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ELECTROPHILIC INSERTION REACTIONS OF SULFUR DIOXIDE
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DISSERTATION
Presented in Partial Fulfillment of the Requirements for
the Degree Doctor of Philosophy in the Graduate
School of The Ohio State University

By
Roland G. Severson, Jr., B.S., M.S.

* * * * *

The Ohio State University
1977

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Chapter I

INTRODUCTION

The insertion of unsaturated molecules into the metal-carbon bond of coordinatively-saturated transition-metal alkyls is a method of preparation of many metal complexes. For example, sulfur dioxide has been shown to react with complexes such as $\gamma^5\text{C}_5\text{H}_5\text{Fe(CO)}_2\text{CH}_3$ to yield the S-sulfinate $\gamma^5\text{C}_5\text{H}_5\text{Fe(CO)}_2\text{SO}_2\text{CH}_3$ (1). Many other compounds (2), including carbon monoxide, tetracyanoethylene, isocyanides, sulfur trioxide, carbon disulfide, dioxygen, chlorosulfonylisocyanate, and germanium(II) and tin(II) chlorides undergo reaction with transition metal-alkyl complexes leading to the interposition of the unsaturated molecule between the metal and alkyl group. These reactions proceed by a variety of pathways and thus the term "insertion reaction" indicates only the structure of the product and implies nothing about the mechanism.

Only the insertion reactions of carbon monoxide (3) and sulfur dioxide (2) have been examined closely enough for a clear picture of their mechanisms to emerge. The carbonyl insertion involves the intramolecular migration of an alkyl group onto a carbonyl carbon atom with the vacated coordination site being occupied by a new ligand such as CO, or a phosphine. The sulfur dioxide insertion reaction is best looked on as an electrophilic cleavage of a metal-carbon bond as will be
shown later.

This thesis includes a description of the enhancement of the reactivity of sulfur dioxide with respect to its insertion into transition metal-carbon bonds in an attempt to broaden the synthetic usefulness of the reaction in the preparation of transition-metal complexes. Also in this study, the insertion reactions of several compounds structurally similar to sulfur dioxide are described which lead to new classes of coordination compounds. Before proceeding to a discussion of these topics, some aspects of electrophilic insertion reactions of coordinatively-saturated transition-metal complexes will be examined.

A. The Sulfur Dioxide Insertion Reaction.

Sulfur dioxide reacts with many transition metal-alkyl complexes to yield an insertion product as depicted in equation (1), where M is

\[
M-R + SO_2 \rightarrow M-(SO_2)-R
\]

a transition metal together with its ancillary ligands and R is an alkyl group. Insertion reactions have been studied quite intensively and there have been several recent review articles (4) on the subject.

In principle there are four monomeric insertion products (4b) which are likely to result from the incorporation of an SO_2 molecule into a metal-carbon bond. As shown in Figure 1 they are the S-sulfinate (I), the O-sulfinate (II), the O,O'-sulfinate (III), and the S-alkoxysulfenate (IV). Examples of all of these linkages for an (SO_2)-alkyl moiety coordinated to a metal have been synthesized but only I, II, and
III have been formed by an insertion route. In the case of sulfur
dioxide insertions into coordinatively-saturated transition-metal alkyls,
only the S-sulfinate has been isolated.

\[
\begin{align*}
\text{M} & \text{-S-R} & \text{M} & \text{-O-S} & \text{M} & \text{-O-S} & \text{M} & \text{-S-O-R} \\
& & & & & & & \\
I & & II & & III & & IV
\end{align*}
\]

Figure 1

The structures of the various sulfinate complexes have been deter­
mined largely on the basis of their IR and \(^1\text{H} \) NMR spectra. Terminal S=O
groups have very strong characteristic stretching absorptions in the
region 1300-1000 cm\(^{-1}\) (4b,e) whereas the coordination of oxygen in an
S-O-M fashion lowers the stretching frequency to the 1100-850 cm\(^{-1}\) region.
The structures of S-sulfinates are readily determined by the presence of
an antisymmetric and a symmetric S=O stretching absorption in their
IR spectra. The presence of a single terminal S=O group as in II or IV
is generally easily verified (4b,e) by the appearance of a strong
stretching absorption in the 1300-1000 cm\(^{-1}\) region. In addition,
arguments based on the chemical shift of the \(\alpha\)-carbon protons of the
sulfinate group have been presented in an attempt to distinguish between
the possible isomers (4b,e). In all cases where structures of sulfinate
complexes of transition metals have been determined by x-ray crystal-
lography they have been in agreement with the structures inferred from
their spectroscopic data (2).

A sulfinate ion can be considered an ambidentate ligand, with the
sulfur atom being essentially a "soft" (5) donor and the oxygens being
"hard" type donors. Thus a more stable sulfur-bonded species is not surprising in conjunction with "soft" low-valent transition metal complexes. As might be expected in a reaction involving "harder" metal centers, such as that found in tetra-valent tin alkyl complexes, O-bonded sulfinate insertion products prevail (4a,e). The fact that a single metal can behave as a "hard" or as a "soft" center with respect to a sulfinate ligand when the metal has different ancillary ligands has been shown by Lindner (6). Equation (2) shows the exchange of four carboxyls for two molecules of THF in an iron sulfinate complex.

\[
\text{CF}_3\text{SO}_2\text{Fe(CO)}_4\text{Cl} + 2\text{THF} \rightarrow \text{CF}_3\text{SO}_2\text{Fe(THF)}_2\text{Cl} + 4\text{CO}
\]

The alteration of the character of the metal center caused the isomerization of the complex from an S-bonded to an O,0'-bonded sulfinate. In some sulfinate complexes the stabilities of the S- and O-sulfinites might be expected to be similar to each other. This proved to be true when Deacon (?) isolated two isomeric forms of phenylmercurybenzene-sulfinate. Both the S- and O-bonded complexes were obtained by crystallizations under different conditions (7).

The insertion of sulfur dioxide into coordinatively saturated transition metal-alkyl bonds is fairly well understood from a mechanistic viewpoint. The kinetics of reaction of \( \gamma^2\text{C}_5\text{H}_5\text{Fe(CO)}_2\text{R} \) (where \( \text{R} \) is an alkyl or an aryl group) and similar metal complexes with liquid SO\(_2\) and solutions of SO\(_2\) have been examined by Jacobson and Wojcicki (8). The stereochemical course of the reaction at the \( \alpha \)-carbon with similar metal-alkyl complexes has been determined by Wojcicki (9), Baird (10),
and Whitesides (11) and the stereochemistry at the metal has been examined both by Wojcicki (12) and Flood and Miles (13).

Table 1 contains data from the kinetic study by Jacobson and Wojcicki (8b). A wide variety of reaction rates were observed for the reaction of sulfur dioxide with $\gamma^5\text{C}_5\text{H}_5\text{Fe(OC)}_2\text{R}$ complexes. The rate data obtained were those for the disappearance of the starting metal-alkyl complex. The observed decrease in reaction rate with increased electron withdrawing ability of the alkyl group is consistent with an electrophilic interaction in the rate determining step of the insertion reaction. It was also shown that the rate decreased with increased bulkiness of the alkyl group. Substitution of methyl groups on the cyclopentadienyl ring increased the rate of insertion into iron alkyl bonds, as did also increased polarity of solvents employed. The reactions were characterized by large negative values of $\Delta S^\ddagger$ (-62 to -43 eu) and low values of $\Delta H^\ddagger$ (2.9 to 7.8 kcal/mole).

In all of the studies concerning the stereochemistry of the $\alpha$-carbon atom of the alkyl group (9,10,11) during the insertion reaction it was determined that there was a high degree of stereospecificity. In the studies by Whitesides and Boschetto (11) it was shown that $\text{SO}_2$ insertion into the metal-carbon bond of three- or erythro-$\gamma^5\text{C}_5\text{H}_5\text{Fe(OC)}_2\text{CHDCHD(CH}_3)_3$ results in $>95\%$ inversion of configuration at the $\alpha$-carbon of the sulfinate product (eq. 3). Sulfur dioxide was also shown to

\[
\text{Fe(CO)}_5\text{Cp} + \text{SO}_2 \rightarrow \text{Fe(CO)}_5\text{Cp} \quad \text{(3)}
\]
Table 1

Rates of Insertion of Some $^5\text{C}_2\text{H}_5\text{Fe(CO)}_2\text{R}$ Alkyls in Liquid $\text{SO}_2$\(^a\)

<table>
<thead>
<tr>
<th>R</th>
<th>Temp. (°C)</th>
<th>$k_{\text{obs}}$ (sec(^{-1}))</th>
<th>Rel. $k_{\text{obs}}$</th>
<th>Taft $\sigma^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$SiMe$_3$</td>
<td>-65</td>
<td>v. fast</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-Pr</td>
<td>-65</td>
<td>v. fast</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Et</td>
<td>-65</td>
<td>v. fast</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Me</td>
<td>-65</td>
<td>$1.1 \times 10^{-3}$</td>
<td></td>
<td>0.00</td>
</tr>
<tr>
<td>-40</td>
<td>$2.8 \times 10^{-3}\text{b}$</td>
<td>340</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH$_2$CH$_4$OMe-$P$</td>
<td>-61</td>
<td>$2.8 \times 10^{-4}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-40</td>
<td>$3.8 \times 10^{-4}\text{b}$</td>
<td>46</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH(Me)Ph</td>
<td>-30</td>
<td>$3.4 \times 10^{-4}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-40</td>
<td>$2.5 \times 10^{-4}\text{b}$</td>
<td>31</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH$_2$Ph</td>
<td>-40</td>
<td>$1.6 \times 10^{-4}$</td>
<td>19</td>
<td>+0.22</td>
</tr>
<tr>
<td>CH$_2$OMe</td>
<td>-40</td>
<td>$8.3 \times 10^{-5}$</td>
<td>1</td>
<td>+0.60</td>
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<tr>
<td>CH$_2$CH$_3$Me$_2$</td>
<td>-10</td>
<td>~75% completion in 2 hr</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH$_2$CH$_2$OMe$_3$</td>
<td>-10</td>
<td>~40% completion in 2 hr</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH$_2$Me$_3$</td>
<td>-10</td>
<td>~22% completion in 30 hr</td>
<td>-0.16</td>
<td></td>
</tr>
<tr>
<td>Me$_3$</td>
<td>25</td>
<td>~11% completion in 48 hr</td>
<td>-0.30</td>
<td></td>
</tr>
<tr>
<td>CH$_2$CN</td>
<td>25</td>
<td>no product observed in 60 hr</td>
<td>+1.30</td>
<td></td>
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\(^a\)From Jacobson (8b), Table from (4b)

\(^b\)Calculated.
insert with inversion at the α-carbon into the metal-carbon bond of
three-\( \gamma^5C_5H_5Fe(CO)_2CHDCDC_6H_5 \) by Slack and Baird (10).

Interestingly, the insertion reaction is also accompanied by a high
degree of stereospecificity at the metal. Flood and Miles have shown
(13) that the reaction depicted in equation (4) occurs well in excess

\[
\begin{align*}
\text{CD spectrum of starting material, the product, and related complexes} & \text{ suggest that the insertion most likely occurs with retention of} \\
& \text{configuration at the metal center. They have also studied the SO}_2
\end{align*}
\]

insertion reaction with the alkyls \( \gamma^5C_5H_5Fe(CO)(PPh_3)CH_2R \) (R=H, CH₃,
CH₂CH₃, CH(CH₂)₃, C₆H₅) where they found the insertion to be >95% stereo-
specific in CH₂Cl₂ solution. In liquid SO₂ the methyl and ethyl derivatives showed 15% and 8% racemization, respectively (14). In the
reactions of the diastereomers of the complex \( \gamma^5C_5H_5Fe(CO)(PPh_3)CH_2CH-
(CH₃)(C₆H₅) \) in liquid sulfur dioxide >95% stereospecificity was observed
by Reich-Rohrwig and Wojcicki (12a). In a similar manner the reaction of
SO₂ in CH₂Cl₂ solution with diastereomeric pairs of the iron-alkyl complex
of the composition shown in equation (5) resulted in >95% stereospecific

\[
\begin{align*}
\text{CD spectra of starting material, the product, and related complexes} & \text{ suggest that the insertion most likely occurs with retention of} \\
& \text{configuration at the metal center. They have also studied the SO}_2
\end{align*}
\]
formation of sulfinate products (12b). When the reaction shown in equation (5) was carried out in liquid SO₂ it resulted in about 80% stereospecific product formation.

A reaction intermediate was observed in many insertion reactions both in liquid SO₂ and in SO₂ solutions (15). The structure proposed for the intermediate on the basis of IR and ¹H NMR spectral data is that of an O-sulfinate.

The generally accepted mechanism for the insertion of sulfur dioxide into coordinatively saturated transition metal-alkyl complexes was proposed by Wojcicki (4b), and is consistent with all available experimental data. The suggested mechanism is shown in equation (6).

\[
\text{M} - \text{C}^\text{R}_2 + \text{SO}_2 \rightarrow [\text{M} - \text{C}^\text{R}_2 \text{SO}^\text{−}]^+ \rightarrow \text{M}^\text{−} \text{O}^\text{−} \text{S}^\text{−} \text{C}^\text{R}^\text{−} \rightarrow \text{M} \text{−} \text{O} \text{−} \text{S}^\text{−} \text{C}^\text{R}^\text{−} \quad (6)
\]

The reaction mechanism is envisaged as an S₂E₂ backside attack of the SO₂ at the α-carbon of the alkyl group resulting in the formation of a tight ion pair. The ion pair quickly rearranges to form the kinetically favored O-sulfinate or collapses to the S-sulfinate directly. The O-sulfinate has a long lifetime only for a few complexes (such as \(\gamma^5\text{C}_5\text{H}_5\text{Fe(CO)}_3\text{OS(O)}\text{CH}_3\)) before it in turn isomerizes to the thermodynamically more stable S-isomer.

In addition to insertion, sulfur dioxide has been shown to interact with transition metal complexes in three other ways. First it can behave as a Lewis acid and coordinate to one of the ligands on the metal
if the ligand is sufficiently polarizable. This was seen to occur (16) in the reaction shown in equation (7). The I-SO\textsubscript{2} group is nonplanar

\[
\text{CH}_3\text{Pt}[\text{P(C}_6\text{H}_5)_3]\text{I} + \text{SO}_2 \rightarrow \text{CH}_3\text{Pt}[\text{P(C}_6\text{H}_5)_3]_2(\text{I-SO}_2)
\]

as would be expected for a simple Lewis acid-base adduct of this type.

The second type of reaction is the addition of SO\textsubscript{2} to the metal center in coordinatively unsaturated compounds. For example, the Vaska-type complexes \([\text{C}_6\text{H}_5\text{P}]_2(\text{CO})\text{ClM} (\text{M=Ir, Rh})\) add SO\textsubscript{2} to form five-coordinate, square-pyramidal complexes with SO\textsubscript{2} at the apex (17). In these complexes the M-SO\textsubscript{2} framework is also non-planar indicating that the metal is acting as a Lewis base and donating a pair of electrons to SO\textsubscript{2}. The coordination of SO\textsubscript{2} in \(\eta^5\text{C}_5\text{H}_5\text{Mn(CO)}_2\text{SO}_2\) (18) is somewhat different in that the M-SO\textsubscript{2} framework is planar. Here the SO\textsubscript{2} can be envisaged as a \(\sigma\)-donor and a \(\pi\)-acceptor. The geometry involved in the bonding of SO\textsubscript{2} to metals has been compared to that of the nitrosyl ligand (19) and has been satisfactorily explained in terms of molecular orbital theory by Ryan and Eller (19).

The third type of reaction is an interaction of SO\textsubscript{2} with an unsaturated group on the organic ligand to give a cycloaddition product (2). An example of this reaction is given in equation (8). The

\[
\eta^5\text{C}_5\text{H}_5\text{Fe(CO)}_2\text{CH}_2\text{C}≡\text{CH}_3 + \text{SO}_2 \rightarrow \eta^5\text{C}_5\text{H}_5\text{Fe(CO)}_2\text{C≡C(CH}_3\text{)S(O)CH}_2
\]

cycloaddition reaction with SO\textsubscript{2} has proven to be quite general for a variety of metal propargyl complexes (2). The implications are that some unsaturated site on organic groups are either sterically more accessible to SO\textsubscript{2} or that they are better nucleophiles than the \(\alpha\)-carbon
toward SO$_2$ or both.

The purpose of this research project was to develop a better understanding of the interaction of electrophiles with organo(transition metal) complexes through a further examination of electrophilic insertion reactions. During this work two specific goals were kept in mind. The first, to promote or catalyze the reaction of SO$_2$ with unreactive organo(transition metal) complexes. The second, to apply the concepts used in attaining the first goal in extending the range of molecules known to undergo an electrophilic insertion reaction with organo-(transition metal) complexes, and thereby develop syntheses of new organometallic species.

B. Sulfur Dioxide and Lewis Acids.

As mentioned above, SO$_2$ shows a wide range of reactivity towards different transition metal complexes in the insertion reaction. The reactivity is dependent not only on the alkyl group bound to the metal, but also on the metal center itself. For example in Table 2 are listed several methyl-metal complexes and their rates of reaction in liquid SO$_2$. The rates are for the disappearance of the starting metal complex and were taken from the work of Jacobson (8c) and Kroll (20). It can be seen that the rate of cleavage of the metal-carbon bond decreased greatly in the tungsten complex as compared to the iron complex. A portion of this thesis deals with approaches aimed at increasing the rate of insertion in very slow reactions.

The rate of reaction of the tungsten complexes could be expected to increase with substitution of a triphenylphosphine ligand for a carbonyl
Table 2
Reactions of Metal Alkyls with Liquid $\text{SO}_2$\textsuperscript{a}

<table>
<thead>
<tr>
<th>$\text{M-CH}_3$</th>
<th>$\text{K}_{\text{obs}} \text{ (sec}^{-1} \text{, -40°C)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma^{\text{5C}_5\text{H}_5\text{Fe(CO)}_2\text{CH}_3}$</td>
<td>$2.8 \times 10^{-3}$</td>
</tr>
<tr>
<td>$\text{Re(CO)}_5\text{CH}_3$</td>
<td>$6.7 \times 10^{-4}$</td>
</tr>
<tr>
<td>$\gamma^{\text{5C}_5\text{H}_5\text{Ru(CO)}_2\text{CH}_3}$</td>
<td>$4.3 \times 10^{-4}$</td>
</tr>
<tr>
<td>$\text{Mn(CO)}_5\text{CH}_3$</td>
<td>$3.8 \times 10^{-4}$</td>
</tr>
<tr>
<td>$\gamma^{\text{5C}_5\text{H}_5\text{Mo(CO)}_2\text{CH}_3}$</td>
<td>$1.8 \times 10^{-4}$</td>
</tr>
<tr>
<td>$\gamma^{\text{5C}_5\text{H}_5\text{N(CO)}_2\text{CH}_3}$</td>
<td>$4 \times 10^{-4}$ (50°C)\textsuperscript{b}</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Jacobson and Wojcicki (8c)

\textsuperscript{b}calculated from data in (20)

The phosphine is a better $\sigma$-donor and a poorer $\pi$-acceptor than carbonyl and so would increase the electron density on the metal. This, in turn, should increase the negative charge on the $\alpha$-carbon atom of the alkyl group (4b). In a similar manner the substitution of methyl groups for protons on the cyclopentadienyl ring would increase the reaction rate (8b) by increasing electron density on the metal. These alternatives amount to making the metal complex a better nucleophile with respect to an interaction with $\text{SO}_2$.

The problem could be approached from the opposite viewpoint; rather than to make the metal more nucleophilic, the $\text{SO}_2$ can be made a better electrophile. If a Lewis acid were available which would coordinate to $\text{SO}_2$ and not be reactive by itself with the metal complex, then perhaps the $\text{SO}_2$ reaction with the more inert metal-alkyl complexes
could be promoted.

The very strong Lewis acid antimony(V) fluoride reacts with sulfur dioxide to yield a stable, colorless, crystalline, one to one adduct. An x-ray diffraction study of this adduct was undertaken by Moore, Baird and Miller (21) and revealed an oxygen to antimony coordination as depicted in Figure 2.

Boron(III) fluoride has also been shown to form a one to one adduct with SO$_2$. Booth and Martin (22) determined that this adduct is largely dissociated above its melting point of -96°C. Presumably this coordination compound is similar in structure to the SbF$_5$-SO$_2$ adduct. The coordination of a Lewis acid to one of the oxygens of SO$_2$ could increase the reactivity of SO$_2$ with an electron rich site on a transition-metal complex.

There is more than one site on many complexes where a strong Lewis acid can attack. In some coordinatively unsaturated systems such as Vaska's compound, BF$_3$ forms a one to one adduct (23) similar to the SO$_2$
adduct. In this case the metal acts as a simple Lewis base, donating two electrons to the acid (eq. 9). Shriver (24) showed that

\[
\begin{array}{c}
\text{Ph}_2\text{P} \\
\text{Ir} \\
\text{Cl} \\
\text{PPh}_3
\end{array}
\quad +
\begin{array}{c}
\text{BF}_3 \\
\text{Cl} \\
\text{PPh}_3
\end{array}
\rightarrow
\begin{array}{c}
\text{Ph}_2\text{P} \\
\text{Ir} \\
\text{Cl} \\
\text{PPh}_3
\end{array}
\quad (9)
\]

\((\gamma^5\text{C}_5\text{H}_5)_2\text{WH}_2\) forms a W-B bond with BF\(_3\) and Kotz and Pedrotty (25) showed that the \((\gamma^5\text{Ph}_3\text{F}^+\text{C}_5\text{H}_4)\text{M(CO)}_3\) (M=Cr, Mo, W) also form M-B bonds with BF\(_3\).

Lewis acids have demonstrated their ability to coordinate to the oxygen atom of a coordinated carbonyl group. Bridging type carbonyls are much more susceptible to a Lewis acid attack than are terminal carbonyl groups owing to the increased electron density on the carbonyl-oxygen atom when the carbonyl is bridging between two metals. For example, in the reaction (26) of \([\gamma^5\text{C}_5\text{H}_5\text{Fe(CO)}_2]_2\) with triethylaluminum, one or two acid units can be incorporated into the product as shown in Figure 3 for the latter case. Boron(III) fluoride and bromide also react

![Figure 3](image_url)

with \([\gamma^5\text{C}_5\text{H}_5\text{Fe(CO)}_2]_2\) (27) to give one to one adducts of a similar structure with the Lewis acid coordinated to a bridging carbonyl group.
With dicobalt octacarbonyl, AlBr$_3$ coordinates to a bridging carbonyl group (27). Lewis acid attacks at electron rich carbonyl oxygens are not uncommon and many examples have now been reported in the literature.

The interaction of the acid BF$_3$ with a metal sulfinate has been reported (28). The iron complexes $\eta^5$C$_5$H$_5$Fe(CO)(PR$_3$)SO$_2$CH$_3$ (R=G$_5$H$_5$, n-C$_4$H$_9$) both absorb one equivalent of BF$_3$ in toluene at 0°C to yield the products $\eta^5$C$_5$H$_5$Fe(CO)(PR$_3$)SO(OBF$_3$)(CH$_3$). The structures of the products were convincingly assigned on the basis of IR spectral data. The corresponding dicarbonyl complexes apparently do not strongly coordinate BF$_3$.

Lewis acids can promote the reactivity of sulfur dioxide. This was shown by Jacobson, Oku and Paquette (29) for the reaction of cyclooctatetraene in liquid SO$_2$ with SbF$_5$ at -70°C. After solvent removal and hydrolysis of the reaction residue, the following two products were obtained. Cyclooctatetraene is unreactive towards SO$_2$ alone. An example of the use of BF$_3$ to promote the reactivity of SO$_2$ in an organometallic system was described by Kaesz (30) and the nature of the product was defined by Churchill and Wormald (31) by a single crystal x-ray diffraction study. Butadienetrichromyliron does not react with SO$_2$ alone, but in the presence of BF$_3$ at -30°C in liquid sulfur dioxide the product shown in Figure 4 is formed. This reaction
can be described as a BF$_3$ assisted SO$_2$ insertion since the SO$_2$ will not undergo the reaction without the acid. The coordination of BF$_3$ to an oxygen in the product is additional evidence that BF$_3$ may coordinate with an oxygen in SO$_2$.

With this background it seemed reasonable that a Lewis acid could promote the insertion of SO$_2$ into a metal-carbon $\sigma$-bond which was inert to SO$_2$ alone. It was desirable to minimize alternative sites for an electrophilic attack on the organo(transition metal) complex. For this reason a coordinatively saturated transition metal alkyl was chosen. As the $\sigma$-bonded ligand also could not contain electron rich sites, a saturated alkyl group containing no heteroatoms was chosen. A very low reactivity towards SO$_2$ was necessary. From these constraints a suitable complex with which to start this investigation was $\eta^5$C$_5$H$_5$W(CO)$_3$CH$_3$.

It should be mentioned that an alternative preparation of $\eta^5$O$_5$H$_5$W-(CO)$_3$SO$_2$CH$_3$ was recently reported by Lorenz and Griesshammer (32) in the reaction of $\eta^5$C$_5$H$_5$W(CO)$_3$H with CH$_3$SO$_2$Cl and N(C$_2$H$_5$)$_3$. The product is presumably formed by a sulfene (CH$_2$=SO$_2$) insertion into a metal-H bond. This is not a general preparative route to metal sulfinate complexes.
C. Imide Derivatives of Sulfur Dioxide.

There are two series of imide derivatives of sulfur dioxide, the N-sulfinylamines RN=S=O, and the sulfur diimides RN=S=NR (where R may be an organic or inorganic species). The N-sulfinylamines are generally prepared by the reaction of an amine such as aniline with thionyl chloride (eq. 11) giving two moles of HCl and the sulfinylamine

\[
C_6H_5NH_2 + SOCl_2 \rightarrow C_6H_5NSO + 2HCl
\]

(11).

The sulfur diimides have normally been prepared by the action of \( \text{SX}_4 \) on amines (34) as shown in equation (12). In the case of bis-N-

\[
3RNH_2 + \text{SX}_4 \rightarrow RN=\text{SX}_2 + 2RNH_3
\]

\[
3RNH_2 + \text{RN}=\text{SX}_2 \rightarrow RN=S=N-R + 2RNH_3
\]

\[ X=F, Cl \]

sulfonylsulfur diimides the treatment of benzene solutions of the corresponding N-sulfinylsulfonamide with a catalytic amount of pyridine (35) induces the diimide to crystallize with the evolution of sulfur dioxide (ε₁, 13). The organic chemistry of the sulfur imide compounds

\[
2\text{RSO}_2\text{NSO} \rightarrow \text{RSO}_2\text{N}=\text{S=NSO}_2\text{R} + \text{SO}_2
\]

(13)

consists largely of additions to the nitrogen-sulfur bond. For example, many of the useful reactions of these compounds involve cycloadditions to dienes. Several review articles covering the reactions of both the sulfinylamines and sulfur diimides have been published (33, 34).
The close structural similarity of the sulfur imides with sulfur dioxide prompted an investigation of the reactions of these compounds with transition metal-alkyl complexes. Reactions of N-sulfinylamines and sulfur diimides with metal complexes have not been extensively studied. N-Sulfinylamines have been shown to form sulfinic acid amides (33) in good yield when allowed to react with organolithium or Grignard reagents followed by hydrolysis of the reaction mixtures (eq. 14).

\[
\begin{align*}
1. \text{R'}\text{Li} & \text{ or } \text{R'}\text{MgBr} & \text{R-N=S=O} & \text{H}_2\text{O} & \text{R-N=S-R'} & + & \text{LiOH} & \text{ or } \text{Mg(OH)Br} \\
2. \text{H}_2\text{O} & \\
\end{align*}
\]

(14)

Sulfur dioxide undergoes a similar reaction with organolithium and Grignard reagents to give sulfinic acids after hydrolysis (36).

The alkyl- or aryl-sulfur diimides were shown by Kuyper and Vrieze (37) to react quantitatively with organolithium and Grignard reagents to yield one to one addition (insertion) products (eq. 15). These products could be isolated only at low temperatures and were very moisture sensitive. The structure of the sulfur diimide addition products could not be unequivocally assigned. The \(^1\text{H NMR data available (38)}\) for the products, however, show that the R groups are equivalent at ambient temperatures. This suggests a monomeric structure for the product with an M-S bond or a dimeric structure with the sulfur diimidate ligand coordinated by nitrogen atoms bridging two metal centers. A structure involving bridging ligands was preferred "in view of the
tendency of the metal atoms for four coordination". \( S,N,N'-\)Substituted
derivatives of sulfur diimidato complexes of Cu\(^I\) and Ag\(^I\) were prepared
(38) as shown in equation (16). The dimeric bridging structure proposed

\[
\text{Li}\left[RNS(R')NR\right] + \left[M\left(O_2CCF_3\right)\right]_n \quad (M=\text{Cu}^I, \text{Ag}^I)
\]

for the complexes was based on molecular weight determinations and the
\(^1H\) NMR spectra of the complexes. The orientation of the \( R' \) group and
the free electron pair on sulfur was shown to be rigid. Rhodium(I)
complexes of \( S,N,N'-\)substituted derivatives of sulfur diimidides were
prepared (38) in a similar reaction shown in equation (17). The products

\[
\frac{1}{2}\left[\text{Rh}(CO)_2\text{Cl}\right]_2 + \text{Li}\left[RNS(R')NR\right] \rightarrow \text{Rh}(CO)_2\left[RNS(R')NR\right] + \text{LiCl} \quad (17)
\]

were characterized by molecular weight determinations and \(^1H\) NMR spectroscopy. They contain a bidentate ligand and are monomeric. Preliminary single crystal x-ray data indicated the structure shown in Figure 5. The sul-

![Figure 5](image)

fur atom is about 0.5 Å out of the \( \text{RhN}_2 \) plane and thus the structure of the
complex shows some resemblance to the structure of \( \gamma^2 \text{allyl} \) complexes (38).
Both the insertion of $\text{SO}_2$ and $\text{C}_6\text{H}_5\text{NSO}$ into a N-Si bond was demonstrated by George, Jones and Lappert (39) in the reactions shown in equation (18).

The structures of the products were proposed on the basis of IR spectra.

An additional example of a reaction of $\text{C}_6\text{H}_5\text{NSO}$ with an organometallic complex (eq. 19) was reported by Robinson and Wojcicki (40). In a

\[
[\text{Fe}] - \text{CH}_2\text{C}=\text{O}-\text{R} + \text{C}_6\text{H}_5\text{NSO} \rightarrow [\text{Fe}] - \text{C} - \text{S} - \text{O} \quad \text{(Ref. 41)}
\]

\[
[\text{Fe}] - \text{CH}_2\text{C}=\text{O}-\text{R} + \text{SO}_2 \rightarrow [\text{Fe}] - \text{C} - \text{S} - \text{O} \quad \text{(Ref. 42)}
\]

\[
[\text{Fe}] = \text{C}_5\text{H}_5\text{Fe(CO)}_2
\]

\[
\text{R=CH}_3, \text{CH}_2[\text{Fe}], \text{C}_6\text{H}_5
\]

cycloaddition to a propargyl complex the course of the reaction of an $\text{N}$-sulfinylamine also parallels that of $\text{SO}_2$. The addition is much
slower for N-sulfinylaniline than for SO₂.

