

# Kinetics and Mechanism of Ligand Substitution in Iron Tricarbonyl 1,4-Diazabutadiene Complexes

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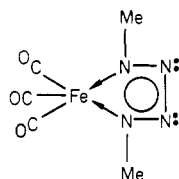
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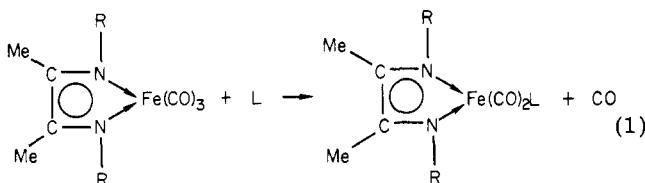
When aryl groups are substituents in the 1,4-positions of the diazabutadiene (DAB) ligand,<sup>2</sup> substitution of carbon monoxide by  $\text{PMe}_3$  in  $\text{Fe}(\text{CO})_3(\text{DAB})$  takes place solely by a second-order process. The rate law is first order in both  $\text{Fe}(\text{CO})_3(\text{DAB})$  and  $\text{PMe}_3$ . Activation parameters for the 4-fluorophenyl derivative in toluene support the associative nature of this reaction:  $\Delta H^\ddagger = 13.6 \pm 1.0$  kcal/mol;  $\Delta S^\ddagger = -34.8 \pm 3.2$  eu. Carbon monoxide replacement rates depend on the nature of the nucleophile, and increase in the series  $\text{PPh}_3 < \text{P}(\text{OMe})_3 < \text{P}(n\text{-Bu})_3 < \text{PMe}_3$ . This rate also increases when the  $\pi$ -acceptor ability of the DAB ligand increases. When bulky *tert*-butyl groups are the substituents in the 1,4-positions of the DAB ligand, steric interactions become important in the six-coordinate transition state. Nucleophilic attack on this complex results in loss of the DAB ligand to give  $\text{Fe}(\text{CO})_3(\text{PMe}_3)_2$ . This reaction obeys a two-term rate law involving both associative ( $\Delta H^\ddagger = 20.4 \pm 0.8$  kcal/mol and  $\Delta S^\ddagger = -18.2 \pm 2.0$  eu) and dissociative ( $\Delta H^\ddagger = 25.0 \pm 1.0$  kcal/mol and  $\Delta S^\ddagger = -8.0 \pm 3.0$  eu) pathways. Factors which facilitate nucleophilic attack on iron in these coordinately saturated metallacycles and in the related  $\text{Fe}(\text{CO})_3(\text{N}_4\text{Me}_2)$  complex are discussed.

## Introduction

In contrast to most other pentacoordinate iron carbonyl complexes,  $\text{Fe}(\text{CO})_3(\text{N}_4\text{Me}_2)$  reacts readily with nucleophiles by an associative ( $\text{S}_{\text{N}}2$ ) mechanism.<sup>3</sup>



We attributed this unusual behavior to the flexible  $\pi$ -acceptor properties<sup>4</sup> of the tetraazabutadiene ligand. Diazabutadiene (or diimine) ligands are also thought<sup>5</sup> to possess strong  $\pi$ -acceptor properties, although not as great as in the tetraazabutadiene metallacyclic systems. These considerations prompted us to examine substitution reactions of analogous iron tricarbonyl 1,4-diazabutadiene complexes (eq 1). Preliminary studies indicated<sup>3</sup> that iron



tricarbonyl 1,4-diphenyl-2,3-dimethyl-1,4-diaza-2,3-butadiene undergoes carbon monoxide replacement in a manner similar to  $\text{Fe}(\text{CO})_3(\text{N}_4\text{Me}_2)$ . In order to probe the role of the metallacycle in promoting nucleophilic attack on iron, we examined substitution reactions of  $\text{Fe}(\text{CO})_3(\text{DAB})$  as a function of the nature of the substituent R. An understanding of how coordinately saturated organometallic complexes react by associative mechanisms is relevant to synthetic and catalytic transformations.<sup>6,7</sup>

