

Contribution from the Department of Chemistry,  
University of California, Riverside, California 92502

## Kinetics and Mechanism of the Substitution Reactions of Bis(mercaptotricarbonyliron) Complexes

P. C. ELLGEN\* and J. N. GERLACH

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The kinetics and mechanisms of the carbonyl-substitution reactions of  $\text{Fe}_2(\text{CO})_6\text{S}_2\text{C}_6\text{H}_5\text{CH}_3$  with  $\text{P}(\text{C}_6\text{H}_5)_3$ ,  $\text{P}(\text{OC}_6\text{H}_5)_3$ ,  $\text{P}(n\text{-C}_4\text{H}_9)_3$ ,  $\text{P}(\text{OCH}_3)_3$ ,  $\text{PH}(\text{C}_6\text{H}_5)_2$ ,  $\text{P}(\text{C}_2\text{H}_5)(\text{C}_6\text{H}_5)_2$ ,  $\text{P}(\text{C}_6\text{H}_{11})_3$ ,  $\text{P}(o\text{-C}_6\text{H}_4\text{CH}_3)_3$ , and  $\text{As}(\text{C}_6\text{H}_5)_3$ ; of  $\text{Fe}_2(\text{CO})_6\text{S}_2\text{C}_6\text{H}_5$  with  $\text{P}(n\text{-C}_4\text{H}_9)_3$  and  $\text{P}(\text{C}_6\text{H}_5)_3$ ; and of the complexes  $\text{Fe}_2(\text{CO})_6(\text{SR})_2$  ( $\text{R} = \text{CH}_3$ ,  $\text{CH}_2\text{CH}_3$ ,  $\text{CH}_2\text{C}_6\text{H}_5$ ,  $\text{C}_6\text{H}_5$ , and  $p\text{-C}_6\text{H}_4\text{CH}_3$ ) with  $\text{P}(\text{C}_6\text{H}_5)_3$  have been investigated in toluene solution by monitoring the volume of carbon monoxide evolved as a function of time. The complexes in which the bridging sulfur atoms are joined by a rigid organic group undergo substitution by a strictly second-order rate law, which is first-order in each reagent and independent of the carbon monoxide concentration. For those complexes in which the bridging sulfur atoms are not joined by a rigid organic group, syn-anti isomerization is possible. Syn and anti isomers can interconvert at rates comparable to those of the carbonyl-substitution reactions; these isomers undergo carbonyl substitution at different rates. For some such complexes, rate experiments were carried out by monitoring pmr spectra as a function of time. Although the syn-anti isomerization can complicate the kinetic analysis, it is shown that the same rate law also applies to the actual substitution step in these cases. Second-order rate constants are sensitive to the nature of the attacking reagent and insensitive to the nature of the solvent. Entropies of activation are notably negative. An  $\text{S}_\text{N}2$  or  $\text{I}_\text{a}$  mechanism with a seven-coordinated activated complex is proposed. The nature of the rate effects ascribable to the mercapto substituents suggests a specific, if speculative, structure for the activated complex for substitution.

### Introduction

Although di- $\mu$ -mercapto-hexacarbonyldiiron complexes have been known for many years,<sup>1</sup> extensive investigations of the structures and substitution chemistry of these complexes have been more recent developments. A determination of the molecular structure of *anti*-di- $\mu$ -(ethyl mercapto)-hexacarbonyldiiron by X-ray diffraction<sup>2</sup> confirmed the presence of the nonplanar  $\text{Fe}_2\text{S}_2$  molecular core inferred from ir and dipole moment data,<sup>3</sup> as well as the syn vs. anti structural assignment for the isomers detected by isolation and pmr spectroscopy<sup>4,5</sup> (Figure 1). The observed iron-iron distance of 2.55 Å implies the presence of the iron-iron bond anticipated from the observed diamagnetism. The molecular structure can be considered to arise from two octahedrally ligated iron atoms sharing an octahedral face. Two sulfur atoms and the bent iron-iron bond occupy the vertices of the shared octahedral face. However, the Fe-S-Fe angles are only 68°, considerably less than the 90° angles expected for a regular octahedron. Dahl and Wei<sup>2</sup> suggested that this distortion results from the existence of the bent iron-iron bond. To achieve good overlap of the octahedrally hybridized iron orbitals forming the iron-iron bond, it is necessary to sacrifice some overlap of octahedrally hybridized iron orbitals with the (presumably) tetrahedrally hybridized sulfur valence orbitals. Thus the iron-sulfur bonds are also bent.

Several reports have documented the displacement of one, two, or three molecules of carbon monoxide from  $\text{Fe}_2(\text{CO})_6(\text{SR})_2$  complexes by tertiary phosphines, phosphites, arsines, and stibines or di(tertiary phosphines and arsines).<sup>6-8</sup> Infra-red, pmr, and Mossbauer spectra of these derivatives imply

that the favored coordination sites for the noncarbonyl ligands are the "apical" positions trans to the iron-iron bond.<sup>7,8</sup> When the ligands are monodentate, the disubstituted derivatives have symmetric structures with one ligand occupying the position trans to the iron-iron bond at each iron atom.<sup>8</sup>

In the course of their investigation of syn-anti isomerism in these systems, Bor and coworkers<sup>9</sup> observed that the rates of substitution reactions were dependent on the nature of the ligand and that substitution reactions of syn isomers were much more rapid than those of anti isomers. The first of these observations raised the possibility that the substitution mechanism might involve a direct bimolecular attack by the incoming ligand on the substrate complex. If true, these systems would be unusual examples of octahedral transition metal complexes undergoing substitution by  $\text{S}_\text{N}2$  mechanisms.<sup>10,11</sup> The second observation suggested that a kinetic study of the carbonyl-substitution reactions in a series of complexes containing different mercapto substituents might provide useful information on the detailed stereochemical course of the substitution process.

This paper reports a detailed mechanistic investigation of the reactions shown in eq 1 and 2. (Quantitative studies of  $\text{Fe}_2(\text{CO})_6(\text{SR})_2 + \text{L} \rightarrow \text{Fe}_2(\text{CO})_5(\text{SR})_2\text{L} + \text{CO}$  (1)  
 $\text{Fe}_2(\text{CO})_6(\text{SR})_2 + 2\text{L} \rightarrow \text{Fe}_2(\text{CO})_4(\text{SR})_2\text{L}_2 + 2\text{CO}$  (2)

disubstitution reactions (eq 2) have been confined to cases in which the monosubstitution (eq 1) is rate limiting.) The results strongly imply that the mechanism is  $\text{S}_\text{N}2$  (or  $\text{I}_\text{a}$ ) and suggest that the seven-coordinate activated complex is best described as an octahedral wedge.

### Experimental Section

**Materials.** Tricyclohexylphosphine<sup>12</sup> and diiron nonacarbonyl<sup>13</sup> were prepared by literature methods. All other ligands were obtained from commercial sources. S. N. P. Aquitaine supplied complimentary

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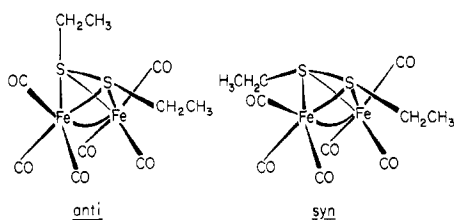


Figure 1.

samples of 1,2-ethanedithiol and 1,2-propanedithiol. Triphenylarsine was recrystallized from methanol, and tributylphosphine, trimethyl phosphite, and triphenyl phosphite were distilled in a nitrogen atmosphere at reduced pressure before use. Solvents were refluxed over calcium hydride or phosphorus pentoxide (nitrobenzene) and distilled in a nitrogen atmosphere. Carbon monoxide was passed through a trap at  $-78^\circ$  before use. Other reagents were used as received.

