra in CH_2Cl_2 exhibit carbon monoxide stretching vibrations shifted to higher energy (2105, 2048 cm^{-1}) compared to the parent compound (2073, 2000 cm^{-1}). Coordination of BF_3 to the carbonyl oxygens may be discounted because the C–O stretching frequencies would be shifted to lower frequency in this instance. The reaction can be partially reversed by subjecting the solid adduct to vacuum.¹⁴ The analogous monosubstitution product $\text{Fe}(\text{CO})_2(\text{PPh}_3)(\text{N}_4\text{Me}_2) \cdot 2\text{BF}_3$ is rapidly formed when PPh_3 is added to a solution of $\text{Fe}(\text{CO})_3(\text{N}_4\text{Me}_2)$ that contains excess BF_3 . Again the ν_{CO} peaks are shifted to higher energy (2033, 1984 cm^{-1}) relative to the uncomplexed monophosphine complex (1994, 1937 cm^{-1}).

Kinetic Procedures. The rates of substitution were measured by observing changes in the visible spectra as a function of time in the thermostated (± 0.5 °C) cell compartment of the Cary 14. The cell, containing a solution of $\text{Fe}(\text{CO})_3(\text{N}_4\text{Me}_2)$, was allowed to thermally equilibrate in the spectrometer for at least 15 min. Reactions were then initiated by injecting neat ligand into the cell with a Hamilton gas-tight microliter syringe. The cell was vigorously shaken, and spectra were recorded as a function of time. A typical experiment may be found in Figure 1 for $\text{L} = \text{PET}_2\text{Ph}$. Isosbestic points are maintained at 483, 417, and 353 nm after injecting the ligand. The ligand-free spectrum does not pass through the isosbestic points at 417 and 353 nm partly because the free ligand contributes to the spectrum in the near UV.

Similar isosbestic points were observed for all reactions studied. Most of the kinetic data was obtained by monitoring the change in absorbance at a constant wavelength (usually between 450 and 550 nm) where both the product and substrate absorb. Reactions were conducted under pseudo-first-order conditions with the ligand concentration at least 1 order of magnitude greater than that of $\text{Fe}(\text{CO})_3(\text{N}_4\text{Me}_2)$. The concentration of $\text{Fe}(\text{CO})_3(\text{N}_4\text{Me}_2)$ was determined by measuring the absorbance of the solution at 467 nm (ϵ 2650)¹¹ before the ligand was added. Plots of $\ln(A_\infty - A_t)$ vs. time were linear ($R^2 > 0.995$) for more than 3 half-lives, and k_{obsd} was determined by calculating the slope of this line by the least-squares method. The rate of substitution for $\text{L} = \text{PMe}_3$ was also measured with the use of Applied Photophysics Ltd. Model 1705 stopped-flow spectrometer which was modified for work with air-sensitive compounds. Rate constants were reproducible to within 5%.

One experiment was conducted in which ca. 10% of the $\text{Fe}(\text{CO})_3(\text{N}_4\text{Me}_2)$ was allowed to decompose (by exposing the solution to the atmosphere) before the substitution kinetics were measured. The rate constant was identical with that previously measured, showing that small amounts of decomposition products would not alter the rate of reaction.

Results

The IR and electronic absorption spectral data for the substitution products are given in Table I. Infrared spectra

Table I. Spectral Data for $\text{Fe}(\text{CO})_2\text{L}(\text{N}_4\text{Me}_2)$ and Rate Constants for Reaction 1

L	λ_{max} , nm (ϵ , $\text{M}^{-1} \text{cm}^{-1}$)	ν_{CO} , cm^{-1} ^a	k , $\text{M}^{-1} \text{s}^{-1}$ ^b
CO	467 (2650)	2070, 2000	
PMe_3	492 (2860)	1989, 1933	41.0
PMe_2Ph	500 (2750)	1991, 1935	3.01
PBU_3	492 (2420)	1988, 1930	0.627
PET_2Ph	498 (2530)	1988, 1933	0.185
PMePh_2	502 (2410)	1991, 1934	1.60×10^{-2}
$\text{P}(\text{OEt})_3$	475 (2820)	2006, 1953	6.38×10^{-2}
$\text{P}(\text{OMe})_3$	473 (3100)	2009, 1952	1.90×10^{-2}
PH_2Ph	498 (1980)	2002, 1950	1.42×10^{-3}
$\text{P}(\text{c-Hx})_3$	492 (1940)	1981, 1923	1.80×10^{-5}
PPh_3	500 (2100)	1994, 1937	2.42×10^{-6}
PPh_3 ^c	514 (1590)	2033, 1984 ^d	3.21
AsMe_3	527 (1860)	1991, 1934	7.80×10^{-4}
AsEt_3	523 (1760)	1992, 1928	1.47×10^{-4}
AsMe_2Ph	529 (1780)	1991, 1934	7.83×10^{-5}
4-CNpy ^e		1995, 1938	7.83×10^{-4}
Me_3CNC		2006, 1962	6.67×10^{-3}
Me_3CNC ^f	520 (2500)	1944 ^g	1.25×10^{-3}