Equations (14), (15), (18), and (19) all demonstrate a close similarity between SO₂ and the sulfinylamines in reactions with organometallic complexes. A further resemblance was found by Blake and Reynolds (43) in the reaction of N-sulfinylamines with coordinatively unsaturated complexes. They found that Vaska's complex would not react with N-sulfinylaniline or p-tolyl-N-sulfinylaniline but did form a weak one to one adduct with p-nitro-N-sulfinylaniline. The exclusion of moisture and O₂ was extremely important, as earlier reports had apparently mistaken SO₂ and SO₄²⁻ complexes for products in these reactions (43 and references therein). The structure of the p-nitro-N-sulfinylaniline product could not be definitely ascertained but only two possible structures (Figure 6) were consistent with the

![Chemical Structures](image-url)
data obtained. Structure VI is analogous to that found for sulfur
dioxide adducts of most coordinatively unsaturated complexes (Ref. 16b
and references therein). A structure similar to VII has been reported
for the $\text{SO}_2$ complex of $\text{Pt}(\text{CH}_3)(\text{PPh}_3)_2\text{I}$ (16). In contrast, the reaction of
substituted $N$-sulfinylaniline with $\text{Pt}(\text{PPh}_3)_2(c_2\text{H}_4)$ resulted (43) in a
substitution product assigned structure VIII from infrared spectral
evidence. A similar substitution product of $p$-tolyl-$N$-sulfinylsulfon-
amide with $\text{Pt}(\text{PPh}_3)_2(c_2\text{H}_4)$ was obtained but a structure could not be
assigned due to a complex sulfur-oxygen stretching region in the IR
spectrum of the product.

The study of the coordination of sulfur diimides in coordinatively
unsaturated transition metal complexes has been undertaken principally
by Kuyper and Vrieze (44). They have shown that a sulfur diimide in the
trans,trans configuration can behave as a mono- or bidentate ligand
(structure XI or XII in Figure 7) in forming addition complexes

![Figure 7]

with $\text{Pt(II)}$ (44c,d,e), $\text{Pd(II)}$ (44b), $\text{Rh(I)}$ and $\text{Ir(I)}$ (44c). When the
ligand is in the cis, trans configuration it can only behave as a
monodentate ligand with two different isomers generally being found since
the two nitrogen atoms are non-equivalent in the cis, trans configuration (structures IX or X in Figure 7). In these complexes only metal-nitrogen bonds were observed. The complexes become fluxional at raised temperatures through inversion (or less likely N=S bond rotation) at the uncoordinated nitrogen atom and by a N-N "jump" mechanism which involves a five coordinate intermediate with an N,N'-bidentate sulfur diimide ligand.

Of more interest to this study is the behavior of the sulfur diimide ligand when bound to coordinatively saturated $M(CO)_5$ and $M(CO)_4$ ($M=Cr$, Mo, W) centers (44a, 45, 46). When the alkyl groups on the diimide are very bulky the ligand prefers the trans, trans configuration and bidentate coordination to $M(CO)_4$ units as in Figure 8.

![Figure 8](image)

Many of the sulfur diimides form fluxional complexes with $M(CO)_5$ ($M=Cr$, Mo, W) centers (47). Here the mechanism is unlikely to involve a bidentate coordination of the ligand since the metal would then have a 20-electron configuration. Instead the likely mechanism is a gliding of the ligand from nitrogen to sulfur and on to the other nitrogen (see Figure 9) in a manner similar to that found in some $\eta^2$allene complexes (48).
At reduced temperatures (-6 to 25°C depending on R) two isomers can be observed in the $^1$H and $^{13}$C NMR spectra of the complexes. These are most likely of structures XIII and XIV (Figure 9), an N- and an S-bonded form, respectively. The S-isomer has equivalent imide carbons and protons and so must have a symmetrical structure. The electronic influence of the sulfur diimide on the M(CO)$_5$ moiety is similar to that of amine ligands, judging by the frequencies of the carbonyl stretching absorptions. With the M(CO)$_4$ group, on the other hand, the ligand (bidentate diimide) acts as a strong π-acceptor group as is reflected in the raised frequencies of the carbonyl stretches compared to those in a similar amine complex.

There have not been reported any insertion reactions of N-sulfinyl-amines or sulfur diimides other that those mentioned earlier in this section. Also the products which may be reasonably expected from an
Insertion reaction of sulfur imide compounds with transition metal-alkyl complexes have not been prepared by alternative methods. Thus the reactivities of these interesting sulfur dioxide analogs with coordinatively saturated transition metal-alkyl complexes were investigated.
A. Reagents and Solvents.

1. Organometallic compounds and their precursors. The following compounds were used as obtained unless otherwise stated. Bis(η^5-cyclopentadienyldicarbonyliron) was obtained from Pressure Chemical Company. The complexes Mn(CO)_5CH_3, Mn(CO)_5CF_3 and η^5-C_5H_5W(CO)_2CH_2CH=CHCH_3 were donated by Dr. S. A. Hallock, Dr. F. A. Hartman and Dr. S. R. Su, respectively. Bis(η-cyclopentadienyltricarbonyltungsten) was obtained from Mr. C. Poffenberger. Aldrich Chemical Company was the source of dicyclopentadiene and 2-chloroethylbenzene. Allied Chemical Company supplied allyl chloride whereas methyl iodide and benzyl chloride were obtained from Eastman Kodak Company and Matheson, Coleman and Bell, respectively. The oxidizing agent m-chloroperoxybenzoic acid was obtained from Aldrich in 85% purity and was used as purchased.

2. Electrophiles and their precursors. Both BF_3 and BCl_3 were obtained from Matheson Gas Products. Matheson, Coleman and Bell supplied p-toluenesulfonyl chloride. Antimony(V) fluoride was obtained from Columbia Organic Chemicals Company. Joseph Dixon Crucible Company was the source of graphite. Aniline hydrochloride and reagent grade pyridine were obtained from J. T. Baker Chemical Company. Fisher Scientific Company supplied reagent grade thionyl chloride and
cyclohexylamine, whereas Eastman Kodak Company was the source of
methanesulfonyl chloride. Sulfur dioxide was obtained from Air Products
and was purified by passing through concentrated $\text{H}_2\text{SO}_4$ and a powdered
$\text{P}_4\text{O}_{10}$ column prior to use.

3. Chromatographic materials. Active neutral alumina was
obtained from Ventron, Alpha Products and was normally deactivated by
the addition of 10% by weight of water. Florisil in 60-100 mesh was
purchased from J. T. Baker Chemical Company whereas silica gel in 100-
200 mesh was supplied by Matheson, Coleman and Bell. All molecular
sieves used were purchased from the Union Carbide Corporation.

4. NMR solvents and standards. Deuterobenzene and hexafluoro-
benzene were purchased from Columbia Organic Chemicals, and deuter-
chloroform and tetramethydisilane were obtained from Merck, Sharpe and
Dohme Canada, Ltd.

5. Solvents and their purification. All solvents were
reagent grade and were used as purchased or are listed below. Tetra-
hydrofuran was dried by refluxing over and distilling from $\text{LiAlH}_4$,
as were toluene, methylcyclohexane and pentane. Xylene was purified by
refluxing over and distilling from sodium. Dimethoxyethane, which
was very wet, was dried first by passing through active alumina
followed by refluxing for at least 24 hours over $\text{CaH}_2$ and finally
distillation from this drying-reducing agent. When very dry benzene
was needed it was also refluxed over and distilled from $\text{CaH}_2$.
Dichloromethane and chloroform were both purified by refluxing over
and distillation from $\text{P}_4\text{O}_{10}$.
B. Instrumentation and Physical Measurements.

Solid state IR spectra were measured on a Perkin-Elmer Model 337 grating spectrophotometer in the 4000 to 400 cm⁻¹ region as Nujol or Fluorolube mulls prepared by grinding the solid sample with the mulling agent between ground glass plates. The spectra were calibrated with polystyrene film at 1601 and 1020 cm⁻¹. Solution spectra were obtained on a Beckman Model IR-9 grating spectrophotometer using matched 0.1 mm KBr cells. This instrument was calibrated with polystyrene film at 1601.4 cm⁻¹.

¹H NMR spectra were measured on a Varian A60 or A60A spectrometer, using internal TMS as a reference. The variable temperature studies were performed on the Varian A60A instrument equipped with a variable temperature controller using a methyl alcohol sample to determine the probe temperature. ¹³C NMR spectra were obtained using CDCl₃ solutions containing TMS as an internal standard on a Fourier transform, proton decoupled, Bruker HX-90 spectrometer by Dr. C. Gottrel.

Mass spectra were collected by Mr. C. Richard Weisenberger on an AEI MS-902 mass spectrometer at 70ev using a source temperature of 80-100°C.

Melting points were determined for samples sealed under argon or vacuum in glass capillaries in a Thomas-Hoover capillary melting point apparatus and are uncorrected.

Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, New York; by Galbraith Laboratories, Inc., Knoxville, Tennessee; or by Pascher Mikroanalytisches Laboratorium, Bonn, Germany. Analyses for carbon were obtained by combustion over V₂O₅.
C. General Experimental Procedures.

Standard techniques for the manipulation of air-sensitive compounds (49) were used in working with Lewis acids, their addition complexes, and other air-sensitive materials. Inert atmospheres were attained by the use of nitrogen or argon.

Complicated manipulations of air-sensitive materials were carried out in an argon filled dry box. The atmosphere in the box was purified by a gas recirculation system which removed water and small vapor molecules with Linde type 4 A molecular sieves (Union Carbide Corporation). Larger vapor molecules were removed with Linde type 13 X molecular sieves (Matheson, Coleman and Bell) whereas oxygen was removed with a Ridox (Fisher Scientific Company) column.

Several inert gas lines to supply argon or nitrogen were used. All of them were equipped with a mercury bubbler to limit the maximum pressure available, and the gas flow rate was observed by the use of mineral oil bubblers.

A general purpose vacuum line (49) was utilized in these studies. The design of the line was unexceptional, containing a grease-free manifold (teflon stopcocks), a trap to trap fractionation manifold and a grease free constant volume tensiometer. The vacuum was attained by the combined use of a mechanical oil pump and a mercury diffusion pump. The normal working pressure was \(10^{-4} - 10^{-5}\) Torr as measured on the main manifold with a 250 ml, permanently attached McLeod gauge.

Three gas bulbs with teflon stopcocks were calibrated for use as standard volumes. The volumes of a 57.64 ml and a 59.53 ml bulb were determined by their weight gain on filling with degassed water.
The third bulb was calibrated at 6.081 ml by its weight gain on filling with mercury.

For the use of Schlenk type apparatus a parallel arrangement of an argon manifold and a vacuum manifold connected by 3-way stopcocks was constructed. The construction and use of this apparatus is adequately described by Shriver (49).

It was found that low temperature filtrations were most easily performed by the use of a polyethylene filter-tube and an inert gas pressure. The tubes were made by heating the center of a three inch section of a \( \frac{1}{2} \) in diameter polyethylene tube over a very small flame from a microburner. When it was well softened the softened portion was drawn out into a long, thick capillary. The large ends of the tube were then packed with cotton and shortened by a perpendicular cut with a sharp knife through the tube and cotton. This resulted in a flat cotton plug of the original diameter of the tube which acted as the filtering medium. Finally the capillary was cut in half to give two filter tubes. The capillary was pulled through a pierced serum cap with a pair of tweezers and the serum cap was fitted to one neck of a two-necked flask. By applying an inert gas pressure at the other neck of the flask, the contents of the flask were easily filtered through the tube. Both the solids and filtrate could be maintained under an inert atmosphere and at the desired temperature.

Solvents were degassed either by several freeze-thaw cycles or by purging them with an inert gas for at least \( \frac{1}{2} \) hour. Solvents used on the vacuum line were refluxed over and distilled from a drying agent (vide supra) under inert atmosphere. After being placed on the
vacuum line they were degassed by the freeze-thaw technique and vacuum transferred to a storage flask in the grease-free portion of the line.

D. Preparation of Organometallic and Electrophilic Reactants.

1. \( \text{W(CO)}_3\text{R}_1 \) \((\text{R}=\text{CH}_3, \text{CH}_2\text{CH}_3, \text{CH}_2\text{C}_6\text{H}_5, \text{CH}_2\text{CH}=\text{CH}_2) \). In general these tungsten-alkyl complexes were prepared by the method of Piper and Wilkinson (50), modified as is shown below for the preparation of the methyl derivative.

A solution of \( \text{NaC}_5\text{H}_5 \) in the solvent 1,2-dimethoxyethane was prepared by the reaction of sodium with the cyclopentadiene monomer in this solvent. The boiling point of 1,2-dimethoxyethane is high enough to insure a good reaction with \( \text{W(CO)}_6 \). The solvent must be carefully dried. One suitable method is to pass the solvent through an active neutral alumina column followed by refluxing for 24 hours with \( \text{LiAlH}_4 \) under argon. Distillation from this reducing agent then yields a good quality solvent. Dicyclopentadiene is best cracked to the monomer in a distillation apparatus with a good vigreux column and a boiling flask of about six times the volume of dimer to be cracked. For safety, a metal basin should be placed under the boiling flask before it is heated gently with an open flame. A few carborundum chips reduce bumping. The monomer distills out slowly at about \( 40^\circ \text{C} \). Freshly distilled monomer may be stored at Dry Ice temperature, and any dimer present precipitates at this temperature. Two equivalents of sodium were scraped clean of oxides and cut in small pieces under pentane. These pieces were placed in an argon filled, two-neck round-bottom flask. After the pentane evaporated, dimethoxyethane
and 1.1 equivalents of cyclopentadiene were added. An exit bubbler was attached, the apparatus was thoroughly flushed with argon and the inert gas flow was stopped. The mixture was stirred with a magnetic stirrer overnight. The reaction was complete since there was no more H₂ being evolved near the pieces of excess sodium. Next about one equivalent of W(CO)₆ was placed in a clean, argon flushed, two-neck flask before the pale pink NaC₅H₅ solution was filtered into it. A reflux condenser was attached and the solution was brought to a boil for 24 hours. A longer reflux period is not harmful. After cooling, 1.5 equivalents of methyl iodide were added and the solution was stirred for one hour and then refluxed for one hour. Sodium iodide did not precipitate. The solvent was removed on a rotary evaporator, the residue was extracted with CH₂Cl₂ and the solvent was removed again to yield a crude product. This resulted in an 80-90% yield based on the starting amount of W(CO)₆.

The other tungsten alkyl complexes were prepared by the addition of allyl chloride, benzyl chloride, or ethyl bromide to a dimethoxymethane solution of the sodium salt of \( \eta^2\)C₅H₅W(CO)₃⁻ under the same conditions as those given for the methyl complex above. The yields were similar except for the allyl complex where a 53% yield was obtained.

2. \( \eta^2\)C₅H₅Fe(CO)₂R, (R=CH₃, CH₂CH₃, CH₂CH₂CH₃). These complexes were synthesized by the method of Bibler (51) involving the reaction of the sodium salt of the iron anion, \( \eta^2\)C₅H₅Fe(CO)₂⁻, with methyl iodide, benzyl chloride, or phenethyl chloride. The metal anion was prepared in THF by the reaction of excess 1% sodium amalgam with \([\eta^2\)C₅H₅Fe(CO)₂]₂⁻.
3. **N-Sulfinylamines.** N-Sulfinylaniline was prepared by the method of Michaelis and Hertz (23) in a reaction of aniline hydrochloride with thionyl chloride in benzene. Cyclohexyl-N-sulfinylamine was prepared by the method of Klamann, Sass and Zelenka (52) in a reaction of cyclohexylamine with SOCl₂ and two equivalents of pyridine in ether solution. The product is unstable at room temperature and was always vacuum transferred to a reaction flask as a final purification step.

The methyl and p-tolyl-N-sulfinylsulfonamides were prepared by the method of Maschke (53) in the reaction of the corresponding sulfonamide with refluxing thionyl chloride. Methanesulfonamide was prepared by the reaction of anhydrous ammonia with methanesulfonyl chloride in benzene. The product sulfonamide and by-product NH₄Cl were separated by Soxlet extraction with benzene. The sulfonamide was filtered off from the benzene and dried on a rotary evaporator at about 50°C for one hour. p-Toluenesulfonamide was prepared by refluxing p-toluenesulfonyl chloride in NH₄OH until it was completely dissolved. After the solution cooled to room temperature the precipitate sulfonamide was collected on a Buchner funnel and dried at 100°C under mechanical vacuum for several hours.

4. **Bis-N-methanesulfonylsulfodiimide.** This was easily prepared from a CHCl₃ or benzene solution of methanesulfonyl-N-sulfinylamine by its pyridine-catalyzed disproportionation to the sulfodiimide and SO₂ as described by Wucherpfennig and Kresse (54). The diimide crystallizes from the reaction solution as colorless crystals.
5. Antimony(V) fluoride intercalated in graphite. This substance was prepared in the manner outlined by Lalancette (55). A 20 g sample of graphite was treated with 100 ml of concentrated HCl at reflux for three hours. The graphite was filtered off the yellow HCl solution and washed with 200 ml of H2O followed in order by 50 ml of acetone, 50 ml of CH2Cl2, 50 ml actone and 200 ml of water. The graphite was finally dried at 110°C under vacuum for 10 hours. A 2.74 g sample of this dry graphite was placed in a flask and the flask was evacuated on the vacuum line. A 5.00 g quantity of SbF5 was vacuum transferred to the flask at -196°C. After sealing the flask with a flame it was placed in a 110°C oil bath for 17 hours. The flask was allowed to cool to room temperature and was opened. The product, a free flowing black powder, was poured in air into a solvaseal flask and evacuated on the vacuum line. After evacuation, argon was admitted to the flask for storage. There was no fuming or other evidence of free SbF5 associated with the product. The product was 65% SbF5 by weight.

E. Interactions of Lewis Acids with Potential Inserting Molecules.

1. Boron(III) fluoride and N-sulfinylaniline, a tensimetric titration. A sample of N-sulfinylaniline (0.305 g, 2.19 mmole) was vacuum transferred at -196°C to the reaction flask which was mounted on the tensimeter section of the vacuum line. The amount was determined by the mass difference of the reaction flask. About three milliliters of benzene was condensed into the flask. The flask was warmed to 7.0°C for one half hour after which the pressure over the
resulting solution was measured. A total of 2.484 mmoles of \( \text{BF}_3 \) was added in this titration in about 0.6 mmolar aliquots at \(-196^\circ\text{C}\).

Following each addition of \( \text{BF}_3 \) the reaction flask was sealed by a teflon stopcock, warmed to \(7.0^\circ\text{C}\) for 45 minutes and then opened to the manometer for 10 minutes before the pressure over the solution was measured. Only a slight excess of \( \text{BF}_3 \) was added since it was evident that at this temperature only a weak interaction of the \( \text{BF}_3 \) with the sulfinylamine occurred. The data are presented in Figure 10 as a comparison of the pressure over the reaction solution with the molar ratio of \( \text{BF}_3 \) to \(\text{N-sulfinylamine}\). The volume of the tensimeter with the same reaction flask was later determined to be 67.60 ml by the weight of \( \text{BF}_3 \) (0.144 g) filling the tensimeter at \(24.50^\circ\text{C}\) and 583.1 Torr. The total pressure that would be expected to be exerted by the quantity of \( \text{BF}_3 \) added in the tensimetric titration, assuming a temperature of \(7.0^\circ\text{C}\) and no solvation or complex formation, would have been 642 Torr. The pressure actually found was 635 Torr. Thus there was at most very little complex formed at \(7.0^\circ\text{C}\).

2. Boron(III) fluoride and \(\text{N-sulfinylcyclohexylamine, a tensimetric titration.}\) A sample of \(\text{C}_6\text{H}_{11}\text{NSO} \) (0.077 g, 0.53 mmole) was vacuum transferred at \(-196^\circ\text{C}\) to the reaction flask of the tensimeter on the vacuum line. The amount was determined by the mass difference of the reaction flask. In addition about one milliliter of toluene was condensed into the reaction vessel, which was subsequently warmed to \(1.0^\circ\text{C}\). During this titration the temperature of the reaction solution was always maintained at \(1.0\pm0.2^\circ\text{C}\) and 30 minutes were allowed between each addition of \( \text{BF}_3 \) for the system to equilibrate before the
THE TENSIMETRIC TITRATION OF \( \text{C}_6\text{H}_5\text{NSO} \) WITH BF₃

Solvent = Benzene
Temperature = 7.0 °C

Figure 10
pressure measurements were taken. A total of 2.215 mmoles of BF$_3$ was added in approximately 0.3 mmolar aliquots. The data are presented in Figure 11 in the form of a comparison of the pressure over the reaction solution with the mole ratio of added BF$_3$ to C$_6$H$_4$NSO.

3. Boron(III) fluoride and N-sulfinyl-p-toluenesulfonamide, a tensiometric titration. A sample of N-sulfinyl-p-toluenesulfonamide (0.211 g, 0.971 mmole) was placed in the reaction vessel in the dry box. After the necessary mass measurements were made the vessel containing the sulfinylsulfonamide was attached to the tensimeter section of the vacuum line and thoroughly evacuated. About three milliliters of toluene were condensed into the flask at -196°C, and the flask was warmed to -22.9°C (CCl$_4$ slush bath). During this titration the temperature of the reaction solution was maintained at -22.9°C, and 30 minutes were allowed for equilibration between BF$_3$ additions and the measurement of the pressure over the reaction solution. A total of 4.55 mmoles of BF$_3$ was added in 11 portions. The data are presented in Figure 12 in the form of a comparison of the pressure over the reaction solution with the mole ratio of added BF$_3$ to CH$_3$C$_6$H$_4$S(0)$_2$NSO.

F. The Synthesis and Reactions of Transition Metal Complexes.

1. \(\eta^5\text{C}_5\text{H}_5\text{W}(\text{CO})_3\text{[CS(OBF$_3$)CH$_3$]}\) \(\rightarrow\) (I). Compound I was prepared many times in this work. Below are described an NMR scale experiment and a much larger, gram-scale preparation and isolation scheme.

A low temperature reaction of \(\eta^5\text{C}_5\text{H}_5\text{W}(\text{CO})_3\) CH$_3$ with boron(III) fluoride in liquid sulfur dioxide typically was carried out as follows. An NMR tube was sealed to a solve-seal joint which allowed the
The tensimetric titration of $C_{6}H_{11}NSO$ with $BF_{3}$

Solvent = Toluene
Temperature = 1.0 ± 0.2°C

Figure 11
THE TENSIMETRIC TITRATION OF \( \text{CH}_2\text{C}_6\text{H}_4\text{S}(\text{O})_2\text{NSO} \) WITH \( \text{BF}_3 \)

Solvent = Toluene
Temperature = -22.9°C

Figure 12
attachment of the tube to the vacuum line. A 0.064 g (0.18 mmole) portion of \( \ce{\text{H}_2\text{W(CO)}_3\text{CH}_3} \) was placed in the tube which was then evacuated on the vacuum line. Sulfur dioxide was condensed onto the solid at -78°C to give a sufficient volume of solution to observe the \(^1\)H NMR spectrum. A small amount of TMS was condensed into the tube at -196°C followed by a 0.18 mmole (57.3 Torr, 57.64 ml, 22.3°C) portion of BF\(_3\) which was also transferred to the tube at -196°C. The tube was then sealed with a flame and stored at -78°C until the spectrum was taken. There was no evidence of reaction at this temperature, the initial yellow solution of the tungsten alkyl remaining unchanged. To run the spectrum the tube was carefully warmed to a temperature of -26°C at which temperature the spectrum was examined. During this warming process the solution suddenly changed color to a clear deep burgundy. In the spectrum only one product was observed, which showed two singlets at \( \gamma \sim 3.99 \), relative intensity 5, and \( \gamma \sim 7.52 \), relative intensity 3.

The best gram-scale preparation of I was found to be that described below. A special apparatus, depicted in Figure 13, was developed for this reaction. The reaction vessel (flask A) was charged with 2.54 g (7.30 mmoles) of \( \ce{\text{H}_2\text{W(CO)}_3\text{CH}_3} \). The apparatus was connected to the vacuum line by the solve-seal joint and the two flexible rubber vacuum hoses as depicted in Figure 13 and the system was pumped down to about 10^{-4} Torr. Sulfur dioxide was condensed at a temperature of -78°C into flask A until it was nearly half full. A flask more than half full of sulfur dioxide is likely to crack in subsequent freeze-thaw procedures. Flask A was warmed to dissolve the tungsten alkyl and was frozen in liquid nitrogen. An equimolar amount of
BF$_3$ was then added (4 additions, total pressure 2343.2 Torr, 23.7°C, 57.64 ml, 7.29 mmoles). The reaction mixture was warmed slowly with stirring to -22.9°C (CCl$_4$ slush bath). During this warming a rapid reaction occurred resulting in the formation of a clear deep burgundy red solution. After allowing 45 minutes to insure complete reaction, 20 ml of dichloromethane was vacuum transferred to the solution at
liquid nitrogen temperature. The reaction mixture was allowed to warm, and the volume of solvent was reduced to about 20 ml by exposure to vacuum. This was followed by the addition of 40 ml of dichloromethane and the reduction of solvent volume to 10 ml. At this time the apparatus was separated from the vacuum line and tilted to filter the solution through the frit from flask A to flask B. This was easily accomplished by the judicious use of cooling baths on the two flasks of the system. Care must be taken that the vapor pressure of the solution is kept low enough to prevent explosion. The solution that passed through the frit to flask B was a deep burgundy red color. By condensing some of the dichloromethane back into flask A all red material can be washed through the frit. This procedure leaves on the frit a variable amount of brown solid residue which was not identified. Addition of 50 ml of pentane to the dichloromethane solution resulted in the formation of a large amount of precipitate. By tilting the apparatus to pour the solution back through the frit to flask A, the red precipitate was collected on the clean side of the frit. This precipitate was then washed with three additional portions of pentane. At this time the apparatus was reconnected to the vacuum line via the solve-seal joint and all volatile materials were removed from the reaction mixture. The solid obtained in this manner was a poorly crystalline red powder which was easily transferred to a Schlenk tube under argon for storage and for transfer to the dry box.

This red material was subsequently characterized as \[\eta^5\left(\text{C}_2\right)_5\text{H}_2\text{W}(\text{CO})_3\left[\text{OS(OBF}_3\right)_2\text{CH}_3\left]\left(\text{I}\right)\right.\] It is extremely difficult to purify this substance. Compound I has been recrystallized rapidly from benzene and pentane
resulting in a very low yield of small red crystals. It has also been recrystallized from a solution of I in a 50:50 mixture of CH$_2$Cl$_2$-C$_6$F$_6$ by solvent removal on a rotary evaporator. This resulted in a good yield of small red crystal clusters. Neither of these methods nor others have proven to be reliable, high-yield crystallization techniques. In no case have large well-formed crystals been obtained. Other examples of the recrystallization attempts were from the solvent mixtures SO$_2$:benzene and CH$_2$Cl$_2$:benzene. From both of these solvent systems, only very poorly formed crystals were obtained. It should be pointed out that in all handling of this substance an inert atmosphere or vacuum must be maintained. The critical factor is exclusion of moisture, not oxygen. A powdered sample of I was exposed to a stream of air dried by passage through a silica gel column and then through a powdered P$_4$O$_{10}$ column. Over a period of three hours no change in appearance was noted. On the other hand a sample of I quickly decomposed in a stream of water-saturated nitrogen to uncharacterized tars. A well crystallized sample of I is stable in vacuum or dry argon at room temperature over a period of at least two years. Pure samples of I have the following physical characteristics:

- Melting Point (argon) 98-99$^\circ$C with gas evolution
- Melting Point (vacuum) 97$^\circ$C with gas evolution
- Analytical Data (three trials)
  - found
    1. 22.48 1.90 10.87
    2. 23.10 1.83 11.07
    3. 23.24 1.86
  - calculated for C$_8$H$_8$BF$_3$O$_{3.5}$
    - $\%$C 22.52 1.68 11.88
    - $\%$H
    - $\%$F
- $^1$H NMR (CDCl$_3$) $\delta$ 4.01, singlet, relative intensity 5
  - 7.52, singlet, relative intensity 3
The reaction of $\eta^5\text{C}_5\text{H}_5\text{W(CO)}_3\text{CH}_3$ in SO$_2$ with a 27% equivalent deficiency of BF$_3$. A sample of $\eta^5\text{C}_5\text{H}_5\text{W(CO)}_3\text{CH}_3$ (1.019 g, 2.928 mmole) was dissolved in 30 ml of liquid sulfur dioxide. At liquid nitrogen temperature boron(III) fluoride (2.30 mmole, 746.1 Torr, 28.0°C, 57.64 ml, a 27% deficiency) was added. The reaction was allowed to proceed under vacuum in refluxing sulfur dioxide for one hour. A deep red solution was produced from the original yellow solution of the tungsten-alkyl complex. All volatile materials were removed on the vacuum line. The $^1$H NMR spectrum of the CDCl$_3$ extract of the reaction residue indicated the presence of only compound I and $\eta^5\text{C}_5\text{H}_5\text{W(CO)}_3\text{CH}_3$. The carbonyl stretching region of the IR spectrum of the reaction residue taken as a Nujol mull indicated that the principal material present was an insertion product (identified as compound I in the $^1$H NMR spectrum). The starting tungsten-alkyl complex was present in a substantially lesser amount as judged by the relative intensities of the carbonyl stretches.
3. The reaction of $^{56}C_{5}H_{5}(CO)_{3}[OS(OBF_{3})CH_{3}]$ (I) with $^{56}C_{5}H_{5}(CO)_{3}CH_{3}$ in SO$_{2}$. About 40 mg of a mixture of roughly equal portions of I and $^{56}C_{5}H_{5}(CO)_{3}CH_{3}$ was placed in the apparatus shown in Figure 14 in the dry box. After attaching the assembly to the vacuum line and evacuating it, a small amount of TMS and sufficient sulfur dioxide for a $^1H$ NMR spectrum were condensed into the vessel at $-78^\circ$C. By closing the stopcock, removing the apparatus from the vacuum line and pouring the solution onto the frit the solution was filtered into the NMR tube. Cooling baths must be used on the NMR tube and dissolution vessel to prevent undue pressure build-up. After washing all of
the soluble material into the NMR tube by repeated vacuum transfers and filtrations the tube was cooled in liquid nitrogen and sealed in a flame. The $^1H$ NMR spectrum showed only the presence of unreacted $^{55}C_5H_5W(CO)_3CH_3$ and I in roughly equal amounts. There was no evidence indicating the presence of the S-sulfinate, $^{55}C_5H_5W(CO)_3S(O)_2CH_3$.

