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Hu, Yeh-Rom

STUDIES OF REACTIONS OF IRON- AND TUNGSTEN-CYCLOALKYL AND PLATINUM-ETA(1)-ALLYL COMPLEXES WITH ELECTROPHILES

The Ohio State University

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STUDIES OF REACTIONS OF IRON- AND TUNGSTEN-CYCLOALKYL AND PLATINUM-n¹-ALLYL COMPLEXES WITH ELECTROPHILES

DISSERTATION

Presented in Partial Fulfillment of the Requirements for the Degree Doctor of Philosophy in the Graduate School of The Ohio State University

By

Yeh-Rom Hu, M.S.

The Ohio State University

1985

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\( FeCHCH_2N(S(O)_2CH_3)SN(S(O)_2CH_3)CH_2 \) and \( n^5-C_5H_5(CO)_2FeCHCH_2N(S(O)_2CH_3)-\)


"Conversion of trans- to cis-\( n^5-C_5H_5(CO)_2Fe-\)


FIELDS OF STUDY

MAJOR FIELD: Organic and Organometallic Chemistry

Professor Andrew Wojcicki
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INTRODUCTION

Reactions of 18-electron transition-metal-\(n^1\)-allyl complexes with unsaturated electrophilic reagents have been extensively investigated in the past two decades.\(^1\)\(^2\) These complexes react with the unsaturated electrophiles generally to yield [3+2] cycloaddition products. A number of metal-\(n^1\)-allyl complexes of iron, tungsten, cobalt, manganese, and chromium enter into these cycloaddition reactions. Among them, iron-\(n^1\)-allyl complexes have been widely studied.

The two classes of unsaturated organic reagents, \(E=\text{Nu}\) (\(E = \) electrophilic part, \(\text{Nu} = \) nucleophilic part), which have received particular attention in the study of this cycloaddition reaction are the olefins and the isocyanates. The addition of olefins to metal-\(n^1\)-allyl complexes leads to the formation of metal-cyclopentyl complexes\(^3\)\(^-\)\(^{13}\) where the added olefin is TCNE, \(\text{O-CI}_{6}\text{H}_4\text{CH}=\text{C(CN)}_2\), \(\text{C}_6\text{H}_5\text{CH}=\text{C(CN)}_2\), \(\text{C}_2\text{H}_5\text{OCH}=\text{C(CN)}_2\), \(\text{CF}_3\text{(CN)C=C(CN)CF}_3\), \(\text{CH}_2\text{=C(CO}_2\text{CH}_3)_2\) or 2,3-dichloro-5,6-dicyano-1,4-benzoquinone. The organic isocyanates, such as \(\text{ClSO}_2\text{NCO}\), \(\text{p-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NCO}\), \(\text{CCl}_3\text{C(0)NCO}\), and \(\text{CH}_3\text{OSO}_2\text{NCO}\), readily react with metal-\(n^1\)-allyl complexes to afford complexes containing a \(\gamma\)-lactam ring.\(^7\)\(^{\text{--}}\)\(^{16}\) Moreover, \((\text{CF}_3)_2\text{C}=\text{O}_6\),\(^8\)\(^{17}\)\(^{18}\)
CH$_3$SO$_2$NSO,$^{19}$ CH$_3$O$_2$CN=SO$_2$·THF,$^{7,20}$ and CH$_2$SO$_2$$^7$ have been found to participate in cycloaddition with one or more of the transition-metal-$^1$-allyl complexes. Recently, it was reported that reactions of $^5$-C$_5$H$_5$(CO)$_2$FeCH$_2$C(R)=CH$_2$ (R=H, CH$_3$) with (CH$_3$SO$_2$N)$_2$S surprisingly yield [3+3] cycloadducts, 1 (eq 1), rather than expected [3+2] cycloadducts.$^{19}$ The structure of $^5$-C$_5$H$_5$(CO)$_2$FeCHCH$_2$N(S(O$_2$)CH$_3$)$_2$CH$_2$ was determined by X-ray diffraction.

$$\eta^5$-C$_5$H$_5$(CO)$_2$FeCH$_2$C(R)=CH$_2$ + (CH$_3$SO$_2$N)$_2$S \rightarrow \eta^5$-C$_5$H$_5$(CO)$_2$FeCH$_2$C(R)=CH$_2$N(S(O$_2$)CH$_3$)$_2$CH$_2$ (1)$$

R = H, CH$_3$

Cycloaddition reactions of metal-$^1$-allyl complexes with unsaturated electrophiles E=Nu or Nu=E=Nu are potentially useful in organic synthesis. There are several methods which may be used for the demetallation of the organic ring in the products.$^{21,22,23}$

Cleavage of the Fe-C σ bond in iron-alkyl complexes effected by protic acids and halogens has been reported.$^{22,23}$ In general, it is a facile process. For example, treatment of $^5$-C$_5$H$_5$(CO)$_2$FeCH$_3$ with CF$_3$COOH readily gives $^5$-C$_5$H$_5$(CO)$_2$FeOC(0)CF$_3$ and CH$_4$.$^{22}$ However,
when the acid-induced cleavage is applied to iron cycloalkyls, in some cases protonation appears to take place instead at a heteroatom in the ring.

Oxidative demetallation has received some attention. Treatment of iron-alkyl complexes with oxidizing reagents in carbon monoxide-saturated alcohol solution leads to the formation of esters. Several years ago Abram and Baker reported that carboalkoxylation of the cycloadduct $\eta^5$-$C_5H_5(CO)_2FeCHCH_2C(CN)_2C(CN)_2CH_2$ by oxidative demetallation afforded a quantitative yield of the appropriate ester (eq 2).^{13}

\[
\begin{align*}
\eta^5-C_5H_5(CO)_2Fe & \xrightarrow{\text{eq 2}} (NH_4)Ce(NO_3)_6 \\
& \xrightarrow{CO} \text{CH}_3\text{OH} \\
& \xrightarrow{H_3COC-CN-CN-CN-CN} \\
\end{align*}
\]

Owing to decomposition of the $\eta^5$-$C_5H_5(CO)_2Fe$ fragment under oxidative conditions, applications of the oxidative cleavage of the Fe-C bond have a limited practical use in stiochiometric synthesis.

With regard to mechanism, these [3+2] cycloaddition reactions appear to proceed in two steps that involve a dipolar metal-$\pi^2$-olefin intermediate (Eq3).
When freshly prepared solutions of \((\eta^5-C_5H_5)(CO)_2FeCH_2C(R^1)=C-(R^2)R^3\) in liquid SO\(_2\) were examined by IR and \(^1\)H NMR spectroscopy, the spectra indicated rapid formation of zwitterionic species, \(^{2,25,26}\) These zwitterions can be trapped by addition of \((CH_3)_3OBF_4\) or \((C_6H_5)_3CCl\) to yield cationic iron-\(n^2\)-olefin complexes, \(3\), isolated as the BF\(_4^-\) or PF\(_6^-\) salts.\(^{11,25,26}\)

\[ \eta^5-C_5H_5(CO)_2Fe=\begin{array}{c} \text{Nu} \\ \text{R}_1 \end{array} \text{R}_2 \text{R}_3 \rightarrow \eta^5-C_5H_5(CO)_2Fe=\begin{array}{c} \text{Nu} \\ \text{R}_1 \end{array} \text{R}_2 \text{R}_3 \]  

Where:

- \(\eta^5-C_5H_5(CO)_2Fe\) is the iron complexes
- \(\text{Nu}\) is the nucleophile
- \(\text{R}_1, \text{R}_2, \text{R}_3\) are the substituents

Equation 3

- \(\eta^5-C_5H_5(CO)_2Fe\) is the iron complexes
- \(\text{Nu}\) is the nucleophile
- \(\text{R}_1, \text{R}_2, \text{R}_3\) are the substituents

Equation 3
However, storage of the solutions of 2 gradually leads to formation of the insertion products $n^5$-$C_5H_5(CO)_2FeSO_2CH_2C(R^1)=C(R^2)-R^3$ and $n^5$-$C_5H_5(CO)_2FeSO_2C(R^2)(R^3)C(R^1)=CH_2$, except when $R^1=R^2=R^3=H$, in which case a more complex behavior obtains.$^{25,26}$

The proposed dipolar mechanism for [3+2] cycloaddition reaction is further supported by the finding that the rate of cycloaddition when $E=\text{Nu}$ is TCNE depends markedly on the nature of the solvent.$^6$ Accordingly, for $n^5$-$C_5H_5(CO)_3MoCH_2CH=C(CH_3)_2$, the rate increases substantially on going from pentane to THF and then to CH$_3$CN.

A study of the reaction of $n^5$-$C_5H_5(CO)_2Fe(\text{E-CH}_2\text{CH}=\text{CH}_2\text{CH}_3)$ with TCNE has demonstrated that the cycloaddition leads to the preservation of the geometrical relationship between the substituent at the $\gamma$-carbon atom of the allyl ligand and the metal.$^7$ This result suggests that the cycloaddition reactions occur stereospecifically by a suprafacial addition of electrophile trans to the metal group (eq 4).
Recently, protonation of the [3+3] cycloadduct in eq 1 was found to induce the opening of the six-membered ring and to result in the formation of a cationic iron-$\eta^2$-olefin species (eq 5).\(^{27}\) The structure of the cationic species, 4, was determined by X-ray diffraction.

\[
\begin{align*}
\eta^5\text{-C}_5\text{H}_5\text{(CO}_2\text{Fe} & \xrightarrow{\text{HPF}_6} \eta^5\text{-C}_5\text{H}_5\text{(CO}_2\text{Fe}+ \text{PF}_6^-} \\
1 & \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quan
Reaction of 16-electron transition-metal-\(n^1\)-allyl complexes with unsaturated electrophiles, unlike reactions of their 18-electron analogues, had not received attention until a few years ago. Recently, reactions of platinum(II)-\(n^1\)-allyl complexes with tetracyanoethylene (TCNE) were found to afford products of [3+2] cycloaddition to the allyl fragment (eq 7).18
In order to explore generality and scope of this type of cycloaddition, reactions of platinum(II)-η¹-allyl complexes with other electrophiles E=Nu were investigated further in this work.

Cycloaddition reactions of 16-electron complexes have considerable potential in organic synthesis because of the propensity of the d⁸-d¹⁰ and d⁸-d⁶ systems to undergo reductive elimination-oxidative addition process. These reactions would lead to a release of the coordinated five-membered organic ring, thus completing a three-step catalytic cycle for preparation of cyclic organic compounds from allyl halides and E=Nu. The net process is shown in eq 8.

\[
\begin{align*}
\text{R}^3\text{R}^2\text{R}^1\text{X} + \text{E=Nu} & \rightarrow \text{Nu}^{\text{Nu}} \text{R}^1\text{R}^2\text{R}^3 \\
X & = \text{Halogen}
\end{align*}
\]

If the three steps in this catalytic cycle are compatible, this cycle might proceed through one of two sequences. (1) A 16-electron transition-metal-η¹-allyl complex first reacts with an electrophile E=Nu to form a cycloadduct. Then oxidative addition of allyl halide to this cycloadduct yields a six-coordinate complex. Finally, reductive elimination releases a five-membered ring compound and
Scheme I

M = Pt, Pd
L = Phosphine
X = Halogen

regenerates the starting metal-$\eta^1$-allyl complex. This sequence is shown in Scheme I. (2) The cycloadduct from reaction of the 16-electron transition-metal-$\eta^1$-allyl complex with an electrophile E=Nu releases a five-membered organic ring by reductive elimination. The resulting platinum(0) complex reacts with allyl halide to give the starting metal-$\eta^1$-allyl complex through oxidative addition. The sequence is shown in Scheme II.

In addition to the synthetic potential of these 16-electron complexes, the mechanism of their cycloaddition reactions is a note
worthy area for exploration in its own right. Since a 16-electron complex is coordinatively unsaturated, the unsaturated electrophile E=Nu may first coordinate to the metal center in the cycloaddition reaction. Alternatively, the reactions may proceed the same way as cycloaddition reactions of the 18-electron complexes with the electrophiles E=Nu, i.e., the electrophile attacks at the allylic terminus first.

In the study of cycloaddition reactions of platinum(II)-n^1-allyl complexes with TCNE,^28 two possible mechanisms, initiated by (i) electrophilic attack of TCNE at the allylic double bond, and
(ii) addition of TCNE to the platinum center, have been proposed. However, experimental evidence for the two mechanisms was not conclusive.

Reactions of sulfur dioxide with platinum-alkyl complexes to yield insertion products have been known for many years.\textsuperscript{29} Isolation of five-coordinate intermediates, RPt(SO\textsubscript{2})L\textsubscript{2}Cl(R=C\textsubscript{6}H\textsubscript{5}, L=P(C\textsubscript{2}H\textsubscript{5})\textsubscript{3}, As(C\textsubscript{2}H\textsubscript{5})\textsubscript{3}, Se(C\textsubscript{2}H\textsubscript{5})\textsubscript{2}, Te(C\textsubscript{2}H\textsubscript{5})\textsubscript{2})\textsuperscript{30} suggests that these insertion reactions proceed through attack of SO\textsubscript{2} on the platinum metal followed by migration of the alkyl group. On the other hand, reactions of platinum(II)-\textsuperscript{\textit{n}}\textsuperscript{1}-allyl complexes with sulfur dioxide have not been examined. It is possible that in these reactions the double bond of the allyl fragment may be the point of attack by SO\textsubscript{2}. If so, a different chemistry can result with respect to product and mechanism when compared with the chemistry of reactions of platinum-alkyl complexes with SO\textsubscript{2}.

The research described in this dissertation focused on (1) the protonation-deprotonation reaction sequence of 18-electron transition metal complexes containing a \textgamma-lactam ring, and (2) reactions of platinum(II)-\textsuperscript{\textit{n}}\textsuperscript{1}-allyl complexes with the unsaturated reagents sulfur dioxide and chlorosulfonyl isocyanate. Protonation of these platinum complexes with hexafluorophosphoric acid was investigated to shed further light on mechanism of addition of electrophilic reagents.
EXPERIMENTAL

I. REAGENTS:
   A. Source of Chemicals
      (1) Organics and Organometallics
          Aldrich Chemical Company supplied methanesulfonyl chloride, allyl chloride, crotyl chloride (which contains 20% H$_2$C=CHCHClCH$_3$), 3-chloropropenyl benzene (cinnamyl chloride), phenylpropionic acid, 1,8-bis(dimethylamino)naphthalene (Proton Sponge), triphenylcarbenium hexafluorophosphate, trifluoroacetic acid, and p-toluenesulfonfyl isocyanate. Fisher Chemical Company supplied thionyl chloride and dimethyl amine. Chlorosulfonylisocyanate, trimethyloxonium tetrafluoroborate, lithium aluminum hydride and iron pentacarbonyl were procured from Alfa Chemical Company. Tungsten hexacarbonyl, dimethylphenylphosphine, triethylphosphine, tri-t-butylphosphine, tri-i-propylphosphine, and tricyclohexylphosphine were purchased from Strem Chemical Company. Triethyloxonium hexafluorophosphate and hexafluorophosphoric acid (HPF$_6$*(C$_2$H$_5$)$_2$O) were received from Columbia Organic Chemical Company. p-Toluidine and 1-chloro-3-methyl-2-butene were procured from Eastman Organic Chemical Company. Sulfur dioxide, from Matheson, was dried over P$_2$O$_5$ and conc. H$_2$SO$_4$ before use. 2-Butyn-1-ol and 3-phenyl-2-propyn-1-ol
were purchased from Wiley Organic Chemical Company. Mallinckrodt Inc. supplied aniline.

(2) Chromatographic Materials

Activated magnesium silicate ("Florisil"), 60-100 mesh, was purchased from J. T. Baker Company. Activated neutral alumina was procured from Aldrich Chemical Company and deactivated with 6% H₂O by weight.

(3) NMR Solvents

Deuterochloroform, acetone-d₆, benzene-d₆, and deuterium oxide (99.8%) were purchased from Aldrich Chemical Company.

B. Solvent Purifications

Benzene, toluene, and n-pentane were purified by distillation from sodium. THF, n-hexane, and 1,2-dimethoxyethane were distilled from potassium. Dichloromethane was distilled from P₂O₅ at 41°C. All solvents were distilled immediately before use under an atmosphere of nitrogen.

II. Instrumentation

All infrared spectra were recorded on a Perkin-Elmer Model 283 or a Perkin-Elmer Model 337 spectrophotometer. Spectra of solids were taken as Nujol mulls by using KBr or CsI windows. Spectra of
solutions were obtained by using matched KBr cells in an appropriate solvent. The instruments were calibrated by a polystyrene standard.

Proton NMR spectra were obtained on Varian Associates EM-390, IBM-NR-80, and Bruker AM-500 FT-NMR spectrometers with use of Me$_4$Si as an internal reference. Deuterium-decoupled spectra were obtained on a General Electric NT-300 spectrometer using a decoupling frequency of 46.06 MHz. Phosphorus-31 NMR spectra were recorded on a Bruker HX-90 at a frequency of 36.43 MHz using (MeO)$_3$P=O as an external reference.

Melting points were measured on a Thomas-Hoover melting point apparatus and are uncorrected.

Mass spectral measurements were made on a Kratos MS-30 spectrometer by Mr. C. Weisenberger.

III. Starting Materials
A. Organometallics

The complexes $[n^5$-C$_5$H$_5$Fe(CO)$_2$]$^2$, $^31$ $[(n^5$-CH$_3$C$_6$H$_5$)Fe(CO)]$^2$, $^32$
$n^5$-C$_5$H$_5$(CO)$_2$FeCH$_2$CH=CH$_2$, $^33$ $n^5$-C$_5$H$_5$(CO)$_2$FeCH$_2$CH=CHCH$_3$, $^33$
$n^5$-C$_5$H$_5$(CO)$_2$FeCH$_2$CH=C(CH$_3$)$_2$, $^18$ $n^5$-C$_5$H$_5$(CO)$_2$FeCH$_2$CH=CHC$_6$H$_5$, $^18$
$[(n^5$-CH$_3$C$_6$H$_4$)(CO)$_2$FeCH$_2$CH=CHC$_6$H$_5$, $^34$ $n^5$-C$_5$H$_5$(CO)$_2$FeCH$_2$C≡CCH$_3$, $^35$
$n^5$-C$_5$H$_5$(CO)$_2$FeCH$_2$C≡CC$_6$H$_5$, $^36$ $n^5$-C$_5$H$_5$(CO)$_2$FeCHCH$_2$N(S(O)$_2$CH$_3$)S(O)CH$_2$, $^19$
The carbonylate salt Na\([n^5-C_5H_5W(CO)_3]\) was prepared by the procedure described by R. B. King. The procedure has been modified to reduce the amount of unreacted W(CO)\_6. A typical procedure is described as follows:

A mixture of 1 equivalent sodium in 100 mL of dry toluene was heated to reflux with vigorous stirring to make sodium granules. After the mixture was cooled to room temperature, the solvent was replaced by 100 mL of dry 1,2-dimethoxyethane with a syringe. A two-fold excess of freshly cracked cyclopentadiene was added dropwise to the mixture. The mixture was stirred at 40°C until all of the sodium dissolved. To the resulting pink mixture at room temperature was added 1 equivalent W(CO)\_6. The reaction mixture was refluxed until CO evolution ceased (about 18 hours).
The carbonyl ate salt Na[n^5-C_5H_5W(CO)_3] made by the above procedure was used to prepare the following tungsten-allyl complexes by the addition of the corresponding organic chlorides: n^5-C_5H_5W-(CO)_3CH=CHCCH_3 and n^5-C_5H_5W(CO)_3CH_2CH=C(CH_3)_2.

B. Other Reagents

N-Sulfinylsulfonamide, CH_3SO_2NSO, was prepared by reaction of CH_3SO_2NH_2 with SOCl_2. The disulfonylsulfur diimide S(NSO_2CH_3)_2 was synthesized from a concentrated solution of CH_3SO_2NSO in dry benzene by the addition of a few drops of pyridine. Phenylpropargyl chloride, C_6H_5C=CCH_2Cl; 1-chloro-2-butyne, CH_3C≡CCH_2Cl; and cis-1-chloro-3-deutero-2-butene, cis-CH_2CH≡CDCH_3 were made from corresponding alcohols by published methods. A mixture DCI-D_2O was prepared by reaction of AlCl_3 and D_2O as described in the literature.

Methyl phenylpropiolate, C_6H_5C≡CCOOCH_3, was synthesized by refluxing C_6H_5C≡CCOOH and CH_3OH in the presence of a catalytic amount of H_2SO_4. The compounds trans-CH_2OHCH=CD_6H_5 was made by the reaction of C_6H_5C≡CCOOCH_3 and LiAlH_4; the reaction mixture was then worked up with DCI-D_2O. The compound trans-CH_2ClCH=CD_6H_5 was prepared by the reaction of trans-CH_2OHCH=CD_6H_5 with SOCl_2 using a procedure analogous to that for trans-CH_2ClCH=CHC_6H_5.
IV. General Experimental Procedures

All reactions were carried out under an atmosphere of nitrogen. Standard Schlenk techniques were routinely used. A drybox purged with argon was utilized for handling of the compounds which were very sensitive to air or moisture.

Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

V. Preparation of Eighteen-Electron Complexes (Iron and Tungsten) and Their Reactions

A. Preparation of Iron-Alkyl Complexes Containing a Five-Membered Ring and Their Reactions Involving Protonation-Deprotonation Sequence

Protonation of $\eta^5$-$\text{C}_5\text{H}_5(\text{CO})_2\text{FeCHCH}_2\text{N}(\text{SO})_2\text{CH}_3\text{S}(\text{SO})_2\text{CH}_2$ with $\text{HPF}_6\cdot(\text{C}_2\text{H}_5)_2\text{O}$

A solution of 0.393 g (1.77 mmol) of $\text{HPF}_6\cdot(\text{C}_2\text{H}_5)_2\text{O}$ in 20 mL of CH$_2$Cl$_2$ at -78°C was added to 0.500 g (1.39 mmol) of the title complex (78:22 mixture of diastereomers) in 45 mL of CH$_2$Cl$_2$ also at -78°C. A yellow precipitate formed immediately. The resulting mixture was stirred at -78°C for 10 min, then the temperature was allowed to rise to 25°C in 20 min, and stirring was continued for 25 min. The precipitate was filtered off and washed with CH$_2$Cl$_2$ (2 x
10 mL) to give 0.610 g (87% yield) of yellow product which was $[n^5$-
\[\text{C}_5\text{H}_5(\text{CO})_2\text{Fe}(\text{n}^2-\text{CH}_2=\text{CHCH}_2\text{S}(\text{O})\text{NH}(\text{SO}_2\text{CH}_3))\] $]^+\text{PF}_6^-$. $^1\text{H}$ NMR (acetone-
d$_6$) $\delta$ 6.03 (s, C$_5$H$_5$), 5.03-5.07 (m, CH$_2$=CH), 3.43-3.11 (m, CH$_2$),
3.08 (s, CH$_3$); IR (Nujol) $\nu$(NH) 3295 (w, br), $\nu$(CO) 2070 (vs), 2035
(vs), $\nu$(SO$_2$) 1356 (vs), 1158 (vs), $\nu$(SO) 1088 (vs, br) cm$^{-1}$.

**Deprotonation of $[n^5$-$\text{C}_5\text{H}_5(\text{CO})_2\text{Fe}(\text{n}^2-\text{CH}_2=\text{CHCH}_2\text{S}(\text{O})\text{NH}(\text{SO}_2\text{CH}_3))\] $]^+\text{PF}_6^-$

with Proton Sponge

To a solution of 0.420 g (0.832 mmol) of the title complex in
40 mL of THF at -78°C was added a solution of 0.210 g (0.870 mmol)
of Proton Sponge in 15 mL of THF also at -78°C. The resulting
mixture was stirred at -78°C for 20 min and then at room temperature
for an additional 30 min. The PF$_6^-$ salt of the protonated Proton
Sponge was filtered off, and the solvent was removed from the yellow
filtrate under reduced pressure. The residue was recrystallized
from 40 mL of 1:2 CH$_2$Cl$_2$-n-pentane to yield 0.170 g (0.474 mmol,
57%) of $n^5$-$\text{C}_5\text{H}_5(\text{CO})_2\text{FeCHCH}_2\text{N}(\text{SO}_2\text{CH}_3)\text{S}(\text{O})\text{CH}_2$ which was
characterized by $^1\text{H}$ NMR spectroscopy as a 95:5 mixture of diastereomers. $^1\text{H}$ NMR (chloroform-$d$) $\delta$ 4.89 (s, C$_5$H$_5$, the peak of the minor
diastereomer was at 4.88), 3.0-4.0 (m, 2 CH$_2$), 3.10 (s, CH$_3$), 2.7-
2.9 (m, CH).
Preparation of $\eta^5$-C$_5$H$_5$(CO)$_2$FeCHCH$_2$C(O)N(S(O)$_2$)NHC$_6$H$_5$CH$_2$

The addition of a solution of 0.976 g (6.90 mmol) of ClSO$_2$NCO in 20 mL of CH$_2$Cl$_2$ at -78°C to a solution of 1.50 g (6.89 mmol) of $\eta^5$-C$_5$H$_5$(CO)$_2$FeCH=CH$_2$ in 30 mL of CH$_2$Cl$_2$ also at -78°C resulted in the formation of a yellow precipitate. The temperature of the resulting mixture was allowed to rise to room temperature. Then the mixture was cooled to -60°C and treated with a solution of 2.0 g (22 mmol) of aniline in 30 mL of CH$_2$Cl$_2$ at -60°C. The mixture was allowed to come to room temperature and stirred at 25°C for 30 min. Subsequently, the mixture was filtered, and the solvent was removed from the filtrate in vacuo. The residue was recrystallized from 40 mL of (1:3) CH$_2$Cl$_2$-n-pentane to give a yellow-brown solid. The solid was washed with 5 mL of CH$_2$Cl$_2$ to yield 2.02 g (4.86 mmol, 70%) of yellow product. The IR and $^1$H NMR spectral data are listed in Tables 1 and 2, respectively.

<table>
<thead>
<tr>
<th>M.P.</th>
<th>106°C (dec.)</th>
</tr>
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<tr>
<td>Mass Spectra (FAB) m/e (relative intensity)</td>
<td></td>
</tr>
<tr>
<td>417 ((M + H)$^+$, 11.53)</td>
<td></td>
</tr>
<tr>
<td>361 ((M + H - 2CO)$^+$, 3.10)</td>
<td></td>
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</table>

Preparation of $\eta^5$-C$_5$H$_5$(CO)$_2$FeCHCH(CH$_3$)C(O)N(S(O)$_2$)NHC$_6$H$_5$CH$_2$

To a solution of 1.97 g (8.50 mmol) of $\eta^5$-C$_5$H$_5$(CO)$_2$FeCH$_2$CH=CH-CH$_3$ (2:1 mixture of E diastereomer and Z diastereomer) in 40 mL of CH$_2$Cl$_2$ at -78°C was added a solution of 1.22 g (8.62 mmol) of
ClSO₂NCO in 20 mL of CH₂Cl₂ at -78°C. A precipitate formed during the addition. The temperature of the mixture was allowed to rise to room temperature over 20 min. Most of the precipitate dissolved after the mixture was stirred at 25°C for 5 min. The reaction mixture was cooled to -78°C again and treated with a solution of 1.60 g (1.72 mmol) of aniline in 20 mL of CH₂Cl₂ at -78°C. After the resulting mixture was stirred at -78°C for 5 min, it was allowed to warm to 25°C and stirring was continued for 50 min. The mixture was filtered to remove C₆H₅NH₃Cl generated in the reaction. The filtrate was filtered on a pad of Florisil again to remove excess aniline. The solvent was then removed from the filtrate in vacuo. The n⁵-C₅H₅ resonances of ¹H NMR spectrum of the yellow-brown residue showed that it was n⁵-C₅H₅(CO)₂FeCHCH(CH₃)C(O)N(S(O)₂NH-C₆H₅)CH₂ with 90% of the trans diastereomer and 10% of the cis diastereomer. The residue was further purified by recrystallization from a mixture of CH₂Cl₂ and n-pentane (1:3) to afford 1.87 g (4.35 mmol, 51%) of yellow product. Chromatography on alumina, eluting first with CH₂Cl₂ and then with acetone, did not separate the two diastereomers. The IR and ¹H NMR spectral data are listed in Tables 1 and 2, respectively.