## Experimental Section

All manipulations were carried out under an atmosphere of prepurified nitrogen by using standard inert atmosphere techniques.<sup>8</sup> Toluene was dried with sodium, methanol with  $\text{Mg}(\text{OMe})_2$ , and acetonitrile with  $\text{P}_2\text{O}_5$ . Solvents were distilled and degassed prior to use. Trimethylphosphine (Strem) was purified by distillation on a vacuum line and triphenylphosphine (Aldrich) was recrystallized from ethanol and dried under vacuum. Trimethyl phosphite and tri-*n*-butylphosphine were distilled from sodium metal. Iron tricarbonyl 1,4-diazabutadiene complexes,  $\text{Fe}(\text{CO})_3(\text{DAB})$ , were prepared by a ligand exchange reaction between iron tricarbonyl benzylideneacetone<sup>9</sup> and an equivalent of the appropriate Schiff base. This procedure avoids the formation of dimeric iron carbonyl products which may result when  $\text{Fe}_2(\text{CO})_9$  is used as the starting material.<sup>10</sup> Exchange reactions were complete in 6–20 h at 60 °C, as determined by IR monitoring. The detailed preparative procedure for the previously unreported 4-fluorophenyl derivative<sup>11</sup> is given below. Other  $\text{Fe}(\text{CO})_3(\text{DAB})$  compounds were prepared similarly, and their IR spectra agreed with those prepared by other procedures.<sup>12–14</sup>

**Preparation of Iron Tricarbonyl 1,4-Bis(4-fluorophenyl)-2,3-dimethyl-1,4-diaza-2,3-butadiene (1a).** A Schlenk flask was charged with 1.50 g (5.5 mmol) of 1,4-bis(4-fluorophenyl)-2,3-dimethyl-1,4-diaza-2,3-butadiene,<sup>15</sup> 1.57 g (5.5 mmol) of iron tricarbonyl benzylideneacetone, and 85 mL of toluene. After the mixture was heated for 12 h at 60 °C, the IR spectrum showed complete loss of starting complex and a red solution was obtained following filtration. The solvent was removed under vacuum and the residue redissolved in 10 mL of toluene–hexane (60:40). Chromatography on Grade III alumina (2.5 × 35 cm column) with the same solvent mixture gave a red band which was collected. Removal of the solvent yielded 0.95 g (42%) of deep red crystalline product, 1a, which may be recrystallized from hexane. Anal. Calcd for  $\text{FeC}_{19}\text{H}_{16}\text{N}_2\text{F}_2\text{O}_3$ : C, 55.37; H, 3.42; N, 6.68. Found: C, 55.19; H, 3.59; N, 6.80.

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(11) For convenience, we shall refer to the  $\text{Fe}(\text{CO})_3(\text{DAB})$  complexes by the name of the alkyl or aryl substituent in the 1,4-positions of the DAB ligand (Table I).

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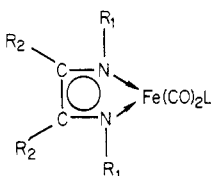
(1) (a) Lanzhou University, People's Republic of China. (b) Northwestern University.

(2) Abbreviations:  $(\text{N}_4\text{Me}_2)$ , 1,4-dimethyltetraazabutadiene; DAB, 1,4-diazabutadiene; Me, methyl; Ph, phenyl; Bu, butyl; L, ligand.

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Table I. Spectral Data<sup>d</sup> for

	R <sub>1</sub>	R <sub>2</sub>	L	λ, nm (ε, M <sup>-1</sup> cm <sup>-1</sup> )	ν <sub>CO</sub> , cm <sup>-1</sup>
1a	4-fluorophenyl	Me	CO	508 (7980), 380 (3830)	2024, 1949
1b	4-fluorophenyl	Me	PMe <sub>3</sub>	522 (6740), 423 (6210)	1960, 1900
1c	4-fluorophenyl	Me	P( <i>n</i> -Bu) <sub>3</sub>	516 (6730), 436 (6370)	1958, 1896
1d	4-fluorophenyl	Me	P(OMe) <sub>3</sub>	498 (8690), 409 (6040)	1979, 1915
1e	4-fluorophenyl	Me	PPh <sub>3</sub>	520 (6100), 445 (5920)	1965, 1905
2a	phenyl	Me	CO	508 (8610), 381 (4030)	2035, 1965 <sup>a</sup>
2b	phenyl	Me	PMe <sub>3</sub>	520 (6180), 422 (4930)	1961, 1900
3a	4-methoxyphenyl	Me	CO	508 (7540), 380 (3970)	2019, 1942 <sup>b</sup>
3b	4-methoxyphenyl	Me	PMe <sub>3</sub>	519 (5560), 419 (4730)	1957, 1896
4a	cyclohexyl	H	CO	505 (7550), 370 (3590)	2018, 1938 <sup>b</sup>
4b	cyclohexyl	H	PMe <sub>3</sub>	503 (6690), 408 (5940)	1946, 1885
4c	cyclohexyl	H	PPh <sub>3</sub>	509 (6500), 435 (4730)	1949, 1889
5a	<i>tert</i> -butyl	H	CO	545 (6220), 377 (2670)	2005, 1926 <sup>c</sup>
5b	<i>tert</i> -butyl	H	PMe <sub>3</sub>	531 (4710), 420 (2030)	1935, 1869
5c	<i>tert</i> -butyl	H	PPh <sub>3</sub>	540 (4350), 448 (2670)	1938, 1876

<sup>a</sup> Reference 12. <sup>b</sup> Reference 13. <sup>c</sup> Reference 14. <sup>d</sup> In toluene solution.