^a Solvent = heptane. ^b 343 K; solvent = toluene. ^c Mole ratio $\text{BF}_3:\text{PPh}_3:\text{Fe}(\text{CO})_3(\text{N}_4\text{Me}_2) = 43:10:1$; $\text{Fe}(\text{CO})_3(\text{N}_4\text{Me}_2) = 2.50 \times 10^{-3}$ M. ^d Solvent = dichloromethane. ^e Reaction did not go to completion. ^f Rate constant for reaction 3. ^g $\text{Fe}(\text{CO})_2(\text{Me}_3\text{CNC})_2(\text{N}_4\text{Me}_2)$.

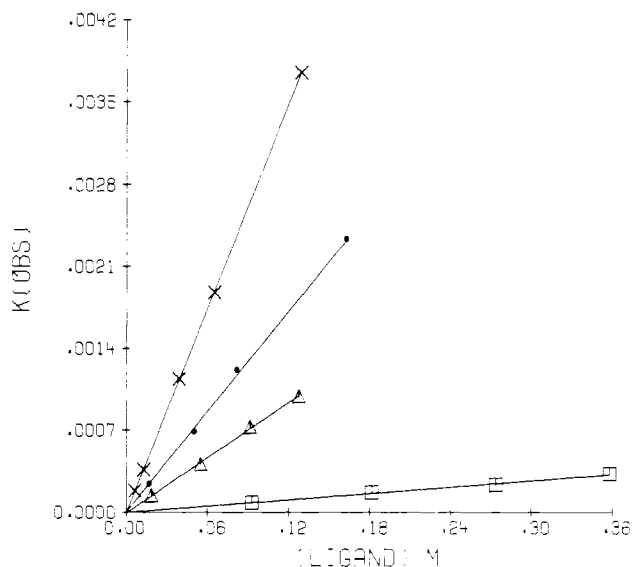


Figure 2. Plot of k_{obsd} (s^{-1}) vs. ligand concentration (M) for reaction 1: (x) $\text{L} = \text{PET}_2\text{Ph}$, $T = 296$ K; (o) $\text{L} = \text{P}(\text{OMe})_3$, $T = 343$ K; (Δ) $\text{L} = \text{Me}_3\text{CNC}$, $T = 343$ K; (\square) $\text{L} = \text{AsMe}_3$, $T = 343$ K.

indicate that monosubstituted products are formed for all the ligands studied. The preparation and complete characterization of the $\text{Fe}(\text{CO})_2\text{L}(\text{N}_4\text{Me}_2)$ compounds ($\text{L} = \text{PMe}_3$, PPh_3 , and $\text{P}(\text{OMe})_3$) will be reported elsewhere.¹⁴ Initial experiments with $\text{L} = \text{PET}_2\text{Ph}$ were carried out to determine the rate law. In addition, k_{obsd} was measured as a function of ligand concentration for $\text{L} = \text{P}(\text{OMe})_3$, Me_3CNC , and AsMe_3 . These results are shown in Figure 2, and the rate constants are available as supplementary material. The reaction is first order in $\text{Fe}(\text{CO})_3(\text{N}_4\text{Me}_2)$ and first order in incoming ligand. The y intercepts of the plots in Figure 2 are 0 for all ligands studied, which shows that there is no ligand independent substitution (i.e., dissociative) path under these experimental conditions. The second-order rate constants for all the ligands studied are presented in Table I. Table II lists the rate constants for the trivalent phosphorus ligands as well as cone angle and basicity data. Activation parameters are given in Table III. Complete tables of the rate constants as a function of temperature are

Table II. Cone Angle, Proton Basicity, and Rate Data for Phosphorus Ligands

ligand	cone angle ^a	ΔHNP^b	$\log k^c$
1 PMe_3	118	114	1.61
2 PMe_2Ph	122	281	0.48
3 $\text{P}(\text{Bu})_3$	132	131	-0.20
4 PEt_2Ph	136	300	-0.73
5 $\text{P}(\text{OEt})_3$	109	520 ^d	-1.20
6 $\text{P}(\text{OMe})_3$	107	580 ^e	-1.72
7 PPh_2Me	136	424	-1.80
8 PH_2Ph	101	917 ^e	-2.85
9 $\text{P}(\text{c-Hx})_3$	170	33	-4.74
10 PPh_3	145	573	-5.62

^a Reference 16. ^b Reference 22. ^c 343 K; solvent = toluene. ^d Value for $\text{P}(\text{OEt})_3$. ^e Estimated value. See ref 22-26.