M.P. 156-160°C with decomposition
Mass Spectrum (FAB) m/e (relative intensity)
Preparation of \( n^5-C_5H_5(CO)F_{e C H C} (CH_3)_2C(O)N(S(O)_{2NHC6H_5})_{CH_2} \)

Addition of 0.976 g (6.89 mmol) of CISO\(_2\)NCO in 15 mL of CH\(_2\)Cl\(_2\) at -78°C to a solution of 1.86 g (6.61 mmol) of \( n^5-C_5H_5(CO)_{2FeCH_2-CH=CH(CH_3)_2} \) in 40 mL of CH\(_2\)Cl\(_2\) also at -78°C resulted in the formation of a yellow precipitate. After 5 min of stirring at -78°C, the mixture was allowed to warm to room temperature. After 5 min at 25°C, the mixture was cooled to -78°C. A solution of 2.5 g (27 mmol) of aniline in 10 mL of CH\(_2\)Cl\(_2\) was added to the reaction mixture at -78°C. The resulting mixture was allowed to warm to room temperature and stirred for 1 hr. The mixture was filtered to remove the H\(_3\)NC\(_6\)H\(_5\)Cl salt produced in the reaction.

The filtrate was filtered by suction through Florisil to remove excess aniline. The filtrate was evaporated to dryness under reduced pressure. The residue was recrystallized from 40 mL of 1:3 CH\(_2\)Cl\(_2\)-n-pentane to give 2.27 g (4.46 mmol, 69%) of a yellow product which was identified by comparison of its \(^1\)H NMR and IR data with those of the compound \( n^5-C_5H_5(CO)_{2FeCHC(CH_3)_2C(O)N(S(O)_{2NHC6H_5})_{CH_2} \) prepared by Yamamoto.\(^{14}\)
Table 1

Major Infrared Absorption Bands for Complexes

\( \eta^5-C_5H_5(CO)_2FeCHCR'^1R'^2C(0)N(S(0))_2NHCH_5CH_2a \)

<table>
<thead>
<tr>
<th>R^1</th>
<th>R^2</th>
<th>( \nu(NH) \text{cm}^{-1} )</th>
<th>( \nu(C=O) \text{cm}^{-1} )</th>
<th>( \nu(C=O) \text{cm}^{-1} )</th>
<th>( \nu(SO_2) \text{cm}^{-1} )</th>
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<tr>
<td>H</td>
<td>H</td>
<td>3315 (ms)</td>
<td>2004 (vs)</td>
<td>1961 (vs)</td>
<td>1716 (s)</td>
</tr>
<tr>
<td>H</td>
<td>CH₃</td>
<td>3218 (s, br)</td>
<td>2003 (s)</td>
<td>1950 (s)</td>
<td>1712 (s)</td>
</tr>
<tr>
<td>CH₃</td>
<td>H</td>
<td>3220 (m, br)</td>
<td>2004 (s)</td>
<td>1950 (s)</td>
<td>1710 (s)</td>
</tr>
<tr>
<td>H</td>
<td>C₆H₅</td>
<td>3265 (s, sharp)</td>
<td>2001 (vs)</td>
<td>1951 (vs, br)</td>
<td>1722 (vs)</td>
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<td>C₆H₅</td>
<td>H</td>
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<td>1950 (vs)</td>
<td>1702 (vs)</td>
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^a As Nujol mull.
<table>
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<tr>
<th>R^1</th>
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<th>C_5H_5 (δ, ppm)</th>
<th>Other Protons (δ, ppm)</th>
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<tr>
<td>H_d</td>
<td>H_e</td>
<td>4.74 (s)</td>
<td>1.98-2.75 (m, H_c, H_d and H_e), 3.14-3.53 (m, H_a)</td>
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<td>3.67-3.97 (m, H_b), 6.46 (s, NH), 6.98-7.53 (m, C_6H_5)</td>
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<td>(trans diastereomer)</td>
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<td>H_d</td>
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<td>4.71 (s)</td>
<td>1.18 (d, CH_3, J=6.7 Hz), 1.83 (m, H_d), 2.04 (m, H_c)</td>
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<tr>
<td>CH_3</td>
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<td>3.43 (q, H_a), 3.79 (q, H_b), 6.47 (s, NH),</td>
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<td>7.13-7.34 (m, C_6H_5)</td>
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<tr>
<td>H_d</td>
<td>C_6H_5</td>
<td>4.43 (s)</td>
<td>2.47 (m, H_c), 3.25 (d, H_d, J(H_c, H_d)=12.3 Hz), 3.46</td>
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<td></td>
<td>(q, H_a, J(H_a, H_b)=9.6 Hz, J(H_a, H_c)=11.6 Hz), 3.90</td>
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<tr>
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<td></td>
<td></td>
<td>(q, H_b, J(H_c, H_d)=9.0 Hz), 6.47 (s, NH), 6.94-7.45</td>
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<td></td>
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<td>(c, C_6H_5 and NC_6H_5)</td>
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</table>
Table 2 (continued)  

\[ \text{H} - \text{S} - \text{N}' \text{H} \]

\[ \text{H} - \text{N} - \text{M R} \text{ Data for Complexes } n^5-\text{C}_6\text{H}_5(\text{CO}_2\text{F}) \]

\[ \text{H} \]

\[ \text{O} \]

\[ \text{N}^\cdots \text{N} \text{ Ph} \]

\[ \text{C} \]

\[ \text{O} \]

\[ \text{N} \]

<table>
<thead>
<tr>
<th>R&lt;sup&gt;1&lt;/sup&gt;</th>
<th>R&lt;sup&gt;2&lt;/sup&gt;</th>
<th>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt; (δ, ppm)</th>
<th>Other Protons (δ, ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;</td>
<td>H&lt;sub&gt;d&lt;/sub&gt;</td>
<td>4.58 (s)</td>
<td>3.04 (m, H&lt;sub&gt;c&lt;/sub&gt;), 3.48 (d, H&lt;sub&gt;d&lt;/sub&gt;, J(H&lt;sub&gt;C&lt;/sub&gt;, H&lt;sub&gt;d&lt;/sub&gt;)=8.4 Hz)</td>
</tr>
<tr>
<td>(cis diastereomer)</td>
<td></td>
<td></td>
<td>3.72 (q, H&lt;sub&gt;a&lt;/sub&gt;, J(H&lt;sub&gt;a&lt;/sub&gt;, H&lt;sub&gt;c&lt;/sub&gt;)=11.8 Hz), J(H&lt;sub&gt;a&lt;/sub&gt;, H&lt;sub&gt;b&lt;/sub&gt;)=10.3 Hz) 3.96 (q, H&lt;sub&gt;b&lt;/sub&gt;, J(H&lt;sub&gt;b&lt;/sub&gt;, H&lt;sub&gt;c&lt;/sub&gt;)=7.7 Hz), 6.49 (s, NH), 6.72-7.40 (c, C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt; and NC&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;)</td>
</tr>
</tbody>
</table>

\[ ^a \text{In CDCl}_3 \text{ solution.} \]
Preparation of trans-n^5-C_5H_5(CO)_2FeCHCH(C_6H_5)C(O)N(S(O)_2NHC_6H_5)CH_2

To a solution of 2.10 g (7.15 mmol) of trans-n^5-C_5H_5(CO)_2FeCH_2=CHC_6H_5 in 30 mL of CH_2Cl_2 at -78°C was added a solution of 1.01 g (7.15 mmol) of ClSO_2NCO in 15 mL of CH_2Cl_2 at -78°C. A yellow precipitate formed immediately. After the mixture was allowed to come to room temperature and stirred at 25°C for 5 min, most of the precipitate dissolved. The mixture was stirred at room temperature for 1 hr, and the C_6H_5NH_3Cl salt was removed from the mixture by filtration. The filtrate was filtered again by suction through Florisil to remove excess aniline, and then the solvent was evaporated under reduced pressure. The residue was recrystallized from 60 mL of 1:3 CH_2Cl_2-n-pentane to afford 2.40 g (4.88 mmol, 68%) of trans-n^5-C_5H_5(CO)_2FeCHCH(C_6H_5)C(O)N(S(O)_2NHC_6H_5)CH_2. The IR and ^1H NMR spectral data are listed in Tables 1 and 2, respectively.

Preparation of n^5-C_5H_5(CO)_2FeCHCH(C_6H_5)C(O)N(S(O)_2NCH_3)_2CH_2

A solution of 1.04 g (7.35 mmol) of ClSO_2NCO in 15 mL of CH_2Cl_2 at -78°C was added to a solution of 2.13 g (7.25 mmol) of n^5-C_5H_5-(CO)_2FeCH_2CH=CHC_6H_5 in 40 mL of CH_2Cl_2 at -78°C. A yellow precipitate formed immediately. After being stirred at 25°C for 5 min, the mixture was cooled to -78°C. A solution of about 1.5 g (33 mmol) of dimethylamine in 20 mL of CH_2Cl_2 at -78°C was added to the mixture also at -78°C. The resulting mixture was allowed to warm to
room temperature, stirred for 3 hours, and then filtered off. The solvent was removed from the filtrate in vacuo. The residue was recrystallized from a mixture of CH$_2$Cl$_2$ and n-pentane (1:3) to yield 1.72 g (3.58 mmol, 49%) of a yellow product. Spectroscopic data: $^1$H NMR (chloroform-d) $\delta$ 7.37-7.58 (m, C$_6$H$_5$), 4.52 (s, C$_6$H$_5$), 3.26-4.29 (m, CH$_2$, FeCH and CHCO), 2.98 (s, CH$_3$); IR (Nujol) $\nu$(C=O) 2000 (vs), 1948 (vs), $\nu$(C=O) 1709 (s), $\nu$(SO$_2$) 1369 (ms), 1158 (s) cm$^{-1}$. M.P.: 180-181°C with decomposition. Anal. Calcd for C$_{19}$H$_{20}$Fe-SN$_2$O$_5$: C, 51.37; H, 4.54. Found: C, 51.27; H, 4.57.

Protonation of trans-$^5$-C$_{5}$H$_5$(CO)$_2$FeCHCH(CH$_3$)C(O)NS(O)$_2$NH$_2$C$_6$H$_5$CH$_2$ with HPF$_6$·(C$_6$H$_5$)$_2$O

A solution of 0.847 g (3.85 mmol) of HPF$_6$·(C$_6$H$_5$)$_2$O in 25 mL of CH$_2$Cl$_2$ at -78°C was added to a solution of 1.05 g (2.43 mmol) of the title complex (90:10 mixture of trans diastereomer and cis diastereomer) in 50 mL of CH$_2$Cl$_2$ also at -78°C. The resulting mixture was stirred at -78°C for 25 min, and the temperature of the mixture was then allowed to rise to room temperature in 20 min. During this process, a large amount of yellow precipitate formed at ca. -30°C. The precipitate dissolved after the mixture was stirred at 25°C for 10 min, and the color of the mixture changed to red. After an additional 5 min of stirring at room temperature, a yellow precipitate started to form slowly. The mixture was continuously stirred
for 1 hour, and the precipitate was then filtered off and washed with \( \text{CH}_2\text{Cl}_2 \) (5 mL x 3) to give 0.810 g (1.41 mmol, 58%) of the cis diastereomer (major diastereomer) of \( \eta^5\text{-C}_5\text{H}_5(\text{CO})_2\text{Fe}(\eta^2\text{-CH}_2=\text{CHCH-}
\text{(CH}_3\text{)C(O)NH(S(O)\text{)}_2\text{NHC}_6\text{H}_5})\text{]}^+\text{PF}_6^- \). The physical properties and IR and \( ^1\text{H NMR} \) spectral data are listed in Tables 3, 4 and 5, respectively.

Deprotonation of cis-\[\eta^5\text{-C}_5\text{H}_5(\text{CO})_2\text{Fe}(\eta^2\text{-CH}_2=\text{CHCH(CH}_3\text{)C(O)NH(S(O)\text{)}_2\text{NHC}_6\text{H}_5})\text{]}^+\text{PF}_6^- \]

To a solution of 0.485 g (0.842 mmol) of the title complex, obtained from the above reaction, in 45 mL of THF at -78°C was added a solution of 0.230 g (0.933 mmol) of Proton Sponge in 15 mL of THF also at -78°C. The temperature of the resulting mixture was then allowed to rise to room temperature over 20 min. A white precipitate formed at ca. -60°C during the process of warming. After being stirred at 25°C for 15 min, the mixture was filtered. The solvent was removed from the filtrate \textbf{in vacuo}. The residue was recrystallized from 50 mL of 1:3 \( \text{CH}_2\text{Cl}_2\)-n-pentane to yield 0.320 g (0.744 mmol, 88%) of yellow crystals of \( \eta^5\text{-C}_5\text{H}_5(\text{CO})_2\text{FeCHCH(CH}_3\text{)C(O)N(S(O)\text{)}_2\text{NHC}_6\text{H}_5})\text{CH}_2 \) (10:90 mixture of the trans and cis diastereomers; the ratio of the two diastereomers was determined by measuring integration of the \( \eta^5\text{-C}_5\text{H}_5 \) and methyl peaks in the \( ^1\text{H NMR} \) spectrum).
analytical data and IR and $^1$H NMR data of the cis diastereomer are listed in Tables 11, 1, and 2, respectively.

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<th>Property</th>
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<tr>
<td>Mass Spectrum (FAB)</td>
<td>m/e (relative intensity)</td>
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<td>431 ((M + H)$^+$, 45.53)</td>
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</tr>
<tr>
<td>375 ((M + H - CO)$^+$, 20.42)</td>
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</table>

Protonation of cis-$^5$-C$_5$H$_5$(CO)$_2$FeCHCH(CH$_3$)C(O)N(S(O)$_2$NHC$_6$H$_5$)CH$_2$ with HPF$_6$·(C$_2$H$_5$)$_2$O and Deprotonation of the Resulting Salt with Proton Sponge

A solution of 0.250 g (1.14 mmol) of HPF$_6$·(C$_2$H$_5$)$_2$O in 25 mL of CH$_2$Cl$_2$ at -78°C was added to a solution of 0.300 g (0.698 mmol) of the title complex (10:90 mixture of trans diastereomer and cis diastereomer) in 40 mL of CH$_2$Cl$_2$ also at -78°C. After the resulting mixture was stirred at -78°C for 15 min, a yellow precipitate formed. More precipitate formed during the process of warming to room temperature. The mixture was stirred at 25°C for 70 min. The color of the solution changed from yellow to red, but the rate of color change was much slower than that for protonation of the trans diastereomer. The yellow precipitate which formed at low temperature did not dissolve at room temperature. After the mixture was filtered, the yellow precipitate was washed with CH$_2$Cl$_2$ (10 mL x 2) to afford 0.242 g (0.420 mmol, 60%) of the cis diastereomer (major
diastereomer) of the protonated salt \([n^{5}-\text{C}_5\text{H}_5(\text{CO})_2\text{Fe}(n^{2}-\text{CH}_2=\text{CHCH-}\
(\text{CH}_3)\text{C(O)NH(S(O)}_2\text{NHC}_6\text{H}_5))]+\text{PF}_6^{-}\). The resulting protonated salt was
deeprotonated with Proton Sponge in THF to give predominately cis-\(n^{5}-\text{C}_5\text{H}_5(\text{CO})_2\text{FeCHCH(}\
\text{CH}_3)\text{C(O)N(S(O)}_2\text{NHC}_6\text{H}_5)\text{CH}_2\). The \(1^H\) NMR spectrum of
the compound showed that it contained 10% of the trans diastereomer and 90% of the cis diastereomer. The ratio of the diastereomers was
determined by measuring integration of the \(n^{5}-\text{C}_5\text{H}_5\) and \(\text{CH}_3\)
resonances in the \(1^H\) NMR spectrum.

**Storage of a Mixture of trans- and cis-\(n^{5}-\text{C}_5\text{H}_5(\text{CO})_2\text{FeCHCH(}\
\text{CH}_3)\text{C(O)N(S(O)}_2\text{NHC}_6\text{H}_5)\text{CH}_2\) in \(\text{CH}_2\text{Cl}_2\)**

A solution of 80 mg of a mixture containing the trans and cis
diastereomers (60:40) of the title complex in 10 mL of \(\text{CH}_2\text{Cl}_2\) was
stirred at room temperature for 20 hours. The solution was then
filtered. The solvent was removed from the filtrate in vacuo. By
measuring the integration of the \(n^{5}-\text{C}_5\text{H}_5\) and \(\text{CH}_3\) peaks in the \(1^H\) NMR
spectrum of the residue, the ratio of the trans to the cis diaster-
emer was shown to be unchanged (60:40). Thus, no conversion
occurred between the trans and the cis diastereomers in the absence
of acid.
Protonation of trans-$n^5$-C$_5$H$_5$(CO)$_2$FeCHCH(CH$_3$)C(O)N(S(O)$_2$NHC$_6$H$_5$)CH$_2$

with HPF$_6$·(C$_2$H$_5$)$_2$O at -10°C

To a solution of 0.407 g (0.944 mmol) of the title complex (90% trans diastereomer/10% cis diastereomer) in 40mL of CH$_2$Cl$_2$ at -78°C was added a solution of 0.225 g (1.02 mmol) of HPF$_6$·(C$_2$H$_5$)$_2$O in 20 mL of CH$_2$Cl$_2$ also at -78°C. The resulting mixture was stirred at -78°C for 20 min, and when no reaction was indicated by the absence of precipitation, the reaction temperature was allowed to warm to -10°C. During the process of warming up, a large amount of yellow precipitate formed at ca. -30°C. The mixture was stirred at -10°C for 40 min. The yellow precipitate was collected by filtration at -10°C and washed with CH$_2$Cl$_2$ (10 mL x 3) to afford 0.270 g (0.469 mmol, 47%) of [n$^5$-C$_5$H$_5$(CO)$_2$Fe(n$^2$-CH$_2$=CHCH(CH$_3$)C(O)NH(S(O)$_2$NH-C$_6$H$_5$))]$^+$PF$_6^-$ (90% trans diastereomer/10% cis diastereomer). The ratio of the two diastereomers was determined by deprotonation of the protonated salt with Proton Sponge in THF. The physical properties and IR and $^1$H NMR spectral data are listed in Tables 3, 4 and 5, respectively.
Table 3
Some Physical Properties and Analytical Data for Complexes

\[ [n^5-C_5H_5(CO)_2Fe(n^2-CH=CHCR_1R_2C(O)NH(S(O)NHC_6H_5))]^+PF_6^- \]

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<th>R(^2)</th>
<th>Color</th>
<th>M.P.</th>
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<th>%C Found</th>
<th>%H Calcd.</th>
<th>%H Found</th>
<th>%N Calcd.</th>
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<tbody>
<tr>
<td>H</td>
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<td>56-58°C (dec.)</td>
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<tr>
<td>H</td>
<td>H</td>
<td>yellow</td>
<td>59-62°C (dec.)</td>
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</tr>
<tr>
<td>CH(_3)</td>
<td>H</td>
<td>yellow</td>
<td>91-93°C (dec.)</td>
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<tr>
<td>CH(_3)</td>
<td>CH(_3)</td>
<td>yellow</td>
<td>decomposed at room temperature</td>
<td>---</td>
<td>---</td>
<td>---</td>
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<td>---</td>
</tr>
<tr>
<td>C(_6)H(_5)</td>
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<td>94-96°C (dec.)</td>
<td>43.28</td>
<td>42.48</td>
<td>3.32</td>
<td>3.28</td>
<td>4.39</td>
<td>4.44</td>
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</table>
Table 4
Major Infrared Absorption Bands for Complexes

\[
[n^5-C_5H_5(CO)_2Fe(n^2-CH_2=CHCR_1R_2C(0)NH(S(0)_2NH_5C_6H_5))]+PF_6^-^a
\]

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<thead>
<tr>
<th>( R^1 )</th>
<th>( R^2 )</th>
<th>( \nu(NH) ) cm(^{-1} )</th>
<th>( \nu(C=0) ) cm(^{-1} )</th>
<th>( \nu(C=0) ) cm(^{-1} )</th>
<th>( \nu(SO_2) ) cm(^{-1} )</th>
<th>( \nu(PF_6) ) cm(^{-1} )</th>
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<tbody>
<tr>
<td>H</td>
<td>H</td>
<td>3317 (m)</td>
<td>2078 (s)</td>
<td>1716 (s)</td>
<td>1365 (s)</td>
<td>851 (s, br)</td>
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<tr>
<td></td>
<td></td>
<td>3248 (m)</td>
<td>2035 (s)</td>
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<td>1165 (s)</td>
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<tr>
<td>H</td>
<td>( \text{CH}_3 ) (trans diastereomer)</td>
<td>3320 (m, br)</td>
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<td>1365 (ms)</td>
<td>841 (s, br)</td>
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<td>3258 (s, br)</td>
<td>2039 (s)</td>
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<td>1174 (s)</td>
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<tr>
<td>( \text{CH}_3 )</td>
<td>H (cis diastereomer)</td>
<td>3500 (w, br)</td>
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<td>1708 (s)</td>
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<td>833 (s, br)</td>
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<td>3220 (s, br)</td>
<td>2034 (s)</td>
<td></td>
<td>1176 (s)</td>
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<tr>
<td>( \text{C}_6\text{H}_5 )</td>
<td>H (cis diastereomer)</td>
<td>3378 (m, sharp)</td>
<td>2078 (vs)</td>
<td>1720 (s)</td>
<td>1366 (s)</td>
<td>842 (s, br)</td>
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<td></td>
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<td>3249 (s, br)</td>
<td>2040 (vs)</td>
<td></td>
<td>1177 (s)</td>
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</table>

^a As Nujol mull.
Table 5

$^1$H NMR Data for Complexes

$[\text{n}^5-\text{C}_5\text{H}_5(\text{CO})_2\text{Fe(n}^2-\text{CH}_2=\text{CHR}_1\text{C}(\text{O})\text{NH(S(O)}_2\text{NH}_2\text{C}_6\text{H}_5))]^+\text{PF}_6^-^a$

<table>
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<tr>
<th>R1</th>
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<th>Other Absorptions</th>
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<td>7.13-7.87 (m, C6H5)</td>
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<td>CH3</td>
<td>5.75 (s)</td>
<td>7.03-7.98 (m, C6H5)</td>
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<td>1.21 (d, J=7 Hz)</td>
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<tr>
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<td>7.03-7.98 (m, C6H5)</td>
<td></td>
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<tr>
<td>CH3</td>
<td>H</td>
<td>5.75 (s)</td>
<td>7.12-7.87 (m, C6H5)</td>
</tr>
<tr>
<td></td>
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<td>1.21 (d, J=7 Hz)</td>
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<tr>
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<td>7.12-7.87 (m, C6H5)</td>
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<tr>
<td>C6H5</td>
<td>H</td>
<td>5.97 (s)</td>
<td>6.97-7.48 (m, C6H5 and NC6H5)</td>
</tr>
</tbody>
</table>

$^a$ In acetone-$_d_6$ solution;

$^b$ Since the complexes decomposed rapidly in acetone-$_d_6$, only major peaks were distinguished.
Storage of trans-[^5-C5H5(CO)2Fe(n2-CH2=CHCH(CH3)C(O)NH(S(O)2NHC6-H5))]\textsuperscript{+}PF6\textsuperscript{-} in CH2Cl2

(a) In the Presence of Acid

To a suspension of 0.160 g (0.278 mmol) of the title complex in 25 mL of CH2Cl2 was added 0.060 g (0.272 mmol) of HPF6\textsuperscript{+}(C2H5)2O at room temperature. The suspension was stirred at 25°C for 7 min as the color changed from light yellow to slightly red. After 10 min of stirring, most of the solid disappeared and the color of the mixture turned red. A large quantity of yellow precipitate formed when the mixture was stirred for an additional 10 min. The mixture was stirred at 25°C for 45 min. The yellow precipitate was then filtered off and washed with 5 mL of CH2Cl2 to give 0.075 g of the yellow product [^5-C5H5(CO)2Fe(n2-CH2=CHCH(CH3)C(O)NH(S(O)2NHC6-H5))]\textsuperscript{+}PF6\textsuperscript{-}. Deprotonation of the yellow precipitate with Proton Sponge in THF showed that the yellow precipitate contained 10% trans diastereomer and 90% cis diastereomer.

(b) In the Absence of Acid

A suspension of 0.200 g (0.347 mmol) of the title complex in 30 mL of CH2Cl2 was stirred at room temperature. After 10 min the suspension showed no apparent change, and the color was still light yellow. However, after 20 min of stirring, the amount of solid in the suspension decreased, and the suspension changed color to
yellow. The mixture was stirred for 45 min and then filtered. The yellow precipitate collected was washed with 5 mL of CH$_2$Cl$_2$ to give 0.140 g (0.243 mmol) of the complex \([\eta^5\text{-C}_5\text{H}_5(\text{CO})_2\text{Fe}(\text{H}_2\text{CH}=\text{CH}-\text{(CH}_3)\text{C}(\text{O})\text{NH}(\text{S}(\text{O})\text{NH}\text{C}_6\text{H}_5))]+\text{PF}_6^-\). Deprotonation of the yellow precipitate with Proton Sponge in THF showed it to contain 45% trans diastereomer and 55% cis diastereomer.

**Protonation of \(\eta^5\text{-C}_5\text{H}_5(\text{CO})_2\text{FeCHCH}_2\text{C(O)N(S(O)NH}\text{C}}_6\text{H}_5)\text{CH}_2\) with \(\text{HPF}_6^-(\text{C}_2\text{H}_5)_2\text{O}\)**

A solution of 0.359 g (1.63 mmol) of \(\text{HPF}_6^-(\text{C}_2\text{H}_5)_2\text{O}\) in 15 mL of CH$_2$Cl$_2$ at -78°C was added to a solution of 0.500 g (1.20 mmol) of the title complex in 40 mL of CH$_2$Cl$_2$ also at -78°C. After the resulting mixture was stirred at -78°C for 5 min, the reaction temperature was allowed to rise to room temperature in 20 min. During the process of warming up, a large quantity of yellow precipitate formed at ca. -30°C. The yellow precipitate remained suspended in solution when the temperature of the mixture reached room temperature. The mixture was continuously stirred at 25°C for 1 hour, and then it was filtered. The yellow precipitate collected was washed with CH$_2$Cl$_2$ (5 mL x 2). This sticky solid was dried under vacuum to give 0.455 g (0.810 mmole, 67%) of a yellow product.
shown to be \([n^5-C_5H_5(CO)_2Fe(n^2-CH_2=CHCH_2C(O)NH(S(O)_2NH-C_6H_5)C(0)NH(S(O)_2NH-C_6H_5))]+PF_6^-\).

The physical properties and IR spectral data are listed in Tables 3 and 4, respectively.

**Deprotonation of \([n^5-C_6H_6(CO)_2Fe(n^2-CH_2=CHCH_2C(O)NH(S(O)_2NH-C_6H_5))]^-PF_6^-\) with Proton Sponge**

To a solution of 0.230 g (0.409 mmol) of the title complex in 40 mL of THF at -78°C was added a solution of 0.099 g (0.41 mmol) of Proton Sponge in 15 mL of THF also at -78°C. After 3 min of stirring at -78°C, the temperature of the mixture was allowed to rise to room temperature. After being stirred at 25°C for 10 min, the mixture was filtered. The solvent was removed from the filtrate in vacuo. The residue was recrystallized from a mixture of CH_2Cl_2 and n-pentane (1:5) to give 0.166 g (0.399 mmol, 98%) of a yellow product. The product was identified by comparison of its \(^1H\) NMR spectrum with that of an authentic sample of \(n^5-C_5H_5(CO)_2FeCHCH_2-C(0)NH(S(O)_2NH-C_6H_5)C(0)NH(S(O)_2NH-C_6H_5)CH_2\).