4. Reactions of $^{55}C_5H_5W(CO)_3[OS(OBF_3)CH_3] (I)$ leading to formation of $^{55}C_5H_5W(CO)_3S(O)_2CH_3$. The treatment of I with amines results in the efficient conversion of I into the S-sulfinate, $^{55}C_5H_5W(CO)_3S(O)_2CH_3$, and the corresponding amine:boron(III) fluoride adduct. The reaction of both aniline and ammonia with I was examined.

A filtered solution of a small amount of I in dichloromethane was prepared in the dry box. The test tube containing this deep red solution was sealed with a serum cap and removed from the dry box. A large excess of aniline was added dropwise with a syringe to this solution. A precipitate started forming within a minute after the addition of the aniline was begun. During the addition of the aniline the solution also changed from a deep red to a light brownish-red color. The white precipitate which had formed was filtered off under nitrogen. Treatment of the filtrate with pentane until the solution began to cloud followed by partial solvent removal on a rotary evaporator induced the crystallization of a yellow compound. The IR spectrum of this crystalline material when prepared as a Nujol mull contained the following significant absorptions: 2039s, (1948vs, 1935vs)doublet, 1190s, 1055s. These bands, particularly the two sulfur-oxygen stretches at 1190 and 1055, indicate that the crystals were $^{55}C_5H_5W(CO)_3S(O)_2CH_3$, the S-sulfinate. An IR spectrum as a Nujol mull
was also obtained of the white material which precipitated from the reaction mixture. This presumably was a product of the interaction of BF₃ with aniline. A similar precipitate was obtained from a reaction where an excess of BF₃ gas was bubbled through a solution of aniline in CH₂Cl₂. A comparison of the IR spectra of these two white precipitates in Nujol mulls in the region 4000-600 cm⁻¹ showed many coincident absorptions. In the spectrum of both of the samples, however, there were absorptions which did not appear in the spectrum of the other precipitate. Because a survey of the literature concerning BF₃:aniline adducts indicated that the adduct is light sensitive (56), is unstable in ether solutions (57), and that judging by UV spectral data at least two different substances have been reported as products of the reaction of BF₃ with aniline (56), the white precipitates obtained in this study were not further characterized.

In the case of the reaction of I with ammonia, however, the products were better defined. In the dry box 0.584 g (1.30 mmoles) of I was placed in a dry flask. The flask was sealed with a stopcock adapter and removed from the dry box. After attaching the flask to the vacuum line, it was evacuated and about 30 ml of dichloromethane was vacuum transferred to the reaction vessel. Compound I dissolved to give the characteristic deep red solution and a small amount of insoluble material. A slight deficiency (1.28 mmoles, 57.64 ml, 25.6°C, 414.1 Torr) of ammonia was then added to the reaction vessel at liquid nitrogen temperature. As the reaction mixture was warmed to room temperature with stirring, a precipitate formed and the solution changed from the deep red color of I to an orange color. After
45 minutes, the contents of the flask were filtered through a frit under argon and the white precipitate was washed with several 15 ml portions of dichloromethane. The filtrate and washes were concentrated on a rotary evaporator to 10 ml. The addition of pentane to this solution induced the crystallization of 0.419 g (1.02 mmoles) of \( \gamma_5^5 \text{H}_5 \text{W(CO)}_3 \text{S(0)}_2 \text{CH}_3 \), an 85% yield. This was identified by its IR spectrum taken as a Nujol mull. An IR spectrum of the white precipitate in a Nujol mull was identical with that of a BF\(_3\) ammonia adduct prepared as follows (58).

A quantity of BF\(_3\) (277 Torr, room temperature, volume of grease-free manifold) was condensed into a flask containing 20 ml of dichloromethane at \(-196^\circ\text{C}\). The flask was warmed to dissolve the BF\(_3\) and refrozen with liquid nitrogen. An approximately equimolar amount of NH\(_3\) (272 Torr, room temperature, same volume) was condensed into the flask. The flask was warmed to room temperature and the volatile materials were removed on the vacuum line leaving behind a white powder. The IR spectrum in Nujol and Fluorolube mulls of this complex was as follows: 3340s, 3270mSh, 2340mBr, 1860wBr, 1590m, 1435s, 1422s, 1210Sh, 1100vsBr, 1020Sh, 990s, 868m, 520m, cm\(^{-1}\).

Several additional reagents and procedures involving I lead to the formation of the very stable S-sulfinate complex, \( \gamma_5^5 \text{H}_5 \text{W(CO)}_3 \text{S(0)}_2 \text{CH}_3 \). In this work the following examples were found.

Grinding the complex I in KBr under argon produced a red powder. This powder was compressed to form a clear red plate in preparation for an IR analysis. In the span of two or three minutes, however, the plates changed color to yellow and the only material observed in the
S=O stretching region was the S-sulfinate, $\gamma^5\text{C}_5\text{H}_5\text{W}(\text{CO})_3\text{S}(\text{O})_2\text{CH}_3$.

The complex I readily dissolved in degassed water to yield a red solution which very quickly turned yellow. Again the only organometallic species observed in the IR spectrum of a Nujol mull of the residue after solvent removal on a rotary evaporator was the S-sulfinate. Exposure of I to water-saturated nitrogen resulted in decomposition of the material into a black gummy tar which was not further characterized.

In a similar manner dissolution of I in acetone under nitrogen gave a red solution which turned yellow in five to ten minutes. In this case, again, the S-sulfinate was the only organometallic material which could be observed in an IR spectrum of the residue after the solvent was removed on a rotary evaporator.

Whenever samples of I were placed on either a Florisil or alumina column, with solvents such as CH$_2$Cl$_2$, the only organometallic species recovered was the S-sulfinate. This was removed from the columns with acetone. Solvent removal from the acetone solution on a rotary evaporator resulted in the isolation of brown solids. These solids when dissolved in dichloromethane and dried over MgSO$_4$ were recovered as a yellow crystalline material after filtration and solvent removal on a rotary evaporator. These crystals were shown to be pure $\gamma^5\text{C}_5\text{H}_5\text{W}(\text{CO})_3\text{S}(\text{O})_2\text{CH}_3$ by their IR spectrum as a Nujol mull.

5. $\gamma^5\text{C}_5\text{H}_5\text{W}(\text{CO})_3[\text{OS(SbF}_5\text{)}_2\text{CH}_3]$(II). The reaction of $\gamma^5\text{C}_5\text{H}_5\text{W}(\text{CO})_3$-CH$_3$ in sulfur dioxide with antimony(V) fluoride was allowed to proceed on the vacuum line in the apparatus shown in Figure 15. This apparatus was designed to allow the determination of the mass of SbF$_5$.
Figure 15 - SbF$_5$:SO$_2$ Reaction Apparatus
used in the reaction in flask A and to introduce the SbF$_5$ as its SO$_2$
adduct to a metal alkyl solution in flask B. Rotation of flask A
around the ground glass joint that attaches it to the rest of the
apparatus facilitated the immersion of flask A in cooling baths and
allowed solutions in flask A to be poured into flask B. A quantity of
SbF$_5$ was vacuum transferred to flask A, indicated in Figure 15. The
weight of SbF$_5$ added, determined by the weight difference of flask A
was 0.382 g (1.76 mmoles). After weighing the SbF$_5$, $\eta^5$C$_5$H$_5$W(CO)$_2$CH$_3$
(0.631 g, 1.81 mmoles) was placed in flask B and the apparatus was
reassembled and evacuated. Sulfur dioxide was transferred into flask B
at -78°C to give 30 ml of tungsten alkyl solution which was maintained
at -78°C throughout this reaction. Sulfur dioxide was transferred
from the solution to flask A by cooling A with liquid nitrogen.
Rotation of flask A, containing the Lewis acid sulfur dioxide adduct,
about the ground glass joint allowed the sulfur dioxide solution of the
Lewis acid to flow into the reaction mixture in flask B. For complete
transfer of SbF$_5$ to flask B this process was repeated several times.
There was a fast reaction which changed the solution in flask B from
yellow to red during the addition of the Lewis acid to the tungsten
alkyl. Reaction was allowed to proceed at -78°C for two hours, after
which the materials volatile at that temperature were removed overnight
to a liquid nitrogen trap. The powdery reddish-brown residue was
warmed to room temperature and placed in the dry box.

A portion of the reaction residue was purified by dissolution in
CH$_2$Cl$_2$ and filtration in the dry box. This left a small amount of
brown solid on the frit, the solution being a deep red color. Hexane
was added and the material was taken from the dry box for solvent removal on a rotary evaporator. After partial solvent removal a large number of small, very dark, plate-like crystals had formed in addition to some brown decomposition products. The remaining hexane was decanted and the crystals were manually separated from the brown decomposed material under argon. These crystals were not very sensitive to the atmosphere and could be handled in air for short periods without any obvious signs of decomposition. The crystals were dissolved in CH$_2$Cl$_2$ under argon, CHCl$_3$ was added and the solvent was partially evaporated in a stream of argon. The flask containing this concentrated solution was stoppered and placed over a -78°C bath for slow cooling. Many very small crystals formed over a period of about an hour after which the round-bottom flask was placed over a Dewer flask of liquid nitrogen. After most of the solution was nearly colorless the mother liquor was decanted under argon and the crystals were collected in a vial and sealed (glass seal) under vacuum. The deep red crystals were small, but regularly formed in a rectangular shape. From pure crystals the following physical data were obtained.

Analytical Data found 17.16% C, 1.98% H, 19.65% Sb calculated for C$_9$H$_8$F$_5$O$_5$SSbW 17.19% C, 1.28% H, 19.36% Sb

$^1$H NMR (CDCl$_3$) $^\tau$ 4.02, singlet, relative intensity 5
7.39, singlet, relative intensity 3

IR (CH$_2$Cl$_2$) 2058s, 1967sBr cm$^{-1}$

IR (Nujol-fluorolube) 3121w, 2933vW, 2050s, 1955vsBr, 1310w, 1070-1030mVBr, 870m, 845Sh, 835Sh, 720w
660vs, 645s, 610w, 545w, 505w, 465w cm$^{-1}$

In a separate experiment the reactivity of Sb$_5$ in graphite was examined. A sample of $^7_{5}C_{9}H_{8}W$(CO)$_{5}$CH$_3$ (0.167 g,
0.480 mmole) was placed in a 50 ml flask. A spatula full of SbF$_5$
intercalated in graphite (65% by weight SbF$_5$) was added under nitrogen.
The solids were not reactive towards each other in the absence of a
solvent. The flask was evacuated on the vacuum line and 15 ml of
liquid SO$_2$ was condensed into the flask at -78°C. The cooling bath
was lowered from the flask which was allowed to warm until the vapor
pressure of the SO$_2$ rose about 400 Torr. The solution slowly took on
a reddish color. The reaction was allowed to proceed for two hours,
after which the SO$_2$ was transferred to a liquid nitrogen trap. The
residue was dissolved in 10 ml CH$_2$Cl$_2$ under nitrogen and filtered to
give a clear red solution. An IR spectrum of this solution in the
carbonyl stretching region indicated a large amount of the starting
tungsten-alkyl complex (2020 vs, 1930 vs Br cm$^{-1}$) and a smaller amount
of an insertion species (2055 m, 1965 m Br cm$^{-1}$). The CH$_2$Cl$_2$ solution
was concentrated to about one milliliter which caused a large amount of
material to crystallize. A fivefold excess of hexane was added and the
resulting yellow solution was pipetted off the red solids. The hexane
solution was rotary evaporated to dryness to isolate 0.073 g (0.21 mmole)
of $\frac{2}{3}$C$_5$H$_7$W(CO)$_2$CH$_3$. The red precipitate was washed with hexane and
dried on the vacuum line to yield 0.032 g (0.051 mmole) of II which
was identified by its Nujol mull IR spectrum.

In an attempt to observe the initial product of this insertion
reaction, a red SO$_2$ solution of the product was prepared in an NMR
tube as follows. Samples of the tungsten alkyl (0.108 g, 0.255 mmole)
and SbF$_5$ intercalated in graphite (0.098 g, 65% by weight SbF$_5$,
0.29 mmole SbF$_5$) were mixed in the dry box in an NMR preparation tube
(Figure 14). The dry powders were unreactive in the absence of solvent, since the alkyl complex retained its yellow color. Sulfur dioxide (0.5 ml) and a small amount of TMS were condensed onto the solids at -196°C on the vacuum line. The tube was stored at -45°C (chlorobenzene slush bath) for seven hours. The reaction mixture was filtered into the NMR tube and the tube was sealed with a flame. The 1H NMR spectrum of the red solution showed unreacted tungsten alkyl complex at 4.48 T and 9.58 T. In addition there was another cyclopentadienyl resonance at 4.03 T, a broad resonance from 6.4 to 7.7 T, and a singlet at 7.85 T. The ring resonance at 4.03 T and the singlet at 7.85 T were in approximate 5:1 intensity ratio. The intensity of the ring resonance at 4.03 T when compared to the total intensity of the region 6.4 to 7.9 T gave a ratio of 5.6:2.3, respectively.

6. $\text{H}_2\text{W(CO)}_3\text{SO}_2\text{CH}_3$. This sulfinate was prepared in the manner described by Kroll (59) in a 43% yield. A 0.365 g (1.05 mmoles) sample of $\text{H}_2\text{W(CO)}_3\text{CH}_3$ dissolved in a 25 ml of liquid SO$_2$ in a 75 ml Whitey bomb was heated in a 50°C oil bath for 82 hours. A small amount of the starting alkyl was isolated from the reaction mixture along with 0.195 g (0.473 mmole) of the yellow-brown crystalline S-sulfinate. The following 1H NMR and IR spectra were obtained from this material and are in agreement with the spectra reported in the literature (20).

$^1$H NMR (CDCl$_3$) T 4.12, relative intensity 5
6.76, relative intensity 3

IR (Nujol) 2050s, 1955vsBr, 1188s, 1050s, 1005s, 938w, 844w cm$^{-1}$

Two additional preparations of the S-sulfinate were carried out on
an NMR scale to obtain a qualitative rate comparison with other metal-carbon bond cleavage reactions and to examine the insertion reaction for the possible appearance of an O-sulfinate intermediate. Two small spatula size samples of $^{75}_{5}C_{3}H_{5}W(CO)_{3}CH_{3}$ were placed in NMR tubes which had been glass-blown onto solve-seal joints for attachment to the vacuum line. The tubes were evacuated and a sufficient quantity of sulfur dioxide was vacuum transferred into the NMR tubes at liquid nitrogen temperature to allow the measurement of the $^{1}H$ NMR spectra. A small amount of TMS was also added and the tubes were sealed in a flame. These two tubes were maintained at different temperatures.

The first tube was stored at room temperature in the dark. There was no immediate evidence of any species other than $^{75}_{5}C_{3}H_{5}W(CO)_{3}CH_{3}$ in the $^{1}H$ NMR spectrum. After six days at room temperature there had been a reaction only to the extent of about 10%, forming the $^{75}_{5}C_{3}H_{5}W(CO)_{3}S(O)_{2}CH_{3}$ species, as observed in the NMR spectrum of the solution. After two months at room temperature the reaction was complete, $^{75}_{5}C_{3}H_{5}W(CO)_{3}S(O)_{2}CH_{3}$ accounting for the two signals observed in the $^{1}H$ NMR spectrum. A small amount of decomposition had occurred in the two-month time interval.

The second tube was stored at $-16^\circ C$ for 27 days. After this period of time there was a 14% yield of the S-sulfinate as observed in the $^{1}H$ NMR spectrum of the solution. There was no evidence of decomposition in this solution.

7. The reactivity of $BF_{3}$ toward $^{75}_{5}C_{3}H_{5}W(CO)_{3}CH_{3}$. The reactivity of $^{75}_{5}C_{3}H_{5}W(CO)_{3}CH_{3}$ with respect to boron(III) fluoride in toluene was examined at room temperature in a tensimetric titration. A quantity
of $\gamma^5C_5H_5W(CO)_2CH_3$ (0.497 g, 1.43 mmole) was placed in a reaction vessel on the tensimeter section of the vacuum line. After evacuating the flask, about 25 ml of toluene was vacuum transferred into the flask. The yellow-orange solution was degassed in three freeze-thaw cycles. The pressure over the solution was measured (30.5 Torr, 26.4°C). Boron(III) fluoride was added in about 0.13 mmolar quantities, allowing 20 minutes for equilibration of the system before measuring the reaction pressure. With the first addition of BF$_3$ a dark brown or black precipitate formed and the solution became red-orange in color. The amount of precipitate and the color of the solution did not change much after this first addition of boron(III) fluoride. The data are presented in Figure 17 (p. 90) as a comparison of the pressure over the solution with the molar ratio of added boron(III) fluoride to $\gamma^5C_5H_5W(CO)_2CH_3$.

Following this titration all of the volatile materials were removed from the reaction mixture on the vacuum line. A Nujol mull of the residue was prepared in the dry box for an examination of the carbonyl stretching region of the IR spectrum. The spectrum indicated that about 95% of the material was the $\gamma^5C_5H_5W(CO)_2CH_3$ complex; however, there was a small amount of an additional substance with raised carbonyl stretches. This material was isolated by precipitation from a dichloromethane solution with pentane. In acetone the carbonyl stretches of this substance appear in the IR spectrum at 2050s, 1959s cm$^{-1}$. It was not further characterized due to the very small quantity available. It should be mentioned that the starting material was contaminated by a small amount of W(CO)$_6$. 

A second tensimetric titration of $\text{C}_5\text{H}_5\text{W(CO)}_3\text{CH}_3$ with BF$_3$ in toluene was done at a reduced temperature. A sample of the tungsten alkyl (0.331 g, 0.951 mmole) was placed in a reaction flask and was well degassed on the vacuum line. Toluene (25 ml) was vacuum transferred to the flask at -78°C. The resulting solution of the tungsten-alkyl complex was warmed in a CC$_4$ slush bath to -23°C and was maintained at that temperature throughout the titration. For the titration, BF$_3$ was drawn from a reservoir cooled to -126°C in a methylcyclohexane slush bath to maintain a convenient pressure of BF$_3$. The pressure over the solution was measured (2.1 Torr, -23°C) and a total of 4.675 mmoles of BF$_3$ was added in 11 aliquots. Thirty minutes was allowed for the equilibration of the system between each addition. There was a slight brown precipitate formed on the addition of the first aliquot of BF$_3$ and the solution took on a reddish-orange color during the titration. The data are presented in Figure 18 (p. 91) as a comparison of the pressure over the solution with the molar ratio of added BF$_3$ to the tungsten alkyl. An IR spectrum in the carbonyl stretching region of a CH$_2$Cl$_2$ solution of the reaction residue after all volatile materials were removed on the vacuum line indicated a trace of a substance absorbing at 2060 cm$^{-1}$ in addition to the starting alkyl complex.

8. $\text{C}_5\text{H}_5\text{W(CO)}_3\text{S(O)(OBF}_3\text{)}\text{CH}_3$, (III). The addition of boron-(III) fluoride to $\text{C}_5\text{H}_5\text{W(CO)}_3\text{S(O)}_2\text{CH}_3$ was examined in a tensimetric titration of a heterogeneous mixture of this S-sulfinate in toluene. A finely ground sample of $\text{C}_5\text{H}_5\text{W(CO)}_3\text{S(O)}_2\text{CH}_3$ (0.678 g, 1.65 mmoles) was placed in the reaction vessel which was then attached to the
tensimeter portion of the vacuum line. The flask was evacuated and
50 ml of toluene was vacuum transferred to the flask. Warming the
vessel to room temperature resulted in a heterogeneous mixture of
$\gamma^{5}C_{5}H_{5}W(CO)_{3}S(O)_{2}CH_{3}$ in a pale yellow solution. This mixture was
degassed in three freeze-thaw cycles. The vapor pressure over the
mixture was measured (30.7 Torr, 24.3°C). In this titration the BF$_3$
aliquots were added to the reaction mixture at liquid nitrogen tempera-
ture and thus a considerable time (30-45 minutes) was required between
each addition to allow the flask to equilibrate to room temperature for
the pressure measurements. The pressures were measured at 25±2°C.
The data are presented in Figure 19 (p. 94) in the form of a comparison of
the pressure over the reaction mixture with the molar ratio of added
boron(III) fluoride to $\gamma^{5}C_{5}H_{5}W(CO)_{3}S(O)_{2}CH_{3}$.

The solvent and all other volatile materials were removed from
the reaction mixture on the vacuum line. The flask containing the
residue was sealed and placed in the dry box. Repeated washing of
the residue with CH$_2$Cl$_2$ left behind a yellow powder. This material
was identified as $\gamma^{5}C_{5}H_{5}W(CO)_{3}S(O)(OBF)_{2}CH_{3}$ (see results and dis-
cussion) and its physical characteristics are listed below.

Melting Point (argon) 100-105°C decomposes
Analytical Data - not obtained due to facile loss of
BF$_3$ in vacuum
$^1$H NMR (CDCl$_3$) $^\delta$ 4.08, singlet, relative intensity 5
6.64, singlet, relative intensity 3
IR (CHCl$_3$) 2050s, 1964sBr cm$^{-1}$
IR (Nujol) 3115m, 2060s, 1980s, 1950s, 1312m, 1200vs,
1142s, 117s, 1070vw, 1060vw, 1010m, 998m, 960m, 890sh,
860sBr, 820sBr, 725m, 690w cm$^{-1}$
The addition of BF$_3$ to $\gamma^{5}C_{5}H_{5}W(CO)_{3}S(O)_{2}CH_{3}$ was also examined in a
reaction occurring in an NMR tube at low temperature in liquid sulfur
dioxide. A sample of $\gamma_{5^2}^2\gamma_{5}^1H_{5}^1W(CO)_3S(O)_2CH_3$ (0.030 g, 0.073 mmole) was
placed in an NMR tube that was sealed to a solve-seal joint for attach-
ment to the vacuum line. The tube was evacuated and an amount of $SO_2$
sufficient for a $^1H$ NMR spectrum was added at $-196^\circ C$. A small amount
of TMS and an equimolar amount of $BF_3$ (24.00°C, 6.081 ml, 224.3 Torr,
0.0736 mmole) relative to the sulfinate complex were also added. The
$^1H$ NMR spectrum was taken at $-161^\circ C$ after sealing the tube in a flame.
In the spectrum at this temperature initially the $\gamma_{5^2}^2\gamma_{5}^1H_{5}^1W(CO)_3S(O)_2CH_3$
species was the principal substance observed ($\gamma_{4.02}$, relative intensity
5, $\gamma_{6.76}$, relative intensity 3). During the next 45 minutes, however,
another pair of resonances appeared at $\gamma_{3.84}$ (relative intensity 5)
and $\gamma_{6.31}$ (relative intensity 3). This pair grew at the expense of
the S-sulfinate until it accounted for roughly 80% of the total
intensity of the spectrum after the 45 minute reaction period. These
resonances are ascribed to the adduct III.

The heterogeneous reaction of $\gamma_{5^2}^2\gamma_{5}^1H_{5}^1W(CO)_3S(O)_2CH_3$ with $BF_3$ in
benzene at room temperature was also examined. A 0.082 g (0.20 mmole)
sample of $\gamma_{5^2}^2\gamma_{5}^1H_{5}^1W(CO)_3S(O)_2CH_3$ was placed in the reaction tube of the
apparatus shown in Figure 14. About 2 ml of benzene was vacuum
 transferred into the tube after it was evacuated. Not all of the
S-sulfinate dissolved at room temperature. An equimolar amount of $BF_3$
(22.50°C, 57.6 ml, 63.8 Torr, 0.199 mmole) was condensed into the tube
at $-196^\circ C$. The solution was warmed to room temperature and reaction
was allowed to proceed for one hour. The tube was cooled to 0°C and all
volatile materials were removed on the vacuum line. A sufficient
amount of SO$_2$ for an NMR spectrum was then condensed onto the residue. The solution formed in this manner was filtered into the NMR tube by cooling the NMR tube with Dry Ice-isopropyl alcohol bath after disconnecting the apparatus from the vacuum line and pouring the solution onto the frit. Care must be taken to prevent undue pressure rises. The SO$_2$ was condensed back into the reaction tube several times in order to wash all soluble material through the frit. When all soluble compounds were washed into the NMR tube it was frozen in liquid nitrogen and a small amount of TMS was condensed in before sealing the tube in a flame. The $^1$H NMR spectrum of the solution was taken at -26±2°C and it indicated that the solution was composed of about 10% III ($\tau$ 3.90, 6.35) and 90% $^5_{\delta}$C$_2$H$_5$W(CO)$_3$S(O)$_2$CH$_3$ ($\tau$ 4.04, 6.72).

9. The isomerization of $^5_{\delta}$C$_2$H$_5$W(CO)$_3$[OS(OBF$_3$)$_3$CH$_3$]$_1$ (I). A sample of I (about 1 g) was dissolved in benzene in the dry box. The solution was placed in the inner tube of the apparatus shown in Figure 16. Pentane was placed in the outer tube and the entire apparatus was wrapped in aluminum foil after assembly. The sample was set aside for 15 days. Within 12 hours a colorless layer had formed over the deep red solution. At the interface of the two solvents there was a hazy zone in which crystals were forming and a sludge was settling to the bottom of the tube. As the days progressed the colorless layer moved downward as did the hazy solvent interface. Any red crystals which formed in the interface turned yellow in the colorless layer. After 15 days the volume of the red solution had been reduced by about one third and all the solvents were poured off. The remaining crystals were dried in a vacuum (in the dry box) and examined. There were
three colors of crystals: yellow, orange, and red. The crystals were separated manually. The yellow crystals, which turned to powder very easily, were obtained primarily from the zone in the tube where the colorless solution had been. They were identified as the S-sulfinic acid on the basis of their IR spectrum taken as a Nujol mull. In a like fashion the dark red crystals were determined to be I and the orange crystals determined to be the isomer of I, III. The principal product was the S-sulfinic acid while almost as much of the orange isomer III was obtained. The overall yield of crystalline products was very low.
10. The conversion of \( \eta^5\text{C}_5\text{H}_5\text{W(CO)}_3\{\text{S(O)(CBF}_3\text{)}\text{CH}_3\}_1 \) (III) to 
\( \eta^5\text{C}_5\text{H}_5\text{W(CO)}_3\text{S(O)}_2\text{CH}_3 \). A sample of III (about 0.25 g) was washed in the dry box with \( \text{CH}_2\text{Cl}_2 \). The resulting yellow powder, which was shown by a Nujol mull IR spectrum to be III, was then dried overnight on the vacuum line. A Nujol mull IR spectrum in the sulfur-oxygen stretching region indicated the presence of only the S-sulfinate \( \eta^5\text{C}_5\text{H}_5\text{W(CO)}_3\text{S(O)}_2\text{CH}_3 \).

11. \( \eta^5\text{C}_5\text{H}_5\text{W(CO)}_3\{\text{OS(OBF}_3\text{)}\text{CH}_3\}_1 \) (IV). The \(^1\text{H} \) NMR spectrum of this complex was needed for comparison with the spectra of related complexes. A sample of \( \eta^5\text{C}_5\text{H}_5\text{W(CO)}_3\text{SO}_2\text{CH}_3 \) (0.075 g, 0.18 mmole) was mixed with SbF\(_5\) intercalated in graphite (0.071 g, 65% by weight SbF\(_5\), 0.21 mmole) in an NMR preparation tube (Figure 14) in the dry box. On the vacuum line 0.5 ml of sulfur dioxide and a small amount of TMS were condensed into the reaction tube at -196°C. Reaction was allowed to proceed for seven hours at -45°C (chlorobenzene slush bath) before the reaction mixture was filtered into the NMR tube. After the tube was sealed in a flame the \(^1\text{H} \) NMR spectrum of the yellow-brown solution was recorded at -40°C. There were two singlets assigned to the cyclopentadienyl and methyl proton resonances of IV in the spectrum. They appeared at 3.95 \( \tau \) and 6.47 \( \tau \) of relative intensity of 5.0 to 3.0 respectively. There were no resonances corresponding to the starting S-sulfinate complex indicating that the reaction had gone to completion.

12. \( \eta^5\text{C}_5\text{H}_5\text{W(CO)}_3\{\text{OS(OBF}_3\text{)}\text{CH}_2\text{C}_6\text{H}_5\}_1 \) (V). A sample of \( \eta^5\text{C}_5\text{H}_5\text{W(CO)}_3\text{CH}_2\text{C}_6\text{H}_5 \) (0.722 g, 1.70 mmole) was placed in a 100 ml flask which was then attached to the vacuum line and evacuated. About 45 ml of liquid SO\(_2\) was condensed onto the alkyl complex at -78°C with the alkyl
dissolving to give a yellowish-orange solution. A total of 1.68 mmole of BF$_3$ was added in two portions (345.8 Torr, 20.50°C, 57.64 ml and 188.9 Torr, 20.10°C, 57.64 ml). As the BF$_3$ was admitted to the reaction flask a beautiful brown crystalline plate-like precipitate formed which reflected light in many sparkles. There was no other evidence of any reaction. The reaction vessel was allowed to warm in the air for about three minutes, and during this period of time the solution changed color to a dark red and the precipitate dissolved. The solution was cooled again with a Dry Ice-isopropyl alcohol bath and about 20 ml of CCl$_4$ was added. The volatile materials were removed on the vacuum line after the cooling bath was again removed. The residue was an oil and was transferred to the dry box for the preparation of samples for instrumental analysis.