**Preparation of  $\text{Fe}_2(\text{CO})_6(\text{SR})_2$  Complexes.** The diiron hexacarbonyl complexes with bridging methyl,<sup>4</sup> ethyl,<sup>5,9</sup> benzyl,<sup>5,9</sup> phenyl,<sup>14</sup> and *p*-tolyl mercapto ligands<sup>14</sup> were prepared by published procedures. Recrystallization by very slow cooling of hexane solutions yielded methyl and benzyl complexes which nmr spectra showed to be the pure syn and anti isomers, respectively. The complexes in which the bridging sulfur atoms are joined by a rigid organic moiety,  $\text{Fe}_2(\text{CO})_6\text{S}_2\text{C}_2\text{H}_4$  ( $\text{R} = \frac{1}{2}\text{C}_2\text{H}_4$ ) and  $\text{Fe}_2(\text{CO})_6\text{S}_2\text{C}_6\text{H}_3\text{CH}_3$  ( $\text{R} = \frac{1}{2}\text{C}_6\text{H}_3\text{CH}_3$ ), were prepared by the following modification of the literature procedure.<sup>15</sup>

Diiron nonacarbonyl (11.6 g, 0.032 mol) was suspended in a benzene (330 ml) solution of 3,4-toluenedithiol (5 g, 0.032 mol) under an inert atmosphere. The suspension was vigorously stirred until carbon monoxide evolution ceased (18 hr, 40% of the theoretical volume). The solvent was then removed *in vacuo* and the resulting black solid was extracted with a total of 400 ml of hexane in small portions. The resulting red-brown solution was filtered through a bed of alumina (*ca.* 30 cm<sup>3</sup>) supported on a sintered-glass filter frit. The filtrate was concentrated to *ca.* 70 ml and cooled slowly to  $-78^\circ$  to give large, dark red crystals. These were recovered, washed with cold ( $-78^\circ$ ) hexane, and vacuum-dried to give 4 g (28% of theoretical) of  $\mu$ -(3,4-toluenedithiolato)-hexacarbonyldiiron (mp  $123^\circ$ , lit.<sup>15</sup> mp  $123$ – $124^\circ$ ).

Reaction of diiron nonacarbonyl and 1,2-ethanedithiol according to the same procedure yielded  $\mu$ -(1,2-ethanedithiolato)-hexacarbonyldiiron in 17% yield (mp  $76^\circ$ ; lit.<sup>15</sup> mp  $76$ – $77^\circ$ ). An attempt to prepare  $\mu$ -(1,2-propanedithiolato)-hexacarbonyldiiron from 1,2-propanedithiol by this procedure was unsuccessful.

Carbon and hydrogen analyses were obtained for most of the  $\text{Fe}_2(\text{CO})_6(\text{SR})_2$  complexes used. In all cases the compositions found were in satisfactory agreement with the calculated values.

**Kinetic Runs.** Most rate experiments were carried out under pseudo-first-order conditions using a large excess of the incoming ligand. The volume of evolved carbon monoxide was monitored as a function of time with a thermostated 5-ml gas buret connected to a thermostated reaction vessel by a short capillary tube.

Reaction mixtures were prepared in the thermostated reaction vessel. An aliquot of a stock solution of the ligand was transferred to the reaction vessel and diluted to the desired concentration. The apparatus was purged with carbon monoxide, bubbled through the vigorously stirred solution for at least 10 min. The reaction was initiated by injection of a 1-ml aliquot of a stock solution of the appropriate  $\text{Fe}_2(\text{CO})_6(\text{SR})_2$  complex.

For experiments at reduced pressure, all parts of the apparatus normally open to the atmosphere were connected by Tygon tubing to a manifold maintained at a constant reduced pressure. The desired pressure reduction was achieved using a mercury-filled manostat connected to an oil pump. A 2-l. ballast bulb to reduce pressure fluctuations and a manometer for determination of the pressure reduction were also included in the system. Reported carbon monoxide pressures were corrected for the vapor pressure of the solvent.<sup>16</sup>

**Identification of Substitution Products.** In all cases, gas evolution proceeded smoothly to give either 1 or 2 equiv of carbon monoxide, thus establishing the stoichiometry of the reaction. Additional structural verification was provided by the carbonyl region infrared spectra obtained for all of the derivatives involved in this study (Table I).

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(15) R. B. King, *J. Amer. Chem. Soc.*, 85, 1584 (1963).

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Table I. Infrared Spectra<sup>a</sup>

Complex	$\nu(\text{CO}), \text{cm}^{-1}$
$\text{Fe}_2(\text{CO})_6\text{S}_2\text{C}_6\text{H}_3\text{CH}_3$	2080 m, 2045 s, 2005 s
$\text{Fe}_2(\text{CO})_5\text{S}_2\text{C}_6\text{H}_3\text{CH}_3\text{P}(\text{C}_6\text{H}_5)_3$	2050 s, 1997 vw, 1984 m, 1945 w
$\text{Fe}_2(\text{CO})_5\text{S}_2\text{C}_6\text{H}_3\text{CH}_3\text{P}(\text{OC}_6\text{H}_5)_3$	2060 s, 2009 s, 1991 s, 1963 m
$\text{Fe}_2(\text{CO})_5\text{S}_2\text{C}_6\text{H}_3\text{CH}_3\text{HP}(\text{C}_6\text{H}_5)_2$	2056 s, 2001 vs, 1989 s, 1948 m
$\text{Fe}_2(\text{CO})_5\text{S}_2\text{C}_6\text{H}_3\text{CH}_3\text{P}(\text{C}_2\text{H}_5)(\text{C}_6\text{H}_5)_2$	2055 s, 1996 vs, 1985 s, 1942 m
$\text{Fe}_2(\text{CO})_5\text{S}_2\text{C}_6\text{H}_3\text{CH}_3\text{As}(\text{C}_6\text{H}_5)_3$	2056 s, 1997 vs, 1987 s, 1947 m
$\text{Fe}_2(\text{CO})_4\text{S}_2\text{C}_6\text{H}_3\text{CH}_3(\text{P}(n\text{-C}_4\text{H}_9)_3)_2$	2000 s, 1953 vs, 1939 m
$\text{Fe}_2(\text{CO})_4\text{S}_2\text{C}_6\text{H}_3\text{CH}_3(\text{P}(\text{OCH}_3)_3)_2$	2014 m, 1980 s, 1939 m
$\text{Fe}_2(\text{CO})_5\text{S}_2\text{C}_6\text{H}_3\text{CH}_3\text{P}(\text{C}_6\text{H}_{11})_3$	2053 s, 1993 vw, 1987 s, 1937 m
$\text{Fe}_2(\text{CO})_6\text{S}_2\text{C}_2\text{H}_4$ <sup>b</sup>	2080 m, 2039 s, 2010 s, 1998 s, 1986 w
$\text{Fe}_2(\text{CO})_5\text{S}_2\text{C}_2\text{H}_4\text{P}(\text{C}_6\text{H}_5)_3$	2052 m, 1985 s, 1964 m, 1930 w
$\text{Fe}_2(\text{CO})_5\text{S}_2\text{C}_2\text{H}_4\text{P}(n\text{-C}_4\text{H}_9)_3$	2050 m, 2043 s, 1987 vs, 1972 w, 1964 s, 1952 m, 1939 vw, 1930 m, 1917 w, 1906 vw
$\text{Fe}_2(\text{CO})_6(\text{SC}_6\text{H}_5)_2$	2077 m, 2040 vs, 2008 s, 2000 s, 1985 w
$\text{Fe}_2(\text{CO})_5(\text{SC}_6\text{H}_5)_2\text{P}(\text{C}_6\text{H}_5)_3$	2055 s, 1991 vs, 1976 w, 1945 w
$\text{Fe}_2(\text{CO})_4(\text{SC}_6\text{H}_5)_2(\text{P}(n\text{-C}_4\text{H}_9)_3)_2$	1985 vs, 1950 s, 1919 m
$\text{Fe}_2(\text{CO})_6(\text{SCH}_2\text{C}_6\text{H}_5)_2$	2073 m, 2039 vs, 2005 s, 1992 s
$\text{Fe}_2(\text{CO})_5(\text{SCH}_2\text{C}_6\text{H}_5)_2\text{P}(\text{C}_6\text{H}_5)_3$	2049 vs, 1988 s, 1980 m, 1967 m
$\text{Fe}_2(\text{CO})_5(\text{SCH}_2\text{C}_6\text{H}_5)_2\text{P}(n\text{-C}_4\text{H}_9)_3$	2040 s, 1984 vs, 1967 s, 1921 m
$\text{Fe}_2(\text{CO})_4(\text{SCH}_2\text{C}_6\text{H}_5)_2(\text{P}(n\text{-C}_4\text{H}_9)_3)_2$	1986 s, 1950 vs, 1923 s
$\text{Fe}_2(\text{CO})_6(\text{SC}_6\text{H}_4\text{CH}_3)_2$	2076 m, 2039 vs, 2007 s, 1999 s, 1992 w
$\text{Fe}_2(\text{CO})_5(\text{SC}_6\text{H}_4\text{CH}_3)_2\text{P}(\text{C}_6\text{H}_5)_3$	2051 s, 1990 vs, 1973 w, 1948 w
$\text{Fe}_2(\text{CO})_5(\text{SC}_6\text{H}_4\text{CH}_3)_2\text{P}(n\text{-C}_4\text{H}_9)_3$	2040 s, 1997 vs, 1969 s, 1928 m
$\text{Fe}_2(\text{CO})_4(\text{SC}_6\text{H}_4\text{CH}_3)_2(\text{P}(n\text{-C}_4\text{H}_9)_3)_2$	1987 s, 1950 vs, 1920 m
$\text{Fe}_2(\text{CO})_6(\text{SC}_2\text{H}_5)_2$	2072 m, 2036 vs, 2001 s, 1992 s
$\text{Fe}_2(\text{CO})_5(\text{SC}_2\text{H}_5)_2\text{P}(\text{C}_6\text{H}_5)_3$	2045 s, 1989 vs, 1984 sh, 1973 sh, 1969 m, 1950 m
$\text{Fe}_2(\text{CO})_5(\text{SC}_2\text{H}_5)_2\text{P}(n\text{-C}_4\text{H}_9)_3$	2043 s, 1983 vs, 1966 s, 1961 sh, 1922 w
$\text{Fe}_2(\text{CO})_4(\text{SC}_2\text{H}_5)_2(\text{P}(n\text{-C}_4\text{H}_9)_3)_2$	1987 s, 1981 sh, 1948 sh, 1942 s, 1923 s, 1915 w
$\text{Fe}_2(\text{CO})_6(\text{SCH}_3)_2$	2072 m, 2038 vs, 1998 s, 1990 s
$\text{Fe}_2(\text{CO})_5(\text{SCH}_3)_2\text{P}(\text{C}_6\text{H}_5)_3$	2048 s, 1988 vs, 1980 w, 1971 m, 1969 sh, 1936 w, 1930 sh