**Protonation of \(n^5-C_5H_5(CO)_2FeCHC(CH_3)_2C(O)NH(S(O)_2NH-C_6H_5)CH_2\) with \(HPF_6^-(C_2H_5)_2O\)**

(a) **At Room Temperature**

To a solution of 0.325 g (0.678 mmol) of the title complex in 25 mL of CH_2Cl_2 at -78°C was added a solution of 0.165 g (0.750
mmol) of HPF$_6^\cdot$(C$_2$H$_5$)$_2$O in 15 mL of CH$_2$Cl$_2$ also at -78°C. After the mixture was stirred at -78°C for 5 min, the reaction temperature was allowed to come to room temperature in 20 min. When the temperature reached around -30°C, a large amount of yellow precipitate formed. After being stirred for 10 min at 25°C, the mixture changed to a red solution. The mixture was then filtered, and the solvent was removed from the filtrate. The red residue was recrystallized from a mixture of CH$_2$Cl$_2$ and n-pentane (3:1) to give 0.090 g (0.30 mmol, 44%) of red crystals of the possible complex n$^5$-C$_5$H$_5$(CO)$_2$FePF$_6$ or (n$^5$-C$_5$H$_5$(CO)$_2$Fe(H$_2$O)PF$_6$). Characterization of the complex: m.p. 128°C dec; $^1$H NMR (acetone-$_d_6$) $\delta$ 5.52 (s, C$_5$H$_5$); IR (Nujol) $\nu$(C=O) 2052 (s), 2000 (s), $\nu$(PF$_6$) 840 (s, br), $\delta$ (PF$_6$) 558 (m) cm$^{-1}$. The complex, n$^5$-C$_5$H$_5$(CO)$_2$FePF$_6$, decomposed in acetone to form [n$^5$-C$_5$H$_5$(CO)$_2$Fe- acetone]$^+PF_6^-$. Spectroscopic data: $^1$H NMR (acetone-$_d_6$) $\delta$ 5.69 (s, C$_5$H$_5$).

(b) At 0°C

To a solution of 0.807 g (1.68 mmol) of the title complex in 50 mL of CH$_2$Cl$_2$ at -78°C was added a solution of 0.561 g (2.55 mmol) of HPF$_6^\cdot$(C$_2$H$_5$)$_2$O in 20 mL of CH$_2$Cl$_2$ also at -78°C. The resulting mixture was stirred at -78°C for 15 min. The reaction temperature was then allowed to rise to 0°C. When the temperature reached about -30°C, yellow precipitate formed. The mixture was stirred at 0°C
for 20 min. Since the yellow precipitate was thermally unstable, the reaction mixture was cooled to -78°C. The yellow precipitate was then filtered off at low temperature and washed with 10 mL of cold CH₂Cl₂ to afford 0.60 g (0.96 mmol, 57%) of \([n^5-C_5H_5(CO)_2Fe(n^2-CH_2=CH(CH_3)C(O)NH(S(O)_2NHC_6H_5))]^{+}\text{PF}_6^-\). The physical properties are listed in Table 3. Because the complex decomposes at room temperature, no satisfactory spectroscopic data could be obtained.

**Deprotonation of \([n^5-C_5H_5(CO)_2Fe(n^2-CH_2=CH(CH_3)C(O)NH(S(O)_2NHC_6H_5))]^{+}\text{PF}_6^-\) with Proton Sponge**

A 100 mL Schlenk flask was charged with 0.60 g (0.96 mmol) of the title complex, prepared from the above reaction, at -78°C under nitrogen. To dissolve the complex, 40 mL of THF at -78°C was added to the flask. A solution of 0.270 g (1.12 mmol) of Proton Sponge in 20 mL of THF at -78°C was then introduced. After 25 min of stirring at -78°C, a white precipitate formed. The temperature of the mixture was allowed to rise to room temperature in 20 min. The mixture was stirred at 25°C for 20 min and filtered. After the solvent was removed from the filtrate under reduced pressure, the residue was recrystallized from 30 mL of a mixture of CH₂Cl₂ and n-pentane (1:2) to afford 0.300 g (0.626 mmol, 65%) of the yellow product \(n^5-C_5H_5(CO)_2FeCHC(CH_3)C(O)N(S(O)_2NHC_6H_5)CH_2\), which was identified by comparison with an authentic sample.
Reaction of $n^5$-$C_5H_5(CO)_2FeCH_3$ with $HPF_6^-(C_2H_5)_2O$

To a yellow-brown solution of 0.500 g (2.60 mmol) of the title complex in 20 mL of $CH_2Cl_2$ at room temperature was added 0.65 g (3.0 mmol) of $HPF_6^-(C_2H_5)_2O$. A gas vigorously evolved immediately, and the resulting mixture changed color to red. The mixture was stirred for 5 min, and the solvent was then removed in vacuo. The red residue was recrystallized from 30 mL of 1:2 $CH_2Cl_2$ and n-pentane to afford 0.740 g (2.30 mmol, 88%) of a red product, $n^5$-$C_5H_5(CO)_2FePF_6$ (or $n^5$-$C_5H_5(CO)_2FePF_6\cdot2H_2O$). IR (Nujol) $\nu(C=O)$ 2052 (s), 2000 (s), $\nu(PF_6)$ 840 (s, br), $\delta(PF_6)$ 558 (m) cm$^{-1}$. Anal. Calcd. for $C_7H_{11}FeO_4PF_6$: C, 23.86; H, 2.87. Found: C, 23.49; H, 2.53.

Protonation of trans-$n^5$-$C_5H_5(CO)_2FeCHCH(C_5H_5)C(O)N(S(O)_2NH)_C_6H_5CH_2$ with $HPF_6^-(C_2H_5)_2O$

A solution of 0.455 g (2.07 mmol) of $HPF_6^-(C_2H_5)_2O$ in 15 mL of $CH_2Cl_2$ at -78°C was added to a solution of 0.500 g (1.01 mmol) of the title complex in 35 mL of $CH_2Cl_2$ at -78°C. The resulting mixture was stirred at -78°C for 20 min, and the temperature of the reaction mixture was then allowed to rise to room temperature in 20 min. When the temperature reached ca. -60°C, a small amount of yellow precipitate formed. After the mixture was stirred at room temperature for 2 min, all of the yellow precipitate dissolved, and the color of the mixture turned red. A large amount of yellow
precipitate formed after the mixture was stirred at room temperature for 15 min. After being stirred for an additional 45 min, the mixture was filtered. The yellow precipitate was washed with CH₂Cl₂ (5 mL x 3) to yield 0.364 g (0.571 mmol, 57%) of the cis-[η⁵-C₅H₅(CO)₂Fe(η²-CH₂=CHCH(C₆H₅)C(O)NH(S(O)₂NHC₆H₅))]+PF₆⁻. The physical properties and IR spectral data are listed in Tables 3 and 4, respectively.

Deprotonation of cis-[η⁵-C₅H₅(CO)₂Fe(η²-CH₂=CHCH(C₆H₅)C(O)NH(S(O)₂NHC₆H₅))]+PF₆⁻ with Proton Sponge

A solution of 0.080 g (0.33 mmol) of Proton Sponge in 15 mL of THF at -78°C was added to a solution of 0.160 g (0.251 mmol) of the title complex, prepared from the above reaction, in 40 mL of THF also at -78°C. After the resulting mixture was stirred at -78°C for 5 min, a white precipitate formed. The temperature of the mixture was allowed to come to room temperature. The mixture was stirred at 25°C for 20 min and then filtered to remove [1,8-N(CH₃)₂C₁₀H₆NH(CH₃)₂]⁺PF₆⁻. Removal of the solvent from the filtrate gave a yellow-brown residue. The residue was recrystallized from 30 mL of a mixture of CH₂Cl₂ and n-pentane (1:3) to yield 0.112 g (0.227 mmol, 91%) of cis-η⁵-C₅H₅(CO)₂FeCHCH(C₆H₅)C(O)N(S(O)₂NHC₆H₅)CH₂. The IR and ¹H NMR data are listed in Tables 1 and 2.

M.P. 181-185°C with decomposition

Mass Spectrum (FAB) m/e (relative intensity)
Protonation of cis-$\eta^5$-C$_5$H$_5$(CO)$_2$FeCHCH(C$_6$H$_5$)C(0)N(S(0)$_2$NH$_2$C$_6$H$_5$)CH$_2$ with HPF$_6$-$(C_2H_5)_2$O and Deprotonation of Resulting Product with Proton Sponge

To a solution of 0.264 g (0.537 mmol) of the title complex in 40 mL of CH$_2$Cl$_2$ at -78°C was added a solution of 0.240 g (1.09 mmol) of HPF$_6$-$(C_2H_5)_2$O in 20 mL of CH$_2$Cl$_2$ also at -78°C. The mixture was stirred at -78°C for 20 min and then allowed to warm to room temperature. During the process of warming, a large amount of yellow precipitate formed at ca. -60°C. The mixture was stirred at room temperature for 10 min and then filtered. The yellow precipitate was washed with CH$_2$Cl$_2$ (5 mL x 2) to give 0.285 g (0.447 mmol, 83%) of cis-$\eta^5$-C$_5$H$_5$(CO)$_2$Fe($\eta^2$-C$_2$=CHCH(C$_6$H$_5$)C(0)NH(S(0)$_2$NH$_2$C$_6$H$_5$))]+PF$_6$-.

The deprotonation of the protonated salt with Proton Sponge in THF only gave cis-$\eta^5$-C$_5$H$_5$(CO)$_2$FeCHCH(C$_6$H$_5$)C(0)N(S(0)$_2$NH$_2$C$_6$H$_5$)CH$_2$ which was identified by comparison of its IR and $^1$H NMR spectra with those of an authentic sample.
Storage of a Mixture of trans- and cis-$n^5$-C$_5$H$_5$(CO)$_2$FeCHCH(C$_6$H$_5$)-C(O)N(S(O)$_2$NH)$_2$CH$_2$ in CH$_2$Cl$_2$

A solution of 100 mg of a mixture containing the trans and cis diastereomers (55:45) of the title complex in 30 mL of CH$_2$Cl$_2$ was stirred at room temperature for 2 days. The solvent was then removed from the solution in vacuo. The $n^5$-C$_5$H$_5$ peaks in the $^1$H NMR spectrum of the residue showed that the ratio between the trans and cis diastereomers was unchanged. The result of this experiment indicated that no conversion occurred between these two diastereomers in the absence of acid.

Protonation of trans-$n^5$-C$_5$H$_5$(CO)$_2$FeCHCH(C$_6$H$_5$)C(O)N(S(O)$_2$NH)$_2$CH$_2$ with HPF$_6^*$(C$_2$H$_5$)$_2$O at 0°C

To a solution of 0.418 g (0.85 mmol) of the title complex in 40 mL of CH$_2$Cl$_2$ at -78°C was added a solution of 0.318 g (1.45 mmol) of HPF$_6^*$(C$_2$H$_5$)$_2$O in 20 mL of CH$_2$Cl$_2$ at -78°C. The resulting mixture was stirred at -78°C for 20 min and then at 0°C for 1 hour. Yellow precipitate formed slowly when the mixture was stirred at 0°C. The solvent was removed by using a syringe. The sticky yellow solid was dried under vacuum to afford 0.250 g (0.390 mmol, 46%) of [n$^5$-C$_5$H$_5$-(CO)$_2$Fe(n$^2$-CH$_2$=CHCH(C$_6$H$_5$)C(O)NH(S(O)$_2$NH)$_2$C$_6$H$_5$)]$^+PF_6^-$•. The result of deprotonation of the yellow solid with Proton Sponge in THF
indicated that the solid was a mixture of the \textit{trans} and \textit{cis} diastereomers (50:50).

\textbf{Protonation of trans-}{\textit{n}}\textsuperscript{5}-C\textsubscript{5}H\textsubscript{5}(CO)\textsubscript{2}FeCHCH(C\textsubscript{6}H\textsubscript{5})C(O)N(S(O)\textsubscript{2}NHC\textsubscript{6}H\textsubscript{5})CH\textsubscript{2}\textit{N} with HPF\textsubscript{6}\textsuperscript{-}((C\textsubscript{2}H\textsubscript{5})\textsubscript{2}O at Room Temperature}

To a solution of 0.400 g (0.813 mmol) of the title complex in 30 mL of CH\textsubscript{2}Cl\textsubscript{2} was added a solution 0.271 g (1.23 mmol) of HPF\textsubscript{6}\textsuperscript{-}((C\textsubscript{2}H\textsubscript{5})\textsubscript{2}O in 10 mL of CH\textsubscript{2}Cl\textsubscript{2} at room temperature. After the addition, the solution became cloudy and its color changed to light red. The mixture was stirred at 25°C for 30 seconds; subsequently, it was cooled to -20°C. After 20 min at -20°C, the solvent was removed by syringe. The precipitate was dried under vacuum to give 0.344 g (0.539 mmol, 66\%) of the yellow product \textit{[n}\textsubscript{5}-C\textsubscript{5}H\textsubscript{5}(CO)\textsubscript{2}Fe(n\textsuperscript{2}-CH\textsubscript{2}=CHCH(C\textsubscript{6}H\textsubscript{5})C(O)NH(S(O)\textsubscript{2}NHC\textsubscript{6}H\textsubscript{5})]\textsuperscript{+}PF\textsubscript{6}\textsuperscript{-}. The result of the deprotonation of the yellow product with Proton Sponge in THF indicated that the product was a mixture of the \textit{trans} and \textit{cis} diastereomers (2:1).

\textbf{Storage of trans-}{\textit{n}}\textsuperscript{5}-C\textsubscript{5}H\textsubscript{5}(CO)\textsubscript{2}Fe(n\textsuperscript{2}-CH\textsubscript{2}=CHCH(C\textsubscript{6}H\textsubscript{5})C(O)NH(S(O)\textsubscript{2}NHC\textsubscript{6}H\textsubscript{5})]\textsuperscript{+}PF\textsubscript{6}\textsuperscript{-} in CH\textsubscript{2}Cl\textsubscript{2} in the Absence of Acid}

A suspension of 0.100 g (0.157 mmol) of the title complex (2 \textit{trans} diastereomer/1 \textit{cis} diastereomer) in 20 mL of CH\textsubscript{2}Cl\textsubscript{2} was stirred at room temperature for 45 min. The suspension first
changed color to red and became clearer, and then turned cloudy. The mixture was filtered to give 0.080 g of a yellow precipitate. The yellow precipitate was identified as \(\text{cis-}[\eta^5-C_5H_5(CO)_2Fe(\eta^2-CH_2=CHCH(C_6H_5)C(O)NH(S(O)_2NHC_6H_5))]^{+}PF_6^-\) by deprotonation with Proton Sponge in THF.

Storage of \(\text{trans-}[\eta^5-C_5H_5(CO)_2Fe(\eta^2-CH_2=CHCH(C_6H_5)C(O)NH(S(O)_2NHC_6H_5))]^{+}PF_6^-\) in \(\text{CH}_2\text{Cl}_2\) in the Presence of Acid

A suspension of 0.045 g (0.071 mmol) of the title complex (2 trans diastereomer/1 cis diastereomer) and 0.012 g (0.055 mmol) of HPF_6^+(C_2H_5)_2O in 20 mL of \(\text{CH}_2\text{Cl}_2\) was stirred at room temperature for 45 min. The yellow mixture cleared somewhat, and then became cloudy and changed color to red. A yellow precipitate formed and was collected by filtration. The result of the deprotonation of the yellow precipitate with Proton Sponge in THF showed that it was \(\text{cis-}[\eta^5-C_5H_5(CO)_2Fe(\eta^2-CH_2=CHCH(C_6H_5)NH(S(O)_2NHC_6H_5))]^{+}PF_6^-\).

Preparation of \(\eta^5-C_5H_5(CO)_2Fe(E-CH_2CH=CDC_5H_5)\)

A solution containing 18.1 mmol of \(\eta^5-C_5H_5Fe(CO)_2Na\) in 90 mL of THF was prepared by sodium amalgam reduction of 3.20 g (9.05 mmol) of the dimer \([\eta^5-C_5H_5Fe(CO)_2]_2\). A solution of 3.00 g (19.5 mmol) of \(E-\text{ClCH}_2\text{CH}=\text{CDC}_5\text{H}_5\) in 10 mL of THF was added to the reaction mixture which was stirred at room temperature for 2 hours. After the
solvent was removed in vacuo, the residue was extracted with petroleum ether (100 mL x 8). The combined extract was filtered on a pad of Grade III Alumina to remove unreacted dimer. The solvent was then removed from the filtrate in vacuo. The yellow-brown residue was washed with 15 mL of petroleum ether at -78°C to afford 3.0 g (10 mmol, 57%) of \( \text{n}^5\text{C}_5\text{H}_5(\text{CO})_2\text{Fe(E-CH}_2\text{CH=CD}_6\text{H}_5) \). 1H NMR (CDCl\(_3\)) \( \delta \) 2.25 (2H, d, \( J = 9.0 \) Hz, CH\(_2\)), 4.68 (5H, s, C\(_5\)H\(_5\)), 6.47 (1H, m, CH), 6.95-7.41 (5H, m, C\(_6\)H\(_5\)).

Preparation of trans-\( \text{n}^5\text{C}_5\text{H}_5(\text{CO})_2\text{FeCHCD(C}_6\text{H}_5)\text{C(O)N(S(O)\text{2NHC}_6\text{H}_5)CH}_2\)

The addition of a solution of 0.585 g (4.14 mmol) of CISO\(_2\)NCO in 20 mL of CH\(_2\)Cl\(_2\) at -78°C to a solution of 1.20 g (4.07 mmol) of \( \text{n}^5\text{C}_5\text{H}_5\text{Fe(CO)}_2(\text{E-CH}_2\text{CH=CD}_6\text{H}_5) \) in 30 mL of CH\(_2\)Cl\(_2\) also at -78°C resulted in the formation of a yellow precipitate. After 5 min at -78°C, the reaction temperature was allowed to rise to room temperature in 20 min. The mixture was stirred at 25°C for 15 min, as most of the yellow precipitate dissolved. The mixture was then cooled to -78°C. A solution of 1.5 g (16 mmol) of aniline in 20 mL of CH\(_2\)Cl\(_2\) was added at -78°C. After the mixture was warmed to room temperature and stirred for 1 hour, C\(_6\)H\(_5\)NH\(_3\)\(^{+}\)Cl\(^{-}\) was filtered off. The filtrate was passed through Florisil again to remove excess aniline. The solvent was removed from the filtrate in vacuo, and the residue was then crystallized from 40 mL of a mixture of CH\(_2\)Cl\(_2\)
and n-pentane (1:3) to give 1.31 g (2.65 mmol, 65%) of a yellow product. The yellow product was characterized by IR, $^1$H NMR and $^2$H NMR spectroscopy. The spectral data are listed in Tables 6 and 7, respectively.

**Mass Spectrum (FAB) m/e (relative intensity)**

- 494 ((M + H)$^+$, 45)
- 438 ((M + H - 2CO)$^+$, 40)
- 345 ((M + H - 2CO - NH$_2$C$_6$H$_5$)$^+$, 32)

**Protonation of trans-\(\text{C}_5\text{H}_5(\text{CO})_2\text{FeCHCD(C}_6\text{H}_5)\text{C(O)N(S(O)\text{NHC}_6\text{H}_5})\text{CH}_2\)**

To a solution of 0.320 g (0.649 mmol) of the title complex in 30 mL of CH$_2$Cl$_2$ at -78°C was added a solution of 0.860 g (3.91 mmol) of HPF$_6^*$(C$_2$H$_5$)$_2$O in 20 mL of CH$_2$Cl$_2$ also at -78°C. The resulting mixture was stirred at -78°C for 20 min, and the temperature of the mixture was allowed to rise to room temperature. In the process of warming up, the mixture became somewhat cloudy at ca. -60°C. However, when the temperature reached room temperature, the mixture changed color to red and became clear. After 20 min of stirring at 25°C, a yellow precipitate suddenly formed. The mixture was continuously stirred for an additional 20 min, and the yellow precipitate was then filtered off and washed with CH$_2$Cl$_2$ (5 mL x 2)
Table 6

Major Infrared Absorption Bands for Complexes

\[
n^5\text{C}_5\text{H}_5(\text{CO})_2\text{Fe}\text{CHCD(C}_6\text{H}_5)\text{C(O)N(S(O))}_2\text{NHC}_6\text{H}_5\text{CH}_2\]

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<th>Diastereomer</th>
<th>(\nu(\text{NH})\text{cm}^{-1})</th>
<th>(\nu(\text{C=O})\text{cm}^{-1})</th>
<th>(\nu(\text{N=O})\text{cm}^{-1})</th>
<th>(\nu(\text{SO}_2)\text{cm}^{-1})</th>
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<td>1722 (vs)</td>
<td>1375 (s)</td>
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<td>1952 (vs)</td>
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<td>cis</td>
<td>3207 (m, br)</td>
<td>2001 (vs)</td>
<td>1702 (s)</td>
<td>1371 (s)</td>
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<td></td>
<td></td>
<td>1950 (vs)</td>
<td></td>
<td>1170 (vs)</td>
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\(^a\) As Nujol mull.
Table 7

$^1$H and $^2$H NMR Data for $\eta^5$-C$_5$H$_5$(CO)$_2$Fe$^{\delta+}$(I)(Ph)

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<th>Diastereomer</th>
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<th>$^2$H NMR (δ, ppm)</th>
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<td>2.47 (q, H$_c$), 3.46 (q, H$_a$, J(H$_a$, H$_c$)=11.6 Hz, J(H$_a$, H$_b$)=9.6 Hz)</td>
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<td>3.90 (q, H$_b$, J(H$_b$, H$_c$)=9.0 Hz), 4.43 (s, C$_5$H$_5$)</td>
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<td>6.47 (s, NH), 6.94-7.45 (m, C$_6$H$_5$ and NC$_6$H$_5$)</td>
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<tr>
<td>cis</td>
<td>3.03 (q, H$_c$), 3.30 (q, H$_a$, J(H$_a$, H$_c$)=11.8 Hz, J(H$_a$, H$_b$)=10.3 Hz)</td>
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</tr>
<tr>
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<td>3.96 (q, H$_b$, J(H$_b$, H$_c$)=7.7 Hz), 4.58 (s, C$_5$H$_5$)</td>
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<tr>
<td></td>
<td>6.49 (s, NH), 6.72-7.40 (m, C$_6$H$_5$ and NC$_6$H$_5$)</td>
<td></td>
</tr>
</tbody>
</table>

*a* In CDCl$_3$ solution.
to afford 330 mg (0.517 mmol, 80%) of cis-$[^{5}\text{C}_5\text{H}_5(\text{CO})_2\text{Fe(}^{2}\text{CH}_2=\text{CH}-\text{CD(C}_6\text{H}_5)\text{C(O)NH(S(O))}_2\text{NH}_6\text{H}_5)]^+\text{PF}_6^-$. The yellow product was characterized by IR. IR (Nujol) ν(NH) 3378 (m, sharp), 3249 (s, br), ν(C=O) 2078 (vs), 2040 (vs), ν(C=O) 1720 (s), ν(SO$_2$) 1366 (s), 1177 (s) cm$^{-1}$.

Deprotonation of cis-$[^{5}\text{C}_5\text{H}_5(\text{CO})_2\text{Fe(}^{2}\text{CH}_2=\text{CH}-\text{CD(C}_6\text{H}_5)\text{C(O)NH(S(O))}_2\text{NH}_6\text{H}_5)]^+\text{PF}_6^-$ with Proton Sponge

A solution of 0.128 g (0.530 mmol) of Proton Sponge in 15 mL of THF at -78°C was added to a solution of 0.320 g (0.517 mmol) of the title complex in 25 mL of THF also at -78°C. The mixture turned to cloudy after it was stirred at -78°C for 2 min. The temperature of the reaction mixture was then allowed to warm to room temperature, over 20 min. After 10 min of stirring at 25°C, the mixture was filtered. The solvent was removed from the filtrate in vacuo. The residue was crystallized from 30 mL of a mixture of CH$_2$Cl$_2$ and n-pentane (1:3) to give 0.200 g (0.407 mmol, 79%) of yellow crystals of cis-$[^{5}\text{C}_5\text{H}_5(\text{CO})_2\text{FeCHCD(C}_6\text{H}_5)\text{C(O)NH(S(O))}_2\text{NH}_6\text{H}_5]{\text{CH}_2}$. The IR and $^1$H NMR and $^2$H NMR spectral data are listed in Tables 6 and 7, respectively.
Preparation of trans-$n^5$-C$_5$H$_5$(CO)$_2$FeCHCH(C$_6$H$_5$)C(0)N(S(0)$_2$NHC$_6$H$_4$CH$_3$-p)CH$_2$.

The addition of a solution of 1.00 g (7.07 mmol) of ClSO$_2$NCO in 20 mL of CH$_2$Cl$_2$ at -78°C to a solution of 2.00 g (6.81 mmol) of $n^5$-C$_5$H$_5$(CO)$_2$Fe(E=CH$_2$CH=CHC$_6$H$_5$) in 50 mL of CH$_2$Cl$_2$ also at -78°C resulted in the formation of a yellow precipitate. The temperature of the resulting mixture was allowed to come to room temperature in 20 min, and the mixture was then stirred for 10 min. A solution of 1.51 g (14.1 mmol) of p-toluidine in 20 mL of CH$_2$Cl$_2$ at -78°C was added to the reaction mixture also at -78°C. After being stirred at 25°C for 3 hours, the mixture was filtered to remove p-CH$_3$C$_6$H$_4$NH$_3^+$Cl$^-$. The filtrate was passed by suction through Florisil to remove excess p-toluidine. The solvent was removed from the filtrate under reduced pressure. The residue was recrystallized from 40 mL of a mixture of CH$_2$Cl$_2$ and n-pentane (1:3) to give 2.9 g (5.7 mmol, 84%) of a yellow product. The IR and $^1$H NMR spectral data are listed in Tables 7 and 8, respectively.

M.P. 80-84°C with decomposition

Mass Spectrum (FAB) m/e (relative intensity)
507 ($M + H^+$, 8.64)
451 ($M + H - 2$CO$^+$, 3.91)
Protonation of trans-\(^\text{n}^5\)-C\(_5\)H\(_5\)(CO)\(_2\)FeCHCH(C\(_6\)H\(_5\))C(O)N(S(O)\(_2\)NHC\(_6\)H\(_4\)CH\(_3\)-p)CH\(_2\)

To a solution of 0.310 g (0.613 mmol) of the title complex in 40 mL of CH\(_2\)Cl\(_2\) at -78°C was added a solution of 0.234 g (1.06 mmol) of HPF\(_6^-\)(C\(_2\)H\(_5\))\(_2\)O in 20 mL of CH\(_2\)Cl\(_2\) also at -78°C. The resulting mixture was stirred at -78°C for 15 min and then warmed to room temperature over 20 min. The mixture turned slightly cloudy in the process of warming up. When the temperature reached room temperature, the mixture changed color to red and cleared up. After 15 min of stirring at 25°C, a large amount of yellow precipitate suddenly formed. The mixture was continuously stirred for an additional 15 min. The yellow precipitate was filtered off and washed with CH\(_2\)Cl\(_2\) (5 mL x 2) to yield 0.190 g (0.291 mmol, 48%) of product. The yellow precipitate was cis-[\(^\text{n}^5\)-C\(_5\)H\(_5\)(CO)\(_2\)Fe(\(\text{n}^2\)-CH\(_2\)=CHCH(C\(_6\)H\(_5\))C(O)NH-(S(O)\(_2\)NHC\(_6\)H\(_4\)CH\(_3\)-p))]\(^+\)PF\(_6^-\). The IR spectroscopic data are listed in Table 10.