$^1$H NMR (CDCl$_3$) $\tau$ 2.8, complex, phenyl protons
4.16, singlet, cyclopentadienyl protons
5.98, 6.29, AB quartet, J=13.4 Torr, methylene protons

The integration was approximate due to impurities in the sample, 5.8:5.1:1.2 respectively

IR (CH$_2$Cl$_2$) 2056s, 1970sBr cm$^{-1}$
IR (neat) 2055vs, 1960vsBr, 1130vsBr, 1060m, 1000m, 950m, 910s, 845sBr, 810sh, 770w, 730s, 698m, 645w, 615w, 548m, 510m, 460m cm$^{-1}$

The reaction of $^5$H$_2$W(CO)$_3$CH$_2$C$_6$H$_5$ in SO$_2$ with BF$_3$ was also examined in a low temperature $^1$H NMR experiment. A sample of the tungsten alkyl complex (0.065 g, 0.15 mmole) was placed in an NMR tube sealed to a solve-seal joint for attachment to the vacuum line. After evacuation a small amount of TMS and sufficient SO$_2$ for an NMR spectrum were condensed into the tube at -78°C. At -196°C, 0.149 mmole (47.7 Torr, 57.64 ml, 22.30°C) of BF$_3$ was condensed into the tube
which was subsequently sealed in a flame. Reaction was nearly complete upon warming the tube to \(-26^\circ\text{C}\), the temperature at which the spectrum was taken. There were two new cyclopentadienyl proton resonances at 4.06 T and 4.26 T with the former responsible for about 95% of the products of this reaction judging by the relative intensities of the two peaks. The resonance at 4.06 T was assigned to the cyclopentadienyl ring protons of \(V\). The spectrum of \(V\) was as follows:

\[ ^1\text{H NMR (SO}_2\text{, -26}\,^\circ\text{C}) \]

- 2.60, complex, phenyl protons
- 4.06, singlet, cyclopentadienyl protons
- 5.98, 6.14, AB quartet, J=13.2 Torr, methylene protons

13. \( \eta^5\text{C}_2\text{H}_5\text{W(CO)}_3\left[\text{OS(OsBF}_3\right]CH_2\text{C}_6\text{H}_5] \) (VI). In a reaction very similar to that described for the preparation of \( \eta^5\text{C}_2\text{H}_5\text{W(CO)}_3\left[\text{OS(OsBF}_3\right]CH_3] \), a 1.156 g (2.726 mmoles) sample of \( \eta^5\text{C}_2\text{H}_5\text{W(CO)}_3\text{CH}_2\text{C}_6\text{H}_5 \) was allowed to react with 0.593 g (2.74 mmoles) of SbF\(_5\) in 10 ml of liquid SO\(_2\) at \(-78^\circ\text{C}\) for 48 hours. Materials volatile at \(-78^\circ\text{C}\) were removed on the vacuum line during the last 10 hours of this reaction period. Extraction of the residue with CH\(_2\text{Cl}_2\) at \(-23^\circ\text{C}\) resulted in a burgundy solution and 0.938 g of a brown residue. A Nujol mull IR spectrum was obtained of this brown residue which contained carbonyl stretches at 2120 cm\(^{-1}\), 2060 s, 1970 s cm\(^{-1}\) and in addition other absorptions at 865 mBr and 665vs cm\(^{-1}\). The band at 665 cm\(^{-1}\) was most likely due to coordinated SbF\(_5\). All further attempts to purify and characterize this material were unsuccessful; however, a small amount of \( \eta^5\text{C}_2\text{H}_5\text{W(CO)}_3\left[\text{OS}_2\text{CH}_2\text{C}_6\text{H}_5 \right] \) was eventually isolated from it.

The burgundy solution mentioned above was evaporated on the vacuum line to yield a massive solid residue varying in color from brownish-orange to burgundy. This was extracted with CH\(_3\text{C}_6\text{H}_{11}\) to remove the
unreacted starting tungsten alkyl of which 0.201 g were recovered. The residue consisted of 0.53 g of a red powder which was identified tentatively as compound VI. An IR spectrum of this powder was obtained as a Nujol mull. The material was slightly soluble in CDCl₃ and a \( ^1H \) NMR spectrum of the powder was recorded in this solvent. An IR spectrum in the carbonyl stretching region was also obtained on the CDCl₃ solution. These spectral results are listed below.

\[ ^1H \text{NMR (CDCl}_3) \]
\[ 2.6, \text{complex, phenyl protons} \]
\[ 4.07, \text{singlet, cyclopentadienyl protons} \]
\[ 5.99, 5.92, \text{center two resonances of an AB quartet due to the methylene protons} \]

Because of the low solubility of this compound, neither an integration nor a determination of the other two peaks of AB quartet could be obtained.

\[ \text{IR (CDCl}_3) \]
\[ 2060s, 1970sBr \text{ cm}^{-1} \]
\[ \text{IR (Nujol)} \]
\[ 3140w, 2070s, 1980sBr, 986m, 890wBr, 850wBr, 770w, 700w, 668sh, 660s \text{ cm}^{-1} \]

In order to observe the initial product of this reaction, an NMR spectrum of a reaction solution was obtained. A sample of \( ^{15}H_2W(CO)_4\)CH₂C₆H₅ (0.108 g, 0.255 mmole) was mixed with SbF₅ intercalated in graphite (0.098 g, 65% by weight SbF₅, 0.29 mmole) in an NMR preparation tube (Figure 14) in the dry box. On the vacuum line 0.5 ml of sulfur dioxide and a small amount of TMS were condensed into the reaction tube at -196°C. Reaction was allowed to proceed for seven hours at -45°C (chlorobenzene slush bath) before the reaction mixture was filtered into the NMR tube. After the tube was sealed in a flame the \( ^1H \) NMR spectrum of the red solution was recorded at -40°C. There was incomplete consumption of the starting metal alkyl in this reaction. In the spectrum resonances corresponding to the alkyl complex appeared
at 2.88, 4.46, 7.10 T. The region of the spectrum from 2.4 to 2.8 T corresponding to phenyl proton resonances was complex, but contained one narrow intense resonance at 2.78 T. The major cyclopentadienyl resonance appeared at 4.28 T with three minor resonances between 4.0 and 4.2 T. There were two singlet resonances at 6.47 and 7.66 T which could be resonances of methylene protons. The most significant resonances and their relative intensities are given below.

\[ ^1\text{H NMR (SO}_2, \text{-40}^\circ\text{C)} T \]

- 2.53, 2.78, complex, phenyl protons
- 4.28, singlet, relative intensity 5
- 6.47, singlet, relative intensity 0.9
- 7.66, singlet, relative intensity 1.7

A sample of \( \text{\(\text{\text{H}_2\text{W(CO)}_3\text{SO}_2\text{C}_2\text{H}_4\text{H}_5\)}} \) (63 mg, 0.15 mmole) was placed in an NMR tube that was sealed to a solve-seal joint. The tube was attached to the vacuum line, evacuated and a sufficient quantity of \( \text{SO}_2 \) for an NMR spectrum was condensed at \(-78^\circ\text{C}\) into the tube which was subsequently sealed with a flame. The \(^1\text{H NMR spectrum of the resulting solution showed the presence of only the starting alkyl complex with resonances at 2.87 T, 4.48 T, and 7.12 T of relative intensities 5, 5, and 2, respectively. After storing the tube for six days at room temperature there were three new resonances at 2.61 T, 4.22 T, and 5.71 T in the intensity ratio of 5:5:2. These resonances corresponded to those of a known sample of the S-sulfinate when it was dissolved in liquid \( \text{SO}_2 \). The intensity of these new resonances compared to those for the starting alkyl complex indicated that about 30\% of the alkyl had reacted to form the S-sulfinate in six days. After storing the tube for two months at room temperature there was little decomposition and the reaction had gone to completion since in the \(^1\text{H NMR spectrum of the solution there were only
the three resonances corresponding to the S-sulfinate complex.

In a separate reaction on a gram-scale a much higher yield was obtained than that found in the standard literature preparation of the S-sulfinate. The reaction was carried out as described by Kroll (20) with the exceptions that a lower temperature and longer reaction time were utilized. A sample of \( \eta^5\text{C}_5\text{H}_5\text{W} (\text{CO})_3\text{C}_2\text{H}_4\text{H}_5 \) (1.008 g, 2.377 mmoles) was placed in a 75 ml Whitey bomb which was then evacuated on the vacuum line. Sulfur dioxide (40 ml liquid) was vacuum transferred to the bomb at -78°C and the bomb was sealed under vacuum. After heating in a 35-40°C oil bath for eight days the bomb was cooled to ice temperature, connected to a mercury bubbler and opened slightly to allow the \( \text{SO}_2 \) to slowly escape. The residue was dissolved in \( \text{CH}_2\text{Cl}_2 \), filtered and reduced in volume to a few milliliters on a rotary evaporator. The addition of 30 ml of pentane induced the precipitation of 1.043 g (2.137 mmoles, 90% yield) of the S-sulfinate which was isolated by filtration, washed with pentane, and dried on the vacuum line. It was identified by two strong sulfur-oxygen stretches appearing in a Nujol mull IR spectrum at 1201 and 1051 cm\(^{-1}\).

15. \( \eta^5\text{C}_5\text{H}_5\text{W} (\text{CO})_3[\text{S(O)}(\text{OBF}_3)\text{C}_2\text{H}_4\text{H}_5] \) (VII). This complex was prepared in an NMR tube and the spectrum was recorded for comparison with the spectra of other complexes. A sample of \( \eta^5\text{C}_5\text{H}_5\text{W} (\text{CO})_3\text{C}_2\text{H}_4\text{H}_5 \) (0.104 g, 0.213 mmole) was placed in an NMR tube sealed to a solve-seal joint. The tube was evacuated on the vacuum line and 0.5 ml of sulfur dioxide was condensed at -196°C. Boron(III) fluoride (131.7 Torr, 29°C, 59.53 ml, 0.416 mmole) and a small amount of TMS were also condensed into the tube at -196°C. The tube was sealed in a flame and
warmed to -45°C (chlorobenzene slush bath) for one hour before the 
$^{1}$H NMR spectrum was recorded at -43°C. The solution was a clear, deep 
red color as compared to the yellow color of the starting tungsten-
alkyl complex. The spectrum contained a complex multiplet at 2.54 T 
and two singlets at 3.93 and 4.89 T. The resonances were in the 
intensity ratio 4.8:5.0:2.2 respectively.

16. $^{5}\text{C}_{5}H_{5}W(\text{CO})_{3}\left\{S(0)(\text{OSbF}_{5})\text{CH}_{2}C_{6}H_{5}\right\}_{3}$ (VIII). A sample of 
$^{5}\text{C}_{5}H_{5}W(\text{CO})_{3}SO_{2}\text{CH}_{2}C_{6}H_{5}$ (0.061 g, 0.12 mmole) was mixed with SbF$_{5}$ 
intercalated in graphite (0.061 g, 65% by weight SbF$_{5}$, 0.18 mmole) 
in an NMR preparation tube (Figure 14) in the dry box. On the 
vacuum line 0.5 ml of sulfur dioxide and a small amount of TMS were 
condensed into the reaction tube at -196°C. The reaction was allowed 
to proceed for seven hours at -45°C (chlorobenzene slush bath) before 
the reaction mixture was filtered into the NMR tube. The solution of 
the product was yellow brown in color. After the tube was sealed in 
a flame the $^{1}$H NMR spectrum of the solution was recorded at -40°C. 
There was complete consumption of the starting metal complex to give 
VIII. The spectrum of VIII consisted of a complex multiplet at 2.53 T 
and two singlets at 4.04 and 5.36 T. These resonances were in a 
5.5:4.5:1.9 intensity ratio.

17. The attempted reaction of C$_{6}H_{5}NO$ with $^{5}\text{C}_{5}H_{5}W(\text{CO})_{3}\text{CH}_{3}$.
About 30 mg of the tungsten alkyl was placed in an NMR tube under 
nitrogen. A sufficient amount of C$_{6}$D$_{6}$ with 1% TMS was added along with 
several drops of C$_{6}H_{5}NO$. The tube was capped, the contents mixed and 
the $^{1}$H NMR spectrum was taken after one hour was allowed for a reaction 
to occur. The spectrum consisted of phenyl resonances of the starting
sulfinylamine and the cyclopentadienyl and methyl singlets of the starting metal alkyl in a five to three ratio at 5.40 T and 9.53 T, respectively.

18. The reaction of C₆H₅NSO with η⁵C₅H₅Fe(CO)₂CH₃. About 60 mg of the iron alkyl was sublimed into an evacuated NMR tube on the vacuum line. The tube was then 3/4 filled with C₆H₅NSO which was vacuum transferred to the tube at 0°C. A small amount of TMS was vacuum transferred to the tube at -196°C and the tube was sealed with a flame. An initial ¹H NMR spectrum showed the phenyl resonances of the sulfinyl amine and the two singlets of the starting metal alkyl in a 5 to 3 ratio at 5.47 T and 9.80 T. After storing the tube at room temperature in the dark for seven hours an additional NMR spectrum was recorded. Although a considerable amount of dark material had precipitated, there was evidence that the iron alkyl had not reacted. In a comparison of the relative intensities of the TMS signal with those of the iron complex in the initial spectrum and the spectrum recorded after seven hours, it was determined that very little if any of the iron alkyl had been consumed. In addition there were no new peaks of significant intensity from 7 to 0 T. After a 46 hour reaction period more material had precipitated and the spectrum peaks were broadened by paramagnetic impurities, but a comparison of the intensities of the TMS peak and those of the starting iron alkyl with the earlier spectra showed that very little of the iron alkyl complex had been consumed.

In a separate reaction a larger quantity of η⁵C₅H₅Fe(CO)₂CH₃ was heated in a C₆H₅NSO solution at 80°C for one hour under vacuum. In the carbonyl stretching region of an IR spectrum of the reaction solution,
bands of the starting iron alkyl were observed at 1990 and 1930 cm\(^{-1}\) in addition to those of a substance with higher carbonyl stretches at 2050 and 2000 cm\(^{-1}\). The products of this reaction could not be isolated or characterized.

\[\text{19. The attempted reaction of } \text{C}_6\text{H}_{11}\text{NSO with } \text{C}_5\text{H}_5\text{W(CO)}_2\text{CH}_3.\]

A sample of the tungsten alkyl (0.053 g, 0.15 mmole) was placed in an NMR tube sealed to a solve-seal joint for attachment to the vacuum line. A quantity of C\(_6\)H\(_{11}\)NSO (0.025 g, 0.17 mmole) was vacuum transferred to the tube along with a small amount of TMS and a sufficient amount of C\(_6\)D\(_6\) to obtain a \(^1\)H NMR spectrum. The tube was sealed under vacuum with a flame. In the spectrum, which was taken about an hour after the sample was warmed to room temperature, there appeared only the resonances of the two starting materials.

\[\text{20. The attempted reaction of } \text{C}_6\text{H}_{11}\text{NSO with } \text{C}_5\text{H}_5\text{Fe(CO)}_2\text{CH}_3.\]

Approximately 30 mg of the iron alkyl and about 10 drops of C\(_6\)H\(_{11}\)NSO were vacuum transferred to an NMR tube on the vacuum line in addition to a small amount of TMS and enough benzene to half fill the tube. The tube was sealed in a flame and the spectrum was taken. The resonances of the starting alkyl were observed at 9.79 and 5.67 \(\tau\) in an approximate 5 to 3 ratio. In addition, there was a broad resonance centered at 8.6 \(\tau\) of the sulfinylamine and another, weaker broad resonance centered at 5.5 \(\tau\). It is not known what compound is responsible for the latter broad resonance, but the resonance did not increase in intensity relative to that of the starting iron alkyl over a period of seven days. The compound was not isolated or characterized. A similar broad resonance was also found in a \(^1\)H NMR spectrum of the C\(_6\)H\(_{11}\)NSO in benzene and
probably is due to an impurity in the unstable \( \text{C}_6\text{H}_{11}\text{NSO} \). This sulfinylamine slowly decomposes at room temperature under vacuum.

21. The attempted reaction of the \( \text{BF}_3 \) adduct of \( \text{C}_6\text{H}_{11}\text{NSO} \) with \( \text{H}^5\text{C}_5\text{H}_5\text{W(CO)}_3\text{CH}_3 \). A sample of \( \text{H}^5\text{C}_5\text{H}_5\text{W(CO)}_3\text{CH}_3 \) (0.087 g, 0.25 mmole) was placed in an NMR tube sealed to a solve-seal joint for attachment to the vacuum line. The tube was evacuated and 0.038 g (0.26 mmole) of \( \text{C}_6\text{H}_{11}\text{NSO} \) was vacuum transferred to the tube at \(-196^\circ\text{C}\) as was a sufficient quantity of \( \text{C}_6\text{D}_6 \) for a \( \text{H} \) NMR spectrum and a small amount of TMS. Finally 0.025 mmole of \( \text{BF}_3 \) (77.10 Torr, 26.4°C, 59.53 ml) was condensed into the tube which was then sealed in a flame. Upon warming the tube to room temperature there was much decomposition in the form of a brown precipitate. In the \( \text{H} \) NMR spectrum of the solution the principal resonances were those of the starting tungsten alkyl \( (5.47 \tau, 9.55 \tau) \). There were two new very low intensity resonances at 5.39 \( \tau \) and 7.00 \( \tau \) which were not further identified.

22. The reaction of the \( \text{BF}_3 \) adduct of \( \text{C}_6\text{H}_{11}\text{NSO} \) with \( \text{H}^5\text{C}_5\text{H}_5\text{Fe(CO)}_2\text{CH}_3 \). A sample of \( \text{H}^5\text{C}_5\text{H}_5\text{Fe(CO)}_2\text{CH}_3 \) (0.191 g, 0.995 mmole) was sublimed into a reaction flask on the vacuum line. A 0.394 g (2.71 mmoles) sample of \( \text{C}_6\text{H}_{11}\text{NSO} \) was vacuum transferred to the flask at \(-78^\circ\text{C}\) followed by 10 ml of toluene. The flask was then submerged in a \( \text{CCl}_4 \) slush bath (-23°C) and 0.990 mmole of \( \text{BF}_3 \) was added in three portions (86.5 Torr, 23.5°C; 106.8 Torr, 23.5°C; and 114.1 Torr, 22.7°C; in each of the three additions the \( \text{BF}_3 \) measurement volume = 59.53 ml). A very fast reaction occurred when \( \text{BF}_3 \) was added to the solution as evidenced by the precipitation of a dark, poorly formed, crystalline appearing substance. After about one hour the mixture was
warmed to room temperature which caused the precipitate to turn into an oil. All materials volatile at 40°C were removed on the vacuum line. The residual oil was transferred to the dry box and a sample of the oil was pressed between KBr plates for an IR spectral analysis. In the carbonyl stretching region of the spectrum there were three bands at 2075s, 2020s, and 1955s cm⁻¹. The S=O stretching region of the spectrum was dominated by a very strong broad absorption from 1150-1000 cm⁻¹, probably caused by boron-fluorine stretching absorptions. An additional sample of the residual oil was dissolved in CH₂Cl₂ and filtered through one cm of Florisil on a frit. The starting iron alkyl was washed from the Florisil with CH₂Cl₂. An orange substance remaining on the Florisil was eluted off with acetone and, after the acetone was removed from the solution on a rotary evaporator, the material was isolated as a brownish-yellow oil. An IR spectrum of a CH₂Cl₂ solution of this oil in the carbonyl stretching region showed two absorptions at 2060 and 2015 cm⁻¹. Satisfactory ¹H NMR and neat IR spectra could not be obtained from this sample. All further attempts to purify, isolate, and characterize this material were futile.

23. $^{5}_{5}C_{5}H_{5}Fe(CO)_{2}[N(SOCH₃)(SO₂C₆H₄CH₃)]_2$, (IXc). This compound was prepared in three different solvents by the reaction of p-toluene N-sulfinylsulfonamide with $^{5}_{5}C_{5}H_{5}Fe(CO)_{2}CH₃$. Two of the reactions, one in CDCl₃ and one in C₆F₆, were carried out in NMR tubes and were followed by the ¹H NMR spectra of the reaction solutions. The third preparation was on a larger scale in THF and the product complex was isolated and characterized from this solution. The reactions are very clean, since only one product was observed in each
of the NMR experiments.

Approximately 50 mg of $^7\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CH}_3$ was placed in an NMR tube in the dry box. A sufficient quantity of $\text{C}_6\text{F}_6$ (with 1% TMS) for an NMR spectrum was added to the tube along with about 40 mg of the solid sulfinylsulfonamide. When the solid sulfinylsulfonamide contacted the solution of the iron complex the solution immediately turned red. The tube was capped, shaken, and the spectrum of the red solution was taken. In a similar manner a solution of the product complex was prepared in CDCl$_3$.

In the larger scale preparation 1.032 g (5.33 mmoles) of the starting iron-alkyl complex and a 1.158-g (5.33 mmoles) sample of p-toluene-N-sulfinylsulfonamide were placed in a flask in the dry box. The flask was removed from the dry box and cooled in an ice bath while 30 ml of dry THF were added under nitrogen. The flask was connected to the vacuum line, partially evacuated and the contents were stirred for one hour at 0°C. Solvent removal resulted in an orange oil which could not be induced to crystallize. The spectra of this material in both CDCl$_3$ and $\text{C}_6\text{F}_6$ were indentical with those obtained in the NMR experiments in those solvents. The compound was characterized by means of the following experimental data:

$^1\text{H NMR (C}_6\text{F}_6)\ 
\begin{align*}
&\text{2.63, singlet, relative intensity 4} \\
&\text{4.72, singlet, relative intensity 5} \\
&\text{7.42, singlet, relative intensity 3} \\
&\text{7.81, singlet, relative intensity 3 (signal slightly broadened)} \\
\end{align*}$

$^1\text{H NMR (CDCl}_3)\ 
\begin{align*}
&\text{2.52, center of AA'B'B' pattern, relative intensity 4.1} \\
&\text{4.83, singlet, relative intensity 4.9} \\
&\text{7.60, singlet, relative intensity 6.0} \\
\end{align*}$

IR (CHCl$_3$) 2060s, 2015s cm$^{-1}$

IR ($\text{C}_6\text{F}_6$) 2055s, 2015s cm$^{-1}$
The reaction of p-toluene-N-sulfinylsulfonamide with $\text{C}_5\text{H}_5\text{Fe}^\text{(CO)}_2\text{CH}_2\text{C}_6\text{H}_5$. In an NMR experiment about 40 mg of the iron alkyl were placed in an NMR tube in the dry box. A sufficient quantity of CDCl$_3$ for an NMR spectrum was added along with a slight excess of the sulfinylsulfonamide. A rapid reaction occurred resulting in a red solution. An NMR spectrum which was slightly broadened owing to paramagnetic impurities was obtained on this solution. Solvent removal on the vacuum line gave a brown glass. Its IR spectrum as a Nujol mull was recorded.

$$\text{IR (Nujol)} \; 3100\text{w}, \; 2050\text{s}, \; 2000\text{s}, \; 1950\text{w}, \; 1600\text{w}, \; 1500\text{w}, \; 1300\text{m}, \; 1280\text{sh}, \; 1145\text{s}, \; 1080\text{s}, \; 1020\text{vw}, \; 960\text{w}, \; 860\text{m}, \; 810\text{m}, \; 705\text{w}, \; 660\text{m}, \; 595\text{s}, \; 575\text{s}, \; 560\text{w}, \; 545\text{s}, \; 525\text{w} \; \text{cm}^{-1}$$

Analytical Data found 44.8% C, 4.18% H, 15.4% S

Calculated for $\text{C}_{15}\text{H}_{19}\text{FeNO}_2\text{S}_2$

44.02% C, 3.6% H, 15.67% S

25. $\text{A 1 g quantity of the orange compound } \text{Fe}^\text{(CO)}_2\text{[SOCH}_3\text{(SO}_2\text{C}_6\text{H}_4\text{CH}_3)}$, which had been stored in the dry box at about 30°C for four months was examined. The sample changed to a dark brown-black, slightly sticky solid from its
original orange color. In an attempt to obtain the N-bonded complex in pure form from this partly decomposed material, a new substance was isolated. The partial dissolution of the dark brown sample on a sintered glass frit with a small amount of CHCl₃ resulted in a mixture of a solid in a brown solution. After the yellow solid was filtered off and washed once quickly with a small amount of CHCl₃ it was dissolved in a few milliliters of CHCl₃ to give a yellow solution. The solution was filtered and the solvent was removed on a rotary evaporator to give a yellow glass. The following spectral data were obtained from solutions of this compound.

\[ ^1H\text{ NMR (CDCl}_3) \tau \]
2.47, center of AA'BB' pattern, relative intensity 4.1
4.69, singlet, relative intensity 4.7
6.65, singlet, relative intensity 2.9
7.63, singlet, relative intensity 3.2

\[ \text{IR (CHCl}_3) \]
2070, 2022 cm⁻¹

\[ \text{IR (Nujol)} \]
3080w, 2075s, 2050s, 2005vs, 1295s, 1280s, 1145s, 1115s, 1088s, 1060vw, 1025s, 1010s, 960m, 940Sh cm⁻¹

26. H₂C₅Fe(CO)₂[N(SO₂CH₃)(SO₂C₆H₅CH₃)]₉ (Xc). A 60 mg (0.14 mmole) sample of H₂C₅Fe(CO)₂[N(SOCH₃)(SO₂C₆H₅CH₃)]₉ was dissolved in two milliliters of CH₂Cl₂. A twofold excess of m-chloroperoxybenzoic acid (0.50 mg, 0.29 mmole) was added and the solution was stirred for one hour. The solvent was removed on vacuum line and 2 g of NaHCO₃ was added to the residue. About four milliliters of methyl alcohol were added and the mixture was stirred for 20 minutes. The solution was filtered from the solid NaHCO₃ and combined with a subsequent two milliliter methyl alcohol wash of the solids. The solvent was removed on a rotary evaporator and a solution of the residue in CH₂Cl₂ was dried with MgSO₄. Filtration of this mixture resulted in a red solution which yielded a
crystalline brownish-red residue when the solvent was removed in an argon stream. The spectral data obtained for this product are given below.

\[ {^1}H \text{ NMR (CDCl}_3) \tau \]

- 2.38, center of AA'BB' pattern, relative intensity 4.2
- 5.08, singlet, relative intensity 4.8
- 6.90, singlet, relative intensity 2.8
- 7.56, singlet, relative intensity 3.2

\[ \text{IR (CDCl}_3) \]

- 2059s, 2014s cm\(^{-1}\)

\[ \text{IR (Nujol)} \]

- 3140w, 3105w, 2048s, 2000s, 1320s, 1300w, 1298w, 1150s, 1140s, 1088m, 1070w, 1020w, 980m, 915s, 905Sh, 845m, 840Sh, 815s, 720mBr, 670s, 629m, 588Sh, 558m, 548m, 530s, 508w, 488w cm\(^{-1}\)

27. The attempted reaction of p-toluene-N-sulfinylsulfonamide with \( \overset{5}{\text{C}_2\text{H}_5\text{W(CO)}_3\text{CH}_3} \). A 40 mg sample of the tungsten alkyl was placed in an NMR tube in the dry box. A sufficient quantity of \( \text{C}_6\text{D}_6 \) (1% TMS) for an NMR spectrum and approximately 30 mg of the sulfinylsulfonamide were added. The solids were dissolved and a spectrum was obtained after allowing about one hour for a reaction to occur. In the \( {^1}H \text{ NMR} \) spectrum of the solution, in addition to the resonances from the starting materials, two very low intensity signals appeared at \( \tau 4.05 \) and \( \tau 8.00 \) with the intensity ratio 5.0:3.1. These signals accounted for less than 5% of the spectrum relative to the starting tungsten-alkyl complex, and the compound corresponding to these signals was not isolated or further characterized.

28. \( \overset{5}{\text{C}_2\text{H}_5\text{Fe(CO)}_3\left[\overset{\text{N(SO}_2\text{CH}_3)}{\overset{\text{SO\text{CH}_3}}{}}\right]} \). In the dry box a 12.0 g (62.5 mmole) sample of \( \overset{5}{\text{C}_2\text{H}_5\text{Fe(CO)}_3\text{CH}_3} \) was placed in a flask and dissolved in 5 ml of toluene. A sample of \( \text{CH}_3\text{SO}_2\text{NSO \ (8.85 g, 62.7 mmole) was syringed into a pressure equalizing dropping funnel and dissolved in 10 ml of toluene. The sulfinylsulfonamide solution} \)
was added dropwise over a period of three hours to the stirred solution of the iron-alkyl complex. A very thick precipitate resulted which was slurried with an additional 10 ml of toluene and the mixture was filtered on a sintered glass frit. The mother liquor was discarded. This resulted, after a pentane wash, in the isolation of 20.3 g (60.9 mmoles, 97% yield based on $\eta^5C_5H_5Fe(\text{CO})_2\text{CH}_3$) of a poorly crystalline product. The product was shown to be a pure material by its $^1H$ NMR spectrum taken in CDCl$_3$. The following physical characteristics were found for this complex.

Melting Point (argon) 105-106°C with gas evolution

Analytical Data found 32.21% C, 3.23% H, 19.18% S calculated for $C_{11}H_{21}FeNO_5S_2$

32.45% C, 3.33% H, 19.25% S

$^1H$ NMR (CDCl$_3$) T 4.77, singlet, relative intensity 5
7.08, singlet, relative intensity 3
7.49, singlet, relative intensity 3

$^{13}C$ NMR (CDCl$_3$, 25°C) 212.2, 211.5 PPM, CO
85.8 PPM, C$_5H_5$
45.1 PPM, (broad), CH$_3$
41.9 PPM, CH$_3$

$^{13}C$ NMR (CDCl$_3$, -50°C) 212.0, 211.3 PPM, CO
85.8 PPM, C$_5H_5$
44.0, 41.2 PPM, CH$_3$

IR (CH$_2$Cl$_2$) 2050, 2000 cm$^{-1}$

IR (Nujol) 3120w, 2050s, 2000s, 1300s, 1135s, 1080s, 1070Sh, 975m, 860sBr, 820m, 750m, 700w, 590s, 560s, 535s, 520m, 440m cm$^{-1}$

Mass Spectrum contains a very weak parent peak at m/e 333 the principal peaks below the parent peak correspond to P-CH$_3$, P-CO, P-2(CO), P-2(CO)CH$_3$

29. $\eta^5C_5H_5Fe(\text{CO})_2[N(\text{SO}_2\text{CH}_3)_2]_2(Xe)$. The iron complex $\eta^5C_5H_5Fe(\text{CO})_2$-$[N(\text{SOCH}_3)(\text{SO}_2\text{CH}_3)]$ (1.00 g, 3.00 mmoles) was dissolved in 3 ml of CH$_2$Cl$_2$ in a round-bottom flask under nitrogen to give a red-orange
solution. To this solution, a solution of \( m \)-chloroperoxybenzoic acid (0.62 g, about a 5\% excess of active peracid) in 5 ml of \( CH_2Cl_2 \) was added under nitrogen from a pressure equalizing dropping funnel. The addition of the peracid solution to the solution of the iron complex took place dropwise over a 30 minute period. The reaction solution turned red with the first few drops of peracid solution, and after most of the peracid had been added a precipitate began to form. After complete addition of the peracid solution the reaction mixture was stirred for 15 hours. The precipitate from this reaction was isolated by filtration and washed with 6 ml of pentane. After drying, the substance was a pinkish-orange powder. An examination under a microscope showed that it was a mixture of orange and white crystals. A \(^1\)H NMR spectrum in \( CDCl_3 \) of this mixture contained phenyl resonances suggesting that the white crystalline material was an acid residue. In addition two resonances appeared at 4.84 \( \tau \) and 6.93 \( \tau \) with relative intensities of 5.0 and 6.0 respectively. An IR spectrum of a Nujol mull of this mixture showed two strong terminal CO stretches at 2050 and 2000 \( cm^{-1} \).