<sup>a</sup> Spectra were recorded in hexane solution and calibrated vs. indene and polystyrene. <sup>b</sup> R. B. King, *J. Amer. Chem. Soc.*, 85, 1584 (1963).

Previous work<sup>7-9</sup> established that these spectra were diagnostic of the number and position of the substituents introduced but insensitive to the identity of the substituent.

Infrared spectra of substitution products were recorded for derivatives prepared *in situ* in hexane solution from the appropriate substrate and a slight excess of the desired ligand. All spectra were calibrated vs. indene.<sup>17</sup> In all cases, the spectra were in agreement with expectations based on previously reported spectra for derivatives of the stoichiometry indicated by the volume of carbon monoxide evolved in the rate experiments.

The conclusion that the preferred substitution site is that trans to the iron-iron bond is also supported by the <sup>13</sup>C nmr spectrum of the triphenylphosphine derivative,  $\text{Fe}_2(\text{CO})_5(\text{S}_2\text{C}_6\text{H}_3\text{CH}_3)\text{P}(\text{C}_6\text{H}_5)_3$ . The

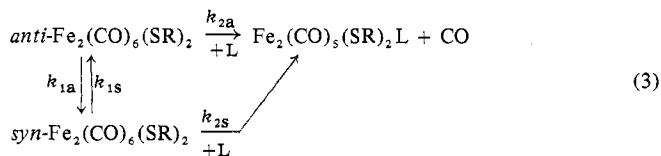
(17) C. N. R. Rao, "Chemical Applications of Infrared Spectroscopy," Academic Press, New York, N. Y., 1963, p 50.

peaks assignable to the carbonyl carbon atoms are very similar to those previously observed for the analogous complex  $\text{Fe}_2(\text{CO})_5(\text{C}_{12}\text{H}_8\text{N}_2)\text{P}(\text{OC}_6\text{H}_5)_3$ .<sup>18</sup> There are two peaks from the carbonyl carbons, one of which shows some indication of splitting, although the splitting is not so distinct as in the case of the  $\text{Fe}_2(\text{CO})_5(\text{C}_{12}\text{H}_8\text{N}_2)\text{P}(\text{OC}_6\text{H}_5)_3$  complex. This spectrum is compatible with the axially substituted structure for which three carbonyl carbon peaks are expected. Five peaks are expected for the alternative isomer in which the triphenylphosphine occupies a site cis to the iron-iron bond; therefore, the cmr spectrum is negative evidence in support of axial substitution.

**Instrumentation.** Infrared spectra were recorded on a Perkin-Elmer Model 621 spectrometer using an expanded linear wave number scale. Pmr spectra were recorded on a Varian A-60D spectrometer. The carbon-13 nmr spectrum of  $\text{Fe}_2(\text{CO})_5(\text{S}_2\text{C}_6\text{H}_3\text{CH}_3)\text{P}(\text{C}_6\text{H}_5)_3$  was obtained at 63.1 MHz by Fourier transform technique.<sup>19</sup>

## Results and Discussion

Because the syn and anti isomers of the di- $\mu$ -mercapto-hexacarbonyldiiron complexes must be expected to undergo substitution reactions at different rates and because these isomers can interconvert at rates comparable to their substitution rates, reasonably complex kinetic data are expected and found for their substitution reactions. Equation 3 indicates



the rate processes possible in such a reaction mixture. Despite this complexity, it has been possible to obtain individual rate constants for several complexes of this type reacting with triphenylphosphine.

These complications cannot occur for the complexes  $\mu$ -(3,4-toluenedithiolato)-hexacarbonyldiiron or  $\mu$ -(1,2-ethanedithiolato)-hexacarbonyldiiron in which rigid organic groups join the bridging sulfur atoms. For this reason, the most extensive kinetic studies have been carried out on the 3,4-toluenedithiol complex. Table II reports all of the pseudo-first-order rate constants obtained in this study.

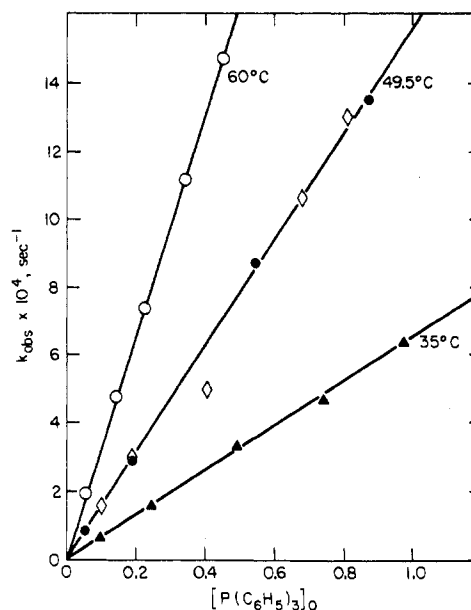
For all reacting ligands, experiments in which  $\text{Fe}_2(\text{CO})_6\text{-S}_2\text{C}_6\text{H}_3\text{CH}_3$  is the substrate give rise to excellent pseudo-first-order kinetic plots. These pseudo-first-order rate constants are strongly dependent on the identity of the incoming reagent, directly proportional to the concentration of the incoming reagent, and independent of the concentration of carbon monoxide over the available range. (See Figure 2.) These results establish a second-order rate law (eq 4) for car-

$$-d[\text{Fe}_2(\text{CO})_6\text{S}_2\text{C}_6\text{H}_3\text{CH}_3]/dt = k[\text{Fe}_2(\text{CO})_6\text{S}_2\text{C}_6\text{H}_3\text{CH}_3] \times [\text{L}] \quad (4)$$

bonyl substitution on  $\text{Fe}_2(\text{CO})_6\text{S}_2\text{C}_6\text{H}_3\text{CH}_3$  by ligands, L. Similar observations are made in all of the reactions of the other rigidly bridged substrate,  $\text{Fe}_2(\text{CO})_6\text{S}_2\text{C}_2\text{H}_4$ . The second order rate constants are given in Table III.