M.P. 82-84°C with decomposition

Deprotonation of cis-[\(^\text{n}^5\)-C\(_5\)H\(_5\)(CO)\(_2\)Fe(\(\text{n}^2\)-CH\(_2\)=CHCH(C\(_6\)H\(_5\))C(O)NH(S(O)\(_2\)-NHC\(_6\)H\(_4\)CH\(_3\)-p))]\(^+\)PF\(_6^-\) with Proton Sponge

A solution of 0.068 g (0.28 mmol) of Proton Sponge in 15 mL of THF at -78°C was added to a solution of 0.177 g (0.271 mmol) of the title complex in 30 mL of THF also at -78°C. The resulting mixture
was then warmed to room temperature over 20 min. A white precipitate formed at ca. -60°C in the process of warming up. After being stirred at room temperature for 5 min, the mixture was filtered. The filtrate was evaporated to dryness. The residue was recrystallized from 30 mL of a mixture of CH₂Cl₂ and n-pentane (1:3) to give 0.096 g (0.19 mmol, 70%) of a yellow product. The yellow product was cis-[n⁵-C₅H₅(CO)₂FeCHCH(C₆H₅)C(O)N(S(O)₂NHC₆H₄CH₃-p)CH₂. The analytical data, IR, and ¹H NMR are listed in Tables 11, 8 and 9, respectively.

M.P. 110-111°C with decomposition

Mass Spectrum (FAB) m/e (relative intensity)
507 ((M + H)⁺, 10.45)
451 ((M + H - 2CO)⁺, 6.54)

Preparation of trans-(n⁵-C₅H₅(CO)₂FeCHCH(C₆H₅)C(O)N(S(O)₂NHC₆H₄-CH₃-p)CH₂

The addition of a solution of 0.977 g (6.90 mmol) of ClSO₂NCO in 20 mL of CH₂Cl₂ at -78°C to 2.13 g (6.92 mmol) of (n⁵-C₅H₅(CO)₂Fe(E-CH₂CH=CHC₆H₅) in 40 mL of CH₂Cl₂ also at -78°C resulted in the formation of a yellow precipitate. The temperature of the mixture was allowed to rise to room temperature over 20 min. The mixture was then cooled to -78°C and treated with a solution of 1.7 g (16 mmol) of p-toluidine in 20 mL of CH₂Cl₂ at -78°C. After
being stirred at 25°C for 4 hours, the mixture was filtered, and the solvent was removed from the filtrate in vacuo. The residue was chromatographed on Florisil (2 x 15 cm) eluting with CH₂Cl₂. After removal of the solvent from the effluent, the oily residue was recrystallized three times from a mixture of CH₂Cl₂ and n-pentane (1:3) to give 1.38 g (2.65 mmol, 38%) of a yellow product. The IR and ¹H NMR spectral data are listed in Tables 8 and 9, respectively.

<table>
<thead>
<tr>
<th>Property</th>
<th>Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>M.P.</td>
<td>103-105°C with decomposition</td>
</tr>
<tr>
<td>Mass Spectrum (FAB)</td>
<td>m/e (relative intensity)</td>
</tr>
<tr>
<td></td>
<td>521 ((M + H)⁺, 14.31)</td>
</tr>
<tr>
<td></td>
<td>465 ((M + H - 2CO)⁺, 7.57)</td>
</tr>
<tr>
<td></td>
<td>358 ((M + H - 2CO - H₂NC₆H₄CH₃)⁺, 5.36)</td>
</tr>
</tbody>
</table>
Table 8

Major Infrared Absorption Bands for Complexes

\[ \text{[M]} \text{CHCH(C_6H_5)C(0)N(S(0))_2NHC_6H_4CH_3-p)CH}_2 \]^a

<table>
<thead>
<tr>
<th>M</th>
<th>Diastereomer</th>
<th>( \nu(\text{NH}) ) cm(^{-1} )</th>
<th>( \nu(\text{C}=\text{O}) ) cm(^{-1} )</th>
<th>( \nu(\text{C}=\text{O}) ) cm(^{-1} )</th>
<th>( \nu(\text{SO}_2) ) cm(^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( n^5-\text{C}_5\text{H}_5(\text{CO})_2\text{Fe} )</td>
<td>\textit{trans}</td>
<td>3280 (s, sharp)</td>
<td>2001 (vs)</td>
<td>1724 (vs)</td>
<td>1349 (s)</td>
</tr>
<tr>
<td>( n^5-\text{C}_5\text{H}_5(\text{CO})_2\text{Fe} )</td>
<td>\textit{cis}</td>
<td>3162 (m)</td>
<td>2000 (vs)</td>
<td>1668 (vs)</td>
<td>1370 (s)</td>
</tr>
<tr>
<td>( (n^5-\text{CH}_3\text{C}_5\text{H}_4)(\text{CO})_2\text{Fe} )</td>
<td>\textit{trans}</td>
<td>3220 (m, sharp)</td>
<td>2004 (vs)</td>
<td>1708 (vs)</td>
<td>1354 (s)</td>
</tr>
<tr>
<td>( (n^5-\text{CH}_3\text{C}_5\text{H}_4)(\text{CO})_2\text{Fe} )</td>
<td>\textit{cis}</td>
<td>3278 (m)</td>
<td>2000 (vs)</td>
<td>1716 (s)</td>
<td>1359 (ms)</td>
</tr>
</tbody>
</table>

^a As Nujol mull.
### Table 9

**1H NMR Data for Complexes**

<table>
<thead>
<tr>
<th>M</th>
<th>Diastereomer</th>
<th>Chemical Shifts (δ, PPM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \eta^5-\text{C}_5\text{H}_5(\text{CO})_2\text{Fe} )</td>
<td>trans</td>
<td>2.37 (s, ( \text{C}_6\text{CH}_3 )), 2.58 (m, ( \text{H}_c )), 3.12-3.63 (m, ( \text{H}_a ) and ( \text{H}_d )), 3.72-4.02 (m, ( \text{H}_b )), 4.52 (s, ( \text{C}_5\text{H}_5 )), 6.46 (s, NH), 6.85-7.52 (m, ( \text{C}_6\text{H}_5 ) and ( \text{NC}_6\text{H}_5 ))</td>
</tr>
<tr>
<td>( \eta^5-\text{C}_5\text{H}_5(\text{CO})_2\text{Fe} )</td>
<td>cis</td>
<td>2.37 (m, ( \text{C}_6\text{H}_5 )), 3.07 (m, ( \text{H}_c )), 3.49 (d, ( \text{H}_d ), ( J(\text{H}_c, \text{H}_d) = 7.2 \text{ Hz} )), 3.58-4.09 (m, ( \text{H}_a ) and ( \text{H}_b )), 4.59 (s, ( \text{C}_5\text{H}_5 )), 6.47 (s, NH), 6.68-7.52 (m, ( \text{C}_6\text{H}_5 ) and ( \text{NC}_6\text{H}_5 ))</td>
</tr>
<tr>
<td>( (\eta^5-\text{CH}_3\text{C}_5\text{H}_4)(\text{CO})_2\text{Fe} )</td>
<td>trans</td>
<td>1.87 (s, ( \text{C}_6\text{CH}_3 )), 2.37 (s, ( \text{C}_6\text{H}_5 )), 2.45 (m, ( \text{H}_c )), 3.22 (d, ( \text{H}_d ), ( J(\text{H}_c, \text{H}_d) = 6.2 \text{ Hz} )), 3.38 (q, ( \text{H}_a )), 3.80 (q, ( \text{H}_b )), 4.30 (m, ( \text{C}_5\text{H}_4 )), 6.46 (s, NH), 6.86-7.50 (m, ( \text{C}_6\text{H}_5 ) and ( \text{NC}_6\text{H}_5 ))</td>
</tr>
</tbody>
</table>
Table 9 (continued)

<table>
<thead>
<tr>
<th>M</th>
<th>Diastereomer</th>
<th>Chemical Shifts (δ, PPM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(n\textsubscript{5}-CH\textsubscript{3}C\textsubscript{5}H\textsubscript{4})(CO)\textsubscript{2}Fe</td>
<td>cis</td>
<td>1.87 (s, C\textsubscript{5}CH\textsubscript{3}), 2.36 (s, C\textsubscript{6}CH\textsubscript{3}), 2.98 (m, H\textsubscript{c})</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.46 (d, H\textsubscript{d}, J(H\textsubscript{c}, H\textsubscript{d})=8.8 Hz), 3.55-4.08 (m, H\textsubscript{a} and H\textsubscript{b}),</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.38 (m, C\textsubscript{5}H\textsubscript{4}), 6.45 (s, NH), 6.63-7.52 (m, C\textsubscript{6}H\textsubscript{5} and NC\textsubscript{6}H\textsubscript{5})</td>
</tr>
</tbody>
</table>

\(a\) In CDCl\textsubscript{3} solution.
Protonation of trans-(\(\eta^5\)-CH\(_3\)C\(_6\)H\(_4\))(CO)\(_2\)FeCHCH(C\(_6\)H\(_5\))C(0)N(S(0)\(_2\)NHC\(_6\)H\(_4\)CH\(_3\)-p))CH\(_3\)-p)CH\(_2\) with HPF\(_6\)\(^{-}\)(C\(_2\)H\(_5\))\(_2\)O

To a solution of 0.205 g (0.394 mmol) of the title complex in 25 mL of CH\(_2\)Cl\(_2\) at -78°C was added a solution of 0.165 g (0.750 mmol) of HPF\(_6\)\(^{-}\)(C\(_2\)H\(_5\))\(_2\)O in 15 mL of CH\(_2\)Cl\(_2\) also at -78°C. The mixture was stirred at -78°C for 5 min, and then the reaction temperature was allowed to rise to room temperature in 20 min. The yellow solution gradually changed to red at room temperature. After 10 min of stirring at 25°C, a yellow precipitate suddenly formed. Following an additional 20 min of stirring, the mixture was filtered. The yellow precipitate was collected and washed with CH\(_2\)Cl\(_2\) (5 mL x 2) to give 0.135 g (0.207 mmol, 53%) of cis-[\(\eta^5\)-CH\(_3\)C\(_6\)H\(_4\))(CO)\(_2\)Fe(\(\eta^2\)-CH\(_2\)=CHCH(C\(_6\)H\(_5\))C(0)NH(S(0)\(_2\)NHC\(_6\)H\(_4\)CH\(_3\)-p))]\(^{+}\)PF\(_6\)\(^{-}\). The IR spectral data are listed in Table 10.

Deprotonation of cis-[\(\eta^5\)-CH\(_3\)C\(_6\)H\(_4\))(CO)\(_2\)Fe(\(\eta^2\)-CH\(_2\)=CHCH(C\(_6\)H\(_5\))C(0)-NH(S(0)\(_2\)NHC\(_6\)H\(_4\)CH\(_3\)-p))]\(^{+}\)PF\(_6\)\(^{-}\) with Proton Sponge

A solution of 0.049 g (0.203 mmol) of Proton Sponge in 10 mL of THF at -78°C was added to a solution of 0.130 g (0.195 mmol) of the title complex in 40 mL of THF also at -78°C. The mixture was then warmed to room temperature in 20 min. A white precipitate formed at ca. -60°C during warming up. After the mixture was stirred for 15 min at 25°C, the white precipitate was filtered off. The solvent
was removed from the filtrate under reduced pressure. The residue was recrystallized from 40 mL of a mixture of CH$_2$Cl$_2$ and n-pentane (1:20). The sticky yellow solid that resulted was further purified by chromatography on Florisil eluting with CH$_2$Cl$_2$. The first yellow band was collected, and the solvent was removed from the effluent in vacuo. The residue was recrystallized from 20 mL of a mixture of CH$_2$Cl$_2$ and n-pentane (1:20) to afford 60 mg (0.12 mmol, 61%) of cis-(n$^5$-CH$_3$C$_5$H$_4$)(CO)$_2$FeCHCH(C$_6$H$_5$)C(0)N(S(0)$_2$NH$_2$H$_4$CH$_3$-p)-CH$_2$. The analytical data, IR and $^1$H NMR, are listed in Tables 11, 8 and 9, respectively.

M.P. 69-70°C with decomposition

Mass Spectrum (FAB) m/e (relative intensity)

521 ((M + H)$^+$, 10.26)
465 ((M + H - 2CO)$^+$, 5.34)
358 ((M + H - 2CO - H$_2$NCH$_2$CH$_3$)$^+$, 5.02)
Table 10

Major Infrared Absorption Bands for Complexes

$$[[\text{M}(\text{n}^2-\text{CH}_2=\text{CHCHC}_6\text{H}_5)\text{C(O)}_2\text{NH}(\text{S(O)}_2\text{NHC}_6\text{H}_4\text{CH}_3-p))]^+\text{PF}_6^-]$$

<table>
<thead>
<tr>
<th>M</th>
<th>Diastereomer</th>
<th>$\nu$(NH) cm$^{-1}$</th>
<th>$\nu$(C=O) cm$^{-1}$</th>
<th>$\nu$(C=O) cm$^{-1}$</th>
<th>$\nu$(SO$_2$) cm$^{-1}$</th>
<th>$\nu$(PF$_6$) cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{n}^5\text{C}_5\text{H}_5(\text{CO})_2\text{Fe}$</td>
<td>cis</td>
<td>3380 (m)</td>
<td>2082 (vs)</td>
<td>1707 (s)</td>
<td>1364 (m)</td>
<td>842 (s, br)</td>
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<tr>
<td></td>
<td></td>
<td>3230 (m)</td>
<td>2044 (vs)</td>
<td></td>
<td></td>
<td>1178 (s)</td>
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<tr>
<td>($\text{n}^5\text{CH}_3\text{C}_5\text{H}_4)(\text{CO})_2\text{Fe}$</td>
<td>trans</td>
<td>3480 (m)</td>
<td>2072 (vs)</td>
<td>1705 (s)</td>
<td>1360 (s)</td>
<td>840 (s, br)</td>
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<tr>
<td></td>
<td></td>
<td>3275 (ms)</td>
<td>2034 (vs)</td>
<td></td>
<td></td>
<td>1177 (s)</td>
</tr>
</tbody>
</table>

$^a$ As Nujol mull.
Table 11

Analytical Data for cis-\([M]\)CHCHR\(^1\)C(O)N(S(O))\(_2\)NHR\(^2\)CH\(_2\)

<table>
<thead>
<tr>
<th>M</th>
<th>R(^1)</th>
<th>R(^2)</th>
<th>%C</th>
<th>%H</th>
</tr>
</thead>
<tbody>
<tr>
<td>(n^5)-C(_5)H(_5)(CO)(_2)Fe</td>
<td>CH(_3)</td>
<td>C(_6)H(_5)</td>
<td>50.25</td>
<td>50.20</td>
</tr>
<tr>
<td>(n^5)-C(_5)H(_5)(CO)(_2)Fe</td>
<td>C(_6)H(_5)</td>
<td>C(_6)H(_4)CH(_3)-p</td>
<td>56.93</td>
<td>57.10</td>
</tr>
<tr>
<td>((n^5)-CH(_3)C(_5)H(_4))(CO)(_2)Fe</td>
<td>C(_6)H(_5)</td>
<td>C(_6)H(_4)CH(_3)-p</td>
<td>57.70</td>
<td>57.41</td>
</tr>
</tbody>
</table>
Protonation of a Mixture of trans-\(\text{C}_5\text{H}_5\)\(\text{FeCHCH(C}_6\text{H}_5\)C(O)N-(S(O)\(_2\)NH\(\text{C}_6\text{H}_5\))\(\text{CH}_2\) and trans-\(\text{C}_3\text{C}_5\text{H}_4\)\(\text{FeCHCH(C}_6\text{H}_5\)C(O)N(S(O)\(_2\)NH\(\text{C}_6\text{H}_5\))\(\text{CH}_2\) with HPF\(_6\)\(.\text{C}_2\text{H}_5\)_\(\text{O}\) \(\)and Deprotonation of the Resulting Protonated Salts with Proton Sponge (Crossover Reaction)

(a) Protonation

To a solution containing 0.400 g (0.769 mmol) of trans-\(\text{C}_5\text{H}_5\)\(\text{FeCHCH(C}_6\text{H}_5\)C(O)N-(S(O)\(_2\)NH\(\text{C}_6\text{H}_5\))\(\text{CH}_2\) and 0.378 g (0.769 mmol) of trans-\(\text{C}_3\text{C}_5\text{H}_4\)\(\text{FeCHCH(C}_6\text{H}_5\)C(O)N(S(O)\(_2\)NH\(\text{C}_6\text{H}_5\))\(\text{CH}_2\) in 40 mL of \(\text{CH}_2\text{Cl}_2\) at -78°C was added a solution of 0.703 g (3.20 mmol) of HPF\(_6\)\(.\text{C}_2\text{H}_5\)_\(\text{O}\) in 20 mL of \(\text{CH}_2\text{Cl}_2\) also at -78°C. After 15 min of stirring at -78°C, the mixture was allowed to come to room temperature over 20 min. The yellow solution gradually turned red at room temperature. The reaction mixture was then stirred for 15 min, as a yellow precipitate suddenly formed. After an additional 15 min, the yellow precipitate was filtered off and washed with \(\text{CH}_2\text{Cl}_2\) (10 mL x 2) to give 0.640 g of yellow protonated products.

(b) Deprotonation

A solution of 0.242 g (1.00 mmol) of Proton Sponge in 15 mL of THF at -78°C was added to a solution of 0.640 g of the protonated salts obtained from the above reaction in 40 mL of THF also at -78°C. The resulting mixture was then warmed to room temperature in 20 min. During warming up, a white precipitate formed at ca.
-60°C. After the mixture was stirred at 25°C for 10 min, it was filtered. The solvent was removed from the filtrate under reduced pressure. The residue was recrystallized from a mixture of CH₂Cl₂ and n-pentane (1:20). The yellow precipitate was further purified by chromatography on a short column of Florisil eluting with CH₂Cl₂ to yield 0.390 g of a yellow solid. The 1H NMR spectrum of this solid indicated that it was a mixture of the cis diastereomers of the complexes studied in this reaction. Major peaks of the mass spectrum of the solid are reported as below:

<table>
<thead>
<tr>
<th>Mass Spectrum (FAB)</th>
<th>m/e (relative intensity)</th>
</tr>
</thead>
<tbody>
<tr>
<td>521 (M₁ + H)⁺, 3.89</td>
<td></td>
</tr>
<tr>
<td>507 (M₂ + H)⁺ and (M₃ + H)⁺, 1.05</td>
<td></td>
</tr>
<tr>
<td>493 (M₄ + H)⁺, 4.98</td>
<td></td>
</tr>
<tr>
<td>465 (M₁ + H - 2CO)⁺, 2.04</td>
<td></td>
</tr>
<tr>
<td>451 (M₂ + H - 2CO)⁺</td>
<td></td>
</tr>
<tr>
<td>and (M₃ + H - 2CO)⁺, 1.01</td>
<td></td>
</tr>
<tr>
<td>437 (M₄ + H - 2CO)⁺, 3.91</td>
<td></td>
</tr>
<tr>
<td>358 (M₂ + H - 2CO - C₆H₅NH₂)⁺, 2.18</td>
<td></td>
</tr>
<tr>
<td>344 (M₄ + H - 2CO - C₆H₅NH₂)⁺, 3.83</td>
<td></td>
</tr>
</tbody>
</table>

M₁: Formula Weight of \( \text{[(n}^5\text{-CH}_3\text{C}_5\text{H}_4)(\text{CO})_2\text{FeCHCH(C}_6\text{H}_5\text{C(O)N(S(O)}_2\text{NH-}
\begin{array}{c}
\text{C}_6\text{H}_4\text{CH}_3\text{-p)}\text{CH}_2
\end{array} \)
M₂: Formula Weight of \( (n^5-\text{C}_5\text{H}_4)(\text{CO})_2\text{FeCHCH(C}_6\text{H}_5)\text{C(O)}\text{N(S(O)}_2\text{NH-} \)
\( \text{C}_6\text{H}_4\text{CH}_2 \)

M₃: Formula Weight of \( n^5-C_5\text{H}_5(\text{CO})_2\text{FeCHCH(C}_6\text{H}_5)\text{C(O)}\text{N(S(O)}_2\text{NH}C_6\text{H}_4 \)
\( \text{CH}_3-p\text{CH}_2 \)

M₄: Formula Weight of \( n^5-C_5\text{H}_5(\text{CO})_2\text{FeCHCH(C}_6\text{H}_5)\text{C(O)}\text{N(S(O)}_2\text{NH}C_6\text{H}_5 \)
\( \text{CH}_2 \)

Protonation of \( n^5-C_5\text{H}_5(\text{CO})_2\text{FeCHCH(C}_6\text{H}_5)\text{C(O)}\text{N(S(O)}_2\text{NH}C_6\text{H}_4 \)
\( \text{CH}_3-p\text{CH}_2 \) with \( \text{HPF}_6^-(\text{C}_2\text{H}_5)_2\text{O} \)

A solution of 0.200 g (0.909 mmol) of \( \text{HPF}_6^-(\text{C}_2\text{H}_5)_2\text{O} \) in 15 mL of \( \text{CH}_2\text{Cl}_2 \) at -78°C was added to a solution of 0.330 g (0.672 mmol) of the title complex in 15 mL of \( \text{CH}_2\text{Cl}_2 \) also at -78°C. The resulting mixture was stirred at -78°C for 30 min, and then the temperature of the mixture was allowed to rise to room temperature. The mixture was stirred at 25°C for 24 hours, as a yellow precipitate formed very slowly. This precipitate was filtered off and washed with \( \text{CH}_2\text{Cl}_2 \) (5 mL x 3) to give 0.124 g (0.19 mmol, 29%) of a yellow product. The product did not dissolve in any common organic solvents. The IR spectrum indicated that it was probably the protonated salt \([n^5-C_5\text{H}_5(\text{CO})_2\text{Fe(n}^2-\text{CH}_2=\text{CHCH(C}_6\text{H}_5)\text{C(O)}\text{NH(S(O)}_2\text{C}_6\text{H}_4-\text{CH}_3-p))]^+\text{PF}_6^- \). IR spectroscopic data: IR (Nujol) \( \nu(\text{NH}) 3532 \text{ (m)}, \nu(\text{C=O}) 2058 \text{ (vs)}, 2004 \text{ (vs)}, \nu(\text{C=O}) 1641 \text{ (s)}, \nu(\text{SO}_2) 1368 \text{ (s)}, 1160 \text{ (s)} \text{ cm}^{-1}. \)
Attempted Protonation of $\eta^5$-C$_5$H$_5$(CO)$_2$FeCHCH(CH$_3$)C(O)N(S(O)$_2$C$_6$H$_4$CH$_3$-p)CH$_2$ with HPF$_6$·(C$_2$H$_5$)$_2$O

To a solution of 0.210 g (0.489 mmol) of the title complex in 30 mL of CH$_2$Cl$_2$ at -78°C was added a solution of 0.146 g (0.663 mmol) of HPF$_6$·(C$_2$H$_5$)$_2$O in 20 mL of CH$_2$Cl$_2$ also at -78°C. The resulting mixture was stirred at -78°C for 20 min, and then at room temperature for 20 hours. The mixture was filtered to remove a precipitate which did not show any signals in the $^1$H NMR spectrum, and no $\nu$(C=O) absorptions in the IR spectrum. Thus, it appeared to be a decomposition material. The solvent was removed from the filtrate in vacuo. The $^1$H NMR spectrum of the brown residue (0.120 g, 57% recovery) showed it to be the starting material.

Protonation of $\eta^5$-C$_5$H$_5$(CO)$_2$FeCHCH(CH$_3$)C(O)N(S(O)$_2$N(CH$_3$)$_2$)CH$_2$ with HPF$_6$·(C$_2$H$_5$)$_2$O

To a solution of 0.450 g (0.843 mmol) of the title complex in 50 mL of CH$_2$Cl$_2$ at -78°C was added a solution of 0.210 g (0.955 mmol) of HPF$_6$·(C$_2$H$_5$)$_2$O in 10 mL of CH$_2$Cl$_2$ also at -78°C. After 20 min of stirring at -78°C, the mixture was stirred at room temperature for 3 hours. A white precipitate that formed was filtered off and washed with CH$_2$Cl$_2$. The $^1$H NMR spectrum of the white precipitate showed it to be H$_2$N(CH$_3$)$_2$+PF$_6$~. The yield was 0.108 g (0.57 mmol, 67%).
Attempted Protonation of $\eta^5$-C$_5$H$_5$(CO)$_2$FeC=C(CH$_3$)C(O)N(S(O)$_2$C$_6$H$_4$CH$_3$-p)CH$_2$ with HPF$_6$·(C$_2$H$_5$)$_2$O

To a solution of 0.202 g (0.473 mmol) of the title complex in 30 mL of CH$_2$Cl$_2$ was added a solution of 0.160 g (0.727 mmol) of HPF$_6$·(C$_2$H$_5$)$_2$O in 15 mL of CH$_2$Cl$_2$ also at -78°C. The resulting mixture was stirred first at -78°C for 20 min and then at room temperature for 24 hours. No precipitate formed during this period. The solvent was removed under reduced pressure. The $^1$H NMR spectrum of the brown residue showed that the starting material was recovered.

Attempted Protonation of $\eta^5$-C$_5$H$_5$(CO)$_2$FeC=C(C$_6$H$_5$)S(O)$_2$CH$_3$CH$_2$ with HPF$_6$·(C$_2$H$_5$)$_2$O

A solution of 0.140 g (0.636 mmol) of HPF$_6$·(C$_2$H$_5$)$_2$O in 20 mL of CH$_2$Cl$_2$ at -78°C was added to a solution of 0.200 g (0.462 mmol) of the title complex in 30 mL of CH$_2$Cl$_2$ at -78°C. The resulting mixture was stirred first at -78°C for 5 min and then at room temperature for 24 hours. The solvent was removed from the reaction mixture in vacuo. The $^1$H NMR spectrum of the residue showed that the starting material was quantitatively recovered.
B. Reactions of Iron-Cycloalkyl Complexes Containing a Six-Membered Ring

Deprotonation of \( [n^5-C_5H_5(CO)_2Fe(n^2-CH_2=CHCH_2N(S(O)_2CH_3)SN(S(O)_2CH_3)]^+PF_6^- \) with Proton Sponge

A solution of 0.150 g (0.622 mmol) of Proton Sponge in 25 mL of THF at -78°C was added to a suspension of 0.287 g (0.493 mmol) of the title complex in 50 mL of THF also at -78°C. The resulting mixture was stirred at -78°C for 10 min and when no reaction was indicated by the absence of precipitation, it was allowed to warm to room temperature. After 20 min of stirring at 25°C, the solvent was removed in vacuo. The residue was then treated with 40 mL of CH_2Cl_2, and was removed in vacuo. The residue was then treated with 40 mL of CH_2Cl_2, and the mixture was filtered to remove the white precipitate \( [1,8-N(CH_3)_2C_{10}H_6NH(CH_3)_2]^+PF_6^- \) which was identified by \(^1\text{H NMR spectroscopy}. \) The filtrate was concentrated to 15 mL, and 30 mL of hexane was added. The resulting mixture was cooled at ca. 0°C for 12 hours to yield 0.185 g (86%) of yellow crystals of \( n^5-C_5H_5(CO)_2FeCHCH_2N(S(O)_2CH_3)SN(S(O)_2CH_3)CH_2 \). The product was identified by comparison of its \(^1\text{H NMR spectrum with that of an authentic sample.} \)
Attempted Reactions of $\eta^5$-C$_5$H$_5$(CO)$_2$FeCHCH$_2$N(S(O)$_2$CH$_3$)SN(S(O)$_2$CH$_3$)-CH$_2$ with (CH$_3$)$_3$OBF$_4$

A solution of 0.096 g (0.22 mmol) of the title complex in 20 mL of CH$_2$Cl$_2$ at -78°C was added to a suspension of 0.070 g (0.47 mmol) of (CH$_3$)$_3$OBF$_4$ in 20 mL of CH$_2$Cl$_2$ also at -78°C. The resulting mixture was stirred first at -78°C for 30 min and then at room temperature for 2 hours. The solvent was removed, and the residue was examined by $^1$H NMR spectroscopy. Its spectrum showed that the starting material was recovered.