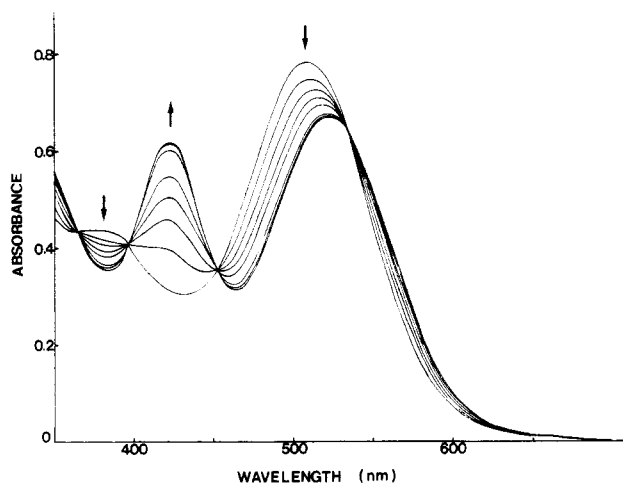
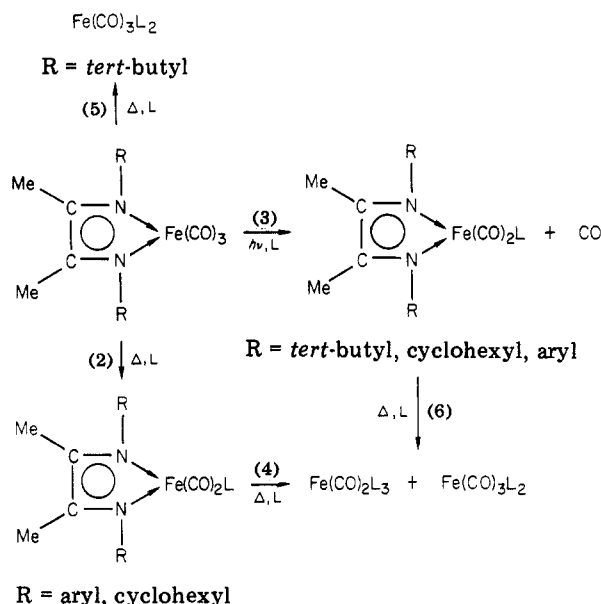


Figure 1. Visible spectral changes during the reaction between  $9.87 \times 10^{-6}$  M 4-fluorophenyl complex (1a) and 0.998 M PMe<sub>3</sub> in toluene solution.

**Spectral Studies.** IR spectra were recorded on a Perkin-Elmer 283 spectrometer using 0.1-mm CaF<sub>2</sub> cells. Visible spectra were recorded on a Cary 14 spectrophotometer using 1.00-cm or 1.00-mm quartz cells modified for work with air-sensitive compounds. Photochemical reactions were carried out by using a 550-W mercury arc lamp and a Corning 0-52 filter ( $\lambda > 340$  nm).

**Kinetic Procedures.** A quartz cell, containing a solution of the ligand in toluene, was allowed to thermally equilibrate in the thermostated ( $\pm 0.5$  °C) cell compartment of the Cary 14 for at least 15 min. Reactions were initiated by injecting a solution of the iron complex into the cell using a Hamilton gas-tight syringe. The cell was vigorously shaken, and then spectra were recorded as a function of time. To avoid competing photochemical reactions, we closed the slit of the Cary 14 between absorption measurements. A typical experiment for reaction of the 4-fluorophenyl complex with PMe<sub>3</sub> is illustrated in Figure 1. Isosbestic points at 528, 453, 395, and 367 nm are maintained throughout the course of the reaction. Similar isosbestic points were observed for all the substitution reactions where the DAB ligand remains coordinated to the metal. Reactions were conducted under pseudo-first-order conditions, with the ligand concentration at least 1 order of magnitude greater than that of the iron complex. Plots of  $\ln(A_{\infty} - A_t)$  vs. time were linear for more than 3 half-lives and  $k_{\text{obsd}}$  was obtained from the slope of this line, as determined by the method of least squares. Although

Scheme I



the statistical error from the analysis was always less than 1% the rate constants,  $k_{\text{obsd}}$ , were realistically reproducible to within  $\pm 5\%$ . The rate of substitution of 1a by P(OMe)<sub>3</sub> and PPh<sub>3</sub> was measured by observing the decrease in intensity of the infrared absorption at 2024 cm<sup>-1</sup>. Reaction products were identified by their infrared, electronic absorption, and mass spectra. Table I contains the visible absorption and IR spectroscopic data for the Fe(CO)<sub>3</sub>(DAB) complexes and their monosubstitution products, Fe(CO)<sub>2</sub>L(DAB).