For  $\text{Fe}_2(\text{CO})_6\text{S}_2\text{C}_6\text{H}_3\text{CH}_3$  rate law 4 is followed even when the reaction entails disubstitution (eq 2), as is observed for the ligands  $\text{P}(n\text{-C}_4\text{H}_9)_3$  and  $\text{P}(\text{OCH}_3)_3$ . This requires that displacement of the first carbonyl group be rate limiting in these cases. Infrared spectra of such reaction mixtures confirm this interpretation, showing no indication of accumulation of monosubstituted complexes at intermediate times.

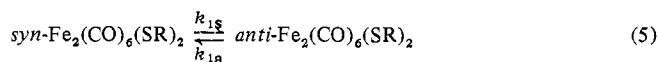
Substrates in which the bridging sulfur atoms are not joined by a rigid organic moiety show more complex kinetic



**Figure 2.** Observed pseudo-first-order rate constants for substitution on  $\text{Fe}_2(\text{CO})_6\text{S}_2\text{C}_6\text{H}_3\text{CH}_3$  plotted vs.  $\text{P}(\text{C}_6\text{H}_5)_3$  concentration. For the solid circles (49.5°) the carbon monoxide pressure is 340 Torr; open rhombuses, 640 Torr.

behavior, which varies both with the identity of the mercapto substituent and with the identity of the attacking ligand. Under the conditions of the rate experiments, triphenylphosphine reacts with the benzyl, methyl, ethyl, phenyl, and *p*-tolyl mercapto derivatives to displace 1 equiv of carbon monoxide. In some of these cases, the rate data do not obey a simple pseudo-first-order rate law over the entire life of the reaction. Instead, rapid evolution of a comparatively small volume can precede the smooth, pseudo-first-order evolution of the major portion of the carbon monoxide. That is, initial portions of pseudo-first-order kinetic plots (as much as 25% of the total volume change) can be severely curved. For these cases, the pseudo-first-order rate constants reported in Table II are obtained from the later, linear portion of the graph. The rate behavior of reactions of  $\text{P}(n\text{-C}_4\text{H}_9)_3$  with these bis(monomercapto) derivatives is generally more complex, because a second substitution occurs at a rate approximately equal to that of the first substitution.

The rate behavior of the triphenylphosphine reactions with bis(monomercapto) derivatives is readily explained by eq 3, once the relationships among the magnitudes of the various rate constants are understood. The necessary understanding follows readily from rate experiments in which the methyl and methylene pmr resonances of  $\text{Fe}_2(\text{CO})_6(\text{SCH}_3)_2$  and  $\text{Fe}_2(\text{CO})_6(\text{SCH}_2\text{C}_6\text{H}_5)_2$  are monitored as a function of time. Samples of essentially pure syn and anti isomers are available for these two substrates, respectively (*vide supra*). Monitoring the equilibration reaction (eq 5) yields a first-order



decay curve, whose apparent first-order rate constant is a sum of  $k_{1s}$  and  $k_{1a}$  (e.g., eq 6). The concentration ratio at

$$\ln \left\{ \frac{[\text{syn}] - [\text{syn}]_\infty}{[\text{syn}]_0 - [\text{syn}]_\infty} \right\} = -(k_{1s} + k_{1a})t \quad (6)$$

infinite time establishes the equilibrium constant and thus the values of the individual rate constants. These rate constants for the isomerization reactions are given in Table IV. The results are in good agreement with earlier qualitative ob-

(18) P. C. Ellgen and S. L. McMullin, *Inorg. Chem.*, **12**, 2004 (1973).

(19) We are indebted to Dr. R. J. Wiersema, Department of Chemistry, University of California at Los Angeles, for this spectrum.

Table II. Pseudo-First-Order Rate Constants for Carbonyl-Substitution Reactions of Bis(mercaptotricarbonyliron) Complexes<sup>a</sup>

Ligand	[Ligand], M	$10^4 k_{\text{obsd}}$ , sec <sup>-1</sup>	$P_{\text{CO}}$ , Torr	Temp., °C	Ligand	[Ligand], M	$10^4 k_{\text{obsd}}$ , sec <sup>-1</sup>	$P_{\text{CO}}$ , Torr	Temp., °C
Fe <sub>2</sub> (CO) <sub>6</sub> S <sub>2</sub> C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub> - P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	0.0942	0.63	690	35	P(OCH <sub>3</sub> ) <sub>3</sub>	0.0819	1.04	690	35
	0.247	1.59	690	35		0.404	4.8	690	35
	0.494	3.3	690	35		0.816	10.8	690	35
	0.740	4.7	690	35	PH(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	0.0140	1.06	690	35
	0.972	6.8	690	35		0.0305	2.6	690	35
	0.101	1.58	645	49.5		0.0923	8.0	690	35
	0.190	3.0	645	49.5		0.143	12.4	690	35
	0.403	5.0	645	49.5	P(C <sub>2</sub> H <sub>5</sub> )(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	0.0117	1.12	690	35
	0.678	10.6	645	49.5		0.0568	5.4	690	35
	0.807	13.0	645	49.5		0.120	11.6	690	35
	0.0573	0.81	340	49.5	P(C <sub>6</sub> H <sub>11</sub> ) <sub>3</sub>	0.173	0.95	690	35
	0.190	2.9	340	49.5		0.406	2.5	690	35
	0.542	8.7	340	49.5	P( <i>o</i> -C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> ) <sub>3</sub>	0.304	No reaction	540	70
	0.871	13.5	340	49.5	As(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	0.497	0.40	540	70
	0.0563	1.94	595	60		0.793	0.67	540	70
	0.147	4.7	595	60	Fe <sub>2</sub> (CO) <sub>6</sub> S <sub>2</sub> C <sub>2</sub> H <sub>4</sub> - P( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub>	0.159	1.03	645	50
	0.226	7.4	595	60		0.480	3.1	645	50
	0.339	11.1	595	60		0.924	5.8	645	50
	0.451	14.7	595	60		0.100	1.22	595	60
	0.111	0.84 <sup>b</sup>		35		0.480	6.1	595	60
	0.324	2.5 <sup>b</sup>		35		0.0201	0.48	540	70
	0.647	5.5 <sup>b</sup>		35		0.129	3.0	540	70
	0.971	8.2 <sup>b</sup>		35		0.258	6.2	540	70
	0.105	0.96 <sup>c</sup>	740	35	P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	0.89	0.62	540	70
	0.405	3.6 <sup>c</sup>	740	35	Fe <sub>2</sub> (CO) <sub>6</sub> (SC <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> - P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	0.0273	2.4	690	35
	0.939	9.2 <sup>c</sup>	740	35		0.100	3.1	690	35
	0.966	0.67	690	35		0.500	4.7	690	35
	0.505	0.94	645	50		0.985	7.4	690	35
1.08	2.2 <sub>3</sub>	645	50						
0.249	0.93	595	60	Fe <sub>2</sub> (CO) <sub>6</sub> (SCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> - P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	0.0273	0.58	690	35	
1.04	4.3	595	60		0.105	1.06	690	35	
0.160	0.96	540	70		0.500	3.3	690	35	
0.508	3.5	540	70		0.984	6.6	690	35	
0.905	6.7	540	70		1.04	6.8	370	35	
0.00899	1.20	700	30						
0.0201	2.3	700	30	Fe <sub>2</sub> (CO) <sub>6</sub> (SC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> - P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	0.150	1.06	690	35	
0.0540	6.3	700	30		0.239	1.50	690	35	
0.106	12.4	700	30		0.785	4.8	690	35	
0.0545	6.7	370	30		0.984	6.1	690	35	
0.0178	0.93	720	20						
0.0537	3.3	720	20	Fe <sub>2</sub> (CO) <sub>6</sub> (SC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> ) <sub>2</sub> - P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	0.0318	2.6	690	35	
0.0995	5.6	720	20		0.399	3.5	690	35	
0.257	14.9	720	20		0.785	4.6	690	35	
0.0429	1.0 <sub>9</sub>	725	10						
0.101	2.6	725	10	<i>syn</i> -Fe <sub>2</sub> (CO) <sub>6</sub> (SCH <sub>3</sub> ) <sub>2</sub> - P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	0.00466	4.5	690	35	
0.196	5.1	725	10		0.0270	26	690	35	
0.370	8.7	725	10	<i>anti</i> -Fe <sub>2</sub> (CO) <sub>6</sub> (SCH <sub>3</sub> ) <sub>2</sub> - P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	0.0219	0.10 <sub>2</sub>	690	35	
					0.102	5.12	690	35	