Table III. Activation Parameters for Reaction 1^a

ligand	$k, \text{M}^{-1} \text{s}^{-1}^b$	$\Delta H^\ddagger, \text{kcal/mol}$	$\Delta S^\ddagger, \text{eu}$
PMe_3	41.0	6.9 ± 0.2	-31.4 ± 0.7
PBu_3	6.27×10^{-1}	7.3 ± 0.3	-38.6 ± 1.1
PEt_2Ph	1.85×10^{-1}	7.3 ± 0.1	-41.1 ± 0.2
$\text{P}(\text{OMe})_3$	1.90×10^{-2}	11.0 ± 0.2	-35.0 ± 0.6
Me_3CNC	6.67×10^{-3}	11.6 ± 0.5	-34.9 ± 1.4
AsMe_3	7.80×10^{-4}	13.3 ± 0.3	-34.3 ± 0.9
AsMe_3^c	1.43×10^{-1}	9.8 ± 0.1	-34.2 ± 0.2
PPh_3^c	6.53×10^{-4}	11.9 ± 0.8	-38.8 ± 1.6

^a Solvent = toluene. ^b 343 K. ^c Solvent = methanol.

Table IV. Rate of Reaction 1 in Various Solvents

solvent	ϵ_s^a $\text{M}^{-1} \text{cm}^{-1}$	$k, \text{M}^{-1} \text{s}^{-1}^b$
<i>n</i> -heptane	1.9	1.23×10^{-2}
toluene	2.4	3.03×10^{-2}
nitromethane	38.6	2.30×10^{-1}
acetonitrile	36.2	2.70×10^{-1}
ethanol	24.3	2.22
methanol	32.6	4.52
methanol- <i>d</i> ₁	32.6	4.40

^a Dielectric constant from ref 36. ^b $\text{L} = \text{PEt}_2\text{Ph}$; 296 K.

available as supplementary material.

When $\text{L} = \text{Me}_3\text{CNC}$, reactions 2-4 are observed. This was

$$\text{Fe}(\text{CO})_3(\text{N}_4\text{Me}_2) + \text{Me}_3\text{CNC} \rightarrow \text{Fe}(\text{CO})_2(\text{Me}_3\text{CNC})(\text{N}_4\text{Me}_2) + \text{CO} \quad (2)$$

$$\text{Fe}(\text{CO})_2(\text{Me}_3\text{CNC})(\text{N}_4\text{Me}_2) + \text{Me}_3\text{CNC} \rightarrow \text{Fe}(\text{CO})(\text{Me}_3\text{CNC})_2(\text{N}_4\text{Me}_2) + \text{CO} \quad (3)$$

$$\text{Fe}(\text{CO})(\text{Me}_3\text{CNC})_2(\text{N}_4\text{Me}_2) + \text{Me}_3\text{CNC} \rightarrow \text{Fe}(\text{Me}_3\text{CNC})_3(\text{N}_4\text{Me}_2) + \text{CO} \quad (4)$$

the only L which exhibited multiple thermal substitution. The rate of reaction 4 is significantly slower than those of reactions 2 and 3. Time-dependent visible spectral changes for these reactions are illustrated in Figure 3. An isosbestic point at 486 nm is observed in the early stages when reaction 2 is dominant and another isosbestic point ($\lambda = 560 \text{ nm}$) appears in the latter stages when reaction 3 predominates. Reaction 4 does not appreciably occur on these time scales.

The substitution reaction with PEt_2Ph was further examined in several different solvents as detailed in Table IV. It should be noted that the electronic spectrum of $\text{Fe}(\text{CO})_3(\text{N}_4\text{Me}_2)$ is insensitive to change in solvent.¹¹ The rate of substitution was also found to be greatly increased, by a factor of 10^6 , when carried out in the presence of BF_3 .