## Results

Thermal and photochemical substitution chemistry of the diazabutadiene complexes is summarized in Scheme I. Efficient visible light photosubstitution of a CO ligand has recently been demonstrated<sup>18</sup> for the phenyl<sup>11</sup> complex.

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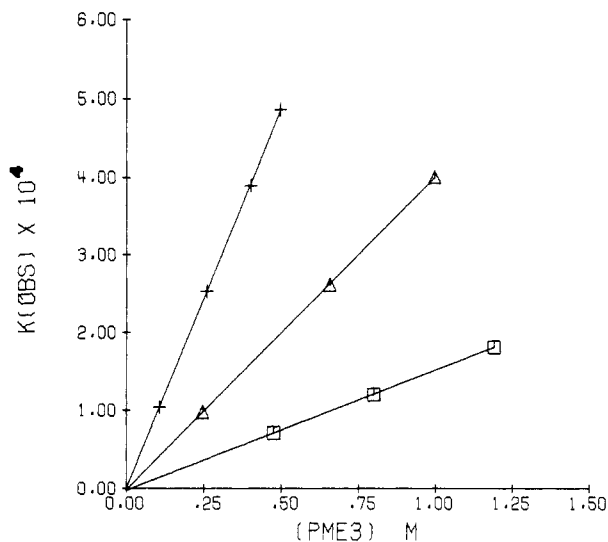


Figure 2. Plot of  $k_{\text{obsd}}$  ( $\text{s}^{-1}$ ) vs.  $\text{PMe}_3$  concentration (M) for the reaction of 4-fluorophenyl complex (1a) with  $\text{PMe}_3$  in toluene solution: (□)  $T = 55.5$  °C; ( $\Delta$ )  $T = 70$  °C; (+)  $T = 85$  °C.

Visible light photolysis of the other  $\text{Fe}(\text{CO})_3(\text{DAB})$  complexes in the presence of an excess of ligand also cleanly leads to  $\text{Fe}(\text{CO})_2\text{L}(\text{DAB})$ . Thermal replacement of CO occurs when the aryl- and cyclohexyl-substituted complexes are treated with  $\text{PMe}_3$ . At elevated temperatures in sealed reaction vessels, these complexes slowly react with additional  $\text{PMe}_3$  to yield  $\text{Fe}(\text{CO})_2(\text{PMe}_3)_3$ <sup>19</sup> and  $\text{Fe}(\text{CO})_3(\text{PMe}_3)_2$ <sup>20</sup> as the metal-containing products. In the case of the cyclohexyl derivative (4a), the rate of reaction (eq 4, Scheme I) is comparable to that of the substitution reaction (eq 2). Qualitatively, the rate of DAB loss (eq 4) increases for changes in R in the order 4-fluorophenyl < phenyl < 4-methoxyphenyl < cyclohexyl. For this reason, the  $\text{PMe}_3$ -substituted cyclohexyl derivative 4b is most conveniently prepared by the photochemical route at room temperature. The  $\text{PPh}_3$  derivative, 4c, can be prepared thermally but the reaction is very slow ( $t_{1/2} \approx 100$  h at 80 °C,  $[\text{PPh}_3] = 0.90$  M).

Simple CO substitution does not occur thermally when the *tert*-butyl derivative (5a) is allowed to react with  $\text{PMe}_3$ ,  $\text{P}(\text{OMe})_3$ , or  $\text{P}(n\text{-Bu})_3$ . Rather, the DAB ligand departs (eq 5) to yield  $\text{Fe}(\text{CO})_3\text{L}_2$  as the only metal carbonyl product. Monosubstituted derivatives of the *tert*-butyl complex can only be prepared by photochemical dissociation of CO in the presence of phosphine ligands. We have studied the kinetics of ligand substitution in detail for the aryl- and *tert*-butyl substituted complexes. Typical plots of  $k_{\text{obsd}}$  (eq 2) vs.  $[\text{PMe}_3]$  for the 4-fluorophenyl compound are given in Figure 2. The y intercept of zero demonstrates that there is no ligand-independent reaction path. Second-order rate constants (eq 2) for the aryl-substituted complexes are provided in Table II, along with the activation parameters and solvent dependence of the substitution rate for the 4-fluorophenyl derivative. In addition, the estimated rate of substitution of CO by  $\text{PMe}_3$  in complex (4a) is recorded in Table II. Only an estimate of this rate was obtained because of competitive secondary reactions of the product. As discussed above, the DAB ligand is lost instead of CO when the *tert*-butyl complex is allowed to react with  $\text{P}(\text{Me})_3$ ,  $\text{P}(\text{OMe})_3$ , or  $\text{P}(n\text{-Bu})_3$ . The rate of this reaction (eq 5) as a function of ligand con-