<sup>a</sup> In toluene solution except as otherwise noted; substrate concentration in the range  $5 \times 10^{-4}$  to  $10^{-2}$  M, but always less than 0.1 [ligand].

<sup>b</sup> In tetrahydrofuran. <sup>c</sup> In nitrobenzene.

servations.<sup>4,5,9</sup> In particular, the methyl mercapto complex isomerizes slowly ( $t_{1/2} = 4.3$  hr at 35°) compared to the benzyl mercapto complex ( $t_{1/2} = 0.84$  hr). In general, it appears that the isomerization rate increases as the size of the mercapto substituent increases (*vide infra*).

When an excess of triphenylphosphine is allowed to react with these substrates at the high concentrations required for monitoring substrate pmr spectra, the *syn* isomers are consumed at a rate large compared to the rate of the isomerization reaction. Moreover, the *syn* isomers react much more rapidly than the *anti* isomers, by factors of 40 and 20 for the benzyl and methyl derivatives, respectively (Table III). This is also in agreement with earlier qualitative observations.<sup>9</sup> It appears that, in general,  $k_{2s} \gg k_{2a}$  for a given substrate.

The rate data obtained in carbon monoxide evolution experiments with bis(monomercapto) substrates fall into two classes. The methyl and ethyl complexes give pseudo-

first-order rate constants which are directly proportional to the ligand concentration. The equilibration of *syn* and *anti* isomers is slow and does not interfere with the evaluation of the second-order rate constants for the ligand substitution processes. That is,  $k_{2a}[\text{P}(\text{C}_6\text{H}_5)_3] \gg k_{1a}$  and  $k_{2s}[\text{P}(\text{C}_6\text{H}_5)_3] \gg k_{1s}$ . The two second-order reactions are not kinetically coupled to one another; if the original substrate sample contains a mixture of *syn* and *anti* isomers, the reaction is observed to take place in two distinct steps.

In contrast, the phenyl, *p*-tolyl, and benzyl derivatives give pseudo-first-order rate constants which are not directly proportional to the ligand concentration. Instead, the rate law appears to contain both a first- and a second-order term (see Figure 3). It appears that the inequalities  $k_{2s} \gg k_{2a}$  and  $k_{2s}[\text{P}(\text{C}_6\text{H}_5)_3] \gg k_{1s}$  also hold for these substrates under the experimental conditions; however, for these substrates,  $k_{2a}[\text{P}(\text{C}_6\text{H}_5)_3]$  is approximately equal to  $k_{1a}$ . When the original

**Table III.** Second-Order Rate Constants and Activation Parameters for Carbonyl-Substitution Reactions of Bis(mercaptotricarbonyliron) Complexes<sup>a</sup>

Complex	Ligand	$10^3 k, M^{-1} \text{sec}^{-1}$	Temp, °C	$P_{\text{CO}}$ , Torr	$\Delta H^\ddagger$ , kcal/mol	$\Delta S^\ddagger$ , eu
$\text{Fe}_2(\text{CO})_6\text{S}_2\text{C}_6\text{H}_5\text{CH}_3$	$\text{P}(\text{C}_6\text{H}_5)_3$	0.65	35	690	12.5	-31
		1.57	49.5	640		
		1.53	49.5	340		
		3.3	60	595		
		0.81 <sup>b</sup>	35			
		0.92 <sup>c</sup>	35	740		
		0.069	35	690		
		0.196	50	645		
		0.39	60	595		
	$\text{P}(\text{OC}_6\text{H}_5)_3$	0.67	70	540	14.4	-29
		2.5	10	725		
		5.8	20	720		
		11.7	30	700		
		12.3	30	385		
		1.23	35	690		
	$\text{P}(n\text{-C}_4\text{H}_9)_3$	8.5	35	690	11.5	-34
		9.6	35	690		
		0.58	35	690		
		No reaction	70	540		
$\text{Fe}_2(\text{CO})_6\text{S}_2\text{C}_2\text{H}_4$	$\text{As}(\text{C}_6\text{H}_5)_3$	0.85	70	540	13.6	-31
		0.64	50	645		
	1.25	60	596			
	2.4	70	540			
	0.072	70	540			
$\text{Fe}_2(\text{CO})_6(\text{SC}_6\text{H}_5)_2$ (anti)	$\text{P}(\text{C}_6\text{H}_5)_3$	0.49	35	690		
	$\text{P}(n\text{-C}_4\text{H}_9)_3$	0.61	35	690		
$\text{Fe}_2(\text{CO})_6(\text{SCH}_2\text{C}_6\text{H}_5)_2$ (anti)	$\text{P}(\text{C}_6\text{H}_5)_3$	0.62	35	370		
		0.66 <sup>d</sup>	35			
$\text{Fe}_2(\text{CO})_6(\text{SCH}_2\text{C}_6\text{H}_5)_2$ (syn)	$\text{P}(\text{C}_6\text{H}_5)_3$	23 <sup>d</sup>	35			
$\text{Fe}_2(\text{CO})_6(\text{SC}_2\text{H}_5)_2$ (anti)	$\text{P}(\text{C}_6\text{H}_5)_3$	0.59	35	690		
$\text{Fe}_2(\text{CO})_6(p\text{-SC}_6\text{H}_4\text{CH}_3)_2$ (anti)	$\text{P}(\text{C}_6\text{H}_5)_3$	0.21	35	690		
$\text{Fe}_2(\text{CO})_6(\text{SCH}_3)_2$ (anti)	$\text{P}(\text{C}_6\text{H}_5)_3$	5.0	35	690		
$\text{Fe}_2(\text{CO})_6(\text{SCH}_3)_2$ (syn)	$\text{P}(\text{C}_6\text{H}_5)_3$	97	35			

<sup>a</sup> Toluene solvent except as noted. <sup>b</sup> Tetrahydrofuran solvent. <sup>c</sup> Nitrobenzene solvent. <sup>d</sup> From rate of disappearance of pmr spectrum.