Discussion

In contrast to iron pentacarbonyl,^{3,4} $\text{Fe}(\text{CO})_3(\text{N}_4\text{Me}_2)$ readily undergoes thermal ligand substitution under mild

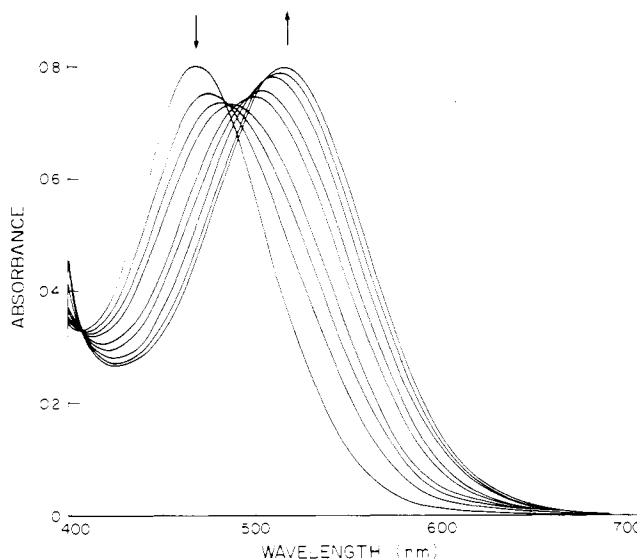


Figure 3. Visible spectral changes during the reaction between $3.09 \times 10^{-4} \text{ M Fe}(\text{CO})_3(\text{N}_4\text{Me}_2)$ and $9.18 \times 10^{-2} \text{ M Me}_3\text{CNC}$ in toluene solution at 373 K.

conditions. The reaction is first order in both $\text{Fe}(\text{CO})_3(\text{N}_4\text{Me}_2)$ and entering ligand, obeying the rate law given in eq 5. As can be seen from Figure 2, there is no ligand-in-

$$-d[\text{Fe}(\text{CO})_3(\text{N}_4\text{Me}_2)]/dt = k[\text{Fe}(\text{CO})_3(\text{N}_4\text{Me}_2)][\text{L}] \quad (5)$$

dependent substitution path even for the poorest nucleophiles studied. Substitution rate constants (Table I) exhibit extreme sensitivity toward the nature of the entering nucleophile, as would be expected for a bimolecular process. Small enthalpies and large negative entropies of activation (Table III) provide further evidence for an associative mechanism (A or I_a in the terminology of Langford and Gray¹⁵ or the classical $\text{S}_{\text{N}}2$ reaction in which a six-coordinate transition state is implicated).

An alternate possibility would be initial dissociation of one end of the N_4Me_2 ligand to yield a coordinately unsaturated complex. This species could then react with L to yield a new five-coordinate species which then quickly expels CO and recoordinates the N_4Me_2 ligand. If the rate of return of the coordinately unsaturated species competed with its associative reaction with L , then second-order kinetics would be found and at high $[\text{L}]$ saturation might be observed. We did not observe saturation behavior for any of the entering nucleophiles; however, this constitutes negative evidence. More direct arguments pertain to the activation parameters. It would be difficult to reconcile the low ΔH^\ddagger and large negative ΔS^\ddagger with a mechanism that involves dissociation of the strongly bound¹¹ tetraazabutadiene ligand. The latter mechanism should lead to a large ΔH^\ddagger and positive ΔS^\ddagger . Further evidence against the intermediacy of a "hot" coordinately unsaturated species derives from the large variation of the rate with entering nucleophile. A highly reactive (coordinately unsaturated) intermediate would not be expected to exhibit such selectivity.

Extensive studies have been made over a period of years on the reactivity of various nucleophiles toward different substrates. In general, the results of those studies show that reactivity depends upon steric and electronic factors. For the reactions of concern here, the effect of ligand size can be examined by comparing Tolman cone angles¹⁶ of several phosphorus ligands with their reactivities (Table II). A plot of this relationship, shown in Figure 4, reveals that cone angles alone do not correlate well with the experimental rate data.

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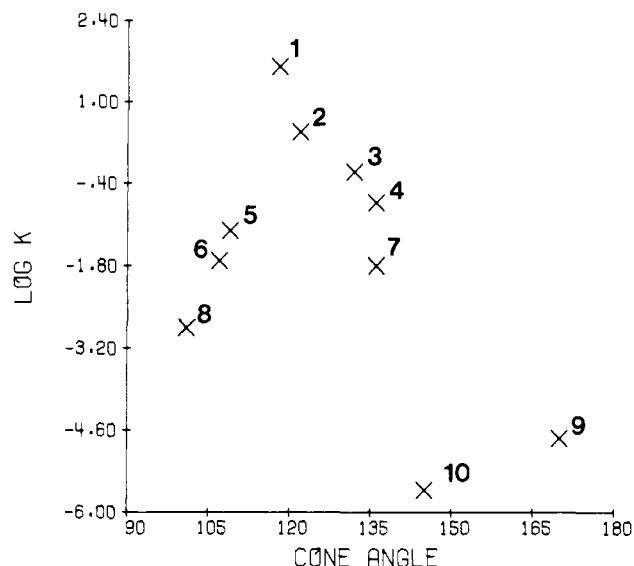


Figure 4. Plot of $\log k$ vs. cone angle for phosphorus ligands. The numbers correspond to those of Table II.