Attempted Reaction of $\eta^5$-C$_5$H$_5$(CO)$_2$FeCHCH$_2$N(S(O)$_2$CH$_3$)SN(S(O)$_2$CH$_3$)-CH$_2$ with (C$_2$H$_5$)$_3$OPF$_6$

To solution of 0.81 g (1.9 mmol) of the title complex in 75 mL of CH$_2$Cl$_2$ at -78°C was added a solution of 0.48 g (1.9 mmol) of CH$_2$Cl$_2$ at -78°C was added a solution of 0.48 g (1.9 mmol) of (C$_2$H$_5$)$_3$OPF$_6$ in CH$_2$Cl$_2$ also at -78°C. The mixture was stirred first at -78°C for 30 min and then at room temperature for 1.5 hours. The solvent was removed in vacuo, and the residue was examined by $^1$H NMR spectroscopy. Its spectrum showed that the starting material was recovered.
C. Preparation of Tungsten Complexes Containing a Five-Membered Ring and Their Reactions Involving a Protonation-Deprotonation Sequence

Preparation of $\eta^5$-C$_5$H$_5$(CO)$_3$W(E-CH$_2$CH=CHC$_6$H$_5$)

A mixture of 0.82 g (35 mmol) of sodium and 100 mL of dry toluene was heated to reflux with vigorous stirring to make sodium granules. After the mixture was cooled to room temperature, the solvent was replaced by 100 mL of dry 1,2-dimethoxyethane with a syringe. To the mixture was added dropwise 3.3 g (50 mmol) of freshly cracked cyclopentadiene solution. The mixture was stirred at 40°C until all of the sodium dissolved. To the resulting pink mixture at room temperature was added 3.61 g (10.3 mmol) of W(CO)$_6$. The reaction mixture was refluxed until CO evolution ceased (about 18 hours). A solution of 7.66 g (50.2 mmol) of E-C$_1$CH$_2$-CH=CHC$_6$H$_5$ was added to the mixture at 25°C, and a white precipitate formed immediately. After 5 hours of stirring, the solvent was removed from the mixture in vacuo. The yellow residue was extracted with petroleum ether (100 mL x 8). The combined extracts were filtered, and then the solvent was removed under reduced pressure. The residue was washed with 10 mL of petroleum ether to afford 3.5 g (8.2 mmol, 80%) of yellow product. Characterization of the product: IR (Nujol) ν(C=O) 2006 (vs), 1922 (s, br) cm$^{-1}$; $^1$H NMR
(CDC\textsubscript{3}) \delta \; 7.49-7.01 (m, C\textsubscript{6}H\textsubscript{5}), 6.66-5.95 (m, CH=CH), 5.30 (s, C\textsubscript{5}H\textsubscript{5}), 2.52 (d, CH\textsubscript{2}).

**Preparation of trans-n\textsuperscript{5}-C\textsubscript{5}H\textsubscript{5}(CO)\textsubscript{3}CHCH(CH\textsubscript{3})C(0)N(S(0))\textsubscript{2}NHCH\textsubscript{3}CH\textsubscript{2}**

To a solution of 1.40 g (3.61 mmol) of n\textsuperscript{5}-C\textsubscript{5}H\textsubscript{5}W(CO)\textsubscript{3}(E-CH\textsubscript{2}CH=-CHCH\textsubscript{3}) in 30 mL of CH\textsubscript{2}Cl\textsubscript{2} at -78°C was added a solution of 0.515 g (3.64 mmol) of ClSO\textsubscript{2}NCO in 20 mL of CH\textsubscript{2}Cl\textsubscript{2} also at -78°C. A yellow precipitate formed immediately. The resulting mixture was allowed to come to room temperature over 20 min, and the yellow precipitate gradually dissolved. After the mixture was cooled to -78°C, a solution of 1.5 g (16 mmol) of aniline in 20 mL of CH\textsubscript{2}Cl\textsubscript{2} was added. The reaction mixture was warmed to room temperature and continuously stirred for 6 hours. The white salt C\textsubscript{6}H\textsubscript{5}NH\textsubscript{3}\textsuperscript{+}Cl\textsuperscript{-} was removed by filtration. The filtrate was suctioned through Florisil to remove excess aniline. The solvent was evaporated under reduced pressure. The residue was chromatographed on Florisil eluting with acetone. After the solvent was removed from the first yellow effluent, the residue was recrystallized from 30 mL of a mixture of CH\textsubscript{2}Cl\textsubscript{2} and n-pentane (1:3) to give 0.820 g (1.39 mmol, 38%) of a yellow product. The physical properties, IR and \textsuperscript{1}H NMR spectral data are listed in Tables 12, 13 and 14, respectively.

**Mass Spectrum (FAB)** m/e (relative intensity)

587 ((M + H\textsuperscript{+}), 7.48)
Preparation of $n^5$-C$_5$H$_5$(CO)$_3$WCHC(CH$_3$)C(O)N[S(O)$_2$NH]$_6$H$_5$CH$_2$

The addition of a solution of 0.535 g (3.78 mmol) of ClSO$_2$NCO in 20 mL of CH$_2$Cl$_2$ at -78°C to a solution of 1.51 g (3.75 mmol) of $n^5$-C$_5$H$_5$(CO)$_3$WCH$_2$=C(CH$_3$)$_2$ in 40 mL of CH$_2$Cl$_2$ also at -78°C resulted in the formation of a yellow precipitate. After the resulting mixture was stirred at -78°C for 15 min, it was allowed to come to room temperature over 20 min. The yellow precipitate disappeared in the process of warming up. The mixture was cooled to -78°C again and to it was added a solution of 0.94 g (1.0 mmol) of aniline in 10 mL of CH$_2$Cl$_2$ at -78°C. The resulting mixture was stirred at -78°C for 20 min and then at 25°C for 40 min. It was then filtered to remove the white solid C$_6$H$_5$NH$_3^+Cl^-$. The solvent was removed from the filtrate in vacuo, and the residue was recrystallized from 40 mL of a mixture of CH$_2$Cl$_2$ and n-pentane to afford 1.98 g (3.30 mmol, 87%) of a yellow product. The physical properties, IR, and $^1$H NMR spectral data are listed in Tables 12, 13 and 14, respectively.

Mass Spectrum (FAB) m/e (relative intensity)

601 ((M + H)$^+$, 4.13)
573 ((M + H - CO)$^+$, 0.37)
445 ((M + H - SO$_2$ - NH$_2$C$_6$H$_5$)$^+$, 1.38)
<table>
<thead>
<tr>
<th>$R^1$</th>
<th>$R^2$</th>
<th>M.P.</th>
<th>%C Calcd.</th>
<th>%H Calcd.</th>
<th>%N Calcd.</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>CH$_3$</td>
<td>80-82°C (dec.)</td>
<td>38.93</td>
<td>3.09</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>39.18</td>
<td>3.06</td>
<td>---</td>
</tr>
<tr>
<td>CH$_3$</td>
<td>CH$_3$</td>
<td>64-66°C (dec.)</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>H</td>
<td>C$_6$H$_5$</td>
<td>72-74°C (dec.)</td>
<td>---</td>
<td>4.32</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4.16</td>
<td>---</td>
</tr>
</tbody>
</table>
Table 13

Major Infrared Absorption Bands for Complexes

$\eta^5-C_5H_5(CO)_3WCHCR^1R^2C(O)N(S(O)_2NH)C_6H_5CH_2$\textsuperscript{a}

<table>
<thead>
<tr>
<th>R\textsuperscript{1}</th>
<th>R\textsuperscript{2}</th>
<th>$v$(NH)$\text{cm}^{-1}$</th>
<th>$v$(C=O)$\text{cm}^{-1}$</th>
<th>$v$(C=O)$\text{cm}^{-1}$</th>
<th>$v$(SO\textsubscript{2}$\text{cm}^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H (trans diastereomer)</td>
<td>CH\textsubscript{3}</td>
<td>3210 (m)</td>
<td>2010 (s)</td>
<td>1718 (ms)</td>
<td>1370 (ms)</td>
</tr>
<tr>
<td>CH\textsubscript{3}</td>
<td>CH\textsubscript{3}</td>
<td>3250 (br)</td>
<td>2005 (vs)</td>
<td>1742 (s)</td>
<td>1388 (ms)</td>
</tr>
<tr>
<td>H (trans diastereomer)</td>
<td>C\textsubscript{6}H\textsubscript{5}</td>
<td>3391 (w)</td>
<td>2009 (vs)</td>
<td>1739 (ms)</td>
<td>1407 (ms)</td>
</tr>
<tr>
<td>C\textsubscript{6}H\textsubscript{5}</td>
<td>H (cis diastereomer)</td>
<td>3325 (w, br)</td>
<td>2005 (vs)</td>
<td>1760 (ms)</td>
<td>1405 (ms)</td>
</tr>
</tbody>
</table>

\textsuperscript{a} As Nujol mull.
Table 14

$^1H$ NMR Data for Complexes $\eta^5$-C$_5$H$_5$(CO)$_3$W

<table>
<thead>
<tr>
<th>$R^1$</th>
<th>$R^2$</th>
<th>C$_5$H$_5$ ($\delta$, ppm)</th>
<th>Other Protons ($\delta$, ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_d$</td>
<td>CH$_3$</td>
<td>5.39 (s)</td>
<td>1.18 (d, J=6.4 Hz CH$_3$), 2.02-2.48 (m, H$_c$), 3.05-4.03 (m, H$_a$, H$_b$ and H$_d$), 6.45 (s, NH), 7.07-7.50 (m, NC$_6$H$_5$)</td>
</tr>
<tr>
<td>CH$_3$</td>
<td>CH$_3$</td>
<td>5.50 (s)</td>
<td>1.04 (s, CH$_3$), 1.24 (s, CH$_3$), 2.58-2.71 (m, H$_c$), 3.58-4.02 (m, H$_a$ and H$_b$), 6.39 (s, NH), 6.63-7.37 (m, NC$_6$H$_5$)</td>
</tr>
<tr>
<td>$H_d$</td>
<td>C$_6$H$_5$</td>
<td>5.11 (s)</td>
<td>2.61-3.06 (m, H$_c$), 3.60-4.52 (m, H$_a$, H$_b$ and H$_d$), 6.42 (s, NH), 6.71-7.50 (m, C$_6$H$_5$ and NC$_6$H$_5$)</td>
</tr>
<tr>
<td>C$_6$H$_5$</td>
<td>$H_d$</td>
<td>5.11 (s)</td>
<td>2.58-3.13 (m, H$_c$), 3.80-4.48 (m, H$_a$, H$_b$ and H$_d$), 6.48 (s, NH), 7.05-7.63 (m, C$_6$H$_5$ and NC$_6$H$_5$)</td>
</tr>
</tbody>
</table>

a In CDCl$_3$ solution.

b The complex contains one THF molecule.
Preparation of trans-$\eta^5$-$C_5H_5(CO)_3WCHCH(C_6H_5)C(O)N(S(O)_2NHC_6H_5)CH_2$

The addition of a solution of 0.580 g (4.10 mmol) of CI$\text{SO}_2\text{NCO}$ in 20 mL of $\text{CH}_2\text{Cl}_2$ at -78°C to a solution of 1.72 g (4.04 mmol) of $\eta^5$-$C_5H_5(CO)_3W(E-\text{CH}_2\text{CH}=\text{CHC}_6\text{H}_5)$ in 40 mL of $\text{CH}_2\text{Cl}_2$ also at -78°C resulted in the formation of a yellow precipitate. The mixture was stirred at -78°C for 10 min and then allowed to warm to room temperature in 20 min. After 10 min of stirring at 25°C, the mixture changed color to green and became clear. The mixture was cooled to -78°C, and a solution of 0.918 g (9.87 mmol) of aniline in 20 mL of $\text{CH}_2\text{Cl}_2$ was added to it. The mixture was first stirred at -78°C for 30 min and then at room temperature for 1.5 hours. A white precipitate formed gradually during this period. The white solid $C_6H_5\text{NH}_3^+\text{Cl}^-$ was then filtered off. The filtrate was passed through a pad of Florisil to remove excess aniline. The filtrate was then evaporated to dryness in vacuo, and the residue was recrystallized from 30 mL of a mixture of $\text{CH}_2\text{Cl}_2$ and n-pentane (1:3). The compound was further purified by chromatography on Florisil eluting with $\text{CH}_2\text{Cl}_2$ to afford 2.0 g (3.1 mmol, 76%) of a yellow product. The physical properties, IR, and $^1\text{H}$ NMR spectral data are listed in Tables 12, 13 and 14, respectively.

Mass Spectrum (FAB) m/e (relative intensity)

649 ((M + H)$^+$, 1.36)
Protonation of trans-$n^5$-C$_6$H$_5$(CO)$_3$WCHCH(C$_6$H$_5$)C(O)N(S(O)$_2$NHC$_6$H$_5$)CH$_2$

with HPF$_6$·(C$_2$H$_5$)$_2$O

To a solution of 0.400 g (0.617 mmol) of the title complex in 30 mL of CH$_2$Cl$_2$ at -78°C was added a solution of 0.240 g (1.09 mmol) of HPF$_6$·(C$_2$H$_5$)$_2$O in 20 mL of CH$_2$Cl$_2$ also at -78°C. The resulting mixture was stirred at -78°C for 20 min. Then the reaction temperature was allowed to rise to room temperature over 20 min, and the mixture was stirred at 25°C for 70 min. A green precipitate formed gradually during this period. The green precipitate was filtered off and washed with 5 mL of CH$_2$Cl$_2$ to afford 0.200 g (0.252 mmol, 41%) of a product which was characterized as cis-[$n^5$-C$_6$H$_5$(CO)$_3$W(n$_2$-CH$_2$=CHCH(C$_6$H$_5$)C(O)NH(S(O)$_2$NHC$_6$H$_5$))]+PF$_6$$. ^1$H NMR spectroscopic data: (acetone-$d_6$) δ 7.77-7.24 (m, C$_6$H$_5$, NH, NC$_6$H$_5$ and NH), 5.65 (s, C$_5$H$_5$), 4.41-3.70 (m, CH$_2$=CH and CH). The IR spectral data are listed in Table 15.

Deprotonation of cis-[$n^5$-C$_6$H$_5$(CO)$_3$W(n$_2$-CH$_2$=CHCH(C$_6$H$_5$)C(O)NH(S(O)$_2$NHC$_6$H$_5$))]+PF$_6$-

A solution of 0.080 g (0.33 mmol) of Proton Sponge in 20 mL of THF at -78°C was added to a solution of 0.257 g (0.324 mmol) of the title complex in 30 mL of THF also at -78°C. After 5 min of
stirring at -78°C, the temperature of the mixture was allowed to rise to room temperature over 20 min. A white precipitate formed in the process of warming up. The mixture was stirred at 25°C for 10 min, and it was then filtered by Schlenk-flask filtration. The solvent was removed from the filtrate under reduced pressure to give 0.095 g (0.15 mmol, 46%) of a yellow product which was characterized as cis-\( \text{n}^5\text{-C}_5\text{H}_5(\text{CO})_3\text{WCH}_2\text{CH(C}_6\text{H}_5)\text{C(O)N(S(O)NHCH}_3\text{H}_5)\text{CH}_3 \). The compound was very air-sensitive. Its \(^1\text{H NMR}\) spectrum showed the presence of one THF molecule. The physical properties and \(^1\text{H NMR}\) and IR spectral data are listed in Tables 12, 16 and 14, respectively.

**Protonation of \( \text{n}^5\text{-C}_5\text{H}_5(\text{CO})_3\text{WCH}(\text{CH}_3)_2\text{C(O)N(S(O)NHCH}_3\text{H}_5)\text{CH}_2 \) with \( \text{HPF}_6^-\text{(C}_2\text{H}_5)_2\text{O} \)**

To a solution of 0.333 g (0.555 mmol) of the title complex in 40 mL of CH\(_2\)Cl\(_2\) at -78°C was added a solution of 0.200 g (0.909 mmol) of \( \text{HPF}_6^-\text{(C}_2\text{H}_5)_2\text{O} \) in 20 mL of CH\(_2\)Cl\(_2\) also at -78°C. After stirring at -78°C for 20 min, the reaction mixture was allowed to warm to 0°C in 20 min. After the mixture was stirred at 0°C for 30 min, it became slightly cloudy. It was then cooled to -78°C and filtered at low temperature (below 0°C) to give about 0.075 g of a yellow-green product which was assumed to be \([\text{n}^5\text{-C}_5\text{H}_5(\text{CO})_3\text{W(\text{n}^2\text{-CH}_2=-\text{CHCH(\text{CH}_3)C(O)N(S(O)NHCH}_3\text{H}_5)})]^+\text{PF}_6^-\). Since the complex decomposed at room temperature in a few seconds, no spectral data were obtained.
The deprotonation of the product was not carried out owing to the low yield and low thermal stability.

**Protonation of trans-\(n^5-C_6H_5(CO)_3WCHCH(CH_3)C(O)N(S(O)_2NHC_6H_5)CH_2\) with HPF\(_6\)'(C\(_2\)H\(_5\))\(_2\)O**

(a) From \(-78^\circ\text{C}\) to \(-10^\circ\text{C}\)

To a solution of 0.175 g (0.297 mmol) of the title complex in 30 mL of CH\(_2\)Cl\(_2\) at \(-78^\circ\text{C}\) was added a solution of 0.095 g (0.43 mmol) of HPF\(_6\)'(C\(_2\)H\(_5\))\(_2\)O in 20 mL of CH\(_2\)Cl\(_2\) also at \(-78^\circ\text{C}\). After the addition, the temperature of the resulting mixture was allowed to come to \(-10^\circ\text{C}\) over 15 min. A precipitate formed at ca. \(-30^\circ\text{C}\) in the process of warming up. The mixture was stirred at \(-10^\circ\text{C}\) for 10 min and then was filtered to give 0.150 g (0.205 mmol, 69%) of a yellow product, which was characterized as trans-[\(n^5-C_6H_5(CO)_3W(n^2-CH_2=CH-CH(CH_3)C(O)NH(S(O)_2NHC_6H_5))\)]\(^+\)PF\(_6^-\). The IR spectroscopic data are listed in Table 15.

(b) From \(-78^\circ\text{C}\) to room temperature

To a solution of 0.200 g (0.341 mmol) of the title complex in 30 mL of CH\(_2\)Cl\(_2\) at \(-78^\circ\text{C}\) was added a solution of 0.157 g (0.714 mmol) of HPF\(_6\)'(C\(_2\)H\(_5\))\(_2\)O in 20 mL of CH\(_2\)Cl\(_2\) also at \(-78^\circ\text{C}\). The mixture was first stirred at \(-78^\circ\text{C}\) for 5 min and then allowed to warm to room temperature and stirred for an additional 45 min. A yellow precipitate formed at ca. \(-30^\circ\text{C}\), and did not dissolve at room
temperature. The mixture was filtered to yield 0.170 g (0.232 mmol, 68%) of a yellow-green product. The deprotonation of the product with Proton Sponge in THF showed that it was more than 90% trans-\([n^5-C_5H_5(CO)_3W(n^2-CH_2=CHCH(CH_3)C(O)NH(S(O)_2NHCH_2CH_3)])^{+PF_6}^-\).

The same procedure was followed for a reaction in which the mixture was stirred at room temperature for 6 hours. A green product was obtained (19%), which was later characterized by deprotonation as a diastereomeric mixture of \([n^5-C_5H_5(CO)_3W(n^2-CH_2=CHCH(CH_3)C(O)NH(S(O)_2NHCH_2CH_3)])^{+PF_6}^-\).

Deprotonation of \([n^5-C_5H_5(CO)_3W(n^2-CH_2=CHCH(CH_3)C(O)NH(S(O)_2NH-C_6H_5)])^{+PF_6}^-\) with Proton Sponge

(a) The transDiastereomer

A solution of 0.048 g (0.198 mmol) of Proton Sponge in 15 mL of THF at -78°C was added to a solution of 0.145 g (0.198 mmol) of the trans diastereomer of the title complex, obtained from the preceding reaction (a), in 20 mL of THF also at -78°C. The temperature of the mixture was allowed to rise to room temperature. A white precipitate was then filtered. The filtrate was evaporated to dryness. The residue was recrystallized from 30 mL of a mixture of CH_2Cl_2 and n-pentane (1:4) to give 0.090 g (0.15 mmol, 76%) of a yellow product. The yellow product was shown to be trans-\(n\)-\(C_5H_5(CO)_3WCHC(CH_3)C(O)N(S(O)_2NHCH_2CH_3)CH_2\) by \(^1\)H NMR spectroscopy.
(b) The Product of the Reaction at Room Temperature for 6 Hours

A solution of 0.015 g (0.062 mmol) of Proton Sponge in 5 mL of THF at -78°C was added to a solution of 0.045 g (0.061 mmol) of the title complex, obtained from the preceding reaction (b) at room temperature for 6 hours, in 10 mL of THF also at -78°C. The mixture was then warmed to room temperature. A white precipitate formed at ca. -60°C. After 5 min of stirring at 25°C, the mixture was filtered. The solvent was removed in vacuo, and the residue was recrystallized from 15 mL of a mixture of CH₂Cl₂ and n-pentane (1:3) to give 0.030 g (0.051 mmol, 82%) of a yellow product. The product contained 30% trans-n⁵-C₅H₅(CO)₃WCHCH(CH₃)C(O)N(S(O)₂NHC₆H₅)CH₂ and 70% possible cis-n⁵-C₅H₅(CO)₃WCHCH(CH₃)C(O)N(S(O)₂NHC₆H₅)CH₂. The complexes were characterized by ¹H NMR spectroscopy.

VI. Preparation and Reactions with Electrophilic Reagents of Platinum(II)-n¹-Allyl Complexes

Preparation of trans-[[(n¹-C₅H₅)Pt(P(C₂H₅)₃)₂Cl]

To a yellow suspension of 1.085 g (1.000 mmol) of [(C₅H₅)PtCl₄] in 30 mL of diethyl ether at 0°C was added a solution of 1.08 g (9.19 mmol) of P(C₂H₅)₃ in 20 mL of diethyl ether also at 0°C over 20 min. The addition resulted in the formation of a white
Table 15

Major Infrared Absorption Bands for Complexes

\[
\left[ n^5-C_5H_5(CO)_3W(n^2-CH_2=CHR^1R^2C(O)N(S(O)_2NH)(C_6H_5)) \right]^+ PF_6^-
\]

<table>
<thead>
<tr>
<th>(R^1)</th>
<th>(R^2)</th>
<th>(v(\text{NH})\text{cm}^{-1})</th>
<th>(v(\text{C}=\text{O})\text{cm}^{-1})</th>
<th>(v(\text{C}=\text{O})\text{cm}^{-1})</th>
<th>(v(\text{SO}_2)\text{cm}^{-1})</th>
<th>(v(PF_6^-)\text{cm}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>CH_3</td>
<td>3335 (s)</td>
<td>2108 (s)</td>
<td>1708 (s)</td>
<td>1362 (s)</td>
<td>845 (s, br)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(trans diastereomer)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>3241 (s, br)</td>
<td>2055 (s)</td>
<td>1195 (s)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(trans diastereomer)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>2000 (s)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C_6H_5</td>
<td>H</td>
<td>3245 (s, br)</td>
<td>2115 (s)</td>
<td>1736 (ms)</td>
<td>1368 (ms)</td>
<td>842 (s, br)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(cis diastereomer)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>3185 (s, br)</td>
<td>2050 (vs)</td>
<td>1193 (ms)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) As Nujol mull.
Table 16

Analytical Data for Complexes trans-[(n\textsuperscript{1}-C\textsubscript{3}H\textsubscript{5})PtL\textsubscript{2}Cl]

<table>
<thead>
<tr>
<th></th>
<th>%C</th>
<th></th>
<th>%H</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Calcd.</td>
<td>Found</td>
<td>Calcd.</td>
<td>Found</td>
</tr>
<tr>
<td>(P(i-C\textsubscript{3}H\textsubscript{7})_3)</td>
<td>42.61</td>
<td>42.44</td>
<td>8.00</td>
<td>8.14</td>
</tr>
<tr>
<td>(P(t-C\textsubscript{4}H\textsubscript{9})_3\cdot CH\textsubscript{2}Cl\textsubscript{2})\textsuperscript{a}</td>
<td>44.18</td>
<td>44.55</td>
<td>8.58</td>
<td>8.44</td>
</tr>
</tbody>
</table>

\textsuperscript{a} This compound was recrystallized from a mixture of CH\textsubscript{2}Cl\textsubscript{2} and n-pentane.

One molecule of CH\textsubscript{2}Cl\textsubscript{2} was associated with the compound.
Table 17

Major Infrared Absorption Bands for Complexes

\( \text{trans-}[\text{(n}^1\text{-CH}_2\text{CH=CR}_1\text{R}_2)\text{PtL}_2\text{Cl}]^a \)

<table>
<thead>
<tr>
<th>( L )</th>
<th>( R^1 )</th>
<th>( R^2 )</th>
<th>( v(\text{C=C}) )</th>
<th>( v(\text{Pt-Cl}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{P(C}_2\text{H}_5)_3 )</td>
<td>H</td>
<td>H</td>
<td>1607 (ms)</td>
<td>258 (m)</td>
</tr>
<tr>
<td>( \text{P(CH}_3)_2\text{C}_6\text{H}_5 )</td>
<td>H</td>
<td>H</td>
<td>1614 (m)</td>
<td>265 (m)</td>
</tr>
<tr>
<td>( \text{P(i-C}_3\text{H}_7)_3 )</td>
<td>H</td>
<td>H</td>
<td>1609 (m)</td>
<td>260 (m)</td>
</tr>
<tr>
<td>( \text{P(t-C}_4\text{H}_9)_3 )</td>
<td>H</td>
<td>H</td>
<td>1631 (w)</td>
<td>253 (m)</td>
</tr>
<tr>
<td>( \text{P(C}_2\text{H}_5)_3 )</td>
<td>D</td>
<td>\text{CH}_3</td>
<td>1645 (w, br)</td>
<td>263 (w)</td>
</tr>
</tbody>
</table>

\( ^a \text{As Nujol mull.} \)
Table 18

$^1$H NMR Data for Complexes $\text{trans-}[(\eta^1-\text{CH}_2\text{CH} = \text{CR}_2^1\text{R}_2)\text{PtL}_2\text{Cl}]^{a,b}$

<table>
<thead>
<tr>
<th>$L$</th>
<th>$R^1$</th>
<th>$R^2$</th>
<th>Chemical Shifts ($\delta$, ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P(C_2H_5)_3$</td>
<td>H</td>
<td>H</td>
<td>$6.17$ (m, 1H, $H_C$), $5.23$-$4.62$ (m, 1H, $H_a$ and $H_b$), $2.31$ (d and $^{195}$Pt-H coupling observed, $J(CH_2, ^{195}$Pt) = 26 Hz), $J(CH_2, H_C) = 7.7$ Hz, $H_d$ and $H_e$), $1.81$ (m, 12H, PCH$_2$), $0.97$ (quintet, 18H, CH$_3$)</td>
</tr>
<tr>
<td>$P(CH_3)_2C_6H_5$</td>
<td>H</td>
<td>H</td>
<td>$7.84$-$6.56$ (m, 10H, C$_6$H$_5$), $5.79$ (m, br, 1H, $H_C$), $4.83$-$4.27$ (m, 2H, $H_a$ and $H_b$), $2.06$ (m, 2H, $H_d$ and $H_e$), $1.49$ (m, 12H, PCH$_3$)</td>
</tr>
<tr>
<td>$P(i-C_3H_7)_3$</td>
<td>H</td>
<td>H</td>
<td>$6.38$-$6.05$ (m, 1H, $H_C$), $5.28$-$4.68$ (m, 2H, $H_a$ and $H_b$), $3.25$-$2.40$ (m, 6H, CH), $2.38$ (d, and $^{195}$Pt-H coupling observed, $J(CH_2, H_C) = 7.2$ Hz, $2H, H_d$ and $H_e$), $1.26$ (q, 36H, CH$_3$)</td>
</tr>
<tr>
<td>$P(t-C_4H_9)_3$</td>
<td>H</td>
<td>H</td>
<td>$6.15$ (m, 1H, $H_C$), $5.40$-$4.90$ (m, br, 2H, $H_a$ and $H_b$), $2.29$ (m, 2H, $H_d$ and $H_e$), $1.55$ (t, 54H, CH$_3$)</td>
</tr>
</tbody>
</table>
Table 18 (continued)

$^1$H NMR Data for Complexes trans-[(n$^1$-CH$_2$CR=CR$^2$)PtL$_2$Cl]$^a$, $^b$

<table>
<thead>
<tr>
<th>L</th>
<th>R$^1$</th>
<th>R$^2$</th>
<th>Chemical Shifts ($\delta$, ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(C$_2$H$_5$)$_3$ D CH$_3$</td>
<td>5.76 (m, 1H, H$_c$), 2.20 (d and $^{195}$Pt-H coupling observed, $J$(CH$_2$, H$_c$) = 6.6 Hz, $J$(CH$_2$, $^{195}$Pt) = 24 Hz, 2H, H$_d$ and H$_e$), 1.80 (m, 12H PCH$_2$), 1.73 (s, 3H, CH$_3$(b)$^d$, 0.96 (quintet, 18H, CH$_3$)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ In C$_6$D$_6$ solution.