The residue from solvent removal on a rotary evaporator of the filtrate of the original reaction mixture was combined with the precipitate from the reaction. The solids were treated with a large excess of \( NaHCO_3 \) and a few milliliters of water to give a pink paste. This paste was placed on a sintered glass frit and washed with water until there was only a red residue remaining on the frit. The residue was dissolved in \( CH_2Cl_2 \), filtered, and dried over anhydrous \( MgSO_4 \). After filtering off the \( MgSO_4 \), a few milliliters of hexane was added to the solution. Small, red crystals were obtained from this solution upon solvent
removal on a rotary evaporator. Recrystallization from a 50:50 CH₆Cl₂/hexane solution at -78°C resulted in 0.3 g of the pure crystalline complex with the following physical characteristics.

Melting Point (vacuum) 129°C with gas evolution

Analytical Data found 30.8% C; 3.10% H, 18.12% S calculated for C₉H₁₁FeNO₅S₂ 30.96% C, 3.18% H, 18.36% S

¹H NMR (CDCl₃) 4.84, singlet, relative intensity 5 6.93, singlet, relative intensity 6

¹³C NMR (CDCl₃) 210.9 PPM, CO 85.6 PPM, C₂H 42.7 PPM, CH₃

IR (CH₂Cl₂) 2070, 2020 cm⁻¹

IR (Nujol) 3140w, 2060s, 2010s, 1321s, 1315s, 1295s, 1135s, 1065w, 1015w, 980w, 970w, 895s, 850m, 840m, 748m, 600w, 595m, 580m, 560m, 540s, 510s cm⁻¹

30. Isomerization of N₂C₅H₅Fe(CO)₂[N(SOCH₃)₂(SO₂CH₃)] to N₂C₅H₅Fe(CO)₂[S(O)(CH₂)(NSO₂CH₃)]. The product of this isomerization has only been observed in the ¹H NMR spectrum of reaction mixtures but chemical shift values assigned to the product are in agreement with those expected from similar compounds. The isomerization was attempted two times. In the first attempt, a small amount of IXa on a spatula was dissolved in CdCl₃ in an NMR tube sealed to a solve-seal joint. The tube was attached to the vacuum line and its contents were degassed before the tube was sealed in a flame. The solution was protected from light by wrapping the tube in aluminum foil. The tube was immersed for 17 hours in an oil bath which was maintained at 35-40°C. When the tube was removed from the oil bath there was a small amount of brown precipitate which was centrifuged to the top of the NMR tube to give a clear, red solution. The ¹H NMR spectrum of the solution was
recorded. A mixture of products was evident in the spectrum with three prominent resonances at 4.78, 7.05, and 7.28 T and three minor resonances at 4.67, 6.57, and 6.94 T.

In the second isomerization attempt 0.93 g of $\eta^5\text{C}_5\text{H}_5\text{Fe(CO)}_2^-$ \([\text{N(SOCH}_3)(\text{SO}_2\text{CH}_3)]\) was dissolved in 30 ml of CHCl$_3$. The flask containing the solution was degassed on the vacuum line and immersed in an oil bath maintained at 50°C for 4.5 hours. The solvent was removed on a rotary evaporator to give a red-brown oil. A portion of this oil was dissolved in CDCl$_3$ and a $^1$H NMR spectrum was recorded. Only two broad major resonances appeared at 4.86 T and 7.02 T in a 5:6 intensity ratio, respectively. A neat IR spectrum of the residue when compared to a spectrum of $\eta^5\text{C}_5\text{H}_5\text{Fe(CO)}_2^-$ \([\text{N(SOCH}_3)(\text{SO}_2\text{CH}_3)]\) indicated that the residue was principally the starting material. The $^1$H NMR spectrum of the pure starting material contains resonances at 4.77, 7.08, and 7.49 T with relative intensities 5:3:3, respectively. Chromatography of the residue on neutral alumina with C$_6$H$_6$CH$_2$Cl$_2$ (70:30) as eluent developed two bands. The first was a small, red, fast moving band and the second an orange nearly stationary band. The first band was collected and shown to be of little interest by its $^1$H NMR spectrum (4.96 T) in CDCl$_3$. The column was then eluted with acetone and the orange band, which was the major complex in the reaction mixture, was collected. This band was identified as slightly impure starting iron complex by its $^1$H NMR spectrum (4.77 T, 7.10 T, 7.41 T relative intensities 5:3:3, respectively). Apparently the chemical shifts of the protons of the starting iron complex, especially of the upfield protons, are concentration and/or impurity dependent. In the earlier isomerization attempt the major
resonances at 4.78, 7.05 and 7.28 T are undoubtedly due to the same complex. The identification of this complex as starting material was verified by its neat IR spectrum. The tail of the orange band was collected separately. The $^1$H NMR spectrum of the residue after solvent removal showed that a mixture of compounds was present; it contained resonances at the following chemical shifts: 4.70, 4.78, 4.94, 6.60, 6.90, 7.00, 7.08 and 7.49 T. Several of the compounds present in the mixture were readily identified. Resonances appearing at 4.78, 7.08, and 7.49 T were assigned to the starting iron complex. The red material isolated by chromatography resonates at 4.96 T. The resonance at 6.90 T is from the methyl protons of $\text{CH}_3\text{SO}_2\text{NH}_2$. The three remaining resonances, 4.70, 6.60, and 7.00 T, are of appropriate chemical shifts and approximate relative intensities for the complex $\eta^5\text{C}_5\text{H}_5\text{Fe(CO)}_2[S(\text{O})(\text{CH}_3)(\text{NSO}_2\text{CH}_3)]$ (see results and discussion). These resonances are similar to the minor product of the first isomerization attempt in an NMR tube (4.67, 6.57 and 6.94 T). Since only a very small quantity of this substance was formed, it was not further purified or characterized.

31. $\eta^5\text{C}_5\text{H}_5\text{Fe(CO)}_2[N(\text{SO}_2\text{CH}_3)(\text{SCH}_3\text{NSO}_2\text{CH}_3)], (\text{XIIa})$. A 30 mg sample of $\text{(CH}_3\text{SO}_2\text{H})_2\text{S}$ was placed in an NMR tube in the dry box. An excess of $\eta^5\text{C}_5\text{H}_5\text{Fe(CO)}_2\text{CH}_3$ (about 50 mg) was added to the tube after a sufficient quantity of CDCl$_3$ for an NMR spectrum had been placed in the tube. Although the colorless diimide was only slightly soluble in CDCl$_3$, it dissolved quickly when the iron complex was added to form a red solution. In the spectrum obtained of this solution there appeared resonances due to the starting metal complex at 5.27 T and 9.84 T in addition to the four singlets ascribed to the product complex listed below.
In a larger scale preparation, 0.30 g of $\eta^5$C$_5$H$_5$Fe(CO)$_2$CH$_3$ dissolved in two milliliters of CHCl$_3$ in the dry box was stirred with an excess of (CH$_3$SO$_2$N)$_2$S overnight. The excess dide was filtered off and the product complex was precipitated by the addition of 10 ml of hexane. The insertion product was filtered off from the yellow solution of unreacted iron-alkyl complex and washed twice with 5 ml portions of hexane. This crude product was recrystallized from CH$_2$Cl$_2$-hexane to give a light orange crystalline product. The $^1$H NMR in CDCl$_3$ was identical with the initial product observed above. The following physical data were obtained for this complex.

$^1$H NMR (CDCl$_3$) $\tau$ 4.70, singlet, relative intensity 4.6
6.91, singlets, relative intensity 6.4
7.04, singlet, relative intensity 3.0

$^1$H NMR (D$_6$-acetone) $\tau$ 4.50, singlet, C$_5$H$_5$
6.98, singlet, CH$_3$
7.17, singlet, CH$_3$
7.33, singlet, CH$_3$

In addition a small resonance occurs at 7.00 in all spectra in acetone.

IR (Nujol) carbonyl region 2042, 2003, 1989 cm$^{-1}$, the lower band is always split in Nujol mull spectra

IR (Nujol) 3100w, 3070w, 2042s, 2003s, 1989s, 1300s, 1280s, 1143sh, 1133sh, 1128s, 1012s, 985w, 978w, 958m, 950m, 944m, 900w, 888w, 854m, 834sh, 820m, 780m, 740w, 725sh, 718w, 590m, 580m, 555m, 540m, 528m, 515m, 508m, 470w, 435w cm$^{-1}$

32. $\eta^5$C$_5$H$_5$Fe(CO)$_2$[(N(SOCH$_2$C$_6$H$_5$))(SO$_2$CH$_3$)]. (IXb). This complex was prepared in a reaction of a solution of 50 mg of $\eta^5$C$_5$H$_5$Fe(CO)$_2$CH$_2$C$_6$H$_5$ in 0.2 ml of CDCl$_3$ with a solution of five drops of CH$_3$SO$_2$NSO in 0.8 ml of CDCl$_3$. The reaction was carried out in an NMR tube in the dry box and produced only one product as evidenced by the NMR spectrum of the solution. The spectrum is listed below.
In those reactions in which neat sulfinylsulfonamide was introduced to the iron-alkyl solution, \( \eta^5C_5H_5Fe(CO)_2\left[N(SO_2CH_3)(SCH_2C_6H_5SO_2CH_3)\right] \) appeared as a by-product. The N-bonded insertion product IXb was later isolated in a larger scale reaction analogous to the NMR-scale preparation above. Solvent removal from the reaction solution on the vacuum line gave the pure product as an orange solid.

\[ ^1H \text{NMR (CDCl}_3) \]

2.65, singlet, relative intensity 4.9
4.94, singlet, relative intensity 5.0
5.72, 6.14, J=12.4 Hz, AB quartet, relative intensity 2.1
7.32, singlet, relative intensity 3.1

IR (CDCl\(_3\)) 2055, 2010 cm\(^{-1}\)

IR (Nujol) 3100w, 2045s, 1995s, 1300s, 1140s, 1080m, 1060m,
960m, 900m, 860w, 810w, 800w, 765m, 730w, 715w,
695m, 590m, 560m, 530m, 515Sh, 475m cm\(^{-1}\)

33. \( \eta^5C_5H_5Fe(CO)_2\left[N(SO_2CH_3)(SCH_2C_6H_5)\right] \). In the dry box a 40 mg sample of \( \eta^5C_5H_5Fe(CO)_2\) dissolved in CDCl\(_3\) in an NMR tube was treated with 5 drops of CH\(_3\)SO\(_2\)NSO. The solution immediately turned red and the tube was shaken to disperse the sulfonamide. A \(^1H\) NMR spectrum of this solution showed complete consumption of the starting metal alkyl, but it was of a poor quality owing to paramagnetic broadening. Since the presence of an excess of sulfinylsulfonamide often caused broadening of the peaks of an NMR spectrum, the excess reactant was removed. The CDCl\(_3\) solution was treated with a 50:50 ethyl alcohol:water solution, decomposing the excess reactant to the sulfonamide and SO\(_2\). The solution was evaporated to dryness on a rotary evaporator. After dissolving the residue in CH\(_2\)Cl\(_2\), it was treated with MgSO\(_4\), filtered, and the solvent again was removed on a rotary evaporator. The residue was an orange-red oil which gave the following \(^1H\) NMR spectrum in CDCl\(_3\).
\[ ^1H\text{NMR (CDCl}_3\text{)} T 2.79, \text{singlet, phenyl protons} \]
\[ 4.89, \text{singlet, cyclopentadienyl protons} \]
\[ 7.10, \text{center of complex symmetrical multiplet, methylene and methyl protons} \]

\[ \eta^5C_5H_5^*Fe(CO)\{N(SO_2CH_3)\{SO_2CH_2C_6H_5\}\}_2 (Xb). \]
A 50 mg sample of \( \eta^5C_5H_5^*Fe(CO)\{N(SO_2CH_2C_6H_5)\{SO_2CH_3\}\}_2 \) was dissolved in three milliliters of CH\(_2\)Cl\(_2\). An excess of m-chloroperoxybenzoic acid was added and the solution was stirred for 10 minutes. The solvent was removed on a rotary evaporator and about one gram of NaHCO\(_3\) was added to the residue along with four milliliters of methyl alcohol. This mixture was stirred for ten minutes and the solids were filtered off. The solid residue was washed once with two milliliters of methyl alcohol and the filtrate and wash were combined. After the solvent was removed on a rotary evaporator, the residue was dissolved in CH\(_2\)Cl\(_2\) and dried over MgSO\(_4\) for ten minutes. This mixture was filtered and the CH\(_2\)Cl\(_2\) solution was evaporated on a rotary evaporator. The red residue was dissolved in CDCl\(_3\) for spectral analysis.

\[ ^1H\text{NMR (CDCl}_3\text{)} T 2.6, \text{complex, phenyl protons} \]
\[ 5.29, \text{singlet, cyclopentadienyl protons} \]
\[ 5.36, \text{singlet, methylene protons} \]
\[ 6.95, \text{singlet, methyl protons} \]

\text{IR (CDCl}_3\text{)} 2056, 2012 cm\(^{-1}\)

\text{IR (Nujol)} 3120w, 2045s, 1990s, 1335w, 1325s, 1298s, 1270w, 1158w, 1145w, 1130s, 1080w, 1040w, 1020w, 1010w, 980w, 970w, 925w, 900s, 850m, 770m, 750w, 720m, 700m, 600m, 590m, 570m, 550m, 525m, 505m cm\(^{-1}\)

\[ \eta^5C_5H_5^*Fe(CO)\{S(O)(CH_2CH_2CH_2)(NSO_2CH_3)\}_2 (XIa). \]
This S-bonded isomer was prepared by crystallization from saturated CHCl\(_3\) solutions of the corresponding N-bonded complex, \( \eta^5C_5H_5^*Fe(CO)_2\{N(SOCH_2CH_2C_6H_5)\{SO_2CH_3\}\}_2 \), at -10°C over a period of several days. All attempts to crystallize the red N-bonded species have resulted only in the crystallization of
the orange-yellow S-bonded isomer. The mother liquor from these crystallizations consisted of a mixture of the S- and N-bonded complexes as was determined by the NMR spectra of the solutions. The following physical data were obtained for the S-bonded complex.

**Melting Point** 100-102°C

$^1$H NMR (CDCl$_3$) $\tau$ 2.52, singlet, relative intensity 4.9

$^1$H NMR (CDCl$_3$) $\tau$ 4.92, singlet, relative intensity 5.2

$^1$H NMR (CDCl$_3$) $\tau$ 5.33, singlet, relative intensity 2.0

$^1$H NMR (CDCl$_3$) $\tau$ 6.99, singlet, relative intensity 2.9

$^{13}$C NMR (CDCl$_3$) 209 PPM, Approximate CO

132.0, 130.2, 129.6, 129.0 PPM, C$_6$H$_5$

87.6 PPM, C$_5$H$_5$

75.9 PPM, CH$_2$

45.6 PPM, CH$_3$

IR (Nujol) 3115w, 3100w, 2065vs, 2005vs, 1320w, 1275vs, 1198w, 1130s, 1105s, 1070w, 1030vsBr, 960m, 935w, 908m, 878m, 860m, 815w, 785m, 770m, 730s, 700s, 645w, 590s, 565w, 555w, 540wSh, 530s, 490s, 470m cm

This compound appeared in irregular amounts as a by-product in the preparation of

$^2$C$_5$H$_5$Fe(CO)$_2$[N(SO$_2$CH$_3$)$_2$(SO$_2$CH$_3$)$_2$]$_2$ (XIIb). This compound was obtained in very concentrated solutions of the reactants were mixed.

A reliable preparation involved the reaction of the diimide ($\text{CH}_3\text{SO}_2\text{N})_2$S with $^2$C$_5$H$_5$Fe(CO)$_2$CH$_2$C$_6$H$_5$. Approximately 30 mg of the diimide was placed in an NMR tube in the dry box and covered with a small amount of CDCl$_3$ in which it is only slightly soluble. A solution of the iron complex in about 0.5 ml of CDCl$_3$ was added to the tube which was capped, shaken, and the $^1$H NMR spectrum of the red solution was taken. The diimide insertion product was purified by crystallization from CHCl$_3$ at -10°C. The physical data obtained for this compound are given below.
Melting Point (vacuum) 148-149°C with gas evolution

Analytical Data found 39.55% C, 3.86% H, 18.92% S
 calculated for C_{16}H_{16}FeN_{0.5}O_{2.6}S_{3}
 39.51% C, 3.73% H, 19.78% S

^1H NMR (CDCl₃) †
 2.63, singlet, relative intensity 5.0
 4.73, singlet, relative intensity 4.8
 5.79, 5.91, J=12.1, AB quartet, relative intensity 2.0
 6.90, singlet, relative intensity 3.1
 7.64, singlet, relative intensity 3.1

^13C NMR (CDCl₃) 212.0, 210.7 PPM, CO
 131.2, 130.7, 129.1, 128.9, 128.2 PPM
 85.8 PPM, C₅H₅
 59.9 PPM, CH₂
 42.8, 42.0 PPM, CH₃

IR (Nujol) 3140w, 3120w, 2050s, 2040sh, 2005s, 1970w, 1330w,
 1310s, 1295s, 1288s, 1270w, 1240w, 1200w, 1150s,
 1140s, 1130sh, 1080w, 1020s, 1010s, 985m, 970m,
 960m, 925vw, 905s, 880s, 850s, 830m, 820w, 800s,
 775m, 750m, 720w, 700s, 660m, 595m, 580m, 570m,
 545s, 525w, 515m, 485m, 448m cm⁻¹

37. \( \text{Co}_{5} \text{Fe(CO)}_{2} \left[ \text{OS(OF)}_{2} \right] \text{CH}_{3} \). A sample of \( \text{Co}_{5} \text{Fe(CO)}_{2} \left[ \text{OS(OF)}_{2} \right] \text{CH}_{3} \)
 0.573 g, 2.98 mmoles) was placed in a reaction flask (Flask A, Figure 13) and the flask was evacuated on the vacuum line.

Approximately 20 ml of liquid sulfur dioxide was condensed into the flask at -196°C and a red solution of \( \text{Co}_{5} \text{Fe(CO)}_{2} \left[ \text{OS(OF)}_{2} \right] \text{CH}_{3} \) was prepared (15) by warming the contents of the flask to -45°C (chlorobenzene slush bath). At that temperature a total of 2.99 mmoles of BF₃ was added in three portions (23.9°C, 457.7 Torr, 57.5 ml; 23.9°C, 444.0 Torr, 57.5 ml; 24.5°C, 60.9 Torr, 57.5 ml). The reaction mixture was maintained at -45°C for two hours after which about 10 ml of benzene was condensed into the flask. The slush bath was removed and the mixture was allowed to warm until the benzene dissolved to give a clear, deep red solution. The volume of the solution was reduced about two-thirds
by exposure to vacuum. Two additional additions of 10 ml of benzene followed by reduction of solvent volume in vacuum resulted with the precipitation of a red powder. The powder was collected on the frit (Figure 13) by filtration and washed twice with benzene condensed back through the frit. This substance had a decomposition point of 73°C. The parent peak and major fragments observed in its mass spectrum corresponded to \( \text{C}_{2}^{5}\text{H}_{5}\text{Fe(CO)}_{2}\text{SO}_{2}\text{CH}_{3} \). Boron was also present as shown in the spectrum by peaks at m/q 10 and 11. An IR spectrum of a CH\(_{2}\text{Cl}_{2}\) solution of the red powder contained strong carbonyl stretching absorptions at 2065 and 2018 cm\(^{-1}\). Attempts to obtain \(^1\text{H}\) NMR spectra in CDCl\(_{3}\) resulted only in resonances at 4.73 and 6.83 \( \tau \) which correspond to the known S-sulfinate \( \text{C}_{2}^{5}\text{H}_{5}\text{Fe(CO)}_{2}\text{SO}_{2}\text{CH}_{3} \) (1). All purification attempts by crystallizations or partial precipitation resulted only in the formation of oils. The IR spectrum of the red powder is compared to that of \( \text{C}_{2}^{5}\text{H}_{5}\text{Fe(CO)}_{2}\text{SO}_{2}\text{CH}_{3} \) (1) in Figure 28.

The reaction of BF\(_{3}\) with \( \text{C}_{2}^{5}\text{H}_{5}\text{Fe(CO)}_{2}\text{OS(OCH}_{3}\) in liquid sulfur dioxide was examined by low temperature NMR spectroscopy. A sample of \( \text{C}_{2}^{5}\text{H}_{5}\text{Fe(CO)}_{2}\text{CH}_{3} \) (0.053 g, 0.28 mmole) was placed in an NMR tube attached to a solve-seal joint. The tube was evacuated and 0.5 ml of SO\(_{2}\) was condensed into the tube with a Dry Ice-isopropyl alcohol bath. An equimolar quantity of BF\(_{3}\) (0.28 mmole; 89.6 Torr, 57.64 ml, 23.0°C) and a small amount of TMS were condensed into the tube at -196°C. The tube was sealed in a flame, warmed to -32°C in the \(^1\text{H}\) NMR spectrometer, and the spectrum of the resulting red solution was recorded. The spectrum contained one cyclopentadienyl resonance at 4.70 \( \tau \). In addition, there were two signals which could be ascribed to methyl protons at 7.07
and 7.52 ppm in the approximate intensity ratio 2:5:2:0, respectively.
These methyl resonances do not correspond with that of the O-bonded
sulfinate starting material.
Chapter III

RESULTS AND DISCUSSION

Intermolecular Electrophilic Enhancement of the Rate of Insertion Reactions by Coordinated Lewis Acids

The objective of the work described in this chapter was to demonstrate that the rate of sulfur dioxide insertion into metal-carbon bonds can be enhanced by the use of Lewis acids. This implies that by using techniques developed here it should be possible to activate other potential inserting agents and thereby extend the range of compounds available through insertion into metal-carbon bonds.

Originally it was felt that a catalytic system to promote the insertion of sulfur dioxide into metal-carbon bonds was desirable. The Lewis acid SbF$_5$ is known to form a stable one to one adduct with sulfur dioxide forming an Sb-O bond (21). It was suspected that the coordination of the SbF$_5$ would be too strong to allow a catalytic process to occur. The weaker Lewis acid BF$_3$ forms a one to one complex with SO$_2$ which is unstable above -96°C (22) and thus was a better candidate for a catalyst in this reaction. The fact that it would be significantly uncomplexed at temperatures where sulfur dioxide, the solvent in these reactions, was liquid suggested that its reactivity with metal alkyls in the absence of SO$_2$ should be examined.
In a tensimetric titration of $\eta^5$C$_5$H$_5$W(CO)$_2$CH$_3$ at 26°C (Figure 17) in toluene with BF$_3$, it was shown that a stable complex was not formed. Since there was an equal time interval between each of the data points, it appears that a slow decomposition reaction occurred. In a second titration at -23°C (Figure 18) there was no evidence of any BF$_3$ complex formation or of any reaction of BF$_3$ with the tungsten-alkyl complex. Thus it is reasonably certain that there will not be a significant reaction of the metal alkyl with the Lewis acid BF$_3$. However, one cannot rule out the possibility that a momentary interaction of BF$_3$ with the metal complex might induce a reaction with SO$_2$.

The reaction of $\eta^5$C$_5$H$_5$W(CO)$_2$CH$_3$ dissolved in SO$_2$ with an equimolar quantity of BF$_3$ was quite rapid at about -40°C. Upon warming a reaction solution from -78°C, the temperature at which the reactants were allowed to dissolve, to about -40°C, there was a fast color change from the yellow of the alkyl solution to the burgundy-red of the product. When the reaction was carried out in a sealed NMR tube, an inspection of the $^1$H NMR spectrum obtained on the sample indicated that only one product (having two singlet resonances) formed and that it must have been quantitatively formed since no material precipitated during the reaction. The isolation of this product was not simple as some decomposition invariably occurred when the solvent sulfur dioxide was removed on a vacuum line, and the residue was often an oil. Techniques were developed (vide supra) for the isolation and purification of this substance. It was obtained as small, dark red crystals, but all attempts to prepare crystals suitable for an x-ray structural study were unsuccessful. The $^1$H NMR spectrum of an SO$_2$ solution of the crystals was recorded. It was
Solvent = Toluene
Temperature = 26.2 ± 0.5°C

Figure 17
THE TENSIMETRIC TITRATION OF $\eta^5$C$_5$H$_5$W(CO)$_3$CH$_3$ WITH BF$_3$

Solvent = Toluene
Temperature = -23°C
(CCl$_4$ slush)

Figure 18
identical with the spectrum of the initial product observed in the
reaction in an NMR tube. The red crystalline product is designated as
compound I. An elemental analysis of I indicated a composition in
agreement with a one to one to one adduct of $\eta^5_{C_5H_5}W(CO)_3CH_3$, $SO_2$, and $BF_3$.

A deficiency (29%) of $BF_3$ was allowed to react with a sulfur dioxide
solution of $\eta^5_{C_5H_5}W(CO)_3CH_3$ under vacuum (Dry Ice as reflux coolant) to
test the possibility of catalysis of $SO_2$ insertion by $BF_3$. The solution
turned a deep red color. The residue remaining after solvent removal
was examined by IR spectroscopic methods. An NMR spectrum of a CDCl$_3$
extract of the residue showed the presence of only I and the starting
tungsten-alkyl complex. An examination of the carbonyl stretching region
of the IR spectrum obtained on a Nujol mull of the residue showed that
an $SO_2$ insertion species was the principal carbonyl containing compound
(i.e., I) and that the starting metal alkyl was present in substantially
lesser amounts. Thus, under these conditions $BF_3$ is definitely not a
catalyst; it is bound too strongly in the product complex. If it were
a catalyst some of the S-sulfinate would have been formed.

In a similar vein, a sample of I mixed with $\eta^5_{C_5H_5}W(CO)_3CH_3$ was
dissolved in $SO_2$ in an NMR tube and the $^1H$ NMR spectrum was recorded at
$-20^\circ C$. Since only the resonances due to I and $\eta^5_{C_5H_5}W(CO)_3CH_3$ appeared
in the spectrum, the $BF_3$ appears to be coordinated too strongly to I
to be able to function as a catalyst in the reaction of the metal-alkyl
complex with $SO_2$. The S-sulfinate $\eta^5_{C_5H_5}W(CO)_3SO_2CH_3$, which would be
formed if the $BF_3$ from I reacted with $SO_2$ and the metal-alkyl complex,
was not observed in the spectrum.
Another Lewis acid, SbF$_5$, reacts in a similar manner with SO$_2$ solutions of H$_5^\text{W(CO)}_3$CH$_3$ to give red solutions. Although experimental handling of SbF$_5$ is more difficult than that of BF$_3$, the product in this case is much easier to work with. Small red crystals of this adduct (compound II) were fairly easily obtained and recrystallizations were possible. The SbF$_5$ is undoubtedly more strongly bonded in this complex than is BF$_3$ in the analogously prepared I since complex II is more stable than I both in solution and in air. The higher Lewis acidity of SbF$_5$ would be expected to lower the rate of its dissociation from the complex as compared to that of BF$_3$. The composition of II is similar to that of I since an elemental analysis of II is in very good agreement with that expected for a one to one adduct of H$_5^\text{W(CO)}_3$CH$_3$, SO$_2$, and SbF$_5$.

During an attempted recrystallization of I from a benzene solution by the slow addition of pentane, an orange crystalline product (compound III) was obtained. It was different from both I and H$_5^\text{W(CO)}_3$SO$_2$CH$_3$ as indicated by its IR and $^1$H NMR spectra. This substance was prepared by an alternative route in a tensimetric titration of H$_5^\text{W(CO)}_3$SO$_2$CH$_3$ with BF$_3$ in a heterogeneous mixture in toluene at 25°C. The curve shown in Figure 19 is indicative of complex formation. This plot shows a coordination of 0.8 mole of BF$_3$ with each mole of the S-sulfinate. This is interpreted as the formation of a one to one complex; the low value of BF$_3$ uptake is undoubtedly due to the heterogeneous nature of the reaction mixture. This result indicates that compounds I and III are isomers since they both contain the units SO$_2$, BF$_3$, and H$_5^\text{W(CO)}_3$CH$_3$. An elemental analysis of III was not obtained since the exposure of III
THE TENSIMETRIC TITRATION OF $\eta^5$-C$_5$H$_5$W(CO)$_3$S(O)$_2$CH$_3$ WITH BF$_3$

Solvent = Toluene
Temperature = 25 ± 2°C

Mole Ratio of BF$_3$ / $\eta^5$-C$_5$H$_5$W(CO)$_3$S(O)$_2$CH$_3$
to vacuum overnight resulted in the quantitative loss of BF$_3$ and the formation of $\eta^5$C$_5$H$_5$W(CO)$_3$SO$_2$CH$_3$.

The complex I was also converted to $\eta^5$C$_5$H$_5$W(CO)$_3$SO$_2$CH$_3$ by the action of amines. From a reaction of a CH$_2$Cl$_2$ solution of I with aniline the only organometallic product obtained was the S-sulfinate. The boron containing products (presumably a BF$_3$-aniline interaction) could not be characterized owing to the known (56, 57) instability of BF$_3$-aniline reaction products. However, in the reaction of NH$_3$ with a CH$_2$Cl$_2$ solution of I the S-sulfinate was isolated in 85% yield along with the NH$_3$BF$_3$ adduct. The IR spectrum of the NH$_3$BF$_3$ adduct agreed with that of a sample of NH$_3$BF$_3$ prepared by the addition of NH$_3$ to a CH$_2$Cl$_2$ solution of BF$_3$ (58). Also, dissolution of I in coordinating solvents, treatment of CH$_2$Cl$_2$ solutions of I with alumina or Florisil, hydrolysis of I, and grinding of I with KBr all resulted in the formation of the S-sulfinate.

The structures of I, II, and III were assigned on the basis of spectral characteristics of these compounds. All three complexes show one sharp and one broad carbonyl stretching absorption in the region 1950-2100 cm$^{-1}$ of the IR spectra. This indicates that the integrity of the $\eta^5$C$_5$H$_5$W(CO)$_3$ group has been retained. The $^1$H NMR spectra of isomers I and III, together with that of the well-known S-sulfinate and of the starting metal alkyl in liquid sulfur dioxide, are shown in Figure 20. It is clear that the methyl group is not bonded to the metal in either isomer I or III because its proton chemical shifts are too far downfield. They are in a region expected for a methyl group bonded to either a sulfur or an oxygen atom. Thus, from these data alone the bonding site
of the methyl group cannot be determined. The cyclopentadienyl proton chemical shifts are significant in that they show that BF$_3$ has not attacked the ring and that the metal centers in I, III, and the S-sulfinate are similar.