For example, the ligands PH_2Ph , $\text{P}(\text{OMe})_3$, and $\text{P}(\text{OEt})_3$ have the smallest cone angles but are not the most reactive. When the basicities are similar, then steric effects are evident, as for the relative rates $\text{PMe}_3 > \text{PMe}_2\text{Ph} > \text{PBu}_3 > \text{PEt}_2\text{Ph} > \text{PPh}_2\text{Me} > \text{P}(\text{c-Hx})_3$ (points 1, 2, 3, 4, 7, and 9 of Figure 4). Increased crowding in the transition state is further indicated by the progressively more negative entropies of activation in the series $\text{PMe}_3 > \text{PBu}_3 > \text{PEt}_2\text{Ph}$. These data support the view that both the size and basicity of the entering ligand effects its reactivity.

Electronic effects on nucleophilic reactivity are much more difficult to assess than are steric factors. It does appear that nucleophilic strengths depend on the proton basicity and the polarizability of the nucleophile.¹⁷⁻¹⁹ This is often discussed in terms of the phenomena of hard and soft²⁰ or E and C.²¹ Transition-metal coordination chemistry abounds with discussions of the relative contributions of σ and π bonding to the coordinate bond. It is possible to make a qualitative assessment of the importance of proton basicity on ligand reactivity toward this substrate from the data plotted in Figure 5. The relative basicity of the phosphorus ligands is given by the difference in half-neutralization potentials, ΔHNP , from that of *N,N'*-diphenylguanidine taken as standard measured in nitromethane (Table II).²²⁻²⁶

The results show that the nucleophilic strengths of phosphorus ligands intensify with increasing proton basicity of the ligand.²⁶ A good correlation is seen (Figure 5) for the five smallest ligands with cone angles less than 122° . Steric repulsions do not appear to be important²⁷ in octahedral cobalt(III) complexes until the cone angle of the bound phosphine exceeds ca. 120° . This provides an analogue to estimate

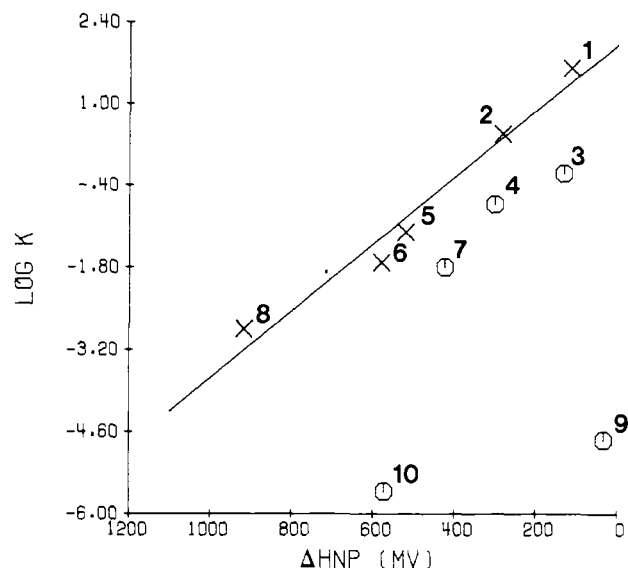


Figure 5. Plot of $\log k$ vs. ΔHNP for phosphorus ligands numbered as in Table II. Small ligands, for which steric effects are expected to be small, are represented by \times and larger ligands by \circ .

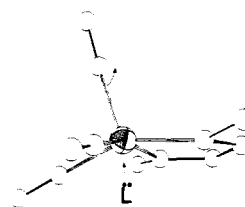


Figure 6. Possible mechanism of attack of donor ligand L on $\text{Fe}(\text{CO})_3(\text{N}_4\text{Me}_2)$. Note that a pseudooctahedral transition state could be achieved with minimal reorganization. The experimental geometry²⁹ of solid $\text{Fe}(\text{CO})_3(\text{N}_4\text{Me}_2)$ was used to construct this figure.

the steric requirements of the presumed pseudooctahedral transition state (Figure 6) in the $\text{Fe}(\text{CO})_3\text{L}(\text{N}_4\text{Me}_2)$ activated complex. As the ligand size increases above the 122° cone angle, substitution proceeds at a significantly slower rate than would be predicted from proton basicity alone. This corresponds to vertical differences of points from the straight line in Figure 5. Note that the vertical difference of the points 3, 4, 7, 10, and 9 from the line of Figure 5 does parallel the relative order of their cone angles. The vertical drop corresponds to a decrease in the rate from that expected on the basis of basicity.