$^b$ Hydrogen letters are assigned as follows:

$^c$ The absorption is very weak and broad.

$^d$ The methyl protons are coupled to deuterium. Since $^3$J(D, CH$_3$) is small, the resonance of the methyl protons appears as a singlet.
precipitate which was not characterized and a colorless solution. The mixture was stirred at room temperature for 18 hours and then filtered. The solvent was pumped off from the filtrate. The white oily residue was recrystallized from 4 mL of n-hexane at -78°C to yield 1.41 g (2.78 mmol, 69%) of white crystals. The product was identified by comparison of its IR and $^1$H NMR spectra with those of an authentic sample prepared by R. G. Pearson.\textsuperscript{40} The IR, $^1$H NMR and $^{31}$P NMR spectra data are listed in Tables 17, 18 and 19, respectively.

**Preparation of trans-[$(\eta^1$-C$_3$H$_5$)Pt(P(CH$_3$)$_2$C$_6$H$_5$)$_2$Cl]$**

To a yellow suspension of 0.826 g (0.760 mmol) of [(C$_3$H$_5$)PtCl]$_4$ in 30 mL of CH$_2$Cl$_2$ at -78°C was added a solution of 0.420 g (3.05 mmol) of the first 4 equivalents of P(CH$_3$)$_2$C$_6$H$_5$ in 25 mL of CH$_2$Cl$_2$ at 30°C over 30 min. The resulting mixture was stirred at room temperature for one day, and a small amount of white precipitate formed which was not characterized. After filtration under nitrogen, a solution of 0.420 g (3.05 mmol) of the second 4 equivalents of P(CH$_3$)$_2$C$_6$H$_5$ in 25 mL of CH$_2$Cl$_2$ was added to the yellow filtrate at room temperature, stirred for one day and then concentrated to 10 mL. Treatment with n-pentane resulted in the formation of a pale yellow precipitate. The precipitate was dried at 55°C \textit{in vacuo} for one day to afford 0.535 g (0.976 mmol, 32%) of
a pale yellow product. The IR, $^1$H NMR and $^{31}$P NMR spectral data are listed in Tables 17, 18 and 19, respectively.

**Preparation of trans-[(η$^3$-C$_3$H$_5$)Pt(P(i-C$_3$H$_7$)$_3$)$_2$Cl]**

Addition over 20 min with stirring of 0.225 g (1.41 mmol) of P(i-C$_3$H$_7$)$_3$ in 25 mL of diethyl ether to a yellow suspension of 0.191 g (0.176 mmol) of [(C$_3$H$_5$)PtCl]$_4$ at room temperature resulted in the formation of a white precipitate which was not characterized and a colorless solution. The mixture was stirred at 25°C for 24 hours and then filtered. The filtrate was evaporated to dryness to give 0.360 g (0.609 mmol, 87%) of a white product. The analytical data, IR, $^1$H NMR and $^{31}$P NMR spectroscopic data are listed in Tables 16, 17, 18 and 19, respectively.

Mass Spectrum (FAB) m/e

558 ((M + H - Cl)$^+$

**Preparation of trans-[(η$^3$-C$_3$H$_5$)Pt(P(t-C$_4$H$_7$)$_3$)$_2$Cl]**

To a suspension of 0.450 g (0.415 mmol) of [(C$_3$H$_5$)PtCl]$_4$ in 30 mL of CH$_2$Cl$_2$ was slowly added a solution of 0.335 g (1.66 mmol) of the first 4 equivalents of P(t-C$_4$H$_7$)$_3$ in 20 mL of CH$_2$Cl$_2$ at -15°C with vigorous stirring over 30 min. The resulting mixture was set aside at -10°C for one day until most of the yellow solid dissolved. The mixture was filtered and a solution of 0.335 g (1.66
mmol) of the second 4 equivalents of \( \text{P(t-C}_4\text{H}_7)_3 \) in 20 mL of \( \text{CH}_2\text{Cl}_2 \) at \(-78^\circ\text{C} \) was added to the filtrate, also at \(-78^\circ\text{C} \) over 30 min. The mixture was kept at \(-78^\circ\text{C} \) overnight and then stirred at \(-10^\circ\text{C} \) for 5 hours. The solvent was pumped off, and the residue was redissolved in a mixture of \( \text{CH}_2\text{Cl}_2 \) and n-pentane (1:3) to precipitate an impurity. The solvent was removed from the solution in vacuo. The yellow residue was washed with 1 mL of diethyl ether to give 0.250 g (0.370 mmol, 22%) of a white product. The IR, \( ^1\text{H NMR} \) and \( ^3\text{P NMR} \) spectroscopic data are listed in Tables 17, 18 and 19, respectively.

Preparation of trans-[\( \text{n}^1\text{-E-CH}_2\text{=CHCDCH}_3\text{)Pt(P(C}_2\text{H}_5)_3\text{)Cl} \)]

To solution of 1.5 g (2.3 mmol) of \( \text{Pt(P(C}_2\text{H}_5)_3}_4 \) in 15 mL of n-hexane was added dropwise a solution of 0.23 g (2.5 mmol) of \( \text{Z-ClCH}_2\text{CH=CDCH}_3 \) in 15 mL of n-hexane. The orange color of the platinum(0) reagent faded after stirring for 10 min to yield a colorless solution. The mixture was stirred at room temperature for 30 min, solvent was removed, and the residue was recrystallized from 5 mL of n-hexane at \(-78^\circ\text{C} \) to yield 0.785 g (1.5 mmol, 65%) of a white product. The \( ^2\text{H NMR} \) spectrum of the product showed a singlet at \( \delta 5.42 \text{ ppm} \). The IR, \( ^1\text{H NMR} \), and \( ^3\text{P NMR} \) spectral data are listed in Tables 17, 18 and 19, respectively.
Reaction of trans-[(η⁵-C₅H₅)Pt(P(CH₃)₂C₆H₅)₂Cl] with SO₂

Dry SO₂ was bubbled through a solution of 0.124 g (0.244 mmol) of the title complex in 30 mL of benzene at room temperature for 5 min. The color of the solution changed to deep yellow and then to light yellow. The solvent was removed under reduced pressure, and the oily residue was washed with 5 mL of n-hexane and dried in vacuo for 6 hours to give 0.135 g (0.236 mmol, 97%) of a solid insertion product, trans-[(CH₂=CHCH₂S(O)₂)Pt(P(CH₃)₂C₆H₅)₂Cl]. The physical properties, IR, ¹H NMR and ³¹P NMR spectroscopic data are listed in Tables 20, 21, 22 and 23, respectively.

Reaction of trans-[(η⁵-C₅H₅)Pt(P(CH₃)₂C₆H₅)₂Cl] with SO₂

Dry SO₂ was bubbled through a solution of 0.203 g (0.371 mmol) of the title complex in 50 mL of benzene at room temperature for 30 min. The color of the solution changed to deep yellow and then to yellow over 1 min. The benzene was removed in vacuo and the residue was recrystallized from 12 mL of a mixture of benzene-n-hexane (1:6) to yield 0.214 g (0.350 mmol, 94%) of an insertion product, trans-[(CH₂=CHCH₂S(O)₂)Pt(P(CH₃)₂C₆H₅)₂Cl], the structure of which was determined by X-ray diffraction. The physical properties, IR, ¹H NMR and ³¹P NMR spectroscopic data are listed in Tables 20, 21, 22 and 23, respectively.
Mass Spectrum (FAB)  m/e (relative intensity)
613 ((M + H)$^+$, 3.38)
508 ((M + H - C$_3$H$_5$ - SO$_2$)$^+$, 5.07)

Reaction of trans-[(n$^1$-C$_3$H$_5$)Pt(P(i-C$_3$H$_7$)$_3$)$_2$Cl] with SO$_2$

Dry SO$_2$ was bubbled through a solution of 0.105 g (0.177 mmol) of the title complex in 30 mL of diethyl ether at room temperature for 4 hours. The reaction proceeded relatively slowly. After 1 hour of bubbling, the $^{31}$P NMR spectrum of the solution showed that half of the starting material remained unreacted. The solvent was removed in vacuo after bubbling SO$_2$ for 4 hours. The residue was redissolved in 3 mL of CH$_2$Cl$_2$, and then 10 mL of n-pentane was slowly added to precipitate an impurity. The solvent was evaporated under reduced pressure to give a light yellow solid which contained a possible insertion product, trans-[(CH$_2$=CHCH$_2$S(O)$_2$Pt(P(i-C$_3$H$_7$)$_3$)$_2$Cl], and some impurities. Since the impurities could not be separated from the product, the $^1$H NMR spectrum was not recorded. The IR and $^{31}$P NMR spectra are listed in Tables 21 and 23, respectively.
Table 19

$^{31}$P NMR Data for Complexes trans-\([(n^{1-}CH_2CH=CR_1R_2)PtL_2Cl]\)\(^a\)

<table>
<thead>
<tr>
<th>L</th>
<th>R(^1)</th>
<th>R(^2)</th>
<th>Chemical Shifts (δ, ppm)</th>
<th>Coupling Constants (J(^{195})Pt-P, Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(C(_2)H(_5))(_3)</td>
<td>H</td>
<td>H</td>
<td>13.32</td>
<td>2902</td>
</tr>
<tr>
<td>P(CH(_3))_2C(_6)H(_5)</td>
<td>H</td>
<td>H</td>
<td>-4.57</td>
<td>2991</td>
</tr>
<tr>
<td>P(i-C(_3)H(_7))(_3)</td>
<td>H</td>
<td>H</td>
<td>28.06</td>
<td>2904</td>
</tr>
<tr>
<td>P(t-C(_4)H(_9))(_3)</td>
<td>H</td>
<td>H</td>
<td>75.21</td>
<td>2948</td>
</tr>
<tr>
<td>P(C(_2)H(_5))(_3)</td>
<td>D</td>
<td>CH(_3) (E)</td>
<td>13.65</td>
<td>2944</td>
</tr>
<tr>
<td>P(C(_2)H(_5))(_3)</td>
<td>CH(_3)</td>
<td>D (Z)</td>
<td>13.48</td>
<td>2925</td>
</tr>
</tbody>
</table>

\(^a\) In C\(_6\)H\(_6\) solution at 298K.
Table 20
Analytical Data for Complexes trans-(CH<sub>2</sub>=CHCR(0)<sub>2</sub>)PtL<sub>2</sub>Cl

<table>
<thead>
<tr>
<th>L</th>
<th>R</th>
<th>%C Calcd.</th>
<th>%C Found</th>
<th>%H Calcd.</th>
<th>%H Found</th>
<th>%S Calcd.</th>
<th>%S Found</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;</td>
<td>H</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>5.60</td>
<td>5.37</td>
</tr>
<tr>
<td>P(CH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;</td>
<td>H</td>
<td>37.36</td>
<td>37.34</td>
<td>4.29</td>
<td>4.36</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>P(C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>32.79</td>
<td>32.68</td>
<td>6.36</td>
<td>6.15</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>
Table 21

Major Infrared Absorption Bands for Complexes

\[
\text{trans-}[(\text{CH}_2=\text{CHR}^1\text{R}^2\text{S(O)}_2\text{PtL}_2\text{Cl})] \]

<table>
<thead>
<tr>
<th>L</th>
<th>R(^1)</th>
<th>R(^2)</th>
<th>(\nu(\text{C=C})\text{cm}^{-1})</th>
<th>(\nu(\text{SO}_2)\text{cm}^{-1})</th>
<th>(\nu(\text{Pt-Cl})\text{cm}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{P(C}_2\text{H}_5)_3)</td>
<td>H</td>
<td>H</td>
<td>1639 (m)</td>
<td>1212 (s)</td>
<td>1076 (s)</td>
</tr>
<tr>
<td>(\text{P(CH}_3)_2\text{C}_6\text{H}_5)</td>
<td>H</td>
<td>H</td>
<td>1634 (m)</td>
<td>1223 (s)</td>
<td>1065 (s)</td>
</tr>
<tr>
<td>(\text{P(i-C}_3\text{H}_7)_3)^b</td>
<td>H</td>
<td>H</td>
<td>1635 (w)</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>(\text{P(C}_2\text{H}_5)_3)</td>
<td>H</td>
<td>\text{CH}_3</td>
<td>1634 (m)</td>
<td>1213 (s)</td>
<td>1065 (s)</td>
</tr>
<tr>
<td>(\text{P(C}_3\text{H}_5)_3)</td>
<td>D</td>
<td>\text{CH}_3</td>
<td>1634 (m)</td>
<td>1213 (s)</td>
<td>1065 (s)</td>
</tr>
</tbody>
</table>

\(^a\) As Nujol mull.

\(^b\) Since the sample contained some impurities which could not be separated, the \(\nu(\text{SO}_2)\) bands were difficult to be assigned.
Table 22

$^1$H NMR Data for Complexes trans-[(CH$_2$=CHR$^1$R$^2$S(0)$_2$)PtLCl]$^{a,b}$

<table>
<thead>
<tr>
<th>L</th>
<th>R$^1$</th>
<th>R$^2$</th>
<th>Chemical Shifts ($\delta$, ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(C$_2$H$_5$)$_3$</td>
<td>H</td>
<td>H</td>
<td>6.22 (m, 1H, H$_c$), 5.56-5.21 (m, 2H, H$_a$ and H$_b$), 3.84 (d, J = 7.0 Hz, 2H, H$_d$ and H$_e$), 2.15 (m, 12H, PCH$_2$), 1.00 (quintet, 18H, CH$_3$)</td>
</tr>
<tr>
<td>P(CH$_3$)$_2$C$_6$H$_5$</td>
<td>H</td>
<td>H</td>
<td>7.84-6.80 (m, 10H, C$_6$H$_5$), 5.68 (m, 1H, H$_c$), 5.15-4.70 (m, 2H, H$_a$ and H$_b$), 3.11 (d, J = 6.8 Hz, 2H, H$_d$ and H$_e$), 1.66 (m, 12H, CH$_3$)</td>
</tr>
<tr>
<td>P(C$_2$H$_5$)$_3$</td>
<td>H</td>
<td>CH$_3$</td>
<td>6.18 (m, 1H, H$_c$), 5.27 (m, 2H, H$_a$ and H$_b$), 3.50 (m, 1H, H$_d$), 1.95 (m, 12H, PCH$_2$), 1.48 (d, J=6.9 Hz, 3H, CH$_3$(e)), 0.96 (quintet, 18H, CH$_3$)</td>
</tr>
<tr>
<td>P(C$_2$H$_5$)$_3$</td>
<td>D</td>
<td>CH$_3$</td>
<td>6.18 (m, 1H, H$_c$), 5.27 (m, 2H, H$_a$ and H$_b$), 1.95 (m, 12H, PCH$_2$), 1.48 (s, J=6.9 Hz, 3H, CH$_3$(e)), 0.96 (quintet, 18H, CH$_3$)</td>
</tr>
</tbody>
</table>

$^a$ In CDCl$_3$ solution.

$^b$ Hydrogen letters are assigned as follows:

$^c$ The methyl protons are coupled to deuterium. Since the coupling constant J(D, CH$_3$) is small, the resonance of the methyl protons appears as a singlet.
Table 23

31P NMR Data for Complexes trans-[(CH₂=CHCR₁R₂S(0)₂)PtL₂Cl]ᵃ

<table>
<thead>
<tr>
<th>L</th>
<th>R¹</th>
<th>R²</th>
<th>Chemical Shifts (δ, ppm)</th>
<th>Coupling Constants (J₁&lt;Pt,P), Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(C₂H₅)₃</td>
<td>H</td>
<td>H</td>
<td>20.2</td>
<td>2705</td>
</tr>
<tr>
<td>P(CH₃)₂C₆H₅</td>
<td>H</td>
<td>H</td>
<td>-3.86</td>
<td>2780</td>
</tr>
<tr>
<td>P(i-C₃H₇)ᵇ</td>
<td>H</td>
<td>H</td>
<td>30.34</td>
<td>2766</td>
</tr>
<tr>
<td>P(C₂H₅)₃</td>
<td>H</td>
<td>CH₃</td>
<td>19.36</td>
<td>2726</td>
</tr>
<tr>
<td>P(C₂H₅)₃</td>
<td>D</td>
<td>CH₃</td>
<td>19.38</td>
<td>2726</td>
</tr>
</tbody>
</table>

ᵃ In C₆H₆ solution unless otherwise specified.
ᵇ In CH₂Cl₂ solution.
Attempted Reaction of trans-\([\eta^1\text{C}_3\text{H}_5]\text{Pt}(\text{t-C}_4\text{H}_9)_3\text{Cl}]\) with SO\(_2\)

Dry SO\(_2\) was bubbled through a solution of 0.040 g (0.059 mmol) of the title complex in 15 mL of benzene at room temperature for 2 hours. The reaction mixture was then kept under a slightly positive pressure of SO\(_2\) for 16 hours. The solvent was removed by a stream of nitrogen gas. The light yellow residue was shown by \(^{31}\text{P}\) NMR spectroscopy to be the starting material.

Reaction of trans-\([\eta^1\text{CH}_2\text{CH}=\text{CHCH}_3]\text{Pt}(\text{P(C}_2\text{H}_5)_3\text{Cl}]\) with SO\(_2\)

Dry SO\(_2\) was bubbled through a solution of 0.200 g (0.383 mmol) of the title complex in 50 mL of benzene at room temperature for 10 min. The solution changed color first to deep yellow and then to light yellow in 5 min. The solvent was pumped off to yield 0.210 g (0.359 mmol, 94%) of a colorless oil which was characterized as the insertion product trans\(-\[(\text{CH}_2=\text{CHCD(CH}_3)S(O)_2)\text{Pt(P(C}_2\text{H}_5)_3\text{Cl}\]. The \(^{2}\text{H}\) NMR and \(^{31}\text{P}\) NMR spectral data are listed in Tables 21, 22 and 23, respectively.

Reaction of trans-\([\eta^1\text{CH}_2\text{CH}=\text{CDCH}_3]\text{Pt}(\text{P(C}_2\text{H}_5)_3\text{Cl}]\) with SO\(_2\)

Dry SO\(_2\) was bubbled through a solution of 0.20 g (0.383 mmol) of the title complex in 25 mL of benzene at room temperature for 15 min. The solution changed color to deep yellow and then to light yellow in 5 min. The solvent was pumped off to afford 0.21 g (0.36
mmol, 94%) of a colorless oil which was characterized as the insertion product \textit{trans}--\((\text{CH}_2=\text{CHCD}(\text{CH}_3)\text{S}(\text{O})_2)\text{Pt}(\text{C}_2\text{H}_5)_3\text{Cl}\). The \(^2\text{H NMR}\) spectrum of the product showed a singlet \(\delta 3.43\) ppm. The IR, \(^1\text{H NMR}\) and \(^{31}\text{P NMR}\) spectral data are listed in Tables 21, 22 and 23, respectively.

\textbf{Protonation of \([n^1-\text{C}_3\text{H}_5]\text{Pt}(\text{C}_2\text{H}_5)_3\text{Cl}\) with \(\text{HPF}_6\cdot(\text{C}_2\text{H}_5)_2\text{O}\) in THF}

To a solution of 0.122 g (0.240 mmol) of the title complex in 1.8 mL of THF in a 10 mm NMR tube at -78°C was added 0.052 g (0.24 mmol) of \(\text{HPF}_6\cdot(\text{C}_2\text{H}_5)_2\text{O}\). The resulting mixture was warmed slowly. The \(^{31}\text{P NMR}\) spectrum of the sample showed that reaction was taking place at -25°C. After the mixture was kept at -15°C for 15 min, the reaction was complete. More than 90% of the product was \textit{trans}--\([n^2-\text{CH}_2=\text{CHCH}_3]\text{Pt}(\text{C}_2\text{H}_5)_3\text{Cl}\)^{\text{+}}\text{PF}_6^-, which was estimated from \(^{31}\text{P NMR}\) spectrum, and the rest was \([n^3-\text{C}_3\text{H}_5]\text{Pt}(\text{C}_2\text{H}_5)_3\text{Cl}\)^{\text{+}}\text{PF}_6^- . The solvent was removed from the mixture in vacuo. Since the THF molecules were associated to the major product, no satisfactory \(^1\text{H NMR}\) or \(^{13}\text{C NMR}\) spectral data were obtained. \(^{31}\text{P NMR}\) (TMS) \(\delta 20.76\) ppm (\(J(^{195}\text{Pt}, \text{P}) = 2067\) Hz), 145 (quintet, \(J(\text{P, F}) = 712\) Hz).
Protonation of trans-[(η^1-C_3H_5)Pt(P(C_2H_5)_3)Cl] with HPF_6·(C_2H_5)_2O in Diethylether

To a solution of 0.230 g (0.453 mmol) of the title complex in 15 mL of diethyl ether at -78°C was added 0.10 g (0.45 mmol) of HPF_6·(C_2H_5)_2O. The resulting mixture was stirred at -78°C for 30 min as a white precipitate formed. The mixture was then allowed to warm to room temperature over 1.5 hours. The precipitate was filtered off and washed with diethyl ether (10 mL x 2) to afford 0.170 g (0.260 mmol, 72%) of a white product, trans-[(η^2-CH_2=CH-CH_3)Pt(P(C_2H_5)_3)_2Cl]^+PF_6. The analytical data, IR, ^31P NMR, ^1H NMR and ^13C NMR spectral data are listed in Tables 24, 25, 26, 27 and 28, respectively.

Mass Spectrum (FAB) m/e (relative intensity)
655 (M + H)^+, 3.32
598 (M + H - 3F)^+, 6.10

Protonation of trans-[(η^1-C_3H_5)Pt(C_6H_{11})_3Cl] with HPF_6·(C_2H_5)_2O

To a solution of 0.210 g (0.252 mmol) of the title complex in 20 mL of toluene at -78°C was added 0.070 g (0.318 mmol) of HPF_6·(C_2H_5)_2O. The resulting mixture was warmed to room temperature over 2 hours. A white precipitate formed at ca. -30°C. The precipitate was filtered off at room temperature and washed with n-pentane (5 mL x 2) to give 0.235 g (0.240 mmol, 95%) of a white
product, trans-\([\text{n}^2-\text{CH}_2=\text{CHCH}_3\text{Pt}(C_6\text{H}_{11})_3\text{Cl}]^+\text{PF}_6^-\). The physical properties, IR, and \(31\text{P NMR}\) spectroscopic data are listed in Tables 24, 25, and 26, respectively.

Reactions of trans-\([\text{n}^1-\text{C}_3\text{H}_5\text{Pt}(\text{P}(\text{C}_2\text{H}_5)_3\text{Cl}] \text{ with } \text{ClSO}_2\text{NCO}\)

Addition of 0.032 g (0.23 mmol) of ClSO\(_2\)NCO to a solution of 0.011 g (0.217 mmol) of the title complex in 2 mL of toluene in a 10 mm NMR tube at -78°C resulted in the formation of an orange precipitate. The \(31\text{P NMR}\) spectrum of the mixture at -75°C showed that it contained three components: (1) \(\delta 19.89 \text{ ppm, } J^{(195\text{Pt, P})} = 2680 \text{ Hz, (2) } \delta 11.98 \text{ ppm, } J^{(195\text{Pt, P})} = 2430 \text{ Hz, (3) } \delta -3.86 \text{ ppm, } J^{(195\text{Pt, P})} = 1700 \text{ Hz. When the temperature of the mixture was raised, the third component gradually started to convert to the second component. After the temperature reached 25°C, all of the third component was converted to the second component. The first compound appeared to be trans-\([\text{P}(\text{C}_2\text{H}_5)_3\text{ClPt}(\text{CHCH}_3\text{C}(\text{O})\text{N(SO}_2\text{Cl})\text{-CH}_2\text{]}], as supported by a comparison of the \(31\text{P NMR}\) data with those of analogous compounds. The second compound was trans-\([\text{P}(\text{C}_2\text{H}_5)_3\text{Cl}_2\text{-PtCl}_2]\], identified by comparison of its \(31\text{P NMR}\) and IR spectral data with those of an authentic sample.\(^{52}\) The ratio of the first compound to the second compound in the mixture was estimated from the \(31\text{P NMR}\) spectrum to be 1 to 3.
Table 24

Analytical Data for Complexes $\text{trans-}[(\eta^2-\text{CH}_2=\text{CHCH}_3)\text{PtL}_2\text{Cl}]^+\text{PF}_6^-$

<table>
<thead>
<tr>
<th>L</th>
<th>%C Calcd.</th>
<th>%C Found</th>
<th>%H Calcd.</th>
<th>%H Found</th>
<th>%S Calcd.</th>
<th>%S Found</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{P(C}_2\text{H}_5)_3$</td>
<td>27.56</td>
<td>27.18</td>
<td>5.55</td>
<td>5.69</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>$\text{P(C}<em>6\text{H}</em>{11})_3$</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>9.50</td>
<td>9.07</td>
</tr>
<tr>
<td>$\text{P(C}<em>6\text{H}</em>{11})_3^a$</td>
<td>41.65</td>
<td>41.33</td>
<td>6.74</td>
<td>6.50</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>

$^a$ One molecule of HPF$_6$ was associated with this compound.
Table 25

Major Infrared Absorption Bands for Complexes

$\text{trans-}[(\eta^2-\text{CH}_2=\text{CHCH}_3)\text{PtL}_2\text{Cl}]^+\text{PF}_6^- \ a$

<table>
<thead>
<tr>
<th>L</th>
<th>$\nu(C=C) \text{cm}^{-1}$</th>
<th>$\nu(\text{PF}_6) \text{cm}^{-1}$</th>
<th>$\delta(\text{PF}_6) \text{cm}^{-1}$</th>
<th>$\nu(\text{Pt-Cl}) \text{cm}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(C$_2$H$_5$)$_3$</td>
<td>1509 (w)</td>
<td>842 (s, br)</td>
<td>557 (m, sharp)</td>
<td>326 (m)</td>
</tr>
<tr>
<td>P(C$<em>6$H$</em>{11}$)$_3$</td>
<td>1510 (w)</td>
<td>838 (s, br)</td>
<td>555 (m, sharp)</td>
<td>325 (m)</td>
</tr>
</tbody>
</table>

$^a$ As Nujol mull
Table 26

$^{31}P$ NMR Data for Complexes $\text{trans-}[\left(n^2-\text{CH}_2=\text{CHCH}_3\right)\text{PtL}_2\text{Cl}]^+\text{PF}_6^-_{a,b}$

<table>
<thead>
<tr>
<th>L</th>
<th>Chemical Shifts ($\delta$, ppm)</th>
<th>Coupling Constants ($J(^{195}\text{Pt},P)$, Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{P(C}<em>6\text{H}</em>{11})_3$</td>
<td>20.92</td>
<td>2017</td>
</tr>
<tr>
<td></td>
<td>20.69</td>
<td>1998</td>
</tr>
<tr>
<td>$\text{P(C}_2\text{H}_5)_3$</td>
<td>18.80</td>
<td>2056</td>
</tr>
<tr>
<td></td>
<td>18.66</td>
<td>2086</td>
</tr>
</tbody>
</table>

---

$^{a}$ In $\text{C}_6\text{H}_6$ solution at 298K.