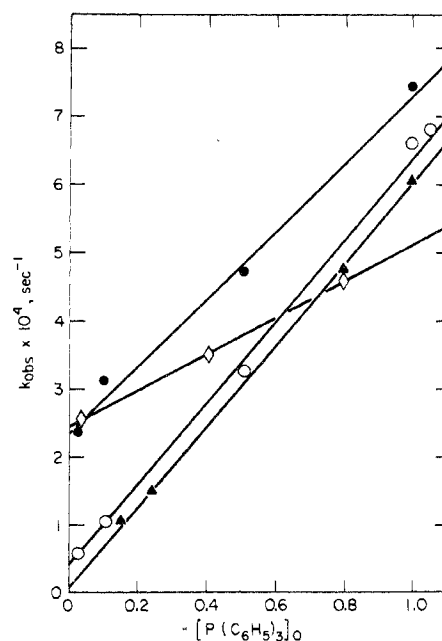
**Table IV.** First-Order Rate Constants for the Syn-Anti Isomerization Reaction<sup>a</sup>

Complex	$10^5 k_{1a}, \text{sec}^{-1}$	$10^5 k_{1s}, \text{sec}^{-1}$
$\text{Fe}_2(\text{CO})_6(\text{SCH}_3)_2$	1.1 <sup>b</sup>	3.4 <sup>b</sup>
$\text{Fe}_2(\text{CO})_6(\text{SCH}_2\text{C}_6\text{H}_5)_2$	4.6 <sup>b</sup>	18.4 <sup>b</sup>
	4.0 <sup>c</sup>	
$\text{Fe}_2(\text{CO})_6(\text{SC}_6\text{H}_5)_2$	24 <sup>c</sup>	
$\text{Fe}_2(\text{CO})_6(p\text{-SC}_6\text{H}_4\text{CH}_3)_2$	25 <sup>c</sup>	
$\text{Fe}_2(\text{CO})_6(\text{SCH}_2\text{CH}_3)_2$	<2	

<sup>a</sup> In toluene solution at 35°. <sup>b</sup> By monitoring pmr spectra. <sup>c</sup> From CO-evolution data according to eq 8.

reaction mixture contains significant quantities of both the syn and anti isomer of the substrate, this interpretation is consistent with initial curvature in pseudo-first-order kinetic plots; the small proportion of the complex originally present as the syn isomer is rapidly converted to product. The later portion of the reaction, which yields a linear pseudo-first-order plot, is due to the anti isomer undergoing substitution by two parallel paths. One of these is the second-order reaction with ligand whose rate constant is  $k_{2a}$  (eq 3); the rate-limiting step for the other is the first-order isomerization to the syn isomer, which is then rapidly converted to the substitution product. This interpretation is equivalent to assuming that the syn isomer's concentration reaches a value well approximated by a steady-state treatment, after an initial induction period in which the initially present syn isomer is essentially completely consumed.

Application of a steady-state treatment to the concentration of syn isomer according to eq 3 yields the expression for the pseudo-first-order rate constant for carbon monoxide



**Figure 3.** Observed pseudo-first-order rate constants for substitution on  $\text{Fe}_2(\text{CO})_6(\text{SR})_2$  complexes plotted vs.  $\text{P}(\text{C}_6\text{H}_5)_3$  concentration: solid circles, R = phenyl; rhombuses, R = *p*-tolyl; open circles, R = benzyl; solid triangles, R = ethyl.

evolution shown as eq 7. Incorporation of the inequalities

$$k_{\text{obsd}} = \frac{(k_{1a}k_{2s} + k_{1s}k_{2a})[\text{P}(\text{C}_6\text{H}_5)_3] + k_{2a}k_{2s}[\text{P}(\text{C}_6\text{H}_5)_3]^2}{k_{1s} + k_{2s}[\text{P}(\text{C}_6\text{H}_5)_3]} \quad (7)$$

above simplifies this to eq 8. Reference to Figure 3 immediately establishes that this result gives a good description of the dependence of the observed pseudo-first-order rate constant on the triphenylphosphine concentration. The values of  $k_{2a}$  obtained in this way for the various substrates are reported in Table III.

$$k_{\text{obsd}} = k_{1a} + k_{2a}[\text{P}(\text{C}_6\text{H}_5)_3] \quad (8)$$

diately establishes that this result gives a good description of the dependence of the observed pseudo-first-order rate constant on the triphenylphosphine concentration. The values of  $k_{2a}$  obtained in this way for the various substrates are reported in Table III.

For the benzyl substrate, independent evidence confirms the validity of this interpretation. The values of  $k_{1a}$  and  $k_{2a}$  obtained from the plot in Figure 3 are in excellent agreement with those obtained independently in reactions monitored by pmr spectroscopy. Reaction mixtures containing high concentrations of both substrate and ligand will lose the bulk of the anti isomer by the second-order path; thus the rate at which anti isomer vanishes from such solutions is expected to yield a good estimate of  $k_{2a}$ . The value obtained agrees well with that from the carbon monoxide evolution experiments (see Table III). Similarly, an independently determined, confirmatory value of  $k_{1a}$  is obtained from the pmr study of the syn-anti isomerization reaction (see Table IV).

For the complexes  $\text{Fe}_2(\text{CO})_6(\text{SC}_6\text{H}_5)_2$  and  $\text{Fe}_2(\text{CO})_6(p\text{-SC}_6\text{H}_4\text{CH}_3)_2$ , this interpretation has some interesting implications. Despite careful efforts, the separation of aryl mercapto complexes into syn and anti isomers has not been achieved, nor has unequivocal spectroscopic evidence for the presence of two isomers been obtained.<sup>9</sup> Although other interpretations are possible, the simplest is that the isomerization equilibrium strongly favors the anti isomer in these cases. The kinetic data for carbonyl substitution reported here strongly support this interpretation. For both of these substrates, the carbon monoxide evolution experiments do not show a significant induction period; pseudo-first-order kinetic plots are linear essentially from the time of mixing. This is consistent with the presence of minimal syn isomer in the initial substrate solution. On the other hand, both of these substrates yield kinetic data which conform to eq 9 with large values of  $k_{1a}$ . That is, even though the syn isomer is not present as a detectable fraction of the total substrate, a substantial portion of the carbonyl-substitution reaction occurs *via* ligand attack on it rather than on the more abundant anti isomer. The values of  $k_{1a}$  for the phenyl and *p*-tolyl mercapto complexes are very similar. For these systems both  $k_{1a}$  and  $k_{1s}$  are larger than for the alkyl mercapto complexes studied.

Thus, for all of the substrates investigated in this study, the carbonyl-substitution process follows a strictly second-order rate law which is first order in both the substrate and the attacking ligand and is independent of the concentration of carbon monoxide. The rate constants for the reactions of  $\text{Fe}_2(\text{CO})_6\text{S}_2\text{C}_6\text{H}_3\text{CH}_3$  are strongly dependent on the nature of the incoming ligand. These results suggest that the reaction mechanism is a bimolecular displacement of the  $\text{SN}2^{20}$  or  $\text{I}_a^{21}$  type. A number of other observations reinforce this conclusion.

It is interesting to compare the  $\text{Fe}_2(\text{CO})_6\text{S}_2\text{C}_6\text{H}_3\text{CH}_3$  substitution reactions to those of  $\text{Co}(\text{CO})_3\text{NO}$ ,<sup>22</sup>  $\text{Fe}(\text{CO})_2(\text{NO})_2$ ,<sup>23</sup> and  $\text{Rh}(\text{C}_5\text{H}_5)(\text{CO})_2$ .<sup>24</sup> These substrates are thought to

undergo carbonyl-substitution reactions by  $\text{SN}2$  mechanisms. They exhibit second-order rate laws, and the second-order rate constants are strongly dependent on the nature of the incoming ligand. For a series of ligands having the same donor atom, a linear free energy correlation relates the second-order rate constants for carbonyl displacement to the nucleophile's basicity toward the proton. A correlation of this type is observed for the reactions of  $\text{Fe}_2(\text{CO})_6\text{S}_2\text{C}_6\text{H}_3\text{CH}_3$  with phosphorus nucleophiles.