Table II. Rate Constants for CO Substitution by Nucleophiles in Toluene According to Eq 1

complex	L	T, °C	$10^4 k, \text{M}^{-1} \text{s}^{-1}$
4-fluorophenyl (1a)	$\text{PMe}_3$	55	$1.54 \pm 0.01$
		55	$1.93^a$
		55	$2.13^b$
		70	$4.02 \pm 0.02$
		85	$9.71 \pm 0.05^c$
		85	0.21
phenyl (2a)	$\text{P}(n\text{-Bu})_3$	85	0.21
		85	0.04
		85	0.01
4-methoxyphenyl (3a)	$\text{PMe}_3$	70	2.48
		70	0.60
cyclohexyl (4a)	$\text{PMe}_3$	70	0.01
		70	$4.10 \times 10^5^d$

<sup>a</sup> Solvent = acetonitrile. <sup>b</sup> Solvent = methanol. <sup>c</sup>  $\Delta H^\ddagger = 13.6 \pm 1.0$  kcal/mol;  $\Delta S^\ddagger = -34.8 \pm 3.2$  eu. <sup>d</sup> Reference 3.  $\Delta H^\ddagger = 6.9 \pm 0.8$  kcal/mol;  $\Delta S^\ddagger = -31.4 \pm 2.1$  eu.

Table III. Rates of DAB Replacement in the *tert*-Butyl Complex 5a by Nucleophiles in Toluene Solution

nucleophile	T, °C	$10^5 k_2, \text{M}^{-1} \text{s}^{-1}$	$10^5 k_1, \text{s}^{-1}$
$\text{PMe}_3$	55.5	$2.36 \pm 0.03$	$0.27 \pm 0.03$
$\text{PMe}_3$	70.0	$9.33 \pm 0.24$	$1.22 \pm 0.13$
$\text{PMe}_3$	77.0	$18.1 \pm 0.2$	$2.94 \pm 0.14$
$\text{PMe}_3^a$	85.0	$34.3 \pm 0.4$	$7.16 \pm 0.35$
$\text{P}(\text{OMe})_3$	77.0	$0.78 \pm 0.05$	$2.00 \pm 0.04$
$\text{P}(n\text{-Bu})_3$	77.0	$0.91 \pm 0.08$	$1.95 \pm 0.05$

<sup>a</sup>  $\Delta H_1^\ddagger = 25.0 \pm 1.0$  kcal/mol;  $\Delta S_1^\ddagger = -8.0 \pm 3.0$  eu.  
<sup>b</sup>  $\Delta H_2^\ddagger = 20.4 \pm 0.8$  kcal/mol;  $\Delta S_2^\ddagger = -18.2 \pm 2.0$  eu.

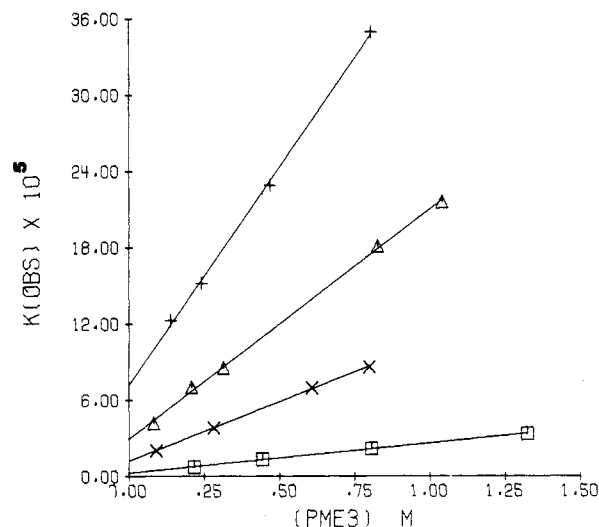


Figure 3. Plot of  $k_{\text{obsd}}$  ( $\text{s}^{-1}$ ) vs.  $\text{PMe}_3$  concentration (M) for the reaction of the *tert*-butyl complex (5a) with  $\text{PMe}_3$  in toluene solution: (□)  $T = 55.5$  °C; (×)  $T = 70.0$  °C; ( $\Delta$ )  $T = 77$  °C; (+)  $T = 85$  °C.

centration and temperature is plotted in Figure 3. Rate constants for the ligand-dependent and ligand-independent mechanisms are collected along with the activation parameters in Table III. The reaction of the *tert*-butyl complex with  $\text{PPh}_3$  was very slow and appeared to involve several competitive pathways, including CO substitution and DAB displacement.