$^{b}$ The absorption of $\text{PF}_6^-$ phosphorus are observed at $\delta$ -145 with a $J(P,F)$ value of 712 Hz.
Table 27

$^1$H NMR Data for Complexes trans-[(n^2-CH_2=CHCH_3)Pt(P(C_2H_5)_3)Cl]^+PF_6^- \text{a,b}

<table>
<thead>
<tr>
<th>Hydrogen</th>
<th>Chemical Shifts ($\delta$, ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>4.08 (d and $^{195}$Pt-H coupling observed, $J(H_a, H_c) = 13.8$ Hz, $J(^{195}$Pt, $H_a) = 75$ Hz)</td>
</tr>
<tr>
<td>b</td>
<td>3.90 (d and $^{195}$Pt-H coupling observed, $J(H_b, H_c) = 7.3$ Hz, $J(^{195}$Pt, $H_b) = 76$ Hz)</td>
</tr>
<tr>
<td>c</td>
<td>5.42 (m)</td>
</tr>
<tr>
<td>d</td>
<td>1.89 (d and $^{195}$Pt-H coupling observed, $J(H_c, CH_3) = 5.9$ Hz, $J(^{195}$Pt, CH_3) = 28 Hz)</td>
</tr>
<tr>
<td>e (or g)</td>
<td>2.12 (m)</td>
</tr>
<tr>
<td>f (of h)</td>
<td>1.21 (m)</td>
</tr>
<tr>
<td>g (or e)</td>
<td>2.00 (m)</td>
</tr>
<tr>
<td>h (or f)</td>
<td>1.18 (m)</td>
</tr>
</tbody>
</table>

\text{a In CDCl}_3 \text{ solution.}

\text{b Hydrogen letters are assigned as follows:}

\begin{center}
\text{[Image of chemical structure]}
\end{center}
Table 28

$^{31}\text{C NMR Data for Complexes trans-[(n}^2\text{-CH}_2\text{=CHCH}_3\text{)Pt(P(C}_2\text{H}_5\text{)}_3\text{Cl}]}^+\text{PF}_6^-\text{a}$

<table>
<thead>
<tr>
<th>Carbon b</th>
<th>Chemical Shifts ($\delta$, ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>93.00 (t) ($J^{195}\text{Pt, C} = 73.8$ Hz)</td>
</tr>
<tr>
<td>2</td>
<td>63.43 (t) ($J^{195}\text{Pt, C} = 79.6$ Hz)</td>
</tr>
<tr>
<td>3</td>
<td>22.35 (s)</td>
</tr>
<tr>
<td>4 (or 6)</td>
<td>14.40 (m)</td>
</tr>
<tr>
<td>5 (or 7)</td>
<td>7.99 (s)</td>
</tr>
<tr>
<td>6 (or 4)</td>
<td>12.20 (m)</td>
</tr>
<tr>
<td>7 (or 5)</td>
<td>7.70 (s)</td>
</tr>
</tbody>
</table>

a In CDCl$_3$ solution.

b Carbon numbers are assigned as follows:

```
Cl — Pt — C^1

C^2 — Pt — C^3

Et$_2$P — C^4 — C^5 — C^6 — C^7
```
When the same reaction was run at room temperature, trans-
\[(P(C_2H_5)_3)_2PtCl_2\] was the only product.

The $^{31}\text{P}$ NMR spectroscopic data of the cycloaddition product are
listed in Table 29.

Reaction of trans-$[\text{n}^1\text{-C}_2\text{H}_5\text{Pt}(\text{C}_6\text{H}_{11})_3\text{Cl}_2]$ with ClSO$_2$NCO

To a solution of 0.030 g (0.036 mmol) of the title complex in
1.6 mL of toluene in a 10 mm NMR tube at $-78^\circ\text{C}$ was added a solution
of 0.008 g (0.06 mmol) of ClSO$_2$NCO in 0.2 mL of toluene also at
$-78^\circ\text{C}$. The color of the solution changed to yellow immediately.
The mixture was slowly warmed to $-30^\circ\text{C}$, and all of the starting
material was converted to a product. The product probably was
trans-$[(\text{P}(\text{C}_6\text{H}_{11})_3)_2\text{PtCl(\text{CHCH}_2\text{C(O\text{N(SO}_2\text{Cl})\text{CH}_2})]}$, as supported by
comparison of the $^{31}\text{P}$ NMR spectral data with those of analogous
compounds. The $^{31}\text{P}$ NMR spectroscopic data are listed in Table 29.

When the same reaction was carried out in a Schlenk flask first
at $-78^\circ\text{C}$ and then with slow warming to room temperature over 1.5
hours, a mixture of the cycloaddition complex and trans-
\[(\text{P}(\text{C}_6\text{H}_{11})_3)_2\text{PtCl}_2\] was obtained.

When the reaction was run at room temperature, the complex
trans-$[(\text{P}(\text{C}_6\text{H}_{11})_3)_2\text{PtCl}_2]$ was the only product. It was identified
by mass spectrum and comparison of its IR and $^{31}\text{P}$ NMR spectral data
with those of an authentic sample.\textsuperscript{53}
Table 29

$^{31}$p NMR Data for Complexes trans-[$\text{Cl}_2\text{PtCHCH}_2\text{C}(\text{O})\text{N(SO}_2\text{Cl})\text{CH}_2$]$^a$

<table>
<thead>
<tr>
<th>L</th>
<th>Chemical Shifts ($\delta$, ppm)</th>
<th>Coupling Constants ($J^{195}$Pt, P, Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{P(C}_2\text{H}_5)_3$</td>
<td>20.09</td>
<td>2677</td>
</tr>
<tr>
<td>$\text{P(i-C}_3\text{H}_7)_3$</td>
<td>27.16</td>
<td>2782</td>
</tr>
<tr>
<td>$\text{P(C}_6\text{H}_11)_3$</td>
<td>16.43</td>
<td>2745</td>
</tr>
</tbody>
</table>

$^a$ In toluene solution at 298K.
Reaction of trans-[{(η^1-C_5H_5)Pt(P(i-C_3H_7)_3)_2Cl}_2] with ClSO_2NCO

To a solution of 0.074 g (0.125 mmol) of the title complex in 1.9 mL of toluene in a 10-mm NMR tube at -78°C was added 0.018 g (0.127 mmol) of ClSO_2NCO. The mixture was then slowly warmed up. The 31P NMR spectra indicated that no reaction occurred below -35°C. The reaction proceeded slowly at -25°C. More product formed in the range of -15°C to -5°C. When the temperature reached 5°C, the second product started to form. The formation of the second product complex predominates at higher temperatures. The first product probably was trans-[{(P(i-C_3H_7)_3)_2Pt(CHCHC(0)N(SO_2Cl)CH_2)_2}] as supported by mass spectrum and comparison of 31P NMR spectral data with those of analogous compounds. The 31P NMR spectroscopic data are listed in Table 29.

Mass Spectrum (FAB) m/e

664 ((M + H)^+)

When the same reaction was carried out in a Schlenk flask, first at -78°C and then with slow warming to room temperature over 2 hours (this included 30 min of stirring at -20°C), it generated a mixture of the cycloaddition complex and trans-[{(P(i-C_3H_7)_3)_2PtCl}_2], detected by its 31P NMR spectrum.

When the reaction was carried out at room temperature, it yielded only the second complex, trans-[{(P(i-C_3H_7)_3)_2PtCl}_2], which
was identified by comparison of its IR and \(^{31}\text{P}\) NMR spectral data with those of an authentic sample.\(^{54}\)

**Attempted Reaction of trans-\([\epsilon^1-\text{C}_3\text{H}_5]\text{Pt}(\text{P}(\text{i-C}_2\text{H}_7)_2\text{Cl})\] with p-Toluenesulfonyl Isocyanate**

A solution of 0.031 g (0.22 mmol) of p-toluenesulfonyl isocyanate in 3 mL of benzene was added to a solution of 0.115 g (0.138 mmol) of the title complex in 40 mL of benzene at room temperature. The resulting mixture was then stirred at 50°C for 27 hours. After the solvent was removed in vacuo, the residue was washed with ethanol (1 mL x 2). It was the starting material as identified by IR and \(^{31}\text{P}\) NMR spectroscopy.

**Attempted Reaction of trans-\([\epsilon^1-\text{C}_3\text{H}_5]\text{Pt}(\text{P}(\text{C}_2\text{H}_5)_3\text{Cl})\] with p-Toluenesulfonyl Isocyanate**

To a solution of 0.162 g (0.329 mmol) of the title complex in 10 mL of toluene was added a solution of 0.063 g (0.32 mmol) of p-toluenesulfonyl isocyanate in 5 mL of toluene. The resulting mixture was stirred at room temperature for 3 days. There was no reaction as indicated by the presence of only the starting material in the \(^{31}\text{P}\) NMR spectrum of the mixture.
RESULTS AND DISCUSSION

I. Reaction Sequence Protonation-Deprotonation on Five- and Six-Membered Ring Metal Complexes

A. Initial Protonation-Deprotonation Studies

It has been reported that protonation of a six-membered ring complex \( n^5-C_5H_5(CO)_2FeCHCH_2N(SO_2CH_3)SN(SO_2CH_3)CH_2 \), 1, with HPF\(_6\)·(C\(_2\)H\(_5\))\(_2\)O results in the formation of a metal-\( n^2 \)-olefin complex \( [n^5-C_5H_5(CO)_2Fe(n^2-CH=CHCH_2N(SO_2CH_3)SNH(SO_2CH_3))]^{PF_6^-} \), 4.\(^{27}\) The structure of 4 determined by X-ray diffraction. Other electrophiles, such as (CH\(_3\))\(_3\)OBF\(_4\) and (C\(_2\)H\(_5\))\(_3\)OPF\(_6\), have been tried in alkylation reactions of the six-membered ring of complex 1 in this research. However, no reactions occurred as indicated by recovery of unreacted starting material.

It was of interest to ascertain whether complex 4 can be converted back to 1 by treatment with base. Deprotonation of various complex cations \( [n^5-C_5H_5(CO)_2Fe(n^2-CH=CHCH_2E)]^+ \) (E = electrophilic fragment) with triethyl amine has been studied by Rosenblum and coworkers.\(^{11}\) These reactions proceed by loss of an allylic proton to yield \( n^5-C_5H_5(CO)_2Fe(n^1-CH=CHCH_2E) \). To avoid removal of allylic protons of the metal-\( n^2 \)-olefin complex 4, a
sterically hindered strong base 1,8-(dimethylamino)naphthalene (Proton Sponge) was chosen to remove the NH proton. The reaction was carried out in THF solution and regenerated the six-membered ring complex 1 in 86% isolated yield (eq 9).

\[
\text{THF} \quad \text{Cp(CO)2Fe} + \text{Proton Sponge} \quad \rightarrow \quad \text{Cp(CO)2Fe} + \text{Proton Sponge}
\]

The successful protonation-deprotonation reaction sequence on complex 1 prompted an extension of this sequence to a five-membered ring cycloadduct, \( \eta^5\text{C}_5\text{H}_5(\text{CO})_2\text{FeCHCH}_2\text{N(S(0)CH}_3\text{S(0)CH}_2\text{)} \), 5.

Reaction of this cycloadduct with \( \text{HPF}_6\cdot(\text{C}_2\text{H}_5)_2\text{O} \) in \( \text{CH}_2\text{Cl}_2 \) proceeds readily at -78°C to give a yellow precipitate, \( [\eta^5\text{C}_5\text{H}_5(\text{CO})_2\text{Fe}(\eta^2\text{CH}_2=\text{CHCH}_2\text{S(0)NH(S(0)CH}_3\text{)})]^+\text{PF}_6^- \), 6, in 87% isolated yield. The structure of the yellow precipitate was assigned from IR and \(^1\text{H}\) NMR spectroscopic data. The IR spectrum revealed \( \nu(\text{CO}) \) absorptions.
typical of complex cations \([\eta^5-C_5H_5(CO)_2Fe(\eta^2-\text{alkene})]^+\) and a \(v(\text{NH})\) band at 3295 cm\(^{-1}\). The \(^1\text{H}\) NMR spectra showed the \(\eta^5-C_5H_5\) and CH\(_2\)=CHCH\(_2\) resonances in the range reported for \([\eta^5-C_5H_5(CO)_2Fe(\eta^2-\text{alkene})]^+\);\(^{11}\) however, the signals were broad possibly owing to low stability of this complex in acetone solution. As a result, no assignments were made of the exact chemical shifts and coupling constants to the various protons of the CH\(_2\)=CHCH\(_2\) fragment.

Deprotonation of 6 with Proton Sponge regenerated the five-membered ring complex. This reaction sequence on \(\eta^5-C_5H_5(CO)_2FeCH-\ch{CH2N(S(O)2CH3)S(O)CH2}\) is shown as follows (eq 10):

\[
\begin{align*}
\text{Cp(CO)2Fe-} & \overset{\text{Proton Sponge}}{\rightleftharpoons} \text{Cp(CO)2Fe}^- \\
\text{HPF6-(C2H5)2O} & \text{PF6}^- \\
5 & \quad \quad 6
\end{align*}
\]

The facile formation of 5 and 6 on removal of the NH proton is relevant to the two-stop dipolar mechanism proposed for cycloaddition reactions of \(\eta^5-C_5H_5(CO)_2Fe(\eta^1-\text{CH}_2\text{CR}^1\text{CR}^2\text{R}^3)\) with various unsaturated electrophiles \(E=\text{Nu}\), i.e.
The close analogy between the second step of this mechanism and the deprotonation of 6 provides additional support for the proposed mechanism of the [3 + 2] cycloaddition reaction.

It is noteworthy that the reaction sequence protonation-deprotonation leads to what appears to be a change in the diastereomeric composition of \( \eta^5-C_5H_5(CO)CH_{2}S(O)N(S(O)_{2}CH_3)CH_2 \). (Chiral centers are present at the CH carbon and the SO sulfur). Complex 5 was obtained from \( \eta^5-C_5H_5(CO)\{\eta^1-CH_2CH=CH_2\} \) and \( CH_3SO_2N=S=O \) as a 78:22 mixture of diastereomers as evidence by the presence of two \( \eta^5-C_5H_5 \) \(^1\)H NMR signals. After protonation-deprotonation, this ratio changes to 95:5. Enrichments of the predominant diastereomer may result from epimerization of 5 during the reaction or some loss of stereospecificity in the two-step reaction sequence, or it simply
reflects greater decomposition of the less abundant isomer of 5 and/or 6.

The success of the reaction sequence on 5 encouraged a further extension of this study to iron complexes containing a \( \gamma \)-lactam ring. However, stirring a solution of \( \ce{[n^5-C_5H_5(CO)_2FeCHCH(CH_3)C(O)N-(S(O)_2C_6H_4CH_3-p)CH_2, 7, and HPF_6^-(C_2H_5)_2O} \) at room temperature for 20 hours gave no reaction as indicated by recovery of the iron complex. Protonation of the analogous complex, \( \ce{[n^5-C_5H_5(CO)_2FeCHCH-(C_6H_5)C(O)N(S(O)_2C_6H_4CH_3-p)CH_2, 8, at room temperature for 24 hours afforded a product, possibly [n^5-C_5H_5(CO)_2Fe(n^2-CH_2-CHCH(C_6H_5)C(O)-NH(S(O)_2C_6H_4CH_3-p))]+PF_6^-, 9, in 29% isolated yield. Since the product does not dissolve in common organic solvents, no \(^1\text{H} \text{NMR}\) spectrum was obtained. For the same reason, deprotonation of the complex was not attempted. The structure of this product was assigned from its IR spectroscopic data. When \( \nu(\text{C=O}) \) absorptions, at 2058 cm\(^{-1}\) and 2004 cm\(^{-1}\), of the product are compared to those of the starting material, they appear at higher frequencies, indicative of a cationic species. A \( \nu(\text{NH}) \) band at 3532 cm\(^{-1}\) further supports the structure of 9.

No observed reaction and a low yield of product on protonation of 7 and 8, respectively, may be due to the presence of nitrogen in the lactam ring that is bonded to two strong electron-withdrawing groups, a carbonyl and a sulfonyl. As a result, the nitrogen is
insufficiently basic to be protonated. Alternatively, it is protonated to open the lactam ring, but easy dissociation of the NH proton leads to the regeneration of the starting material.

In order to reduce the electron-withdrawing ability of the sulfonyl group, the iron complex was modified by replacement of the toluene group with a dimethylamino group. However, protonation of \( \text{n}^5\text{C}_5\text{H}_5(\text{CO})_2\text{FeCHCH(C}_6\text{H}_5)\text{C}(\text{O})\text{N(S(O)}_2\text{N(CH}_3)_2\text{)}\text{CH}_2 \) occurred at the nitrogen of the dimethylamino group rather than the nitrogen of the lactam ring and resulted in decomposition of the metal complex, even at -78°C, as indicated by the formation of a white precipitate, \( \text{H}_2\text{N(CH}_3)_2\text{PF}_6 \). The isolated \( \text{H}_2\text{N(CH}_3)_2\text{PF}_6 \) was identified by \(^1\text{H NMR}\) spectroscopy. The result may be rationalized by the nitrogen of the dimethylamino group being more basic than the nitrogen of the lactam ring. To avoid protonation at the amino group, the complex was further modified by replacement of the dimethylamino group with an anilino group. Complexes \( \text{n}^5\text{C}_5\text{H}_5(\text{CO})_2\text{FeCHCR}_1\text{R}_2\text{C}(\text{O})\text{N(S(O)}_2\text{NHC}_6\text{H}_5)\text{CH}_2 \) have been found to give good yields of iron-\( \text{n}^2\)-olefin complexes \( [\text{n}^5\text{C}_5\text{H}_5(\text{CO})_2\text{Fe(n}^2\text{-CH}_2=\text{CHCR}_1\text{R}_2\text{C}(\text{O})\text{N(S(O)}_2\text{NHC}_6\text{H}_5))]^{+}\text{PF}_6^- \) upon treatment with \( \text{HPF}_6 \).
B. Reaction Sequence Protonation-Deprotonation on Complexes

\[ \eta^5-C_5H_5(CO)\_2FeCHCR\_1R\_2C(O)N(S(O)\_2NHC_6H_5)CH\_2 \]

i. Preparations

Complexes 10, 11, 12 and 13 were prepared via reactions first of \( \text{ClSO}_2\text{NCO} \) with appropriate iron-\( \eta^2 \)-allyl compounds and then with aniline. Although complexes 11 and 12 have been reported,\(^{14}\) a modified method in which the cycloadduct \( \eta^5-C_5H_5(CO)\_2FeCHCR\_1R\_2C(O)N(S(O)\_2\text{Cl})CH\_2 \) was not isolated was used in the preparation of both complexes. This modified procedure simplifies the original method and affords a better yield. Comparison of the two procedures showed that the modified method improves yield by at least 15%.
The same modified procedure was applied to the preparation of complexes 10 and 13. Reaction of iron-$\eta^1$-allyl complexes with ClSO$_2$NCO in CH$_2$Cl$_2$ at -78°C immediately led to the formation of a yellow precipitate. The yellow precipitate dissolved upon warming the suspension to room temperature. It is reported here for the first time. An attempt to isolate the yellow precipitate was unsuccessful.

For complexes 10 and 11, there are two chiral centers at the FeCH and CHR carbons; therefore, an alkyl group trans and cis to the $\eta^5$-C$_5$H$_5$(CO)$_2$Fe group results in the formation of different diastereomers. The reaction of $\eta^5$-C$_5$H$_5$(CO)$_2$FeCH$_2$CH=CHCH$_3$ with tetracyanoethylene (TCNE) has been demonstrated to occur stereospecifically; namely, the reaction of a mixture of $E$ and $Z$ isomers of $\eta^5$-C$_5$H$_5$(CO)$_2$FeCH$_2$CH=CHCH$_3$ with TCNE gave the same ratio of diastereomers of the cycloadduct. In the preparation of 10, a quite different result was obtained. The reaction of $\eta^5$-C$_5$H$_5$(CO)$_2$FeCH$_2$CH=CHCH$_3$, containing the $E$ and $Z$ isomers in a 2:1 ratio, first with ClSO$_2$NCO and then with aniline yielded a mixture of 10 in a 90:10 trans/cis ratio.

The foregoing stereochemical assignments are primarily based upon the positions of the methyl proton resonances. The major product exhibits a methyl doublet absorption at $\delta$ 1.18 while the minor product shows this doublet at $\delta$ 0.82. When the methyl group
is in a region of space close to the fivefold cyclopentadienyl-iron axis, the methyl protons are relatively shielded. Thus, the high and low field resonances in the $^1$H NMR spectrum of the cycloadducts are assigned to methyl protons cis and trans, respectively, of the $\eta^5$-C$_5$H$_5$(CO)$_2$Fe group. The ratio of the two isomers was determined by the integration of two $\eta^5$-C$_5$H$_5$ $^1$H NMR signals present in the spectrum. Characterization of the trans and cis isomers will be further discussed in a later section.

The apparent inconsistency between the result of the reaction of the iron-$\eta^1$-crotyl complex with TCNE and that with ClSO$_2$NCO may have resulted from low reactivity of the iron-$\eta^1$-(Z-crotyl) complex or from its decomposition during the reaction. The reaction of the pure Z isomer of the iron-$\eta^1$-crotyl complex with ClSO$_2$NCO and aniline gave an unusually low yield (23%) of the cycloadduct in a 3:2 trans/cis ratio. This result indicates that the iron-$\eta^1$-(Z-crotyl) complex did not behave cleanly in the reaction. Part of the Z isomer was converted to the E isomer during the course of the reaction. A further study is needed to understand the details of this reaction.

Although complex 11 was prepared by Yamamoto, no stereochemistry of its formation was discussed. Unlike the preparation of 10, the reaction of pure $\eta^5$-C$_5$H$_5$(CO)$_2$Fe(E-CH$_2$CH=CHC$_6$H$_5$) with ClSO$_2$NCO yielded only the trans cycloadduct. The crystal structure of
trans-11 was determined by x-ray diffraction. Characterization of
this complex will be discussed later.

The structure of complex 13 was determined by the IR, $^1$H NMR
and mass spectra. The elemental analysis confirmed its formula.

(ii) Protonation-Deprotonation Reaction Sequence

As mentioned in the preceding section, treatment of several
iron complexes containing γ-lactam ring with acid does not give a
clean opening of the ring except for the complexes $n^5$-C$_5$H$_5$(CO)$_2$Fe-
CHCR$_1^2$C(0)N(S(O)$_2$NH)$_6$H$_5$CH$_2$.

Since a metal-$\eta^2$-olefin complex can be attacked by a nucleo­
phile at the olefinic carbons or at the metal center followed by
dissociation of the olefin, an acid with a non-nucleophilic counter­
ion is necessary for the study of the protonation reaction in
point. To meet this requirement, HPF$_6$*(C$_2$H$_5$)$_2$O was chosen through­
out this research.

A closer look into the progress of protonation of trans-10
revealed that there are three stages of this process which depend on
the temperature. The reaction mixture underwent no apparent change
when it was maintained at -78°C. When the temperature of the
mixture was raised to -30°C, a yellow precipitate formed. After
being stirred at room temperature for a few minutes, the mixture
turned red and became clear. Continuous stirring of the red solution for an additional 15 min led to the formation of a second yellow precipitate. The first yellow precipitate can be isolated if the reaction mixture is maintained at -10°C.

The IR spectra revealed ν(C=O) absorptions typical of complex cations \([\eta^5-C_5H_5(CO)_2Fe(\eta^2\text{-alkene})]^+\) for both precipitates, and a ν(NH) band at 3320 cm\(^{-1}\) for the first precipitate and at 3500 cm\(^{-1}\) for the second precipitate. Therefore, both precipitates are considered as isomers of the iron-\(\eta^2\)-olefin complex 14.

\[
\begin{align*}
\eta^5-C_5H_5(CO)_2Fe & \quad \text{PF}_6 \\
\text{trans} & \quad \text{cis} = 90:10
\end{align*}
\]

Deprotonation of the first precipitate with Proton Sponge regenerated the complex trans-10 in the same ratio of diastereomers (trans:cis = 90:10). Surprisingly, deprotonation of the second precipitate gave complex 10 predominantly as the cis isomer, the trans/cis ratio being 10:90. Since in both cases the deprotonation proceeded very readily at ca. -60°C, it seems unlikely that isomerization took place during the course of deprotonation. Based upon
the results of the deprotonation, the first precipitate is considered to be mainly trans-14 while the second precipitate is largely the cis isomer of 14.

It is of interest that the foregoing reaction sequence leads to a change in the diastereomeric composition of 10. Although the IR spectra of trans- and cis-10 are very similar, in the $^1$H NMR spectra of 10 different methyl proton resonances, which have been discussed earlier on page 116, and $\eta^5$-C$_5$H$_5$ resonances allow a facile determination of their diastereomeric composition. The $^1$H NMR spectra of the isomeric mixtures before and after the reaction sequence are shown in Figures 1 and 2.

To rule out the possibility of transformation between trans- and cis-10 in the absence of acid, a diastereomeric mixture of 10 in 60:40 trans/cis ratio was dissolved in CH$_2$Cl$_2$, and the resulting solution was stirred at room temperature for 20 hours. No change in the ratio of diastereomers was observed by $^1$H NMR.