It also appears that for low-valent metal complexes such as $\text{Fe}(\text{CO})_3(\text{N}_4\text{Me}_2)$ the polarizability of the ligand atom is important.¹⁷⁻¹⁹ Thus, 4-cyanopyridine reacts much slower than expected from its proton basicity ($\Delta\text{HNP} \approx 280$).²³ As expected, the highly polarizable arsenic ligands, because of their low proton basicity,²⁸ react slower than do corresponding phosphorus ligands.

As can be seen in Figure 6, the iron center²⁹ in $\text{Fe}(\text{CO})_3(\text{N}_4\text{Me}_2)$ is sterically accessible for nucleophilic attack. In contrast, the less accessible "piano stool"-type $\text{Fe}(\text{CO})_3(1,3\text{-diene})$ complexes are unreactive.⁶⁻⁸ Substitution reactions³⁰ of iron tricarbonyl 1,4-diphenyl-2,3-dimethyl-1,4-diaza-1,3-butadiene, $\text{Fe}(\text{CO})_3(\text{DAB})$ (isostructural with $\text{Fe}(\text{CO})_3(\text{N}_4\text{Me}_2)$) appear to take place by an associative mechanism. The substitution rates are approximately 3 orders of magnitude lower, possibly due to the diminished π -acceptor ability of DAB relative to that of the tetraazabutadiene ligand.

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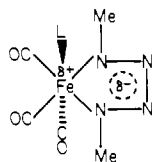
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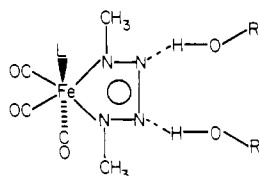
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The rate of substitution additionally depends on the bulk dielectric constant of the solvent, as shown in Table IV. Solvents of higher polarity would be expected to stabilize a polar transition state, in which the tetraazabutadiene ligand accepts electron density from the iron (vide infra), thereby increasing the reaction rate.

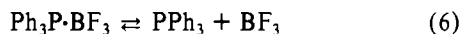


The similarity of the rate constants in acetonitrile and nitromethane seems to preclude nitrile coordination as a rationale for the increased rate. In methanol and ethanol, substitution proceeds much faster than can be accounted for simply by their polarity. This rate enhancement may be caused by hydrogen bonding of the alcohols to the 2,3-nitrogen atoms of the tetraazabutadiene ligand.

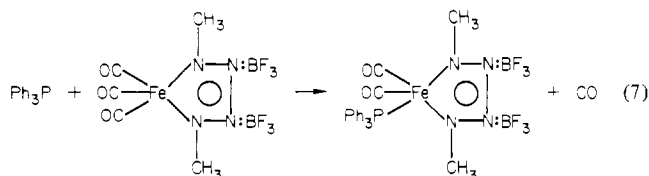


The hypothesis that the inductive effect at iron accelerates the rate (and not some solvation entropy factor) derives support from the similar activation entropies in the two solvents. Hydrogen bonding could decrease the transition-state energy by stabilizing excess electron density on the tetraazabutadiene ligand. Evidence for hydrogen bonding was not observed in the ^1H NMR of a toluene solution of $\text{Fe}(\text{CO})_3(\text{N}_4\text{Me}_2)$ and methanol; however, this does not preclude hydrogen bonding in the transition state which should be a better hydrogen bond acceptor than the ground state. No solvent isotope effect was observed when the substitution was carried out in MeOD , but this type of effect is usually small.³¹

Coordination of the tetraazabutadiene ligand to the strong Lewis acid BF_3 results in an even more dramatic enhancement in the rate of substitution. When excess BF_3 is added to a solution of $\text{Fe}(\text{CO})_3(\text{N}_4\text{Me}_2)$, the carbonyl stretching vibrations shift to higher frequency, indicative of BF_3 coordination to the 2,3-nitrogen atoms of the tetraazabutadiene ligand.^{32,33} When ligand substitution is carried out in the presence of excess BF_3 , the rate of triphenylphosphine substitution is increased by a factor of 1.3×10^6 , even though the uncomplexed phosphine concentration must be small as seen in reaction 6.



The ability of the Lewis acid to withdraw electrons from iron through the tetraazabutadiene ligand must greatly facilitate nucleophilic attack at the iron center in order to account for the millionfold increase in rate of reaction 7. These results



provide further support for the preceding explanation of the

rate acceleration in methanol.

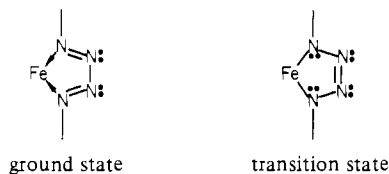
Our study of $\text{Fe}(\text{CO})_3(\text{N}_4\text{Me}_2)$ contrasts with the kinetic studies of $\text{Fe}(\text{CO})_5$ ³⁴ and $\text{Fe}(\text{CO})_4\text{PPh}_3$,³⁵ for which dissociative mechanisms were observed. It should be noted that the iso-electronic complex $\text{Mn}(\text{CO})_4(\text{NO})$ undergoes substitution by an $\text{S}_{\text{N}}2$ mechanism.³⁴ In this instance, localization of a lone pair of electrons on the nitrosyl ligand in the transition state was postulated.