For chemical reasons, it is highly unlikely that the methyl group in I could be bonded to an oxygen atom. There are several established reactions of I leading to the formation of the S-sulfinate (vida supra). They all occur under very mild conditions, and it is improbable that a methyl group could migrate from an oxygen to a sulfur atom under such conditions (for example, CH$_2$Cl$_2$ solution at room temperature over alumina). Since in the S-sulfinate the methyl group is bound to the sulfur atom, it almost certainly must be in I also. In addition, by analogy with all known reactions of sulfur dioxide involving its insertion into metal-carbon bonds, the methyl group should be bound to the sulfur atom in the product I. Similarly for III, which can be prepared from the S-sulfinate, the methyl group is certainly bonded to the sulfur atom.
The addition of BF₃ to \( \eta^5\text{C}_5\text{H}_5\text{W(CO)}_3\text{SO}_2\text{CH}_3 \) would be expected to result in the structure shown in Figure 21 for III. A similar complex

![Structure](image)

**Isomer III**

Figure 21

has been prepared by the addition of BF₃ to \( \eta^5\text{C}_5\text{H}_5\text{Fe(CO)}(\text{PR}_3)_2\text{SO}_2\text{CH}_3 \) \( (R=\text{C}_6\text{H}_5, \text{C}_7\text{H}_9) \) by Ross and Wojcicki (28) and assigned the analogous structure on the basis of IR spectral data. The \(^1\text{H NMR} \) spectrum of III is consistent with this structure; the coordination of a Lewis acid to a sulfinate oxygen would be expected to deshield the methyl group protons, and perhaps also to a lesser extent the cyclopentadienyl group protons, by withdrawing electron density from these atoms.

It is reasonable to propose that the isomer I has one of the structures shown in Figure 22 for several reasons. First, the removal

![Possible structures](image)

**Possible structures of Isomer I**

Figure 22
of BF$_3$ from I by amines resulted in the formation of the S-sulfinate. In the proposed structures, removal of BF$_3$ would result in the formation of an O-bonded sulfinate which would be expected to isomerize to the S-sulfinate rapidly (15). Second, the $^1$H NMR spectra reported (15) for (methanesulfinate)-O complexes of similar metal complexes in liquid SO$_2$ have methyl proton chemical shifts about 0.9 ppm to higher field than the corresponding (methanesulfinate)-S complexes. Isomer I has a chemical shift 0.75 ppm to higher field than $\eta^2$C$_5$H$_5$W(CO)$_3$SO$_2$CH$_3$. This argument suggests that structure A is more likely than structure B (Figure 22) for I, since a strong electrophile bonded at the sulfur would be expected to cause a large downfield shift of the methyl resonance. However, from the $^1$H NMR data alone the structure of I cannot be inferred.

The IR solution spectra of compounds I, II, III, and $\eta^2$C$_5$H$_5$W(CO)$_3$SO$_2$CH$_3$ in the carbonyl stretching region are listed in Table 3. From

**Table 3**

Infrared Spectra of CH$_2$Cl$_2$ Solutions of $\eta^2$C$_5$H$_5$W(CO)$_3$R Complexes

<table>
<thead>
<tr>
<th>Complex #</th>
<th>R</th>
<th>$\nu_{CO}$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>OS(OBF$_3$)CH$_3$</td>
<td>2052s, 1960sBr</td>
</tr>
<tr>
<td>II</td>
<td>OS(0sBF$_3$)CH$_3$</td>
<td>2058s, 1967sBr</td>
</tr>
<tr>
<td>III</td>
<td>-S(O)(OBF$_3$)CH$_3$</td>
<td>2050s, 1964sBr</td>
</tr>
<tr>
<td></td>
<td>-SO$_2$CH$_3$</td>
<td>2046s, 1955sBr</td>
</tr>
</tbody>
</table>

the carbonyl stretching absorptions it can be assumed that the Lewis acid is not bonded to a carbonyl group since this would result in a large decrease in one of the carbonyl absorptions (26, 27, 60). Coordination
of the Lewis acid to the complexes at a site other than a carbonyl
group would be expected to cause a small rise in the stretching fre-
quencies of the carbonyls resulting from reduced π bonding to the metal.

The primary structural information is found in the IR spectra of
these complexes in the region 1300-650 cm\(^{-1}\) which are shown in Figure 23.
In this region are found B-F, Sb-F, and S=O stretching absorptions. The
very strong terminal S=O stretching bands occur at 1250-1000 cm\(^{-1}\) (4b).
Unfortunately in this region B-F absorptions can also occur. By com-
paring the spectra of isomers I and III with similar (Table 4) coordin-
ated BF\(_3\) species the bands at 1140-1100 and 870-840 cm\(^{-1}\) are tentatively
assigned to B-F stretching absorptions. It should be emphasized that
the sulfur-oxygen stretching frequency probably is below about 1140 cm\(^{-1}\)
(28) when the oxygen is bonded to both sulfur and metal or Lewis acid,
a situation which occurs in the possible structures of I and III
(Figure 21, 23).

Typical sulfur-oxygen terminal stretching absorptions for a metal
sulfinate are those in the spectrum of \(\eta^5\)C\(_5\)H\(_5\)W(CO)\(_3\)SO\(_2\)CH\(_3\), which is shown
in Figure 23. The absorptions occur at 1188 and 1054 cm\(^{-1}\) (antisymmetric
and symmetric stretches, respectively) and are characteristic of S-sul-
finite complexes (1, 20). In the spectrum of III there is only one
strong absorption which may be ascribed to a terminal sulfur-oxygen
stretch. It is at 1198 cm\(^{-1}\). In the spectrum of I there is no terminal
sulfur-oxygen stretching absorption apparent. Although in the spectrum
of I the B-F stretching absorption near 1120 cm\(^{-1}\) could mask an S=O
stretching absorption, this is unlikely since in the spectrum of II no
sulfur-oxygen stretches occur above 1000 cm\(^{-1}\). The complex II, prepared
IR Spectra of Tungsten Complexes

Figure 23
Table 4

B-F Stretching Frequencies of Some BF₃ Adducts

<table>
<thead>
<tr>
<th>baseᵃ</th>
<th>B-F asymmetric (cm⁻¹)</th>
<th>B-F symmetric (cm⁻¹)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CpW(CO)₃S(O)(O)CH₃ᵇ</td>
<td>1142-1117</td>
<td>860-820</td>
<td>this work</td>
</tr>
<tr>
<td>(CH₃)₂S</td>
<td>1270-1181</td>
<td>838-833</td>
<td>61</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>1077-1040</td>
<td>887-854</td>
<td>62</td>
</tr>
<tr>
<td>η⁵C₅H₅W(CO)₃OS(O)CH₃ᶜ</td>
<td>1132-1105</td>
<td>870</td>
<td>this work</td>
</tr>
<tr>
<td>(C₂H₅)₂O</td>
<td>1065-1025</td>
<td>900-976</td>
<td>62</td>
</tr>
<tr>
<td>η⁵C₅H₅Fe(CO)(FPh)₃S(O)(O)CH₃</td>
<td>1165-1090</td>
<td>890</td>
<td>28</td>
</tr>
<tr>
<td>PhP</td>
<td>1150-1100</td>
<td>915-888</td>
<td>63</td>
</tr>
<tr>
<td>C₂H₅N</td>
<td>1165-1125</td>
<td>912-893</td>
<td>62</td>
</tr>
<tr>
<td>Fe(CNR)₄(CN)₂</td>
<td>1160-1040</td>
<td>930-900</td>
<td>64</td>
</tr>
<tr>
<td>Cl₃PO</td>
<td>1062-1030</td>
<td>955-936</td>
<td>62</td>
</tr>
</tbody>
</table>

ᵃunderlined atom(s) indicate site(s) of BF₃ coordination;
ᵇisomer III
ᶜisomer I
in a manner strictly analogous to I, most probably has a structure similar to that of I. The structures shown in Figure 23 for the compounds I, II, and III are the only structures which are consistent with the data presented here. The reactions of $\eta^5C_5H_5W(CO)_3CH_3$ and related complexes are summarized in Figure 24.

It was of interest to obtain a quantitative estimate of how much the use of BF$_3$ increased the rate of cleavage of the metal-carbon bond in $\eta^5C_5H_5W(CO)_3CH_3$. A solution of the tungsten alkyl was sealed in an NMR tube which was maintained at -15°C for 27 days. After this reaction period there was no decomposition, and a 16% yield of the S-sulfinate was observed. In a similar experiment at room temperature the reaction was 10% complete in six days, and complete conversion of the alkyl to the S-sulfinate had occurred by the end of two months with little decomposition. The reaction in the presence of an equimolar quantity of BF$_3$ at -26°C is complete in less than 40 minutes.
Thus, the use of a Lewis acid was shown greatly to increase the rate of reaction of sulfur dioxide with a \( \eta^5C_5H_5W(CO)_3 \)-alkyl complex. To demonstrate the generality of this reaction and to test whether the presence of a phenyl group would affect the course of the reaction, an investigation of the reactions of the sulfur dioxide-boron(III) fluoride adduct with \( \eta^5C_5H_5W(CO)_3CH_2C_6H_5 \) was undertaken.

Yellow solutions of \( \eta^5C_5H_5W(CO)_3CH_2C_6H_5 \) in sulfur dioxide rapidly turn red at \(-20^\circ C\) in the presence of an equimolar quantity of boron(III) fluoride. It was observed by \(^1\)H NMR spectroscopy that the reaction occurs at a much slower rate at \(-45^\circ C\). At that temperature the tungsten alkyl is consumed within two hours to give the single product V. Upon solvent removal V was recovered as a red oil which could not be induced to crystallize.

Carbonyl stretching absorptions of V, appearing at 2056s and 1970sBr cm\(^{-1}\), are similar to those found for the \( \eta^5C_5H_5W(CO)_3CH_3 : BF_3 : SO_2 \) insertion product I. This indicates that the \( \eta^5C_5H_5W(CO)_3 \) unit is intact in V and that BF\(_3\) is not coordinated to one of the carbonyl oxygens. The neat IR spectrum of V in the S=0 stretching region is also similar to that of I, with the B-F stretches dominating the spectrum with their absorptions at 1130 and 850 cm\(^{-1}\). There is not an S=0 terminal stretching absorption in the spectrum unless it is buried under the 1130 cm\(^{-1}\) B-F absorption.

The \(^1\)H NMR spectrum of V contains a complex resonance at 2.8 \( \tau \) due to the phenyl protons, a singlet at 4.16 \( \tau \) resulting from the cyclopentadienyl protons, and an AB quartet centered at 6.13 \( \tau \). The quartet in the spectrum results from magnetically non-equivalent methylene
protons in V. A chiral center in a molecule is necessary in order to have magnetically nonequivalent methylene protons. This requirement is met in a structure analogous to I, the $\text{BF}_3\cdot\text{SO}_2$ insertion product of $\eta^5\text{C}_5\text{H}_5\text{W}((\text{CO})_3\text{CH}_3$. It is also met in the S-sulfinate-$\text{BF}_3$ adduct type structure analogous to III. A structure involving a sulfur-boron bond

![Possible Structures of V](image)

as in Figure 25 is a third configuration with a chiral sulfur atom.

The product V was shown to have the structure similar to that of I (Figure 25) when the $\text{BF}_3$ adduct of $\eta^5\text{C}_5\text{H}_5\text{W}((\text{CO})_3\text{SO}_2\text{CH}_2\text{C}_6\text{H}_5$ (VII) was prepared. The addition of a slightly less than twofold excess of $\text{BF}_3$ to an $\text{SO}_2$ solution of $\eta^5\text{C}_5\text{H}_5\text{W}((\text{CO})_3\text{SO}_2\text{CH}_2\text{C}_6\text{H}_5$ at $-40^\circ\text{C}$ resulted in the disappearance of the resonances associated with the S-sulfinate and the appearance of three new resonances. The spectrum of VII contained a complex multiplet at $2.54\ \tau$ of the phenyl protons, and two singlets at $3.93$ and $4.89\ \tau$ resulting from the cyclopentadienyl and methylene protons, respectively. The structure of VII probably is analogous to that of III (Figure 25), since the preparations of III and VII were similar. It is interesting that the methylene proton resonance of VII in its NMR spectrum is not an AB quartet. Although the sulfur atom is chiral in
structure III (Figure 25), the chemical shift difference of the methylene protons is apparently too small, as compared to the coupling constant between the two protons, for a Varian A60 spectrometer to resolve the multiplet. Evidently the coordination of BF$_3$ to an S-sulfinate oxygen does not alter the chemical environment of one of the methylene protons much more than the other. A rapid intra- or inter-molecular exchange of BF$_3$ would also result in equivalent methylene protons.

The Lewis acid SbF$_5$ was also shown to enhance the reactivity of sulfur dioxide. The insertion product $\eta^5$C$_5$H$_5$W(CO)$_3[OS(CSbF_5)CH_3]$ (II) was mentioned previously. It was prepared by the action of SbF$_5$ on a sulfur dioxide solution of $\eta^5$C$_5$H$_5$W(CO)$_3CH_3$ and is strictly analogous to the BF$_3$:SO$_2$ insertion product I.

The corresponding red benzyl complex (VI) was prepared in a reaction of an SO$_2$ solution of $\eta^5$C$_5$H$_5$W(CO)$_3CH_2CH_3$ with SbF$_5$:SO$_2$. The infrared spectra of II and VI closely resemble each other, with a strong carbonyl stretching absorption near 2060 cm$^{-1}$, a strong, broad carbonyl absorption near 1970 cm$^{-1}$, and Sb-F stretching absorptions at 660 cm$^{-1}$. There were also absorptions of moderate intensity for both complexes at 990 and 890 cm$^{-1}$. In the spectra of these complexes there were no S=O terminal stretching absorptions. In the $^1$H NMR spectrum of VI in CDCl$_3$, resonances of the methylene protons appear as an AB quartet. The above data suggest that the structures of II and VI are as shown in Figure 26.

The synthesis of the two complexes IV and VIII in Figure 27 provided further evidence that the above structures for II and VI are correct. In a reaction of SbF$_5$ with the corresponding S-sulfinate in SO$_2$, the simple Lewis acid adducts were prepared quantitatively as was
observed in the $^1$H NMR spectra of the reaction solutions. The chemical shifts of the protons in IV and VIII, along with those of other tungsten complexes prepared in this study appear in Table 5.

From the $^1$H NMR spectra in SO$_2$ three generalizations can be made. The most obvious is that in species containing a metal-oxygen linkage, invariably the resonances of the protons α to the sulfur atom occur at a higher field than those of similar complexes containing a metal-sulfur linkage. The reason for this effect is not clear but could perhaps involve the metal to sulfur π bonding, anisotropic effects of the S=O double bonds, or the nonbonding electron pair on sulfur. The structures of the O- and S-bonded sulfinates containing a benzyl group are
<table>
<thead>
<tr>
<th>Complex #</th>
<th>R</th>
<th>Chemical Shifts in ′ Units</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>CH₃</td>
<td></td>
<td>2.87</td>
</tr>
<tr>
<td>CH₂C₆H₅</td>
<td></td>
<td>2.60</td>
</tr>
<tr>
<td>SO₂CH₃</td>
<td></td>
<td>2.60</td>
</tr>
<tr>
<td>SO₂CH₂C₆H₅</td>
<td></td>
<td>2.54</td>
</tr>
<tr>
<td>I</td>
<td>OS(OBF₃)CH₃</td>
<td>3.98</td>
</tr>
<tr>
<td>II</td>
<td>OS(OSbF₅)CH₃</td>
<td>3.96 (4.03)&lt;sup&gt;f&lt;/sup&gt;</td>
</tr>
<tr>
<td>V</td>
<td>OS(OBF₃)CH₂C₆H₅</td>
<td>2.60</td>
</tr>
<tr>
<td>VI</td>
<td>OS(OSbF₅)CH₂C₆H₅&lt;sup&gt;d&lt;/sup&gt;</td>
<td>2.60</td>
</tr>
<tr>
<td>III</td>
<td>S(0)(OBF₃)CH₃</td>
<td>3.84</td>
</tr>
<tr>
<td>IV</td>
<td>S(0)(OSbF₅)CH₃</td>
<td>3.95</td>
</tr>
<tr>
<td>VII</td>
<td>S(0)(OBF₃)CH₂C₆H₅</td>
<td>2.54</td>
</tr>
<tr>
<td>VIII</td>
<td>S(0)(OSbF₅)CH₂C₆H₅</td>
<td>2.53</td>
</tr>
</tbody>
</table>

<sup>a</sup>complex multiplet, prominent peak listed; <sup>b</sup>singlet; <sup>c</sup>AB quartet; <sup>d</sup>CDC₁₃ solution; <sup>e</sup>center two peaks of AB quartet; <sup>f</sup>initial product of reactions in liquid SO₂
distinguished in these examples by the nature of their methylene proton resonances. When the sulfinate group is O-bonded to the metal, and thus has a nonbonded pair of electrons on the sulfur atom, the chirality of the sulfur atom is observed in the $^1H$ NMR spectrum of the methylene protons in the complex. When the sulfinate is S-bonded, the methylene proton resonance appears as a singlet in the NMR spectrum. The coordination of a Lewis acid to an oxygen evidently does not significantly differentiate the chemical shifts of the two methylene protons. Another observation is that in $SO_2$ solution the $SbF_5$ adducts always have $\alpha$-proton chemical shifts at higher field than the corresponding $BF_3$ adduct even though $SbF_5$ is a stronger Lewis acid.

All of the boron(III) fluoride adducts in Table 5 are the initial products of reaction of the metal alkyls or metal sulfinates with $BF_3$ in $SO_2$ solution. This was observed in the $^1H$ NMR spectra of the reaction solutions. The initial products of the same metal complexes with the stronger Lewis acid $SbF_5$ were also examined by $^1H$ NMR spectroscopy with somewhat different results as described below.

In order to study the reaction of $SbF_5$ it was desirable to be able to control the quantity of the Lewis acid present in a reaction mixture. Antimony(V) fluoride is a difficult substance to handle. It is very rapidly hydrolyzed in moist air which results in HF formation. Since protic acids tend to cleave metal-alkyl bonds, the formation of HF must be avoided. Also, the $SO_2:SbF_5$ adduct is too reactive to allow mass determinations in the dry box. When this was attempted the adduct fumed in the dry box atmosphere. Owing to the low vapor pressure of $SbF_5$ at room temperature, it is difficult to measure quantities of the acid
by normal pressure, temperature, and volume measurements on a vacuum line. Manipulations of this reagent on a vacuum line are also hampered by its high reactivity with mercury. It was found that SbF$_5$ could be handled very easily when it was intercalated into the graphite lattice. A black, free-flowing powder of graphite containing 65% by weight SbF$_5$ was prepared in the manner outlined by LaLancette in a patent. Heating a mixture of 2.7 g of purified graphite with 5.0 g of SbF$_5$ in a sealed flask under vacuum at 110°C for 17 hours, produced a free-flowing, lustrous black powder which did not fume in moist air. In the absence of solvents, this intercalation product does not discolor the yellow $\eta^5$C$_5$H$_5$W(CO)$_3$-alkyl complexes over a period of two days when they are mixed together and stored under vacuum.

Mixtures of a slight excess of SbF$_5$ intercalated in graphite and the $\eta^5$C$_5$H$_5$W(CO)$_3$ alkyls and S-sulfinates were prepared in the dry box. The reaction vessels were removed from the dry box and, after evacuating the mixtures on the vacuum line, sulfur dioxide was added as solvent. Reactions were allowed to proceed at -45°C for seven hours, after which the solutions were filtered at low temperature into $^1$H NMR tubes. The spectra of the resulting solutions were obtained.

In these reactions the S-sulfinates were completely consumed with the formation of a single yellow-brown product in each case. The structures of these products are given in Table 5 as IV and VIII for the addition products of the methane- and benzenesulfinato-S reactants, respectively. The structure assignments are based on the $^1$H NMR spectra and by analogy with the BF$_3$ addition products of sulfinates.
The reactions of the tungsten-alkyl complexes were different in
that only incomplete consumption of the starting alkyl occurred and
the expected insertion products were not observed in the \(^1\)H NMR spectra
of the deep red \(\text{SO}_2\) reaction solutions. In the reaction of \(\eta^5\text{C}_5\text{H}_5\text{W}(\text{CO})_3\text{-CH}_3\) with \(\text{SbF}_5\text{-SO}_2\), only one product cyclopentadienyl resonance at 4.03 \(\tau\)
of relative intensity 5 was observed. In addition, there was a resonance
at 7.85 \(\tau\) with a relative intensity of 1. There were several product
cyclopentadienyl resonances resulting from the reaction of \(\eta^5\text{C}_5\text{H}_5\text{W}(\text{CO})_3\text{-CH}_2\text{C}_6\text{H}_5\) with \(\text{SbF}_5\text{-SO}_2\), but only one major resonance. It appeared at
4.28 \(\tau\) with a relative intensity of 5. The phenyl proton resonance region
of the spectrum was complex and there were only two possible methylene
proton resonances at 6.47 and 7.66 \(\tau\) of relative intensities 0.9 and
1.7, respectively.

The reasons for this difference in behavior between \(\text{BF}_3\text{-SO}_2\) and
\(\text{SbF}_5\text{-SO}_2\) insertion reactions are not clear but are probably related to
the higher Lewis acidity of \(\text{SbF}_5\) as compared to \(\text{BF}_3\). It is possible
that the tight ion pair proposed by Wojcicki (4b) as a transient
intermediate in \(\text{SO}_2\) insertion reactions is stabilized by \(\text{SbF}_5\) in \(\text{SO}_2\)
solution to the extent that it does not collapse to the \(\text{O}\)- or \(\text{S}\)-bonded
sulfinate type structure. The removal of the \(\text{SO}_2\) solvent could effect
the collapse of the ion pair since \(\text{SO}_2\) is a good anion solvating agent
(65). If this is the case a tight ion pair must still be invoked to
explain the difference in cyclopentadienyl resonances between the methyl
and benzyl derivatives. The abnormally high shielding of the methyl-
and methylene protons may indicate the presence of a negative charge near
those groups. Since the \(\text{SbF}_5\text{-SO}_2\) insertion products of both \(\eta^5\text{C}_5\text{H}_5\text{W}(\text{CO})_3\text{-CH}_3\)
and \(-\text{CH}_2\text{C}_6\text{H}_5\) have been isolated, it is likely that the substances responsible for the resonances observed in the spectrum of the \(\text{SO}_2\) reaction solutions are intermediates of the insertion reaction. The appearance of two methylene resonances in the reaction of the benzyl complex may indicate that two competing reactions occur. This is supported by the fact that a large amount of brown unidentifiable material results from the reaction of \(\text{SbF}_5\cdot\text{SO}_2\) with \(\eta^5\text{C}_5\text{H}_5\text{W(CO)}_3\text{CH}_2\text{C}_6\text{H}_5\) when the products are isolated (see experimental section). A reaction of the Lewis acid or its \(\text{SO}_2\) adduct at the phenyl ring is possible and may account for one of the methylene resonances.

In summary, the Lewis acid promoted \(\text{SO}_2\) insertion reaction is viewed as proceeding analogously to the "normal" \(\text{SO}_2\) insertion mechanism except that the O-bonded sulfinic species is stabilized by the coordinated Lewis acid (eq. 20). The stabilization of the O-bonded sulfinates by

\[
\begin{align*}
M - \text{C} \rightleftharpoons \text{R} & + \text{OSOA} \rightarrow M \rightleftharpoons \text{C} \rightleftharpoons \text{OSO} \\
\text{R} & \rightleftharpoons \text{R}' \rightleftharpoons \text{R}'' \\
\text{M} - \text{O} \rightleftharpoons \text{S} - \text{CRR'}\text{R}'' & \leftarrow \left[ \text{H}^+ \right] \left[ \text{RR'}\text{R''OSOA} \right]^{-}\text{tight ion pair}
\end{align*}
\]

\(A=\text{Lewis acid}\)

Lewis acids also satisfactorily accounts for the failure of several workers (15) to isolate O-bonded isomers of \(\text{SO}_2\) insertion reactions.
For example, when $\eta^5\text{C}_5\text{H}_5\text{Fe(CO)}_2\text{CH}_3$ is dissolved in SO$_2$, only the O-sulfinate is initially present. Removal of the solvent SO$_2$, which is also a Lewis acid, results in the isolation of only the S-isomer. The SO$_2$ undoubtedly acts as a Lewis acid to stabilize the O-sulfinate in SO$_2$ solutions. When it is removed by evaporation, the stable S-isomer is formed.

If the O-bonded sulfinate $\eta^5\text{C}_5\text{H}_5\text{Fe(CO)}_2[\text{OS(O)}\text{CH}_3]$ were stabilized by the Lewis acid SO$_2$, it seems reasonable that it could also be stabilized by BF$_3$. From a solution of the O-sulfinate in liquid SO$_2$ which was treated with an equimolar quantity of BF$_3$, a red powder was isolated. The expected structure of this compound was that of a BF$_3$ stabilized O-bonded sulfinate. The IR spectrum of this material in the region 1300 to 800 cm$^{-1}$ when compared to the similar spectrum of I (Figure 28) suggests that the two compounds do have similar structures. The stability of the iron containing product apparently was lower than that of the corresponding tungsten complex since all attempts at purification by recrystallization resulted only in impure oils. A reduced stability was also reflected in a melting point with decomposition at 73°C for the iron product as compared to 97-99°C for I.

The reaction of $\eta^5\text{C}_5\text{H}_5\text{Fe(CO)}_2\text{CH}_3$ with SO$_2$·BF$_3$ in liquid SO$_2$ was later shown to be complex when a low temperature $^1$H NMR spectral examination of the reaction solution demonstrated that at least two types of methyl groups were present in approximately equal amounts. This behavior is similar to that observed for reactions of SbF$_5$·SO$_2$ with $\eta^5\text{C}_5\text{H}_5\text{W(CO)}_3\text{CH}_3$ when the low temperature $^1$H NMR spectra of the SO$_2$ reaction solutions were obtained. Because of the low stability of the
products and the apparent complexity of the reaction, it was not further studied.
IR Spectra of Complexes with a \(-\text{OS(OBF}_3\text{)}\text{CH}_3\) Ligand

A) $\eta^2\text{C}_5\text{H}_5\text{W(CO)}_3\text{OS(OBF}_3\text{)}\text{CH}_3$

B) $\eta^2\text{C}_5\text{H}_5\text{Fe(CO)}_2\text{OS(OBF}_3\text{)}\text{CH}_3$

Figure 28
Chapter IV

RESULTS AND DISCUSSION

Intramolecular Enhancement of the Rate of Insertion Reactions by the Selection of Substituent Groups

A. Reactions of Alkyl- and Aryl-N-Sulfinylamines with Transition Metal-Alkyl Complexes.

The N-sulfinylamines were thought to be rather unreactive toward insertion reactions on the basis of preliminary experiments by Robinson (66). Robinson indicated that all attempts to prepare insertion products of C$_6$H$_5$NSO with $\eta^5$C$_5$H$_5$Fe(CO)(PPh$_3$)$_3$CH$_3$ resulted in formation of the S-sulfinate, probably via an SO$_2$ insertion reaction. Sulfur dioxide could originate in a reaction of moisture with the sulfinylamine or in a base (PPh$_3$) catalysed disproportionation of the sulfinylamine to give SO$_2$ and diphenylsulfur diimide. No reactions of sulfur diimides with transition metal alkyls had been reported prior to this study.

The reactivities of N-sulfinylaniline (C$_6$H$_5$NSO) and cyclohexyl-N-sulfinylamine with $\eta^5$C$_5$H$_5$W(CO)$_2$CH$_3$ and $\eta^5$C$_5$H$_5$Fe(CO)$_2$CH$_3$ were examined in this study. All reactions were carried out with strict exclusion of moisture to prevent the formation of sulfur dioxide. In most cases the reactants were mixed and allowed to react, either neat or in C$_6$D$_6$ or C$_6$H$_6$ solutions, under static vacuum. In reaction times varying from one hour
to seven days at room temperature, there was no conclusive evidence that
the starting metal alkyls had participated in a reaction. Observations
were largely made by $^1$H NMR spectroscopic techniques on solutions
sealed in NMR tubes. The N-sulfinylamines partly decomposed at the
longer reaction times.

A sample of $\eta^5C_5H_5Fe(CO)_2CH_3$ was allowed to react in neat $C_6H_5NSO$
at $80^\circ$C for an hour. An examination of the carbonyl stretching region
of the IR spectrum of the reaction mixture indicated that the starting
metal-alkyl complex was the principal organometallic species present.
In addition to the two very strong absorptions at 1990 and 1930 cm$^{-1}$
resulting from the carbonyl stretches of the starting material, there
were two weak absorptions at 2050 and 2000 cm$^{-1}$. The frequencies of
these new absorptions are similar to those for the S-sulfinate ($\nu CO,$
$CHCl_3$ solution of $\eta^5C_5H_5Fe(CO)_2SO_2CH_3$, 2063, 2053, 2015, 2009, vs, cm$^{-1}$; Ref. 1) and thus may correspond to an insertion type of product. This
material could not be isolated or further characterized.

B. Lewis Acid Promoted Reactions of N-Sulfinylamines with Transition
Metal Alkyls.

The alkyl and aryl N-sulfinylamines show a considerably reduced
reactivity with transition metal-alkyl complexes compared to sulfur
dioxide. Presumably a Lewis acid coordinated to an N-sulfinylamine
would promote its reactivity in an electrophilic insertion-type reaction
in a manner analogous to that found for Lewis acid promoted reactions
of SO$_2$. Boron(III) fluoride etherate has been shown to promote the
reaction of N-sulfinylaniline (67) in a Diels-Alder type reaction as is
shown in equation (21). In the absence of the BF$_3$ etherate, only a red

\[
\begin{array}{c}
\text{C}_6\text{H}_5 + \text{C}_6\text{H}_5\text{N}=\text{SO} \xrightarrow{\text{BF}_3\text{C}(\text{C}_2\text{H}_5)_2} \text{C}_6\text{H}_6 \\
\text{C}_6\text{H}_5 \xrightarrow{\text{C}_6\text{H}_6} \\
\text{C}_6\text{H}_5 \xrightarrow{\text{SO}_2} \text{C}_6\text{H}_5
\end{array}
\]

charge transfer complex was formed. However, the presence of the Lewis acid in a refluxing benzene solution of the reactants resulted in a good yield of the product 1,2,3-triphenylisoindole. Only this product was observed; the intermediates shown in equation (21) were proposed as a likely reaction pathway. The interaction of N-sulfinylamines with Lewis acids has not been extensively studied. Methyl-N-sulfinylamine is known to form a 1:1 adduct with BF$_3$ which is completely dissociated in the vapor phase at 50°C and has a dissociation pressure of 7 Torr at 15.4°C (68). An investigation of the reactivity of other N-sulfinylamines with BF$_3$ was undertaken.