### Discussion

In accord with our preliminary observations,<sup>3</sup> the phenyl-substituted  $\text{Fe}(\text{CO})_3(\text{DAB})$  complex reacts with  $\text{PMe}_3$  by an associative mechanism. This behavior resembles that observed for  $\text{Fe}(\text{CO})_3(\text{N}_4\text{Me}_2)$ . As illustrated in Figure 2, the rate of substitution depends directly on the ligand concentration. The rate law for this process is given in eq

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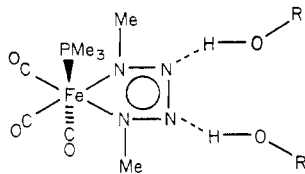
7. The small enthalpy and large negative entropy of  $-d[\text{Fe}(\text{CO})_3(\text{DAB})]/dt = k[\text{Fe}(\text{CO})_3(\text{DAB})][\text{L}]$  (7)

activation (Table II) for CO replacement in the 4-fluorophenyl complex further indicate an associative process. An alternative mechanism involving bond rupture of one end of the DAB chelate ring, followed by CO replacement and ring closure, would be expected to exhibit a large  $\Delta H^\ddagger$  and little variation in rate with different nucleophiles. This contrasts with the observed  $\Delta H^\ddagger$  and the sensitivity of the rate to the nature of the nucleophile. The large negative  $\Delta S^\ddagger$  observed also would not be expected for a dissociative mechanism. In addition, our synthetic results suggest that a unidentate DAB ligand is readily displaced by phosphine ligands. These substitution reactions appear to proceed by a classical  $\text{S}_{\text{N}}2$  mechanism via a six-coordinate transition state.

As would be expected for an associative process, rates of substitution depend on the size and the basicity of the entering nucleophile. Relative rates of carbon monoxide displacement at 85 °C increase in the series  $\text{PPh}_3$  (1) <  $\text{P}(\text{OMe})_3$  (4) <  $\text{P}(n\text{-Bu})_3$  (21) <  $\text{PMe}_3$  (971). A similar reactivity sequence was observed<sup>3</sup> for  $\text{Fe}(\text{CO})_3(\text{N}_4\text{Me}_2)$ , although the magnitude of the difference was significantly larger in the latter system. This suggests that bond making occurs to a greater extent in the transition state of the  $\text{N}_4\text{Me}_2$  system compared to the DAB complexes.

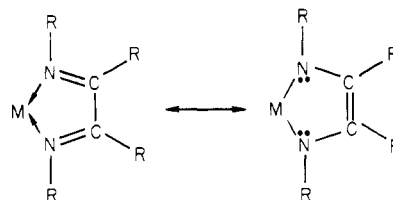
Although similar associative mechanisms appear to be operative, the rates of CO substitution in the aryl DAB complexes are approximately 5 orders of magnitude slower than in the previously studied<sup>3</sup>  $\text{Fe}(\text{CO})_3(\text{N}_4\text{Me}_2)$  complex. Examination of the activation parameters (Table II) for these two systems reveals that the difference in reactivity rests largely in the enthalpy term. This suggests to us that the reduced reactivity of the aryl-substituted  $\text{Fe}(\text{CO})_3(\text{DAB})$  compounds may be attributed to electronic factors as opposed to steric considerations. Recent theoretical<sup>4</sup> and experimental<sup>16</sup> investigations indicate that the  $\pi$ -acceptor ability of the tetraazadiene ligand rivals that of CO. With use of CO stretching frequencies of the  $\text{Fe}(\text{CO})_3$  moiety as a guide, the  $\text{N}_4\text{Me}_2$  ligand (weighted average  $\bar{\nu}_{\text{CO}} = 2019 \text{ cm}^{-1}$ ) appears to be a significantly stronger  $\pi$  acceptor than the DAB moiety ( $\bar{\nu}_{\text{CO}} = 1983 \text{ cm}^{-1}$ ). Thus, the electrophilic  $\text{Fe}(\text{N}_4\text{Me}_2)$  metallacycle can better accommodate increased electron density on iron in the transition state than can the  $\text{Fe}(\text{DAB})$  metallacycle.