Similarly $\text{Co}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)$, which is pseudoisoelectronic with $\text{Fe}(\text{CO})_5$, exhibits a bimolecular substitution process.³⁵ Transfer of electrons to the cyclopentadiene moiety was suggested to take place in the transition state.



In a similar manner, the tetraazabutadiene ligand may facilitate nucleophilic attack on iron due to its great π -acceptor ability.¹¹



These valence bond structures, while convenient for electron bookkeeping, are of uncertain physical significance. The common thread of flexible metal-ligand π bonding does appear to be an important feature for permitting associative mechanisms in 18-electron systems. Our early work³⁷ on the kinetics and mechanism of ligand substitution reactions provides several examples where 18-electron systems, capable of localizing a pair of electrons on a ligand (e.g., NO, cyclopentadiene, and arene), react by associative processes. These observations now receive support from studies³⁸ which obtain evidence for species of the type previously inferred from kinetic studies. It now appears that one could cautiously propose the "rule" that *substitution reactions of 18-electron transition-metal organometallic compounds may proceed by an associative mechanism provided the metal complex can delocalize a pair of electrons onto one of its ligands.*

Acknowledgment. This work was supported in part by the National Science Foundation, and acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society. We thank Nankai University for the leave of absence given C.-Y.C. and Y.-T.C. and the Ministry of Education of the People's Republic of China for their support. We also thank the National Science Foundation for a Graduate Fellowship awarded to T.G.R.

Registry No. $\text{Fe}(\text{CO})_3(\text{N}_4\text{Me}_2)$, 38668-89-2; PMe_3 , 594-09-2; PMe_2Ph , 672-66-2; PBU_3 , 998-40-3; PEt_2Ph , 1605-53-4; PMePh_2 , 1486-28-8; $\text{P}(\text{OEt})_3$, 122-52-1; $\text{P}(\text{OMe})_3$, 121-45-9; PH_2Ph , 638-21-1; $\text{P}(\text{c-Hx})_3$, 2622-14-2; PPh_3 , 603-35-0; AsMe_3 , 593-88-4; AsEt_3 , 617-75-4; AsMe_2Ph , 696-26-4; 4-CNpy, 100-48-1; Me_3CNC , 7188-

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38-7; Fe(CO)₂PMe₃(N₄Me₂), 76299-42-8; Fe(CO)₂PMe₂Ph(N₄Me₂), 78328-92-4; Fe(CO)₂PBu₃(N₄Me₂), 78328-93-5; Fe(CO)₂PEt₂Ph(N₄Me₂), 78328-94-6; Fe(CO)₂PMePh₂(N₄Me₂), 78328-95-7; Fe(CO)₂P(OEt)₃(N₄Me₂), 78328-96-8; Fe(CO)₂P(OMe)₃(N₄Me₂), 76299-41-7; Fe(CO)₂PH₂Ph(N₄Me₂), 78328-97-9; Fe(CO)₂P(c-Hx)₃(N₄Me₂), 78328-98-0; Fe(CO)₂PPh₃(N₄Me₂), 76299-43-9; Fe(CO)₂AsMe₃(N₄Me₂), 78328-99-1; Fe(CO)₂AsEt₃(N₄Me₂), 78329-00-7; Fe(CO)₂AsMe₂Ph(N₄Me₂), 78329-01-8; Fe(CO)₂(4-

CNpy)(N₄Me₂), 78329-02-9; Fe(CO)₂Me₃CNC(N₄Me₂), 78329-03-0; Fe(CO)(Me₃CNC)₂(N₄Me₂), 78329-04-1; BF₃, 7637-07-2; Fe(Me₃CNC)₃(N₄Me₂), 78329-05-2.

Supplementary Material Available: Listings of rate constants for reaction 1 as a function of Fe(CO)₂(N₄Me₂) concentration, ligand concentration, and temperature (2 pages). Ordering information is given on any current masthead page.