In a series of tensimetric titrations of representative sulfinylamine compounds with BF$_3$, differences in base strength relative to this
Lewis acid were found. Cyclohexyl-N-sulfinylamine was shown to form a weak one to one adduct with BF\(_3\) at 1\(^\circ\)C in toluene. N-Sulfinylaniline did not form a complex with BF\(_3\) at 7\(^\circ\)C in benzene solution, as was also the case with p-toluene-N-sulfinylsulfonamide (p-CH\(_2\)C\(_6\)H\(_4\)SO\(_2\)NSO) at -23\(^\circ\)C in toluene. Since cyclohexyl-N-sulfinylamine did form a reasonably stable complex at 1\(^\circ\)C, the reactivity of BF\(_3\):C\(_6\)H\(_{11}\)NSO with \(\eta^5\)C\(_5\)H\(_5\)Fe-(CO)\(_2\)CH\(_3\) and \(\eta^5\)C\(_5\)H\(_5\)W(CO)\(_3\)CH\(_3\) was examined.

It was shown in an experiment carried out in an NMR tube that the BF\(_3\) adduct of C\(_6\)H\(_{11}\)NSO did react at least partly with \(\eta^5\)C\(_5\)H\(_5\)W(CO)\(_3\)CH\(_3\) in C\(_6\)D\(_6\) at ambient temperatures. A large amount of material precipitated from solution and was centrifuged to the top of the tube. In the NMR spectrum of the solution, the principal resonances present corresponded to the starting tungsten-alkyl complex. In addition, however, there were two new very low intensity signals at 5.39 \(\tau\) and 7.00 \(\tau\), which could have corresponded to an insertion product. From this reaction no compounds were isolated. Since there was only partial consumption of the starting tungsten-alkyl complex, the more reactive \(\eta^5\)C\(_5\)H\(_5\)Fe(CO)\(_2\)CH\(_3\) was studied.

A solution of \(\eta^5\)C\(_5\)H\(_5\)Fe(CO)\(_2\)CH\(_3\) and a threefold excess of C\(_6\)H\(_{11}\)NSO in toluene at -28\(^\circ\)C was treated with an equimolar (relative to the iron complex) quantity of BF\(_3\). Poorly formed, crystalline-appearing material precipitated from solution, but warming the reaction mixture to room temperature caused the precipitate to change into an oil. From this oil both the starting iron-alkyl complex and a product complex were isolated as oils. The product showed two carbonyl absorptions at 2060 and 2015 cm\(^{-1}\) in its IR spectrum. These frequencies are roughly what would
be expected of an insertion product. Satisfactory $^1$H NMR and neat IR spectra could not be obtained from this sample, and all attempts to isolate and characterize the substance were futile owing to the reactivity of the coordinated BF$_3$.

Thus, alkyl- and aryl-N-sulfinylamines showed very little, if any, reactivity toward metal-alkyl complexes. The reactivity of the alkyl-N-sulfinylamine used in this study was greatly increased by the use of a Lewis acid, but the reactions were not clean and the products were difficult to isolate or characterize.

C. Intramolecular Promotion of Electrophilic Character of N-Sulfinylamines.

N-Sulfinylamines as a class of compounds are more versatile than SO$_2$ in that they are available in a wide variety of reactivities. The nature of R in RNSO determines the reactivity of the N-sulfinylamines. In this study it was shown that the use of a Lewis acid with C$_6$H$_{11}$NSO increased its reactivity. The Lewis acid was presumably coordinated to the nitrogen in C$_6$H$_{11}$NSO. A similar complex has been reported (68) for the addition of BF$_3$ to CH$_3$NSO and a nitrogen-boron linkage was inferred by comparison with other BF$_3$ complexes. The same effect of enhanced reactivity should result from an increase in the electron-withdrawing ability of the R group in RNSO. In addition, since the coordination of a Lewis acid to a complex often leads to experimental difficulties in purification and handling of products, serious experimental problems would be avoided if the insertion reaction was promoted by a more electrophilic R group. This reasoning led to the examination of the reactivity of N-sulfinylsulfonamides with metal-alkyl complexes.
D. New Reactions of N-Sulfinylsulfonamides with \( \eta^5 C_5 H_5 Fe(CO)_2 \) -alkyl Complexes.

The reactions of the N-sulfinylsulfonamides \( p-CH_3 C_6 H_4 SO_2 NSO \) and \( CH_3 SO_2 NSO \) with \( \eta^5 C_5 H_5 Fe(CO)_2 R \) \( (R=CH_3, CH_2 C_6 H_5, CH_2 CH_2 C_6 H_5) \) were examined. Solutions of equimolar quantities of the metal complexes and the electrophiles in solvents such as toluene or \( CHCl_3 \) reacted very quickly to give red solutions of a one to one adduct. In several cases the compositions of these products were verified by elemental analysis, but their \(^1 H \) NMR spectra also established a one to one adduct nature for these products, assuming that no fragmentation of the reactants occurred during the reaction.

The carbonyl stretching region of the IR spectra and the \( \eta^5 C_5 H_5 \) proton resonance region of NMR spectra suggested that the products contain the \( \eta^5 C_5 H_5 Fe(CO)_2 \) group. The carbonyl stretching frequencies are indicative of a non-alkyl species, since they appear at about 2000 and 2050 cm\(^{-1}\). The stretching absorptions for the alkyl complexes are about 1950 and 2000 cm\(^{-1}\). If the products are one to one adducts no longer containing a metal-alkyl bond, an insertion reaction has occurred.

There are several possible structures for a one to one insertion product in reactions of this type. The most reasonable structures are shown in Figure 29. The ligand can be only monodentate; if the metal center of the products is \( \eta^5 C_5 H_5 Fe(CO)_2 \), as suggested by the \(^1 H \) NMR spectra and the carbonyl stretching region of the IR spectra, it can accommodate only one electron pair without exceeding the 18 electron configuration associated with stable, low-valent, transition metal complexes. Of these structures, all except the first two can be
discounted relatively easily. In the sulfur oxygen stretching region (1350-1000 cm\(^{-1}\)) of the IR spectra, three strong absorptions appear for the products which could be ascribed to three terminal sulfur-oxygen bonds. For example, in the reaction of \(\eta^5\)C,H,Fe(CO),CH, with CH,SO,NSO or p-CH,C,H,SO,SO the products have bands near 1300, 1140, and 1080 cm\(^{-1}\). These compare favorably with those found by Kresze et al for products of additions of dienes and N-sulfinylsulfonamides. In the heterocyclic products (Figure 30), the sulfonyl functional group stretching absorptions occur at about 1350 and 1165 cm\(^{-1}\) and the sulfinyl functional group
absorptions occur near 1080 cm\(^{-1}\) (53). This implies that none of the oxygens in the product are involved in a metal-O-S linkage. It is possible, but unlikely, that this reaction is drastically different than both the SO\(_2\) insertion reaction and the reaction of organolithium or Grignard reagents with SO\(_2\) and RNSO compounds. In both reaction types the alkyl group derived from the metal is bound to the sulfur atom in the product. Also, if the alkyl were bound to an oxygen, one of the S=O stretching bands in the IR spectrum should be shifted to a lower frequency. Thus, the likely structures are A and B (Figure 29) which cannot be readily distinguished on the basis of IR, \(^1\)H NMR, or \(^{13}\)C NMR spectral evidence.

In the reaction of \(\gamma^{5}\)\(\delta^{5}\)Fe(CO)\(_2\)CH\(_3\) with CH\(_3\)SO\(_2\)NSO there is a unique opportunity easily to determine the structure of the insertion product (IXa). If IXa is the N-bonded isomer (A, Figure 29), and if the sulfur atom of the N-bonded isomer could be oxidized, a symmetrical bis(methylsulfonyl)amido ligand would be formed as is shown in Figure 31. The \(^1\)H NMR spectrum of this complex would show two singlets in 5:6 ratio for the cyclopentadienyl and equivalent methyl groups, respectively. In the case of the S-bonded (B, Figure 29) isomer, it is unlikely that
the ligand could be oxidized without its destruction. If it were oxidized, a symmetrical ligand containing two methyl groups would not be formed. A problem arises in that the insertion product could isomerize in the presence of an oxidizing agent. It is believed that the likely direction of isomerization would be from N-bonded to S-bonded since the "soft" sulfur center should form a thermodynamically more stable bond with the "soft" iron center than the nitrogen would. A similar effect was noted (vide supra) in the isomerization of transition-metal O-sulfinites to S-sulfinites. An isomerization in the opposite direction has been observed, however, in the formation of $\eta^5\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{NCS}$ in the solid state at 40°C from $\eta^5\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{SCN}$ (69). This problem is discussed more fully in a later section of this thesis.

In the reaction sequence shown in equation (22) the insertion

$$\eta^5\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CH}_3 + \text{CH}_3\text{SO}_2\text{NSO} \rightarrow \eta^5\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2-(\text{CH}_3\text{SO}_2\text{NSO})\text{-CH}_3$$

$$\text{IXa}$$

$$\text{CH}_2\text{Cl}_2$$

$$\text{IX} + \text{m-ClC}_6\text{H}_4\text{CO}_2\text{H} \rightarrow \eta^5\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{N(SO}_2\text{CH}_3)_2$$

$$\text{Xa}$$
product (IXa) of the reaction of $^5\eta^5C_5H_5Fe(CO)\_2CH\_3$ with CH$_3$SO$_2$NSO was oxidized. The oxidizing agent was m-chloroperoxybenzoic acid, which has been shown to be a mild agent for the oxidation of sulfur compounds (70). The product of this oxidation, Xa, was isolated as a red crystalline material in good yield. The structure of X was determined to be that of a disulfonamidato complex on the basis of its elemental analysis and its IR, $^1$H NMR, and $^{13}$C NMR spectral characteristics. The full characterization of this and similar complexes is related in a later section of this thesis. The oxidation of IXa not only shows that it does not have structure B (Figure 29), but also convincingly rules out all structures with an N-alkyl or O-alkyl bond (C,E, Figure 29) by demonstrating that the alkyl group derived from the starting metal-alkyl complex is in fact bonded to a sulfur atom in IXa and Xa.

In the reaction of a concentrated solution of $^5\eta^5C_5H_5Fe(CO)\_2CH\_2C\_6H\_5$ with CH$_3$SO$_2$NSO there were two initial products, F and G. Attempts to separate and isolate these two products by chromatography resulted in little separation and the formation of a third species, H. By a series of low temperature crystallizations, one of the initial products F, and an orange material, which was the third species, H, were isolated. In a later experiment in the reaction of dilute CHCl$_3$ solutions of $^5\eta^5C_5H_5Fe(CO)\_2CH\_2C\_6H\_5$ and CH$_3$SO$_2$NSO only one product was observed. It was the other initial product, G, observed in the earlier reaction.

By analogy with the reaction of $^5\eta^5C_5H_5Fe(CO)\_2CH\_3$ with CH$_3$SO$_2$NSO, G should have been the N-bonded insertion product. The IR and NMR spectra of G were in agreement with this assignment as will be discussed later, and in addition, the product was easily oxidized by m-ClC$_6$H$_4$CO$_2$H to
give a red-orange solid, I. In G, an AB quartet was observed for the methylene proton resonance in the $^1$H NMR spectrum, indicative of a chiral center, as expected for an N-bonded insertion product, whereas in I the methylene protons gave a singlet suggesting the lack of a chiral center as found in a dialkanesulfonamidato ligand. The structures of G and I are shown in Figure 32.

![Chemical structures](https://example.com/structures.png)

Figure 32

The product H, which formed during purification steps and was obtained in a crystalline form is an isomerization product of G. On the basis of IR, $^1$H NMR, and $^{13}$C NMR spectral evidence the structure of H is thought to be that of the S-sulfinimido complex shown in Figure 32.
The characterization of this complex is discussed later.

The product F of the insertion reaction of a concentrated solution of \( \eta^5\text{C}_5\text{H}_5\text{Fe(CO)}_2\text{CH}_2\text{C}_6\text{H}_5 \) and CH$_3$SO$_2$NSO was later prepared directly by the reaction of \( \eta^5\text{C}_5\text{H}_5\text{Fe(CO)}_2\text{CH}_2\text{C}_6\text{H}_5 \) with the sulfur diimide (CH$_3$SO$_2$N)$_2$S. The characterization of this complex on the basis of IR, $^1$H NMR, $^{13}$C NMR, and analytical data will be discussed later. The data suggest that F is the N-bonded insertion product shown in Figure 32.

The four structures shown in Figure 32 are representative of four new types of complexes prepared in this study. Their preparations and characterizations are discussed in the next four sections of this thesis.

E. Preparation and Characterization of N-(Alkylsulfinyl)alkanesulfonamidato-N Complexes (IX).

Complexes of the general structure shown in Figure 33 were best prepared in the following manner. A 1.5-mmole sample of \( \eta^5\text{C}_5\text{H}_5\text{Fe(CO)}_2 \)alkyl complex was dissolved in 10 ml of a solvent such as toluene or CHCl$_3$. A slight excess of the N-sulfinylsulfonamide dissolved in 20 ml
of the solvent was added dropwise under an inert atmosphere to the
stirred solution of the iron-alkyl complex. The reaction was complete
within an hour. The use of at least this much solvent was desirable
since it reduced the formation of the diimide from the sulfinylsulfon-
amide. The solvent was removed on a rotary evaporator and the residue
was treated with 5 ml of 10% H₂O in acetone to destroy excess N-sulfinyl-
sulfonamide. The solvent was again removed and the residue was dissolved
in CHCl₃. The solution was dried over MgSO₄ and the drying agent was
filtered off to give a red-orange solution of the N-bonded insertion
product. Some of the derivatives were very difficult to crystallize,
but could be obtained as pure glasses on solvent removal. Satisfactory
elemental analysis for one to one insertion products were obtained for
two of the new complexes.

These complexes are susceptible to oxidation by m-ClC₆H₄CO₂H
although they are relatively stable both in the solid state and in
solutions to exposures of at least several minutes to air. The complexes
can also be recovered unchanged from aqueous solutions. The fact that
they are oxidizable to a bis(alkylsulfonyl)amido type of species was of
great importance in the definite determination of their structure. In
the reaction shown in equation (23) the formation of a symmetrical ligand
by oxidation was ascertained by the appearance of equivalent methyl
groups in both the ¹H- and ¹³C NMR spectra of Xa. This indicated
several things about the structure of these insertion products. First,
the alkyl group derived from the metal is certainly bonded to a sulfur
atom in the product. It is very unlikely that upon oxidation the alkyl
group will migrate from a nitrogen or oxygen to a sulfur. It also
demonstrates that the ligand is bound to the metal by a metal-nitrogen bond. An isomerization from a sulfur-bonded to a nitrogen-bonded species during the oxidation is unlikely since the sulfur-metal bond is thought to be thermodynamically more stable than a nitrogen-metal bond (vide supra). Several of these N-bonded insertion products have demonstrated a tendency irreversibly to isomerize to what is undoubtedly the S-bonded isomer. A rapid equilibrium between S- and N-bonded isomers cannot exist if both isomers can be isolated.

The IR spectra of the N-bonded insertion products show carbonyl stretching absorptions at 2050 and 2000 cm\(^{-1}\) which are only slightly affected by changing the alkyl groups on the newly formed ligand. These absorptions are about 40 cm\(^{-1}\) higher than those found in \(\eta^5\)\(\text{C}_2\text{H}_5\)Fe(CO)\(_2\)-alkyl complexes indicating that this N-bonded ligand is a poorer donor than an alkyl group. Several examples of the IR spectra in Nujol mulls
of these complexes are shown in Figure 34. In the sulfur-oxygen stretching region of the spectra these complexes have three distinctive very strong absorptions at 1300, 1140, and 1080 cm\(^{-1}\). They are assigned to the antisymmetric and symmetric sulfonyle functional group stretches and sulfinyl functional group stretch, respectively. In some complexes, these absorptions have shoulders. The assignments are in good agreement with those found (33) for similar compounds which were the products of the reaction of dienes with N-sulfinylsulfonamides as shown in Figure 35.

![Chemical structure](image)

\[
\nu (SO_2) \text{ antisymmetric } 1350 \text{ cm}^{-1} \\
\nu (SO_2) \text{ symmetric } 1165 \text{ cm}^{-1} \\
\nu (SO) \text{ } 1080 \text{ cm}^{-1}
\]

Figure 35

In the \(^{13}\)C NMR spectrum of \(\gamma^{5}\)C\(_2\)H\(_5\)Fe(CO)\(_2\)[N(SOCH\(_2\))\(_2\)(SO\(_2\)CH\(_2\))] (IXa) in CDCl\(_3\) at 25\(^{\circ}\)C, the sulfinyl methyl carbon resonance is broadened by the nuclear quadrupole moment of the nitrogen atom. When the temperature was reduced to -50\(^{\circ}\)C the signal narrowed and became similar in appearance to that of the other methyl carbon. In the oxidized product of this compound the methyl resonance is a sharp singlet. These data suggest that a sulfonyle functional group between nitrogen and carbon reduces the interaction of the nuclear spins of carbon and nitrogen atoms as compared to a sulfinyl functional group.
IR Spectra of $\text{C}_5\text{H}_5\text{Fe(CO)}_2[N(SOR_m)(SO_2R_1)]$ Complexes

A) $R_m=\text{CH}_3; R_1=\text{CH}_3$ (IXa)
B) $R_m=\text{CH}_2\text{C}_6\text{H}_5; R_1=\text{CH}_3$ (IXb)
C) $R_m=\text{CH}_3; R_1=\text{C}_6\text{H}_4\text{CH}_3$ (IXc)
D) $R_m=\text{CH}_2\text{C}_6\text{H}_5; R_1=\text{C}_6\text{H}_4\text{CH}_3$ (IXd)

Figure 34
The $^1$H NMR spectra of a series of complexes of structure IX are listed in Table 6. The assignments of the observed signals are straightforward except for the methyl resonances. By comparing the spectra listed it is possible to assign the methyl resonances as follows:

- $\text{SO}_2\text{CH}_3$: 7.0-7.3 $\tau$
- $\text{SOCH}_3$: 7.49-7.60 $\tau$
- $\text{C}_6\text{H}_4\text{CH}_3$: 7.61 $\tau$

The general utility of the insertion reactions of N-sulfinylsulfonamides with $\gamma^5\text{C}_5\text{H}_2\text{Fe(CO)}_2$-alkyl complexes has been demonstrated. It is possible to design a ligand with many different alkyl groups by the techniques described here. The probable limitation to the usefulness of this insertion reaction for the preparation of N-(alkylsulfinyl)-alkanesulfonamidato-N complexes is that a more reactive site than the metal-carbon bond with respect to the electrophile cannot be introduced in the $\eta^1$-aliphatic group of the starting metal complex. For example, it can be expected that the N-sulfinylsulfonamides will undergo many cycloaddition reaction with metal-propargyl complexes in a manner similar to sulfur dioxide and N-sulfinylaniline (vide supra).

F. The Preparation and Characterization of N-(Alkylsulfonyl)alkane-
sulfonamidato-N Complexes, (X).

Complexes of the structure shown in Figure 36 were prepared by the
Table 6

$^1$H NMR Spectra of $\eta^5$C$_5$H$_5$Fe(CO)$_2$[N(SOR$_m$)(SO$_2$R$_1$)]$^a$ Complexes in CDCl$_3$

<table>
<thead>
<tr>
<th>$R_m$</th>
<th>$R_1$</th>
<th>Chemical Shifts in $\tau$ Units</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$\text{C}_6\text{H}_4$ $^b$</td>
</tr>
<tr>
<td>CH$_3$</td>
<td>CH$_3$</td>
<td>4.77</td>
</tr>
<tr>
<td>CH$_3$</td>
<td>CH$_3$C$_6$H$_4$</td>
<td>2.52</td>
</tr>
<tr>
<td>CH$_2$C$_6$H$_5$</td>
<td>CH$_3$</td>
<td>2.65</td>
</tr>
<tr>
<td>CH$_2$C$_6$H$_5$</td>
<td>CH$_3$C$_6$H$_4$</td>
<td>2.5</td>
</tr>
<tr>
<td>CH$_2$CH$_2$C$_6$H$_5$</td>
<td>CH$_3$</td>
<td>2.79</td>
</tr>
</tbody>
</table>

$^a_{R_m}$ = alkyl derived from metal-alkyl, $R_1$ = alkyl derived from inserting compound; $^b$ value given is center of AA'BB' multiplet; $^c$ AB quartet, $J$=12.4 Hz; $^d$ broad; $^e$ center of complex multiplet containing $\text{CH}_2\text{CH}_2$ and $\text{CH}_3$ resonances
oxidation of the corresponding metal complexes of structure IX (vide supra). A general procedure for these reactions using m-chloroperoxybenzoic acid as an oxidizing agent was developed. A 1.5 mmolar sample of the N-(alkylsulfinyl)alkanesulfonamidato complex dissolved in 5 ml of CH$_2$Cl$_2$ was treated with a slight excess of m-ClC$_6$H$_4$CO$_2$H dissolved in 15 ml of CH$_2$Cl$_2$. The resulting red solution was stirred for one hour after which the solvent was removed on a rotary evaporator. The residue was treated with a large excess (2.0 g) of NaHCO$_3$ and 5 ml of methyl alcohol, and was stirred one hour. The excess NaHCO$_3$ was filtered off and washed once with 2 ml of methyl alcohol. The filtrate and wash were combined and the solvent removed on a rotary evaporator. The residue was taken up in CH$_2$Cl$_2$ and the solution was dried over MgSO$_4$. Solvent removal resulted in the red crystalline product in good yield.

The structure of the oxidized product with two methyl substituent groups was easily identified by its composition as determined by elemental analysis; by the presence of two singlet resonances of 5:6 intensity ratio in its $^1$H NMR spectrum; and by the appearance of three singlets in its $^{13}$C NMR spectrum which were assigned to the carbonyl, cyclopentadienyl, and methyl carbons. That the $^{15}$cyclopentadienyldicarbonylimony unit has not been disrupted is evident in the cyclopentadienyl-proton singlet in the NMR spectrum of all of these N-(alkylsulfonyl)-alkanesulfonamidato-N complexes and in the two carbonyl stretches appearing at about 2060 and 2010 cm$^{-1}$ in their IR spectra. The carbonyl stretching absorptions appear at higher frequencies by 5 to 20 cm$^{-1}$ than the corresponding N-(alkylsulfinyl)alkanesulfonamidato-N derivatives. These stretching frequencies are somewhat lower than those reported (72)
for the similar complex $\eta^5{\text{C}}_5{\text{H}}_5{\text{Fe(CO)}}_2{\text{N(SO}}_2{\text{F}})_2$ (2068, 2033 cm$^{-1}$). This would be expected since the FSO$_2$ group is more electron-withdrawing than an alkyl- or aryl-SO$_2$ group. Oxidation of the ligand would be expected to make it a poorer donor and thus raise the carbonyl stretching frequencies.

The sulfur-oxygen stretching region of the IR spectra is characterized by two ranges of strong absorptions, at 1330-1290 and 1150-1130 cm$^{-1}$ (Figure 37). These bands are often split, especially in nonsymmetrical ligands and are assigned to the antisymmetric and symmetric sulfonyl sulfur-oxygen stretches, respectively. In the compound $\eta^5{\text{C}}_5{\text{H}}_5{\text{Fe(CO)}}_2{\text{N(SO}}_2{\text{F}})_2$, the sulfonyl stretching absorptions appear at 1418, 1398, 1221, and 1184 cm$^{-1}$ (71). In the region near 1080 cm$^{-1}$, where the sulfinyl functional group absorption appears in the N-(alkylsulfinyl)alkanesulfonamidato-N derivatives, there are no strong bands in the spectra of N-(alkylsulfonyl)alkanesulfonamidato-N complexes.

The $^1$H NMR spectra of several complexes of structure X are listed in Table 7. The assignments of the proton resonances are straight-
IR Spectra of $\eta^5\text{C}_5\text{H}_5\text{Fe(CO)}_2[N(\text{SO}_2\text{CH}_3)(\text{SO}_2\text{R})]$ Complexes

A) $R=\text{CH}_3$ (Xa)  B) $R=\text{CH}_2\text{C}_6\text{H}_5$ (Xb)  C) $R=\text{C}_6\text{H}_4\text{CH}_3$ (Xc)

Figure 37
forward and are in agreement with those found in the nonoxidized ligand (vide supra). The methyl resonances at 6.90-7.0 \( \tau \) are from the \( \text{SO}_2\text{CH}_3 \) groups and the one at 7.56 \( \tau \) is the tolyl methyl resonance. The oxidation of N-sulfinylamine insertion products has proven to be a general method for the preparation of symmetrical and unsymmetrical N-(alkylsulfonyl)alkanesulfonamidato-N derivatives of \( \eta^5\text{C}_5\text{H}_5\text{Fe(CO)}_2\text{R} \).

G. The Preparation and Characterization of N-(Alkylsulfonyl)alkane-
sulfimidato-S Complexes (XI).

Three of such S-bonded complexes (Figure 38) have been prepared in this study. Two were found accidentally while attempting to isolate the corresponding N-bonded complex whereas the third was detected in a designed isomerization of an N-bonded complex. The complex XIa was obtained by crystallization at -10°C from a CHCl₃ solution of \( \eta^5\text{C}_5\text{H}_5\text{Fe(CO)}_2[N(\text{SOCH}_2\text{CH}_2\text{SO}_2\text{CH}_3)] \). This S-bonded complex was identified by

\[
\begin{align*}
\text{Fe} & \quad \text{S} \quad \text{R}_m \\
\text{CO} & \quad \text{CO} \quad \text{N} \\
0 & \quad \text{S} \quad \text{R}_1 \\
\text{XIa}, \text{b}, \text{c} & \\
\text{R}_m & = \text{alkyl group derived from the metal alkyl} \\
\text{R}_1 & = \text{alkyl group derived from the inserting compound}
\end{align*}
\]

\[
\begin{align*}
\text{a} & \quad \text{CH}_2\text{C}_6\text{H}_5 \quad \text{CH}_3 \\
\text{b} & \quad \text{CH}_3 \quad \text{C}_6\text{H}_4\text{CH}_3 \\
\text{c} & \quad \text{CH}_3 \quad \text{CH}_3 \\
\text{Figure 38}
\end{align*}
\]
its $^1$H and $^{13}$C NMR spectral characteristics as well as by its IR spectrum. These results will be discussed later. The similar complex Xib was isolated from a sample of $\eta^5$C$_5$H$_5$Fe(CO)$_2[N(SOCH$_3$)(SO$_2$C$_6$H$_4$CH$_2$)] that had been stored at 30°C for two months in the dry box. In this case the low solubility of the corresponding S-bonded isomer in acetone allowed its isolation by partial dissolution of the sample in acetone followed by filtration. The S-bonded isomer was recovered as a yellow powder and identified by its IR and $^1$H NMR spectral characteristics.

The complex Xic was prepared by the thermal isomerization of $\eta^5$C$_5$H$_5$Fe(CO)$_2[N(SO$_2$CH$_3$)(SOCH$_3$)] (IXa) in CHCl$_3$ solution. The solution was maintained at 50°C for 4.5 hours. Chromatography of the reaction mixture on alumina with a 60% benzene:40% dichloromethane solution developed two bands: a small, fast-moving red band and a broad, nearly stationary orange band. A $^1$H NMR spectrum of the red materials showed only the presence of cyclopentadienyl type protons (4.96 \text{\textmu}T) of an unidentified complex. The orange band was removed with acetone and was shown to be the starting metal complex IXa. The trailing edge of the orange band was collected separately and the solvent was removed. A $^1$H NMR spectrum of the residue contained resonances characteristic of the unidentified red material and IXa. Several additional singlets were observed with resonances at 4.70, 6.60, and 7.00 \text{\textmu}T. These chemical shifts are compatible with those expected for the compound Xic as will be shown. The same resonances were observed in the spectrum of a solution of IXa in CDCl$_3$ which had been sealed in an NMR tube and heated at 35-40°C for 17 hours.

The structures of these complexes are suggested by their IR, $^1$H and $^{13}$C NMR spectral characteristics. The IR solution spectrum of the
carbonyl stretching region of the complex Xlb in CDCl_3 shows two sharp carbonyl stretching absorptions at 2070 and 2022 cm\(^{-1}\). In the Nujol mull spectra of this complex, however, the high frequency carbonyl band is split into two equal-intensity bands at 2075 and 2050 cm\(^{-1}\) whereas the low frequency band is not split in the solid state and appears at 2005 cm\(^{-1}\). Two sharp carbonyl stretching absorptions occur in the Nujol mull IR spectrum of XIa at 2065 and 2005 cm\(^{-1}\). These carbonyl stretches and the singlets observed for the cyclopentadienyl proton resonances in the NMR spectra of these complexes indicated that the \(\eta^5\)C\(_5\)H\(_5\)Fe(CO)\(_2\) unit is intact.

It may be assumed that these complexes are monomeric. If they were dimeric the cyclopentadienyl groups in the dimer would have to be magnetically equivalent, since only one singlet for the cyclopentadienyl protons is observed in the NMR spectra. The \(\eta^5\)C\(_5\)H\(_5\)Fe(CO)\(_2\) center may only accommodate one additional ligand without exceeding the stable 18 electron configuration associated with low-valent transition-metal complexes. Thus, dimerization would have to occur through a reaction at the ligand and in such a way as to retain a plane of symmetry between the two metals. Without such a plane of symmetry more signals for the cyclopentadienyl and alkyl groups would appear in the \(^1H\) NMR spectra of the complexes and perhaps the carbonyl stretching absorptions would also be split. Also, such a dimerization would have to occur in such a manner that no protons are lost from the complex since the integrations of the \(^1H\) NMR spectra show the appropriate intensity ratios for the suggested monomeric complexes.
If a monomeric structure is assumed, and if it is also assumed that the alkyl groups have not migrated from a sulfur to an oxygen or nitrogen atom, then the number of reasonable structures for these complexes is reduced to those shown in Figure 39. The IR spectra of complexes

\[
\begin{align*}
M-S-R_m & \quad M-O-S=N-S-R_1 \\
\text{Figure 39}
\end{align*}
\]

XIa and Xib are shown in Figure 40. The bands near 1270 and 1120 cm\(^{-1}\) may be assigned to the antisymmetric and symmetric stretching absorptions of the sulfonyl group. These absorptions are similar to by 10-30 cm\(^{-1}\) lower than, those ascribed to the sulfonyl linkage in the N-(alkylsulfanyl)alkanesulfonamidato-N and N-(alkylsulfonyl)alkanesulfonamidato-N complexes (vide supra). There is an additional region of absorption at about 1030 cm\(^{-1}\). The structure K may well be unstable relative to J (Figure 39), since K is analogous to an O-bonded sulfinate (Figure 41).

\[
\begin{align*}
R \\
M-O-S=O \\
\text{Figure 41}
\end{align*}
\]

These O-sulfinites have been observed coordinated to metal centers such as 755\(^5\)HFe(CO)\(_2\) (15) in liquid SO\(_2\), but always isomerize to the S-bonded isomer on solvent removal. It was found in the earlier portion
IR Spectra of $\eta^5$C$_5$H$_5$Fe(CO)$_2[S(0)(R_m)(NSO_2R_1)]$ Complexes

A) $R_m=\text{CH}_2\text{C}_6\text{H}_5$; $R_1=\text{CH}_3$ (XIa)

B) $R_m=\text{CH}_3$; $R_1=\text{C}_6\text{H}_4\text{CH}_3$ (XIb)

Figure 40
of this study that Lewis acids coordinated to the terminal oxygen of an O-sulfinate ligand (Figure 42) exert a stabilizing influence on that linkage and allow its isolation and characterization. It may be that the electrophilic sulfonyl group bonded to the nitrogen could likewise 

![Figure 42](image)

stabilize an O-bonded structure. It is believed that the ligand is S-bonded since the absorption at 1030 cm\(^{-1}\) and one of the bands near 1110 cm\(^{-1}\) may best be interpreted as the antisymmetric and symmetric stretching absorptions of an O=S=N linkage as found in structure J. The IR spectra of the three products derived from the insertion of CH\(_3\)SO\(_2\)NSO into the metal-carbon bond of \(\eta^5\)C\(_5\)H\(_5\)Fe(CO)\(_2\)CH\(_2\)C\(_6\)H\(_5\) are shown in Figure 43. In all three complexes the sulfonyl sulfur-oxygen stretching absorptions occur near 1300 and 1140 cm\(^{-1}\). In IXb, the sulfinyl sulfur-oxygen stretching absorption occurs near 1080 cm\(^{-1}\). In Xb only sulfonyl group sulfur-oxygen stretching absorptions occur whereas in XIA absorptions near 1110 and 1030 cm\(^{-1}\) can be assigned to the antisymmetric and symmetric absorptions of the O=S=N linkage.