The negative activation entropies obtained for the substitution reactions of  $\text{Fe}_2(\text{CO})_6\text{S}_2\text{C}_6\text{H}_3\text{CH}_3$  imply considerable loss of freedom in going from reactants to the activated complex. The entropies of activation for the dinuclear iron complex are somewhat more negative than those for the mononuclear species. This can be reasonably ascribed to greater crowding in the seven-coordinate activated complex for substitution on  $\text{Fe}_2(\text{CO})_6\text{S}_2\text{C}_6\text{H}_3\text{CH}_3$  than is found in the five-coordinate activated complexes for the mononuclear species.

The phosphines  $\text{P}(\text{C}_6\text{H}_{11})_3$  and  $\text{P}(o\text{-C}_6\text{H}_4\text{CH}_3)_3$  are relatively unreactive toward  $\text{Fe}_2(\text{CO})_6\text{S}_2\text{C}_6\text{H}_3\text{CH}_3$ . Thus  $\text{P}(\text{C}_6\text{H}_5)_3$  reacts readily, but  $\text{P}(o\text{-C}_6\text{H}_4\text{CH}_3)_3$  does not. This large difference in reactivity cannot be ascribed to an inductive effect. Similarly, the reactivity of  $\text{P}(\text{C}_6\text{H}_{11})_3$  is much less than expected from its basicity on the basis of the linear free energy correlation or from the reactivity of tri(*n*-butyl)phosphine. The only phosphorus-donor ligands less active than  $\text{P}(\text{C}_6\text{H}_{11})_3$  are  $\text{P}(\text{OC}_6\text{H}_5)_3$  and  $\text{P}(o\text{-C}_6\text{H}_4\text{CH}_3)_3$ .

The anomalously low reactivities of  $\text{P}(\text{C}_6\text{H}_{11})_3$  and  $\text{P}(o\text{-C}_6\text{H}_4\text{CH}_3)_3$  appear to be a consequence of their large steric requirements. Tolman<sup>25</sup> has defined a "cone angle" for phosphorus-donor ligands which roughly measures the volume about the phosphorus atom from which a Lewis acid would be excluded. These two phosphines have particularly large cone angles. Their low reactivity is consistent with the assumption that steric hindrance provides a major obstacle to their attack on  $\text{Fe}_2(\text{CO})_6\text{S}_2\text{C}_6\text{H}_3\text{CH}_3$  to give a seven-coordinate activated complex.

The rate constant for the reaction of  $\text{Fe}_2(\text{CO})_6\text{S}_2\text{C}_6\text{H}_3\text{CH}_3$  with  $\text{P}(\text{C}_6\text{H}_5)_3$  is insensitive to variation of the solvent from toluene to tetrahydrofuran or nitrobenzene. This indicates that neither the coordinating ability of the solvent nor the dielectric constant of the medium have an important effect on the reaction rate. These results are expected for an  $\text{SN}2$  mechanism involving little charge development in going from the reactants to the activated complex.

A remarkable feature of the second-order rate constants in Table III is their insensitivity to the nature of the mercapto substituent. There is a substantial difference in the reactivities of syn and anti isomers with a given phosphine; this must be ascribed to a steric effect (*vide infra*). But if the rate constants for the anti isomers of bis(monomercapto) complexes reacting with  $\text{P}(\text{C}_6\text{H}_5)_3$  are compared, the differences are small. These data imply that there is very little effect on the reaction rate attributable to the inductive properties of the mercapto substituent. Although *anti*- $\text{Fe}_2(\text{CO})_6(\text{SCH}_3)_2$  reacts significantly faster than the other substrates, the pattern of the data suggests that even this difference is more likely to reflect a steric than an inductive effect.

Now, the reactivity of  $\text{Fe}_2(\text{CO})_6\text{S}_2\text{C}_6\text{H}_3\text{CH}_3$  with  $\text{P}(\text{C}_6\text{H}_5)_3$  is very similar to that of the *anti*-bis(monomercapto) complexes. In view of the absence of a significant inductive effect from the mercapto substituent, this implies that there is no particular rate effect associated with the fact that the two bridging sulfur atoms are joined by a rigid organic group.

(20) Reference 10, p 137.

(21) C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, New York, N. Y., 1965, Chapter 1.

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This conclusion has an interesting and important mechanistic consequence. The structures of these dinuclear complexes are strongly influenced by the presence of the iron-iron bond (*vide supra*); the presence of the iron-iron bond results in bent iron-sulfur bonds and in distorted iron-sulfur-iron and sulfur-iron-sulfur angles.<sup>2</sup> If the iron-iron bond were broken without breaking the iron-sulfur bonds, the resulting, high-energy species would be expected to have a more nearly planar Fe<sub>2</sub>S<sub>2</sub> core, because such rearrangement would reduce the total angle strain in the four iron-sulfur bonds.<sup>26</sup> In particular, attack by ligand on the dinuclear complex could form an activated complex (or a reactive intermediate) in which the iron-iron bond is broken. The substitution process would be completed by re-forming the iron-iron bond with concomitant expulsion of a carbon monoxide ligand.

However, if this were the mechanism, a means would exist for stabilizing the activated complexes for the bis(monomercapto) substrates that does not exist for those complexes in which the bridging sulfur atoms are joined by a rigid organic moiety. The activated complex for the bis(monomercapto) complexes could be stabilized by reorganization of the Fe<sub>2</sub>S<sub>2</sub> core; the activated complexes in which the sulfur atoms are bridged by a rigid organic group could not undergo such reorganization. Hence, this mechanism would predict that Fe<sub>2</sub>(CO)<sub>6</sub>S<sub>2</sub>C<sub>6</sub>H<sub>3</sub>CH<sub>3</sub> should react more slowly than analogous bis(monomercapto) complexes. The fact that this is not true is evidence against a substitution mechanism involving an activated complex, or a reactive intermediate, in which the iron-iron bond is completely broken. A similar argument suggests that iron-sulfur bond breaking cannot play an important role in the activation process.

This interpretation concludes that no particular rate effect results from joining the bridging sulfur atoms with a rigid organic group. Since the data also imply that the mercapto substituent has little inductive effect on the substitution rate, the data for substitution on Fe<sub>2</sub>(CO)<sub>6</sub>S<sub>2</sub>C<sub>2</sub>H<sub>4</sub> are particularly puzzling. At 35°, the second-order rate constant for reaction of this complex with P(*n*-C<sub>4</sub>H<sub>9</sub>)<sub>3</sub> is *ca.* 80 times slower than that of Fe<sub>2</sub>(CO)<sub>6</sub>S<sub>2</sub>C<sub>6</sub>H<sub>3</sub>CH<sub>3</sub>. Comparison of activation parameters shows that this is due to a significantly larger activation enthalpy; activation entropies are not greatly different.

That *syn*-di- $\mu$ -mercapto-hexacarbonyliron complexes are substituted more rapidly than their *anti* isomers must be ascribed to a steric effect. The relative unreactivity of the *anti* isomer focuses attention on the octahedral face defined by the bridging sulfur atoms and the apical carbonyl; it is this region of the original complex which is significantly less accessible in the *anti* isomer than in the *syn* isomer. This octahedral face is also the locus of a small, but distinct, difference in the steric requirements of the 3,4-tolyl and 1,2-ethyl bridges between the sulfur atoms. Both of these bridging ligands project over this octahedral face. The difference in the extent to which these bridges project over the octahedral face is small, but examination of molecular models shows that the van der Waals radius of the hydrogen atoms

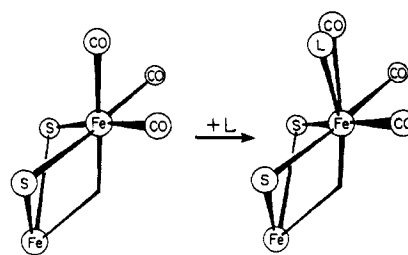


Figure 4. Proposed structure of the activated complex for substitution on Fe<sub>2</sub>(CO)<sub>6</sub>S<sub>2</sub>C<sub>6</sub>H<sub>3</sub>CH<sub>3</sub>. For clarity, only the groups in the immediate vicinity of the iron atom undergoing substitution are shown.

in the 1,2-ethyl bridge extends approximately 0.5 Å further than does the van der Waals thickness of the 3,4-tolyl ring. Now, except for *syn* isomers, this face would appear to be too crowded to be the site of incoming group attack or leaving group departure. But these considerations lead to a plausible structure for the activated complex. This structure is a distorted octahedral wedge<sup>27</sup> in which the entering and leaving groups lie on an edge which is parallel to the edge defined by the two bridging sulfur atoms (see Figure 4). This structure for the activated complex provides an explanation for the difference in reactivity between the 3,4-tolyl- and the 1,2-ethyl-bridged complexes. The hydrogen atoms of the 1,2-ethyl bridge extend only very slightly further than does the 3,4-tolyl bridge, but they are directed exactly toward the sites occupied by the entering and the leaving group in the proposed activated complex. Although the steric difference between these two substrates is slight, it would occur in exactly the critical region and might thus lead to a significant rate effect.