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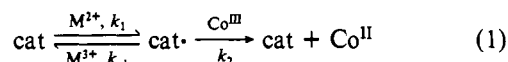
Electron Transfer. 49. Redox Catalysis by Pyridinecarboxylic Acids in Which Conjugation Is Interrupted¹

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The reductions of Co(NH₃)₃py³⁺ and Co(en)₃³⁺ with Eu²⁺ are strongly catalyzed by a number of carboxylate derivatives of pyridine in which the carboxyl group is separated from the ring by a saturated fragment of one to four atoms. The effectiveness of this group of "interrupted catalysts", each of which features a —C(=O)O— or —C(=O)N— group in the 4-position of the pyridine ring, exceeds that of a series of fully conjugated carboxylate catalysts described earlier.¹² Such effectiveness depends mainly on the ease with which these catalysts undergo 1e reduction to radical intermediates, cat· (k₁ in sequence 1). Observed enhancements of k₁ resulting from interposition of "insulating" side chains are attributed to intervention of homoallylic intermediates of types VIII and IX, in which europium is bound to the carboxyl but interacts with the pyridine ring as well. Catalytic potency in this series is quite insensitive to the length of the insulating chain but is found to decrease when branching is introduced or, more markedly, when a peptide linkage is incorporated into this chain. The isonicotinoyl derivatives of glycolic and lactic acids (I and II) are somewhat more effective than the *N*-(carboxymethyl) catalyst, Inic⁺CH₂COOH (VII) and, at the same time, suffer much less serious attrition under conditions of use. Arguments are presented that this improvement in recycling properties reflects more strongly negative values of E°_{cat} for 1e reductions of ester catalysts I and II, leading to lower steady-state concentrations of the catalytic radical intermediates (cat·) in reaction mixtures where these catalysts are operating.

The various substituted pyridines which markedly catalyze the outer-sphere reductions of cobalt(III) complexes³ appear to fall into two categories. In the first class are compounds in which a carboxyl or related function (ester, amide, or nitrile) lies in direct conjugation with the ring nitrogen. The second group consists of bipyridyls, fused bipyridyls, and dipyrindyl-ethylenes in which the two ring nitrogens are in conjugation. Catalysts in both groups operate through preliminary reduction to a radical, "cat·" (sequence 1), but the carboxyl derivatives



are generally the more effective catalysts for their side chains can assume the role of "lead-in groups", thus allowing the initial reduction (k₁) to proceed via a facile inner-sphere path, whereas all catalytic steps with the bipyridyl-related catalysts are necessarily outer sphere.^{3a,b} Note that the most powerful catalysts thus far encountered are derived from 2,4-pyridinedicarboxylic acid, in which both carboxyl groups are conjugated with the hetero nitrogen.^{3c,4}

The impetus for the present work was our finding that certain carboxylate derivatives of pyridine, in which the carboxyl group was separated from the ring by a saturated fragment, were, when ligated to Co^{III}, remarkably effective

mediators for inner-sphere reduction by Eu²⁺ and, further, that such reactions were strongly autocatalytic.⁵ Since the initial step in autocatalytic sequences of this sort is the 1e reduction of the ligand released as a result of the primary electron transfer (i.e., the same process as that initiating catalytic sequence of (1)) it appeared likely that these ligands featuring interrupted conjugation would, when uncoordinated, catalyze electron transfer to such sluggish oxidants as Co(NH₃)₆³⁺, Co(en)₃³⁺, and Co(py)(NH₃)₅³⁺. We here compare the action exhibited by several members of this more recent class of catalysts.

Experimental Section

Inorganic Materials. Solutions of Eu(ClO₄)₃, the primary reductant, were prepared as described.⁶ (Pyridine)pentaamminecobalt(III) perchlorate, Co(NH₃)₅py(ClO₄)₃,⁷ and tris(ethylenediamine)cobalt(III) perchlorate, Co(en)₃(ClO₄)₃,⁸ the primary oxidants, were prepared by published procedures.

Catalysts. Isonicotinate esters of α- and β-hydroxy acids were prepared by a procedure analogous to that of Irikura and co-workers⁹ in which aqueous solutions of sodium isonicotinate and the sodium salt of the appropriate chloro- or bromo-substituted aliphatic acid were mixed, brought to pH 8, and then kept at 85 °C for 5 h. The mixture was then cooled, the desired carboxylalkyl isonicotinate precipitated by addition of HCl, and the product recrystallized from dilute aqueous HClO₄.

Isonicotinylglycine (V) was prepared by the procedure of Gardner and co-workers.¹⁰ *N*-(2-Carboxybenzyl)isonicotinamide (VI) was

(1) Sponsorship of this work by the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.
(2) On leave from Vivekananda College, Mylapore, Madras, India.
(3) See, for example: (a) Fanchiang, Y.-T.; Thomas, J. C.; Neff, V. D.; Gould, E. S. *Inorg. Chem.* 1977, 16, 1942. (b) Fanchiang, Y.-T.; Gould, E. S. *Ibid.* 1977, 16, 2516. (c) Fanchiang, Y.-T.; Heh, J. C.-K.; Gould, E. S. *Ibid.* 1978, 17, 1142.
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