The rate of substitution in  $\text{Fe}(\text{CO})_3(\text{N}_4\text{Me}_2)$  depends on both the polarity and hydrogen-bonding ability of the solvent.<sup>3</sup> Relative rates of substitution in methanol, acetonitrile, and toluene are 149:9:1.<sup>3</sup> Polar solvents should stabilize a polar transition state; however, the dramatic rate enhancement in methanol was attributed to hydrogen bonding to the 2,3 nitrogen atoms of the  $\text{Fe}(\text{N}_4\text{Me}_2)$  metallacycle.



This contrasts with the insensitivity to solvent seen for  $\text{Fe}(\text{CO})_3(\text{DAB})$  in which the relative substitution rates in methanol, acetonitrile, and toluene are 1.4:1.3:1. We suggest that the pseudooctahedral transition state is less polar in  $\text{Fe}(\text{CO})_3(\text{DAB})$  than in  $\text{Fe}(\text{CO})_3(\text{N}_4\text{Me}_2)$ . In addition, there is no opportunity for hydrogen bonding to the DAB ligand as there is for the tetraazabutadiene ligand.

Further support that electron-withdrawing abilities of the metallacycle affect the rate of displacement of CO was obtained by studying derivatives with different DAB ligands. For example, the substitution rate is reduced by a factor of 4 when the electron-donating methoxy group is placed in the para position of the phenyl ring (3a). A much larger rate reduction results when the phenyl ring is replaced by the cyclohexyl group (4a). Thus, the substitution lability of these complexes parallels the ability of the metallacycle to accept electron density in the pseudooctahedral transition state. The importance of electron delocalization to ligands in 18-electron systems which react by associative mechanisms was first recognized for nitrosyl<sup>17</sup> and for cyclopentadienylmetal<sup>18</sup> complexes. The diazabutadiene complex could add a ligand and still maintain an 18-electron configuration by delocalizing a pair of electrons onto the metallacycle.



In contrast to the simple CO substitution process observed for the above complexes, treatment of the *tert*-butyl compound 5a with nucleophiles leads to loss of the DAB moiety (eq 5). The substitution products 5b and 5c are not inherently unstable but can only be prepared by the photochemical reaction (eq 3), which proceeds via a dissociative mechanism. In the thermal reactions,  $\text{Fe}(\text{CO})_3\text{L}_2$  is the sole product observed by IR and mass spectroscopy. No intermediates could be detected in the infrared spectrum of the reaction mixture. The kinetics of DAB replacement in the *tert*-butyl complex exhibits both ligand-dependent and ligand-independent pathways (Figure 3) that follow the rate law (eq 8). Rate constants for this  $-d[\text{Fe}(\text{CO})_3(\text{DAB})]/dt =$

$$k_1[\text{Fe}(\text{CO})_3(\text{DAB})] + k_2[\text{Fe}(\text{CO})_3(\text{DAB})][\text{L}] \quad (8)$$

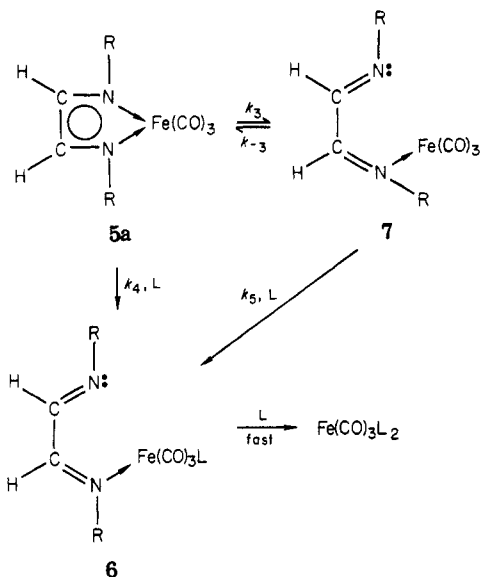
process are presented in Table III as a function of temperature for  $\text{PMe}_3$  and for  $\text{P}(\text{OMe})_3$  and  $\text{P}(n\text{-Bu})_3$ . Analysis of the rate data as a function of temperature and ligand concentration for  $\text{L} = \text{PMe}_3$  permits an estimate of the activation parameters for the two pathways. The dissociative ( $k_1$ ) route exhibits a large enthalpy of activation ( $\Delta H_1^\ddagger = 25.0 \pm 1.0 \text{ kcal/mol}$ ) and a small entropy of activation ( $\Delta S_1^\ddagger = -8.0 \pm 3.0 \text{ eu}$ ). This contrasts with the associative path ( $k_2$ ) which possesses a smaller enthalpy of activation ( $\Delta H_2^\ddagger = 20.4 \pm 0.8 \text{ kcal/mol}$ ) and a larger negative entropy of activation ( $\Delta S_2^\ddagger = -18.2 \pm 2.0 \text{ eu}$ ). These values are consistent with the mechanism proposed below.