The chemical shifts of the \(^1\)H NMR spectra of these complexes argue against an O-bonded structure. The data are listed in Table 8. In the
IR Spectra of Derivatives of \( \eta^5\text{C}_5\text{H}_5\text{Fe(CO)}_2\text{CH}_2\text{C}_6\text{H}_5 \)

**Figure 43**

- **A)** \( \eta^5\text{C}_5\text{H}_5\text{Fe(CO)}_2[N(\text{SOCH}_2\text{C}_6\text{H}_5)(\text{SO}_2\text{CH}_3)] \) (IXb)
- **B)** \( \eta^5\text{C}_5\text{H}_5\text{Fe(CO)}_2[N(\text{SO}_2\text{C}_6\text{H}_5)(\text{SO}_2\text{CH}_3)] \) (Xb)
- **C)** \( \eta^5\text{C}_5\text{H}_5\text{Fe(CO)}_2[S(\text{O})(\text{CH}_2\text{C}_6\text{H}_5)(\text{NSO}_2\text{CH}_3)] \) (XLa)
<table>
<thead>
<tr>
<th>Complex #</th>
<th>$R_m$</th>
<th>$R_1$</th>
<th>Chemical Shifts in T Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>XIb</td>
<td>CH$_3$</td>
<td>CH$_3$C$_6$H$_4$</td>
<td>2.47 4.69 6.65 7.63</td>
</tr>
<tr>
<td>Xla</td>
<td>CH$_2$C$_6$H$_5$</td>
<td>CH$_3$</td>
<td>2.52 4.92 5.33 6.99</td>
</tr>
<tr>
<td>XIc</td>
<td>CH$_3$</td>
<td>CH$_3$</td>
<td>4.70 6.60 7.00</td>
</tr>
</tbody>
</table>

$^a$ $R_m$ = alkyl derived from metal-alkyl complex, $R_1$ = alkyl derived from inserting compounds
$^b$ value given is center of AA'BB' multiplet
The fact that the methylene proton resonances appear as a singlet in the NMR spectrum of compound XIa also argues against an O-bonded structure. In the complexes M-OS(O)CH$_2$C$_6$H$_5$ (M=Fe(CO)$_2$, Mo(CO)$_2$, W(CO)$_2$) the methylene proton resonance appears as an AB quartet because of the chirality of the sulfur atom. Also, in the compounds $\eta^5$C$_5$H$_5$W(CO)$_2$S(OA)CH$_2$C$_6$H$_5$ (A=BF$_3$, SbF$_5$) the methylene proton resonance appears as an AB quartet (vide supra). Interestingly, the methylene protons in the corresponding S-bonded complexes $\eta^5$C$_5$H$_5$W(CO)$_2$S(OA)-CH$_2$C$_6$H$_5$ show a singlet for their resonances in the NMR spectra even though the sulfur is still a chiral center (vide supra). The influence of a non-bonded electron pair on the sulfur may be important in establishing a chemical shift difference between the two protons of the methylene group. The $\alpha$-toluenesulfinato-O complexes and Lewis acid adducts of $\alpha$-toluenesulfinato-O complexes with a structure similar to K show an AB quartet for the methylene protons in their $^1$H NMR spectra. The com-
plexes of structure IX derived from insertion reaction of metal-benzyl complexes contain an AB quartet in one case and a broadened singlet in the other, which result from the methylene proton resonances. The Lewis acid adducts of S-benzyl sulfinates of a structure similar to J show a singlet for the methylene protons. It would seem likely in light of these facts that the structure of XIa is that shown in Figure 38. This is not regarded as a structural proof, but it lends support to the structure involving a metal-sulfur bond. Further evidence for the S-bonded structure is presented in a later section of the $^{13}$C NMR spectra of these complexes.


Bis(methylsulfonyl)sulfur diimide readily undergoes an insertion reaction with $\eta^5C_2H_3^5Fe(CO)_2$-alkyl complexes. The general procedure used in this study was to allow a CHCl$_3$ solution of an iron complex to react with an excess of the solid diimide. Bis(methylsulfonyl)sulfur diimide is only slightly soluble in CHCl$_3$ and thus dissolves as the reaction progresses. When dissolution of the diimide ceases, the reaction is complete. The excess diimide was filtered off from the red solution of the insertion product. The products of structure XII were isolated as oils on removal of the solvent. The pure products were obtained by low temperature crystallizations from CHCl$_3$ solution.

The product of an insertion reaction of a bis(alkylsulfonyl)sulfur diimide with a transition-metal alkyl complex is likely to have one of the two structures which are shown in Figure 44. The alkyl group derived
from the starting metal-alkyl complex almost certainly is bonded to the sulfur atom in the product by analogy with the following known reactions.

a) Alkylations of SO₂ (36), N-sulfinylamines (33), and sulfur diimides (37) with lithium alkyls or Grignard reagents all occur at the sulfur atom.  
b) All insertion reactions of SO₂ (2) or N-sulfinylsulfonamides (vide supra) with transition-metal alkyl complexes result with the alkyl group bonded to the sulfur.  

There is little likelihood that the product diimide ligand is coordinated via a sulfonyl oxygen atom since this linkage was not observed for N-sulfinylsulfonamide insertion products and since S-O-metal linkages are known to be unstable relative to S-metal coordination in low-valent transition metal complexes (vide supra).
The diimide insertion products were shown to contain the \( \eta^2\text{C}_5\text{H}_5\text{Fe}-(\text{CO})_2 \) moiety by the singlet appearing for the cyclopentadienyl proton resonance in their NMR spectra (Table 9) and by the two strong carbonyl stretching absorptions appearing near 2050 and 2005 cm\(^{-1}\) in their IR spectra. Since a one to one addition product is indicated both by elemental analysis and the relative intensities of the peaks appearing in the NMR spectra of the products, and since the \( \eta^2\text{C}_5\text{H}_5\text{Fe}-(\text{CO})_2^+ \) metal center can accept only one electron pair without exceeding an 18 electron configuration, the ligand in the product must be monodentate.

To determine the structure of the product of the sulfur diimide insertion reaction it is necessary to distinguish between the N-bonded form \( \text{L} \) and the S-bonded form \( \text{M} \). All previously reported \( S,N,N' \)-substituted sulfur diimide derivatives have involved coordination through both nitrogen atoms (38). However, in the diimide insertion products prepared

<table>
<thead>
<tr>
<th>( \text{R}_m )</th>
<th>( \text{R}_1 )</th>
<th>Chemical Shifts in ( \gamma ) Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{C}_6\text{H}_5 )</td>
<td>( \text{C}_5\text{H}_5 )</td>
<td>( \text{CH}_2 )</td>
</tr>
<tr>
<td>( \text{CH}_3 )</td>
<td>( \text{CH}_3 )</td>
<td>4.70</td>
</tr>
<tr>
<td>( \text{CH}_2\text{C}_6\text{H}_5 )</td>
<td>( \text{CH}_3 )</td>
<td>2.63</td>
</tr>
</tbody>
</table>

---

\(^a\) \( \text{R}_m = \text{alkyl derived from metal-alkyl complex, } \text{R}_1 = \text{alkyl derived from inserting compounds; } \text{b} J=12.1 \)
here, coordination to the metal center occurs only through one atom of the substituted diimide ligand. The demonstrated preference of the S,N,N'-substituted diimide ligand for coordination through nitrogen suggests that the insertion products prepared in this study may involve an N-bonded structure (I). The fact that the initial insertion product of N-sulfinylsulfonamides with $\gamma^2_5 \mathrm{H}_5 \mathrm{Fe}(\mathrm{CO})_2$-alkyl complexes is a N-bonded rather than an S-bonded species also is an indication that the product in the similar reaction of sulfur diimides contains a metal-nitrogen linkage.

The $^1\text{H} \text{NMR}$ spectra in $\text{CDCl}_3$ of the complexes prepared in this study are listed in Table 9. There are several structural inferences which may be drawn from these data. The two methyl sulfonyl groups in the complex with $R_m = \text{CH}_2\text{C}_6\text{H}_5$ are in different environments judging by the 0.74 ppm difference in their chemical shifts. This is a strong indication that the ligand is coordinated through one of the nitrogen atoms in an unsymmetrical fashion (I). It is possible that restricted rotation about the S-N bonds in conjunction with a slow rate of inversion at the nitrogen atoms of complexes of structure $M$ could result in a nonsymmetrical ligand, but in that case two isomers would likely be observed in the $^1\text{H} \text{NMR}$ spectra of the complexes.

The appearance of the methylene proton resonances as an $\text{AB}$ quartet in the NMR spectrum of the diimide insertion product with $R_m = \text{CH}_2\text{C}_6\text{H}_5$ also suggests that the ligand in the product is coordinated to the metal by a nitrogen. An examination of the $^1\text{H} \text{NMR}$ spectra of related complexes suggests that a non-bonded electron pair on the central sulfur atom of the ligand may play a significant role in determining the chemical shift.
difference between the resonances of the two methylene protons. The following complexes have been shown to have chiral sulfur atoms and the methylene proton resonances appear as AB quartets in their $^1$H NMR spectra: 

$\text{M-}[\text{OS(O)CH}_2\text{C}_6\text{H}_5]$ (M = $^5\text{C}_5\text{H}_5\text{Fe}[\text{CO}]_2$, $^5\text{C}_5\text{H}_5\text{Mo}[\text{CO}]_3$, $\text{Mn}[\text{CO}]_5$) (15); $^5\text{C}_5\text{H}_5\text{W}[\text{CO}]_3[\text{OS(OA)CH}_2\text{C}_6\text{H}_5]$ (A=BF$^3$, SbF$^5$) (vide supra). The complexes $^5\text{C}_5\text{H}_5\text{N}[\text{CO}]_3[\text{S(O)(OA)CH}_2\text{C}_6\text{H}_5]$ (A=BF$^3$, SbF$^5$), although containing a chiral sulfur atom, show only a singlet for the methylene proton resonances in their NMR spectra (vide supra). In addition, the methylene proton resonances of the complex $^5\text{C}_5\text{H}_5\text{Fe}[\text{CO}]_2[\text{S(O)(CH}_2\text{C}_6\text{H}_5\text{N}(\text{SO}_2\text{CH}_3)]$, which was assigned the S-bonded structure (vide supra) and contains a chiral center, appear as a singlet in its NMR spectrum. An inspection of the above complexes shows that the chirality of the sulfur atom appears as a chemical shift difference of the methylene protons only for the complexes with a non-bonded electron pair on the sulfur. The compound presently under discussion, $^5\text{C}_5\text{H}_5\text{Fe}[\text{CO}]_2-[\text{N(SO}_2\text{CH}_3\text{SCH}_2\text{C}_6\text{H}_5\text{NSO}_2\text{CH}_3)]$ fits this pattern assuming an N-bonded structure. This certainly is no proof of the structure, but the close similarity of the complexes compared above suggests that this is a useful correlation.

The infrared spectra of two sulfur diimide insertion products are shown in Figure 45. Two regions of strong absorptions resulting from the sulfur-oxygen stretching vibrations appear near 1300 and 1130 cm$^{-1}$. These frequencies are similar to those found in the complexes $^5\text{C}_5\text{H}_5\text{Fe}[\text{CO}]_2-[\text{N(SO}_2\text{R})(\text{SO}_2\text{R}')]$ and $-[\text{N(SOR)(SO}_2\text{R}')]$, and are about 10-30 cm$^{-1}$ higher than those found for the S-bonded complexes $^5\text{C}_5\text{H}_5\text{Fe}[\text{CO}]_2-[\text{S(O)(R)(NSO}_2\text{R}')]$ (vide supra). An additional strong absorption occurs
IR Spectra of \( \gamma^5C_5H_5Fe(CO)_2\left[N(SO_2CH_3)(SRNSO_2CH_3)\right] \) Complexes

A) \( R=CH_3 \) (XIIa)

B) \( R=CH_2C_6H_5 \) (XIIb)

Figure 45
at 1020 cm\(^{-1}\), about 60 cm\(^{-1}\) lower than the sulfinyl sulfur-oxygen stretching frequency in \(\eta^5C_5H_5Fe(CO)_2[N(SOR)(SO_2R')]\). This stretching absorption may be assigned to the S=N stretching vibration of the uncomplexed nitrogen of the N-bonded ligand with structure I. The assignments of these three bands are in good agreement with those found (35) in related compounds which are the products of the reaction of dienes with bis(alkylsulfonyl)sulfur diimides as shown in Figure 46.

\[
\begin{align*}
\text{[\text{dienes}]} + (\text{RSO}_2\text{N})_2\text{S} & \rightarrow \text{[insertion products]} \\
\text{(SO}_2\text{)}\text{ of } \text{N-SO}_2\text{-group} & 1345-1370 \text{ cm}^{-1} \\
& 1160-1180 \text{ cm}^{-1} \\
\text{(SO}_2\text{)}\text{ of } =\text{N-SO}_2\text{-group} & 1280-1310 \text{ cm}^{-1} \\
& 1120-1160 \text{ cm}^{-1} \\
\text{(S=N)} & 975-1010 \text{ cm}^{-1} \\
\end{align*}
\]

**Figure 46**

The above data indicate that the structure of the diimide insertion products is of the form \(\eta^5C_5H_5Fe(CO)_2[N(SOR)(SR'NSO_2R')]\).

I. \(^{13}\text{C NMR Spectral Assignments of Sulfur Imide Insertion Products.}\)

Additional evidence supporting the structures which were proposed for N-sulfinylsulfonamide and sulfur diimide insertion products was found in their \(^{13}\text{C NMR spectra. A consistent assignment of the chemical shifts of the cyclopentadienyl carbons which differentiates between sulfur-bonded and nitrogen-bonded ligands was possible for the series of closely related complexes prepared in this study. As can be seen in**
Table 10

\[ \text{\(^{13}\)C NMR Spectra of Iron Complexes} \]

<table>
<thead>
<tr>
<th>Compound</th>
<th>R_m</th>
<th>R_1</th>
<th>CO</th>
<th>Aromatic</th>
<th>( \text{O(\text{MX})}_{\text{H}} )</th>
<th>M - S - CH_3</th>
<th>XSO_2CH_3</th>
<th>X - S - CH_3</th>
<th>Other CH_3</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{M[NSO}_2^m\text{R}_1^m\text{(SO}_2\text{R}_1^m)} )</td>
<td>CH_3</td>
<td>CH_3</td>
<td>211.5, 212.2</td>
<td>-</td>
<td>85.8</td>
<td>-</td>
<td>45.1</td>
<td>41.9^c</td>
<td>-</td>
</tr>
<tr>
<td>( \text{M[NSO}_2^m\text{R}_1^m\text{(SO}_2\text{R}_1^m)} )</td>
<td>CH_3</td>
<td>CH_3</td>
<td>211.5, 212.2</td>
<td>131.4, 130.5, 66.0, 65.1Br</td>
<td>128.8, 128.0</td>
<td>-</td>
<td>43.1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>( \text{M[NSO}_2^m\text{R}_1^m\text{(SR}_n\text{NSO}_2\text{R}_1^m)} )</td>
<td>CH_3</td>
<td>CH_3</td>
<td>210.9</td>
<td>-</td>
<td>85.6</td>
<td>-</td>
<td>42.7</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>( \text{M[NSO}_2^m\text{R}_1^m\text{(SR}_n\text{NSO}_2\text{R}_1^m)} )</td>
<td>CH_3</td>
<td>CH_3</td>
<td>210.9</td>
<td>131.8, 130.5, 66.0, 60.2</td>
<td>128.8</td>
<td>-</td>
<td>42.1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>( \text{M[S(O)(R}_m\text{NSO}_2\text{R}_1^m)} )</td>
<td>CH_3</td>
<td>CH_3</td>
<td>212.0, 210.7</td>
<td>131.2, 130.7, 85.8, 59.9</td>
<td>128.9, 128.2</td>
<td>-</td>
<td>42.8, 42.0</td>
<td>39.1</td>
<td>-</td>
</tr>
<tr>
<td>( \text{M[SO}_2^m\text{R}_1^m\text{]} )</td>
<td>CH_3</td>
<td>CH_3</td>
<td>208.8, 208.0</td>
<td>143.0, 141.5, 129.0, 126.5</td>
<td>75.9</td>
<td>59.4</td>
<td>-</td>
<td>-</td>
<td>21.4</td>
</tr>
<tr>
<td>( \text{M[SO}_2^m\text{R}_1^m\text{]} )</td>
<td>CH_3</td>
<td>CH_3</td>
<td>208.8, 208.0</td>
<td>132.0, 130.2, 87.6, 75.9</td>
<td>129.6, 129.0</td>
<td>-</td>
<td>45.6</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

^a\text{CDCl}_3\text{ solution, ppm downfield from TMS (50); b}\text{M=}{\eta}^5\text{C}_5\text{H}_5\text{Fe(CO)}_2, X=remainder of ligand, R_m=alkyl group derived from the initial metal complex, R_1=alkyl group derived from inserting compound; c\text{broad at ambient temperature, sharp at -50°C; dsignal too weak for accurate measurement; e}\text{in}\eta^5\text{C}_5\text{H}_5\text{Fe(PPPh}_3\text{)(CO)SO}_2\text{CH}_3\text{ the methyl carbon resonance is at 58.9 s (14).}
Table 10, all of the N-bonded complexes which were examined by $^{13}$C NMR spectroscopy have cyclopentadienyl carbon chemical shifts ranging from 85.6 to 86.0 $\delta$. In contrast, all complexes assigned an S-bonded structure, including several similar S-sulfinate complexes, have cyclopentadienyl carbon chemical shifts ranging from 87.2 to 87.9 $\delta$. The sulfur-coordinated ligands are capable of $\sigma$ and $\pi$ bonding with the metal in contrast to the nitrogen coordinated ligands where only a $\sigma$ bond is formed. The sulfur would be expected to delocalize electrons associated with the metal in a $d_{\delta-d\pi}$ back-bonding fashion. Such a delocalization should result in a lowering of the energy of electronic excited states with a concomitant increase in the paramagnetic shift of the resonances of the cyclopentadienyl carbons, which are also involved in the delocalized system.

An opposite effect is observed in the chemical shifts of the carbonyl carbons. Their $^{13}$C chemical shifts range from 212.2 to 210.7 $\delta$ for complexes with N-bonded ligands and 209.7 to 208.0 $\delta$ for S-bonded complexes. A linear relationship between the $^{13}$C chemical shifts of carbonyl carbons and the Cotton-Kraihanzel force constants for closely related complexes has been observed (73). With an increased force constant, the chemical shift of a carbonyl carbon is decreased. A reduction of carbonyl-metal $\pi$-bonding would result from competition for $\pi$-electron density with the sulfur atom in complexes with a sulfur-bonded ligand. Thus a sulfur-bonded ligand, by delocalizing $\pi$-electron density, should reduce the degree of metal-carbonyl $\pi$-bonding, raise the carbonyl stretching frequencies (Table 11) and force constants, and thereby cause a shielding of the carbonyl-carbon atoms.
Table 11

Carbonyl Stretching Frequencies of S- and N-Bonded Complexes

<table>
<thead>
<tr>
<th>Complex #</th>
<th>Compound</th>
<th>Medium</th>
<th>Frequencies (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>XIa</td>
<td>$M[S(O)(CH₂C₆H₅)(NSO₂CH₃)]$</td>
<td>Nujol</td>
<td>2065, 2005</td>
</tr>
<tr>
<td>IXb</td>
<td>$M[N(SO(CH₂C₆H₅)(SO₂CH₃)]$</td>
<td>Nujol</td>
<td>2045, 1995</td>
</tr>
<tr>
<td>XIb</td>
<td>$M[S(O)(CH₃)(NSO₂C₆H₄CH₃)]$</td>
<td>CHCl₃</td>
<td>2070, 2022</td>
</tr>
<tr>
<td>IXc</td>
<td>$M[N(SOCH₃)(SO₂C₆H₄CH₃)]$</td>
<td>CHCl₃</td>
<td>2060, 2015</td>
</tr>
</tbody>
</table>

\[ a_{M=\eta^5C₅H₅Fe(CO)} \]

In the insertion products of sulfur dioxide, N-sulfinylsulfonamides and sulfur diimides, the alpha carbon of the starting metal-alkyl complex is bonded to a sulfur atom. In a series of insertion products resulting from the same metal-alkyl complex, the $^{13}$C chemical shifts of the alpha carbon is dependent on the manner of coordination of the product ligand to the metal atom. In Table 10, a series of insertion products of $\eta^5C₅H₅Fe(CO)₂CH₂C₆H₅$ is listed. The chemical shift of the $\alpha$-carbon ranges from 65.1 to 59.9 $\delta$ when the ligand is nitrogen bonded to the metal whereas it ranges from 78.0 to 75.9 $\delta$ when the sulfur is bonded to the metal. The reason for such a large deshielding of the methylene carbon is not clear, but the shift may be a useful empirical rule in the structural assignments of similar complexes. Carbon atoms $\beta$ to a metal are known to give rise to $^{13}$C resonances shifted down-field as compared to the shifts found for hydrocarbon analogs (72).

The "$\beta$-effect" may well be involved in the deshielding of the $\alpha$-carbon in the S-bonded complexes. The shift difference is not caused only by
a change of coordination number of the sulfur atom, since both three- and four-coordinate sulfur atoms are included in the group of non-sulfur bonded ligands whereas in the sulfur-bonded complexes the sulfur is four-coordinate.

A similar large deshielding of the methyl carbon derived from \( \text{H}_{5}C_{5}H_{5}Fe\)\(_{(2)}\text{CH}_{3} \) was observed for the insertion products containing a metal-sulfur bond as compared to that found for the products with a metal-nitrogen bond. The \( ^{13}\text{C} \) chemical shift of a methyl carbon bonded to a metal-coordinated sulfur ranges from 59.4 to 60.6 \( \delta \) whereas the \( ^{13}\text{C} \) resonances of the other methyl carbons which are bonded to sulfur range from 39.1 to 45.6 \( \delta \). It is difficult to assign the chemical shifts of sulfinyl- and sulfonyl-type groups since they are expected to fall in the same range. For example, in substituted phenylmethyl-sulfoxides and sulfones the shift ranges for the methyl carbons are 44.0 to 44.3 \( \delta \) and 43.7 to 44.8 \( \delta \), respectively (74). The assignments of the sulfinyl- and sulfonyl-bonded methyl carbons given in Table 10 should be considered tentative and were made in such a manner as to maintain an internal consistency in the shift data found for these closely related complexes. From this study it appears that the \( ^{13}\text{C} \) chemical shift in an \( \text{N-SO}_{2}\text{-CH}_{3} \) group occurs in the region 45.1 to 42.0 \( \delta \) whereas in an \( \text{N-S(0)CH}_{3} \) group it occurs from 41.9 to 39.1 \( \delta \).

The \( ^{13}\text{C} \) NMR spectra thus will likely be useful in structural assignments of similar N-sulfinylsulfonamide and sulfur diimide insertion products. The formation of a metal-sulfur bond results in a deshielding of the cyclopentadienyl and a shielding of the carbonyl carbons in a regular manner as compared to nitrogen-bonded complexes. Even more markedly affected is the \( \alpha \)-carbon of an organic group that is also
bonded to the sulfur atom. The formation of a metal-sulfur bond resulted in a deshielding of 10-20 ppm of the $\alpha$-carbon as compared to the shift found for the same ligand coordinated to the metal through a nitrogen atom.
SUMMARY

Reactions involving the insertion of sulfur(IV) compounds into the metal-carbon σ bond of \( \eta^5C_5H_5W(CO)_3R \) (Ia, Ib) and \( \eta^5C_5H_5Fe(CO)_2R \) (IIa, IIb) \((R_a=CH_3, R_b=CH_2COCH_3)\) were studied. The focus of this study was the enhancement of the rate of slowly occurring reactions. Since the insertion of \( \text{SO}_2 \) is known to involve an electrophilic cleavage of the metal-carbon bond, an attempt was made to increase the electrophilicity of the inserting sulfur(IV) compounds.

Sulfur dioxide is known to insert into complexes I and II to yield the corresponding sulfinato-S complexes which contain a metal-S(0)\(_2\)-R linkage. Although the rate of the reaction of IIa is too fast to measure by conventional techniques in refluxing \( \text{SO}_2 \), the reaction of Ia is very slow. A solution of Ia in liquid \( \text{SO}_2 \) was maintained at -15°C for 27 days and in that time the formation of the S-sulfinate \( \eta^5C_5H_5W(CO)_3\text{SO}_2\text{CH}_3 \) (IIIa) was 16% complete. In contrast, in the reaction of an equimolar solution of Ia and BF\(_3\) in \( \text{SO}_2 \) at -26°C, all starting Ia was consumed to form a single red product (IVA) in less than 40 minutes. Thus, there was a considerable enhancement by BF\(_3\) of the rate of the reaction of Ia with \( \text{SO}_2 \).

Similar fast reactions and red products were obtained when the Lewis acid SbF\(_5\) was used rather than BF\(_3\) and also when the metal alkyl Ib was mixed with either acid in \( \text{SO}_2 \) solution. The products (IV) of these reactions are of the structure \( \eta^5C_5H_5W(CO)_3\text{OS(OA)}R \)
The products of the insertion of SO\textsubscript{2} into I or II in the absence of a Lewis acid are the S-sulfinate. The S-sulfinate III\textsubscript{a} was obtained in 85\% yield by treating IV\textsubscript{a} with NH\textsubscript{3} in CH\textsubscript{2}Cl\textsubscript{2} solution at 25°C. The addition of a Lewis acid to the S-sulfinate complexes \( \text{H}_2\text{C}_\text{H}_2\text{W}(\text{CO})_3\text{SO}_\text{R} \) (III\textsubscript{a}, III\textsubscript{b}) (\( R_\text{a}=\text{CH}_3, R_\text{b}=\text{CH}_2\text{C}_6\text{H}_5 \)) resulted in the formation of Lewis acid-base adducts \( \text{H}_2\text{C}_\text{H}_2\text{W}(\text{CO})_3\text{SO}(\text{OA})R \) (V) (A=Sb\textsubscript{F}\textsubscript{3}, BF\textsubscript{3}; R=CH\textsubscript{3}, CH\textsubscript{2}C\text{H}_5\text{H}_5). Adducts of structure V containing BF\textsubscript{3} revert to an S-sulfinate structure (III) upon exposure to vacuum. Recrystallization of IV\textsubscript{a} from a benzene-pentane mixture resulted in the conversion of IV\textsubscript{a} to its isomer of structure Va (A=BF\textsubscript{3}, R=CH\textsubscript{3}). These transformations for complexes with A=BF\textsubscript{3} and R=CH\textsubscript{3} are summarized below.

The similar sulfur(IV) compounds, the N-sulfinylamines (\( R'_\text{N}=\text{S}=\text{O}, R'_\text{=}\text{alkyl or aryl} \)), showed little tendency to react with complexes I or
II when mixed at 25°C. The reactivity of cyclohexyl-N-sulfinylamine with complex IIa under similar conditions was greatly increased by the utilization of BF₃ in the reaction solution, and cleavage of the metal-carbon bond was rapid as observed in the carbonyl stretching region of the IR spectra of reaction mixtures. Cyclohexyl-N-sulfinylamine was shown to form a 1:1 adduct with BF₃ and this adduct is thought to be the reactive species. Products of these reactions could not be isolated because of their low stability and were not characterized except by spectral analysis of reaction mixtures.

Since the coordination of a Lewis acid greatly increased the reactivity of N-sulfinylamines, the utilization in the insertion of a more electron-withdrawing substituent on the sulfinylamine was examined. The N-sulfinylsulfonamides, R'SO₂N=S=O (R' = alkyl or aryl group) react very quickly with II to yield complexes of the type \( \eta^2\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2[N(\text{SOR})(\text{SO}_2R')] \) (VI) (R = alkyl derived from the metal complex, R' = alkyl or aryl group of the inserting sulfur compound).

The sulfinyl-sulfur atoms of complexes VI were oxidized with m-CIC₆H₄CO₂H to form the bis-sulfonylamidato complexes \( \eta^2\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2[N(\text{SOR})(\text{SO}_2R')] \). In addition, the N-bonded insertion products VI isomerized to form complexes with the S-bonded structure \( \eta^2\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2[S(\text{O})(\text{R})(\text{NSO}_2R')] \). Methanesulfonylsulfur diimide (CH₃SO₂N=S=NSO₂CH₃) was shown to undergo a similar insertion reaction with complexes II to yield \( \eta^2\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2[N(\text{SO}_2\text{CH}_3)S(\text{R})\text{NSO}_2\text{CH}_3] \).

Thus, the Lewis acid adducts of SO₂ and RN=S=O are much more reactive with respect to electrophilic cleavage/insertion reactions than these sulfur compounds alone. In a similar manner the reactivity
of N-sulfinylamine compounds is greatly increased by the incorporation of the electron-withdrawing sulfonyl group in the N-sulfinylsulfonamides. These effects may be thought of as inter- and intra-molecular enhancements of the rate of electrophilic insertion reactions. By the application of this principle representatives of the several new classes of compounds were prepared.
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