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**Registry No.** Fe<sub>2</sub>(CO)<sub>6</sub>S<sub>2</sub>C<sub>6</sub>H<sub>3</sub>CH<sub>3</sub>, 19964-06-8; Fe<sub>2</sub>(CO)<sub>6</sub>S<sub>2</sub>C<sub>6</sub>H<sub>3</sub>CH<sub>3</sub>P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>, 41539-10-0; Fe<sub>2</sub>(CO)<sub>6</sub>S<sub>2</sub>C<sub>6</sub>H<sub>3</sub>CH<sub>3</sub>P(OC<sub>6</sub>H<sub>5</sub>)<sub>3</sub>, 41539-11-1; Fe<sub>2</sub>(CO)<sub>6</sub>S<sub>2</sub>C<sub>6</sub>H<sub>3</sub>CH<sub>3</sub>HP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>, 41539-12-2; Fe<sub>2</sub>(CO)<sub>6</sub>S<sub>2</sub>C<sub>6</sub>H<sub>3</sub>CH<sub>3</sub>P(C<sub>2</sub>H<sub>5</sub>)(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>, 41539-13-3; Fe<sub>2</sub>(CO)<sub>6</sub>S<sub>2</sub>C<sub>6</sub>H<sub>3</sub>CH<sub>3</sub>As(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>, 41543-15-1; Fe<sub>2</sub>(CO)<sub>6</sub>S<sub>2</sub>C<sub>6</sub>H<sub>3</sub>CH<sub>3</sub>[P(*n*-C<sub>4</sub>H<sub>9</sub>)<sub>3</sub>]<sub>2</sub>, 41543-16-2; Fe<sub>2</sub>(CO)<sub>6</sub>S<sub>2</sub>C<sub>6</sub>H<sub>3</sub>CH<sub>3</sub>[P(OCH<sub>3</sub>)<sub>3</sub>]<sub>2</sub>, 41562-30-5; Fe<sub>2</sub>(CO)<sub>6</sub>S<sub>2</sub>C<sub>6</sub>H<sub>3</sub>CH<sub>3</sub>-P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>, 41543-17-3; Fe<sub>2</sub>(CO)<sub>6</sub>S<sub>2</sub>C<sub>2</sub>H<sub>4</sub>, 15492-14-5; Fe<sub>2</sub>(CO)<sub>6</sub>S<sub>2</sub>C<sub>2</sub>H<sub>4</sub>P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>, 41543-19-5; Fe<sub>2</sub>(CO)<sub>6</sub>S<sub>2</sub>C<sub>2</sub>H<sub>4</sub>[P(*n*-C<sub>4</sub>H<sub>9</sub>)<sub>3</sub>]<sub>2</sub>, 41543-20-8; Fe<sub>2</sub>(CO)<sub>6</sub>(SC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>, 15634-63-6; Fe<sub>2</sub>(CO)<sub>6</sub>(SC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>, 27220-99-1; Fe<sub>2</sub>(CO)<sub>6</sub>(SC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>[P(*n*-C<sub>4</sub>H<sub>9</sub>)<sub>3</sub>]<sub>2</sub>, 41543-23-1; Fe<sub>2</sub>(CO)<sub>6</sub>(SCH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>, 41543-24-2; Fe<sub>2</sub>(CO)<sub>6</sub>(SCH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>, 41543-25-3; Fe<sub>2</sub>(CO)<sub>6</sub>(SCH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>[P(*n*-C<sub>4</sub>H<sub>9</sub>)<sub>3</sub>]<sub>2</sub>, 41543-26-4; Fe<sub>2</sub>(CO)<sub>6</sub>(SCH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>[P(*n*-C<sub>4</sub>H<sub>9</sub>)<sub>3</sub>]<sub>2</sub>, 41543-27-5; Fe<sub>2</sub>(CO)<sub>6</sub>(SC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)<sub>2</sub>, 41543-28-6; Fe<sub>2</sub>(CO)<sub>6</sub>(SC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)<sub>2</sub>P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>, 41562-31-6; Fe<sub>2</sub>(CO)<sub>6</sub>(SC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)<sub>2</sub>[P(*n*-C<sub>4</sub>H<sub>9</sub>)<sub>3</sub>]<sub>2</sub>, 41543-29-7; Fe<sub>2</sub>(CO)<sub>6</sub>(SC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)<sub>2</sub>[P(*n*-C<sub>4</sub>H<sub>9</sub>)<sub>3</sub>]<sub>2</sub>, 41543-30-0; Fe<sub>2</sub>(CO)<sub>6</sub>(SC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)<sub>2</sub>, 15634-62-5; Fe<sub>2</sub>(CO)<sub>6</sub>(SC<sub>2</sub>H<sub>5</sub>)<sub>2</sub>P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>, 36419-09-7; Fe<sub>2</sub>(CO)<sub>6</sub>(SC<sub>2</sub>H<sub>5</sub>)<sub>2</sub>[P(*n*-C<sub>4</sub>H<sub>9</sub>)<sub>3</sub>]<sub>2</sub>, 36419-07-5; Fe<sub>2</sub>(CO)<sub>6</sub>(SC<sub>2</sub>H<sub>5</sub>)<sub>2</sub>[P(*n*-C<sub>4</sub>H<sub>9</sub>)<sub>3</sub>]<sub>2</sub>, 41543-34-4; Fe<sub>2</sub>(CO)<sub>6</sub>(SCH<sub>3</sub>)<sub>2</sub>, 14878-96-7; Fe<sub>2</sub>(CO)<sub>6</sub>(SCH<sub>3</sub>)<sub>2</sub>P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>, 36419-05-3; P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>, 603-35-0; P(OC<sub>6</sub>H<sub>5</sub>)<sub>3</sub>, 101-02-0; P(OCH<sub>3</sub>)<sub>3</sub>, 121-45-9; *anti*-Fe<sub>2</sub>(CO)<sub>6</sub>(SCH<sub>3</sub>)<sub>2</sub>, 19976-87-5; *anti*-Fe<sub>2</sub>(CO)<sub>6</sub>(SCH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>, 18771-08-9; *anti*-Fe<sub>2</sub>(CO)<sub>6</sub>(SC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>, 41543-39-9; *anti*-Fe<sub>2</sub>(CO)<sub>6</sub>(*p*-SC<sub>6</sub>H<sub>4</sub>-CH<sub>3</sub>)<sub>2</sub>, 41543-40-2; *anti*-Fe<sub>2</sub>(CO)<sub>6</sub>(SCH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>, 18771-06-7; *syn*-Fe<sub>2</sub>(CO)<sub>6</sub>(SCH<sub>3</sub>)<sub>2</sub>, 19976-88-6; *syn*-Fe<sub>2</sub>(CO)<sub>6</sub>(SCH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>, 18771-09-0.

(26) Compare N. G. Connelly and L. F. Dahl, *J. Amer. Chem. Soc.*, **92**, 7472 (1972).

(27) Reference 10, p 145.