Ring opening has been observed<sup>21</sup> when compounds of the type  $\text{Fe}(\text{CO})_3(1,4\text{-heterodiene})$ , where heterodiene is an unsaturated aldehyde, ketone, or Schiff base, are treated with nucleophiles. These complexes also react according to a two-term rate law involving partial dissociation of the heterodiene ligand.<sup>22</sup> Our kinetic data can be accommodated by the mechanism given in Scheme II. The 18-electron intermediate 6 can be obtained by either a dissociative or an associative route. In the former, partial dissociation of the DAB ligand leads to the coordinately

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Scheme II



unsaturated intermediate 7, which rapidly adds L to yield 6. Alternatively, direct nucleophilic attack on 5a would lead to a pseudooctahedral transition state which is sterically crowded because of the bulky *tert*-butyl substituents. Dissociation of one end of the DAB ligand would reduce the steric strain and produce 6. This intermediate can then react with another molecule of L, following dissociative loss of the monodentate DAB ligand, to give the observed product. With the assumption that the steady-state approximation holds for 7 and that  $k_5[L] \gg k_{-3}$ , then  $k_{\text{obsd}}$  conforms to eq 9.

$$k_{\text{obsd}} = k_3 + k_4[L] \quad (9)$$

Note (Table III) that the ligand-dependent term dominates only in the case of the small, strongly basic  $\text{PMe}_3$  nucleophile. The dissociative pathway prevails for larger

( $\text{P}(n\text{-Bu})_3$ ) or less basic ( $\text{P}(\text{OMe})_3$ ) ligands. Partial dissociation and subsequent loss of the DAB ligand seems to be a result of the steric bulk of the *tert*-butyl group. It is reasonable that a transition state of increased coordination should be susceptible to steric effects. Recall that the photochemical preparation of the monosubstituted *tert*-butyl derivatives 5b and 5c avoids the six-coordinate transition state.

These studies show that both steric and electronic factors may influence the thermal substitution chemistry of coordinately saturated  $\text{Fe}(\text{CO})_3(\text{DAB})$  complexes. Nucleophilic substitution occurs by an associative mechanism for this 18-electron system which may delocalize electron density onto the DAB ligand.<sup>18</sup> Consequently the rate of substitution increases with the ability of the metallacycle moiety to accept electron density. With bulky substituents in the 1,4 positions of the DAB ligand, steric interactions dominate and lead to DAB loss rather than CO substitution.

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**Registry No.** 1a, 81847-60-1; 1b, 81847-61-2; 1c, 81847-62-3; 1d, 81847-63-4; 1e, 81847-64-5; 2a, 15651-58-8; 2b, 81847-65-6; 3a, 65016-01-5; 3b, 81847-66-7; 4a, 54446-63-8; 4b, 81856-96-4; 4c, 81875-57-2; 5a, 65036-35-3; 5b, 81847-67-8; 5c, 81847-68-9;  $\text{PMe}_3$ , 594-09-2;  $\text{P}(\text{OMe})_3$ , 121-45-9;  $\text{P}(n\text{-Bu})_3$ , 998-40-3; iron tricarbonyl benzylideneacetone, 53861-80-6.

**Supplementary Material Available:** Tables of observed rate constants for CO substitution according to eq 1 and for DAB replacement in the *tert*-butyl complex 5a (2 pages). Ordering information is given on any current masthead page.

## Synthesis of $\beta$ -Keto Sulfides and Thioesters from the Reaction of $\alpha$ -Thiocarbanions with Iron Pentacarbonyl

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$\alpha$ -Thiocarbanions, generated from the reaction of sulfides with organolithium reagents or lithium diisopropylamide, react with iron pentacarbonyl and then with methyl iodide, to give  $\beta$ -keto sulfides. Disulfides were obtained as byproducts of these reactions and as the only product when iodine was used as the electrophile. The utilization of acid halides as the electrophilic reagent afforded thioesters in fine yields.

There have been extensive investigations of the reactions of organolithium compounds<sup>2</sup> and Grignard reagents<sup>2-4</sup> with iron pentacarbonyl. The products of these reactions

are acyltetracarbonylferrates (1) which are useful reagents in their own right being able, for example, to convert halides to ketones (2),<sup>2,3</sup> imidoyl chlorides to mesoionic 1,3-oxazol-5-ones (3),<sup>5</sup> and epoxides to  $\alpha,\beta$ -unsaturated ketones (4).<sup>6</sup>

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