In contrast to the protonation of trans-10, the protonation of cis-10, containing 10% of the trans isomer, produced a yellow precipitate at -78°C, and this yellow precipitate did not dissolve even when the mixture was warmed to room temperature. The IR spectrum of the yellow precipitate showed it to be cis-14. Deprotonation of this precipitate by use of Proton Sponge regenerated cis-10 without changing its diastereomeric ratio. The
experiment demonstrates that the transformation from trans-10 to cis-10 through the sequence protonation-deprotonation is not reversible. There are three observable stages in the course of protonation of trans-10: formation of a yellow precipitate, dissolution to a red solution, and formation of a second precipitate. However, only one stage was observed for the protonation of cis-10, i.e., the formation of a yellow precipitate, cis-14. There is no interconversion between trans-10 and cis-10 in solution. When these results are considered together, they clearly indicate that the change in geometry from trans to cis in the protonation-deprotonation sequence takes place during the conversion of one yellow precipitate to the other. The first yellow precipitate trans-14 in this protonation is the kinetic product. When the reaction mixture is warmed to higher temperature, it rearranges to the thermodynamic product cis-14. This argument is supported by an experiment in which isolated trans-14 in an acidic solution at room temperature for 45 min converted to cis-14. Solid trans-14 has also been found to be less stable than solid cis-14. Solid trans-14 decomposed after one day at room temperature, but solid cis-14 is stable at room temperature for several months. This series of experiments is summarized in Scheme III.
Scheme III

\[ \text{trans: cis = 90:10} \]

\( Fp = \eta^5-C_5H_5(CO)_2Fe \)
Figure 1. The $^1$H NMR spectrum of a diastereomeric 90:10 trans/cis mixture of $n^5$-C$_5$H$_5$(CO)$_2$FeCHCH(CH$_3$)C(O)N(S(O)$_2$NHC$_6$H$_5$)CH$_2$ in CDCl$_3$ solution.
Figure 2. The $^1$H NMR spectrum of a diastereomeric 10:90 trans/cis mixture of $n^5$-C$_5$H$_5$(CO)$_2$FeCHCH(CH$_3$)C(O)N(S(O)$_2$NHC$_6$H$_5$)CH$_2$ in CDCl$_3$ solution.
When the same reaction sequence protonation-deprotonation was applied to the complex trans-11, a similar result was obtained. In the course of the protonation of trans-11, there were also three distinguished reaction stages. However, the amount of the first precipitate which formed at low temperature was relatively small. The mixture turned red and became clear after being stored at room temperature for a few minutes. Continuous stirring for an additional 15 min suddenly resulted in the formation of the second yellow precipitate. This observation is analogous to that for the protonation of trans-10. Progress of the protonation of trans-11 in CD₂Cl₂ followed at low temperature by ¹H NMR spectroscopy. A downfield shift of the n⁵-C₅H₅ signal from δ 4.58 to 4.66 at -73°C is consistent with the protonation occurring readily at nitrogen of the lactam ring. When the reaction mixture was slowly warmed up, the intensity of this n⁵-C₅H₅ signal gradually decreased and at the same time the intensity of a new signal at δ 5.48 gradually increased. The signal at δ 4.66 completely disappeared when the temperature reached 0°C. This observation agrees with the opening of the protonated lactam ring as the temperature of the reaction mixture increased. A comparison of the IR spectra of the second yellow precipitate and cis-14 suggests that the yellow precipitate is the metal-±²-olefin complex 15. This is based on the values of the
ν(C=O) absorptions and the presence of two ν(NH) bands at 3378 and 3249 cm⁻¹. Complexes 14 and 15 very rapidly decomposed in acetone-d₆ solution. Therefore, only major peaks, such as those of η⁵-C₅H₅, CH₃ and C₆H₅ were observed in their ¹H NMR spectra.

Deprotonation by treatment of 15 with Proton Sponge can proceed in two ways: (1) Removal of the proton on the nitrogen which is bonded to the carbonyl and sulfonyl groups and (2) Removal of the NH proton of the anilino group. The former will lead to ring closure with the regeneration of 11, and the latter will lead to the formation of a seven-membered ring complex. From the thermodynamic viewpoint, the proton of the nitrogen bonded to two electron-withdrawing groups is more acidic than that of the anilino group. From the kinetic viewpoint, cyclization to a five-membered ring is faster than that to a seven-membered ring. Hence, it seems that the formation of a five-membered ring complex is more probable. However, taking into consideration that the phenyl group at the β carbon
bonded to the carbonyl group of trans-11 may hinder approach of a bulky base, the formation of a seven-membered ring complex is also possible.

Deprotonation of 15 by use of Proton Sponge gave a surprising result that the reaction went readily to form pure cis-11. A definite proof of the structure was provided by an X-ray crystallographic analysis which is considered in the next section. In addition, the result of the deprotonation suggested that the second precipitate formed in the protonation of trans-11 is cis-15.

A closer examination of the $^1$H NMR spectra of trans- and cis-11 shows that the two isomers can be easily distinguished by their $^5$-C$_5$H$_5$ signals at $\delta$ 4.43 and 4.58, respectively. In order to characterize the first precipitate in the protonation of trans-11, deprotonation was carried out on the precipitate collected from the protonation at 0°C for 1 hour. It gave a mixture of 11 in a trans/cis ratio of 1:1. This result indicates that half of the metal-$\pi^2$-olefin complex trans-15 has already converted to cis-15 during the reaction period at 0°C. If the mixture was not kept at 0°C for such a long time, only a small amount of precipitate formed. To increase the proportion of the trans diastereomer of 15, HPF$_6^\ast$(C$_2$H$_5$)$_2$O was introduced to a solution of trans-11 at room temperature and the reaction was quenched at -20°C. Deprotonation of the precipitate isolated from this reaction yielded a 2:1
trans/cis diastereomeric mixture of 11. When a CH$_2$Cl$_2$ solution of 15 in 2:1 trans/cis ratio was stirred at room temperature for 45 min in the absence of acid, it afforded only cis-15 which was confirmed by deprotonation. Under similar reaction conditions except in the presence of acid, cis-15 was still the only product. These experiments suggest that in the protonation of trans-11 rearrangement from trans-15 to cis-15 occurs readily.

Experiments similar to those conducted with cis-10 were performed on cis-11. When the latter complex was treated with HPF$_6$·(C$_2$H$_5$)$_2$O, a yellow precipitate formed at -60°C. As the temperature of the suspension was warmed to room temperature, this yellow precipitate remained undissolved. This result is to be contrasted with the protonation of the trans isomer of 11. Deprotonation of the yellow precipitate regenerates cis-11. The results of this series of reactions are summarized in Scheme IV.

In contrast, protonation of 12, which has two methyl groups at the β carbon bonded to the carbonyl group, is somewhat different from those of trans-10 and trans-11. The formation of a yellow precipitate took place at ca. -30°C, but when the temperature of the reaction mixture reached room temperature, the yellow precipitate dissolved and did not reform on storage of the resulting red solution. The yellow precipitate isolated at low temperature was very unstable at room temperature. Because of lack of thermal
stability of the precipitate, no spectroscopic data were obtained. Deprotonation was carried out at low temperature to regenerate 12. As a result, the yellow precipitate is deduced to be the iron-$\eta^2$-olefin complex 16.

\[
\begin{align*}
\eta^5\text{C}_5\text{H}_5(\text{CO})_2\text{Fe}^+ & \quad \text{H}^+ \\
\text{H} & \quad \text{N} \quad \text{N} \\
\text{H} & \quad \text{S} \quad \text{N} \\
\text{Ph} & \quad \_ \\
\text{C}_5\text{H}_5(\text{CO})_2\text{Fe}^+ & \quad \text{PF}_6^-
\end{align*}
\]

Since the species $\eta^5\text{C}_5\text{H}_5(\text{CO})_2\text{Fe}^+$ in solution has a red color, it was thought that the metal-olefin bond of 16 underwent dissociation at room temperature. After the solvent was removed from the red solution, the residue was recrystallized to give red crystals. The red crystals were possibly $\eta^5\text{C}_5\text{H}_5(\text{CO})_2\text{FePF}_6$ or $\eta^5\text{C}_5\text{H}_5(\text{CO})_2\text{Fe(H}_2\text{O})\text{PF}_6^-$, since its analogue $\eta^5\text{C}_5\text{H}_5(\text{CO})_2\text{FeBF}_4$ is known to be extremely hygroscopic. The $^1\text{H}$ NMR spectrum of the red crystals in acetone-$d_6$ shows a $\eta^5\text{C}_5\text{H}_5$ signal at $\delta 5.52$. The mass spectrum exhibits a peak at m/e 177 corresponding to the fragment $\eta^5\text{C}_5\text{H}_5(\text{CO})_2\text{Fe}^+$. The IR spectrum reveals two $\nu(\text{C}=\text{O})$ absorptions at 2052 and 2000 cm$^{-1}$, one $\nu(\text{PF}_6)$ band at 840 cm$^{-1}$ and one $\delta(\text{PF}_6)$ band at 558 cm$^{-1}$. These IR data are identical to those of an independently synthesized $\eta^5\text{C}_5\text{H}_5(\text{CO})_2\text{FePF}_6$ (or $\eta^5\text{C}_5\text{H}_5(\text{CO})_2\text{Fe(H}_2\text{O})\text{PF}_6$)
Scheme IV

\[
\begin{align*}
\text{Fp} = \eta^5-C_5\text{H}_5(\text{CO})_2\text{Fe} & \quad \underset{-60 \text{ to } -10^\circ C}{\xrightarrow{\text{HPF}_6}} \quad \text{trans:cis = 1:1} \\
\end{align*}
\]

\[
\begin{align*}
\text{Conditions} & \\
(1) \text{ In the absence of } H^+ \quad & (2) \text{ In the presence of } H^+ \\
\end{align*}
\]

\[
\begin{align*}
\text{Red Solution} & \quad \underset{25^\circ C}{\xrightarrow{\text{25^\circ C}}} \\
\end{align*}
\]

\[
\begin{align*}
\end{align*}
\]
from \( \eta^5-C_5H_5(CO)_2FeCH_3 \) and HPF\(_6\). The formation of the \( \eta^5-C_5H_5(CO)_2FePF_6 \) species is another evidence in support of the above argument.

In the protonation of the complex \( \eta^5-C_5H_5(CO)_2FeCH\_2\_C(O)N-(S(O)\_2NHCH\_6H_5)CH_2 \), 13, which has only one chiral center, precipitate formed at \(-30^\circ C\). Unlike 16, the resulting yellow precipitate stayed in suspension as the temperature reached 25\(^\circ C\). Its IR spectrum revealed \( \nu(C=O) \) absorptions typical of complex cations \([\eta^5-C_5H_5(CO)_2Fe(\eta^2-alkene)]^+\) and \( \nu(NH) \) bands at 3317 and 3248 cm\(^{-1}\). Similarity of the IR spectra of 14, 15 and the yellow precipitate supports structure 17 for the last species. Deprotonation of 17 to regenerate 13 is effected by use of Proton Sponge.

\[
\eta^5-C_5H_5(CO)_2Fe^{\text{PF}_6} \text{ (iii) Characterization of the cis and trans Diastereomers}
\]

The usual conversion of trans-10, 11 to cis-10, 11 via the reaction sequence protonation-deprotonation is a very interesting aspect in this research. Before discussing its mechanism, characterization of these isomers is described. The X-ray structures of
trans- and cis-11 are examined. The IR and $^1$H NMR spectra of trans-10, 11 and cis-10, 11 are inspected to discover distinguishing spectroscopic features of these diastereomers and establish criteria for the determination of the stereochemistry of these complexes.

The $^1$H NMR spectra of the isomers of 10 were briefly discussed in the preceding section. According to the position of their methyl proton resonances the two isomers are assigned a trans or a cis structure. After the trans and cis structures have been assigned on this basis, the $\eta^5$-C$_5$H$_5$ signal of the cis isomer is found 0.06 ppm downfield from that of the trans isomer.

Pure cis-10 was successfully obtained from a predominantly cis-diastereomeric mixture by slow recrystallization from a 1:2 CH$_2$Cl$_2$-n-pentane mixture. For pure cis-10, the assignment of each $^1$H resonance was made with the aid of homonuclear decoupling experiments on a 500-MHz NMR spectrometer. These spectra are shown in Figure 3. Irradiation at the frequency of the $\delta$ 2.31 signal collapses the $\delta$ 0.80 doublet to a singlet. Irradiation at the $\delta$ 2.78 multiplet results in the collapse of the doublet of doublets at $\delta$ 3.42 to a doublet ($J = 10.4$ Hz) and the collapse of the doublet of doublets at $\delta$ 3.74 to a doublet ($J = 10.4$ Hz). According to the structure of cis-10, each of the proton signals can be assigned as follows:
Figure 3. The $^1$H NMR spectra of \( \text{cis-}n^5\text{-C}_5\text{H}_5(\text{CO})_2\text{FeCHCH(CH}_3\text{)}\text{-C(O)N(S(O)\text{)}_2\text{NHC}_6\text{H}_5\text{)}\text{CH}_2 \) in CDCl$_2$ solution: (a) Without decoupling. (b) Irradiation at the $\delta$ 2.31 signal (c) Irradiation at the $\delta$ 3.42 signal.
$^{1}$H NMR NMR (CD$_2$Cl$_2$) δ 0.80 (d, J(CH$_3$, H$_d$) = 7.5 Hz, CH$_3$), 2.31 (m, H$_d$), 2.78 (m, H$_c$), 3.42 (dd, J(H$_a$, H$_b$) = 10.4 Hz, J(H$_a$, H$_c$) = 11.8 Hz, H$_a$), 3.74 (dd, J(H$_a$, H$_b$) = 10.4 Hz, J(H$_b$, H$_c$) = 7.3 Hz, H$_b$), 4.80 (s, C$_5$H$_5$), 7.18-7.35 (m, NH and C$_6$H$_5$). Because CD$_2$Cl$_2$ was used as a solvent, the chemical shifts are a little different from those obtained in CDCl$_3$ solution and reported in Table 2. The IR spectra of trans- and cis-10 are almost identical except for a slightly different shape of the ν(NH) absorption band. The ν(NH) band of the cis isomer is a little broader than that of the trans isomer.

For complex 11, which does not have a methyl group at the β carbon atom bonded to the carbonyl group, it is not easy to distinguish between the trans and the cis isomer from their $^{1}$H NMR spectra. Hence, the molecular structures of trans- and cis-11 were determined by X-ray crystallography. Crystals of both complexes were grown by the method of slow solvent diffusion in which the sample was crystallized from a 1:2 CH$_2$Cl$_2$-n-pentane mixture. The X-ray structure determinations were performed by Dr. M. Calligaris at the University of Trieste, Italy. The molecular structure of trans-11 is shown in Figures 4 and 5. Selected bond distances and angles for trans-11 are listed in Tables 30 and 31, respectively. The molecular structure of cis-11 is shown in Figures 6 and 7. Selected bond distances and angles for cis-11 are listed in Tables 32 and 33. Most of the bond angles of these two complexes are comparable.
Figure 4. The Molecular Structure of \textit{trans-}n^5-C_5H_5(CO)_2Fe-
\textit{CH}_2CH\textit{CH}_2C_6H_5C(O)N(S(0)_2NH)C_6H_5CH_2 with Selected
Bond Distances and Angles.
C–C (Cp) 1.388(5) – 1.418(5)
Fe–C (Cp) 2.096° – 2.109°
Fe–C3–C6–C7 75.5°
Fe–C3–C6 119.6°
C3–C6–C7 75.5°
Figure 5. The Molecular Structure of $\text{trans-}^{5}\text{C}_5\text{H}_5(\text{CO})_2\text{Fe-}$
$\text{CHCH(C}_6\text{H}_5)\text{C}(\text{O})\text{N}(\text{S(})_2\text{NHC}_6\text{H}_5)\text{CH}_2$ with Projection
Down the C(6)-C(3) Axis.
Table 30

Selected Bond Distances for $\text{trans-}^{5}\text{-C}_5\text{H}_5(\text{CO})_2\text{FeCCH}(\text{C}_6\text{H}_5)\text{C}(\text{O})\text{N}(\text{S}(\text{O})_2\text{NH})\text{C}_6\text{H}_5\text{CH}_2$ in Angstroms

<table>
<thead>
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<th>Distances</th>
<th>Bond</th>
<th>Distance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-C(1)</td>
<td>1.748 (4)</td>
<td>C(3)-C(4)</td>
<td>1.520 (3)</td>
</tr>
<tr>
<td>Fe-C(2)</td>
<td>1.748 (4)</td>
<td>C(3)-C(6)</td>
<td>1.541 (3)</td>
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<tr>
<td>Fe-C(3)</td>
<td>2.049 (2)</td>
<td>C(4)-N(1)</td>
<td>1.428 (3)</td>
</tr>
<tr>
<td>S-O(4)</td>
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<td>C(5)-N(1)</td>
<td>1.397 (3)</td>
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<td>S-O(5)</td>
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<td>C(5)-C(6)</td>
<td>1.526 (3)</td>
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<tr>
<td>S-N(1)</td>
<td>1.646 (2)</td>
<td>C(5)-O(3)</td>
<td>1.205 (3)</td>
</tr>
<tr>
<td>S-N(2)</td>
<td>1.619 (2)</td>
<td>C(6)-C(7)</td>
<td>1.508 (4)</td>
</tr>
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</table>

Numbers in parentheses are estimated standard deviations in the least significant digits.
Table 31

Selected Bond Angles for 
\( \text{trans-}^5\text{C}_5\text{H}_5(\text{CO})_2\text{FeCHCH(C}_6\text{H}_5)\text{C}(\text{O})\text{N}(\text{S(0)}_2\text{NHC}_5\text{H}_5)\text{CH}_2 \) in Degrees

<table>
<thead>
<tr>
<th>Angle</th>
<th>Bond Angle</th>
<th>Angle</th>
<th>Bond Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(1)-Fe-C(2)</td>
<td>94.5 (2)</td>
<td>C(4)-N(1)-S</td>
<td>124.2 (2)</td>
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<tr>
<td>C(1)-Fe-C(3)</td>
<td>91.1 (1)</td>
<td>C(5)-N(1)-S</td>
<td>123.0 (2)</td>
</tr>
<tr>
<td>C(2)-Fe-C(3)</td>
<td>86.4 (1)</td>
<td>C(5)-C(6)-C(7)</td>
<td>112.1 (2)</td>
</tr>
<tr>
<td>C(3)-C(6)-C(5)</td>
<td>103.2 (2)</td>
<td>C(6)-C(5)-N(1)</td>
<td>106.5 (2)</td>
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<tr>
<td>C(3)-C(6)-C(7)</td>
<td>116.3 (2)</td>
<td>C(6)-C(5)-O(3)</td>
<td>129.0 (2)</td>
</tr>
<tr>
<td>C(3)-C(4)-N(1)</td>
<td>102.1 (2)</td>
<td>N(1)-C(5)-O(3)</td>
<td>124.5 (2)</td>
</tr>
<tr>
<td>C(4)-C(3)-C(6)</td>
<td>103.4 (2)</td>
<td>Fe-C(3)-C(6)</td>
<td>119.6 (2)</td>
</tr>
<tr>
<td>C(4)-N(1)-C(5)</td>
<td>112.6 (2)</td>
<td>Fe-C(3)-C(4)</td>
<td>113.8 (2)</td>
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</table>

Numbers in parentheses are estimated standard deviations in the least significant digits.
Figure 6. The Molecular Structure of \textit{cis}-^5\textit{C}_5\textit{H}_5\textit{CO})_2\textit{Fe}-
\textit{CHCH}_5\textit{C(0)}N(S(O)_2\textit{NH}_6\textit{H}_5\textit{CH}_2 with Projection
Down the \textit{C}(6)-\textit{C}(3) Axis.
Figure 7. An ORTEP Drawing of \( \text{cis-}n^5\text{-C}_5\text{H}_5(\text{CO})_2\text{FeCHC-} \)
\( \text{(C}_6\text{H}_5)\text{C(O)N(S(O)_2}\text{NH}_5\text{C}_6\text{H}_5)\text{CH}_2 \) Showing the Atom
Numbering Scheme Including All Non-Hydrogen
Atoms.
Table 32

Selected Bond Distances for

\[
\text{cis-}n^5\text{-C}_5\text{H}_5(\text{CO})_2\text{FeCHCH(C}_6\text{H}_5)\text{C}(0)\text{N(S(O)}_2\text{NHC}_6\text{H}_5)\text{CH}_2
\]

in Angstroms

<table>
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<tbody>
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<td>Fe-C(3)</td>
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<tr>
<td>S-O(4)</td>
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</tr>
<tr>
<td>S-O(5)</td>
<td>1.41 (1)</td>
</tr>
<tr>
<td>S-N(1)</td>
<td>1.66 (1)</td>
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<td>S-N(2)</td>
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<tr>
<td>C(3)-C(4)</td>
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<td>C(3)-C(6)</td>
<td>1.52 (2)</td>
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<td>C(4)-N(1)</td>
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<td>C(5)-N(1)</td>
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<td>C(5)-C(6)</td>
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<td>C(5)-O(3)</td>
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<tr>
<td>C(6)-C(7)</td>
<td>1.53 (2)</td>
</tr>
</tbody>
</table>

Numbers in parentheses are estimated standard deviations in the least significant digits.
Table 33

Selected Bond Angles for

cis-n\textsuperscript{5}-C\textsubscript{5}H\textsubscript{5}(CO)\textsubscript{2}FeCHCH(C\textsubscript{6}H\textsubscript{5})C(O)N(S(0)\textsubscript{2}NHC\textsubscript{6}H\textsubscript{5})CH\textsubscript{2} in Degrees

<table>
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<th>Angle</th>
<th>Bond Angle</th>
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<th>Bond Angles</th>
</tr>
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<tbody>
<tr>
<td>C(1)-Fe-C(2)</td>
<td>97 (1)</td>
<td>C(4)-N(1)-S</td>
<td>119 (1)</td>
</tr>
<tr>
<td>C(1)-Fe-C(3)</td>
<td>91.9 (8)</td>
<td>C(5)-N(1)-S</td>
<td>128 (1)</td>
</tr>
<tr>
<td>C(2)-Fe-C(3)</td>
<td>93.6 (8)</td>
<td>C(5)-C(6)-C(7)</td>
<td>109 (2)</td>
</tr>
<tr>
<td>C(3)-C(6)-C(5)</td>
<td>104 (1)</td>
<td>C(6)-C(5)-N(1)</td>
<td>106 (1)</td>
</tr>
<tr>
<td>C(3)-C(6)-C(7)</td>
<td>121 (2)</td>
<td>C(6)-C(5)-O(3)</td>
<td>129 (2)</td>
</tr>
<tr>
<td>C(3)-C(6)-N(1)</td>
<td>102 (1)</td>
<td>N(1)-C(5)-O(3)</td>
<td>126 (2)</td>
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<tr>
<td>C(4)-C(3)-C(6)</td>
<td>103 (2)</td>
<td>Fe-C(3)-C(6)</td>
<td>125 (1)</td>
</tr>
<tr>
<td>C(4)-N(1)-C(5)</td>
<td>113 (1)</td>
<td>Fe-C(3)-C(4)</td>
<td>113 (1)</td>
</tr>
</tbody>
</table>

Numbers in parentheses are estimated standard deviations in the least significant digits.
except for the angles C(3)-C(6)-C(7) and Fe-C(3)-C(6). These two angles for \textit{cis-11} are 121(2)° and 125(1)°, respectively. The bond angles C(3)-C(6)-C(7) and Fe-C(3)-C(6) for \textit{trans-11} are 116.3(2)° and 119.6(2)°, respectively. The larger bond angles of the \textit{cis} isomer are attributed to the repulsion of the phenyl group at the B carbon bonded to the carbonyl group and the \(\eta^5\)-C\(_5\)H\(_5\)(CO)\(_2\)Fe group. The dihedral angle between the planes defined by C(3)-C(6)-C(7) and Fe-C(3)-C(6) for \textit{trans-11} is 75.5°. The same dihedral angle for \textit{cis-11} is -45.2°.

The arrangement around the atom N(1) is trigonal planar for both complexes. This geometry, together with the values of the S-N(1) bond distances, suggests some double bond character in the S-N bonds.\(^{58,59}\) In fact, the values of 1.646 (2) Å for S-N(1) of \textit{trans-11} and 1.66 (2) Å for S-N(1) of \textit{cis-11} are significantly shorter than 1.76 (2) Å expected for a single S-N bond.\(^{60}\) Moreover, they are comparable to the value of 1.677 (7) Å found in the cation \([\eta^5\text{C}_5\text{H}_5\text{CO})_2\text{Fe}(\eta^2\text{CH}_2\text{-CH}_2\text{N}(\text{S}(\text{O})_2\text{CH}_3))\text{SNH}(\text{S}(\text{O})_2\text{CH}_3)]^+\) where S-N partial double bonds are present.\(^{27}\) On the other hand, the C(5)-O(3) distances of 1.205 (3) Å for \textit{trans-11} and 1.18 (2) Å for \textit{cis-11} are close to the value of 1.20 Å for a normal C=O double bond.\(^{61}\) These results suggest that no significant conjugation occurs over the O(3)-C(5)-N(1) bonds and that the lone pair of electrons on N(1) is more delocalized over the sulfonyl group. This argument can
explain that replacement of the anilino group by a somewhat electron-withdrawing toluene group next to the sulfonyl group results in a low yield of product or no reaction upon protonation of the metal-γ-lactam complex. The toluene group is expected to substantially increase the double bond character of the S-N(1) bond.

With the structure of two isomers determined by X-ray crystallography, the IR and ¹H NMR spectra of trans- and cis-11 can be analyzed and compared. The IR spectra of both isomers are quite similar except for the ν(NH) band. The ν(NH) band at 3207 cm⁻¹ for the trans isomer is strong and sharp, whereas the ν(NH) band at 3207 cm⁻¹ for the cis isomer is of medium intensity and broad as shown in Figure 8. This difference may be due to the formation of a hydrogen bond between the carbonyl group and the NH group in the cis isomer. This difference in the IR spectra provides a simple method for distinguishing the two isomers. The ⁵-C₅H₅¹H NMR signal of cis-11 is 0.15 ppm downfield from that of trans-11. This is similar to what has been found in the spectra of trans- and cis-10. Another feature of the ¹H NMR spectra is the difference in the absorption patterns of the phenyl group of the two isomers as shown in Figures 9 and 11. The chemical shifts of the ⁵-C₅H₅ proton and the resonance patterns of the phenyl groups provide another method for differentiating the isomeric configurations. The assignment of the signals to various protons of the lactam ring of trans-11 were made
by use of the homonuclear decoupling technique on a 500-MHz NMR instrument. These spectra are shown in Figure 10. Irradiation at the frequency of the δ 2.47 multiplet collapses the δ 3.25 doublet to a singlet, the δ 3.46 doublet of doublets to a doublet (J = 9.6 Hz), and the δ 3.90 doublet of doublets to a doublet (J = 9.6 Hz). Irradiation at the δ 3.25 signal simplifies the δ 2.47 multiplet to a doublet of doublets. Irradiation at the δ 3.46 signal results in a collapse of the δ 3.90 doublet of doublets to a doublet (J = 7.7 Hz). Irradiation at the δ 3.90 signal collapses the δ 3.46 doublet of doublets to a doublet (J = 11.6 Hz). According to the structure of trans-11, the signal of Ha should be at a higher field than that of Hb, since Ha is shielded by the cyclopentadienyl group. The coupling constant J(Ha, Hc) should be larger than J(Hb, Hc). The resonance of Hc is a multiplet, whereas Hd is coupled to Hc (J = 12.3 Hz). Based on the above analysis, the proton resonance

\[
\text{trans-11}
\]
assignments of trans-11 are listed in Table 2 of Experimental Section.

The homonuclear decoupling technique has also been applied to the assignment of resonances to the protons on the lactam ring of cis-11. The spectra are shown in Figure 12. Thus, irradiation at the frequency of the δ 3.04 signal results in collapses of the δ 3.48 doublet to a singlet, the δ 3.72 doublet of doublets to a doublet (J = 10.3 Hz), and the δ 3.96 doublet of doublets to a doublet (J = 10.3 Hz). Irradiation at the δ 3.48 signal simplifies the δ 3.04 multiplet to a doublet of doublets. Irradiation at the δ 3.72 signal collapses the δ 3.96 doublet of doublets to a doublet (J = 7.7 Hz, one peak looks like a doublet owing to off-resonance effect). Irradiation at δ 3.96 signal collapses the δ 3.72 signal of doublet of doublets to a doublet (J = 11.8 Hz, one peak looks like a doublet owing to off-resonance effect). According to the structure of cis-11, H_a is shielded by the cyclopentadienyl group; therefore, its resonance is at a somewhat higher field than that of H_b. The coupling constant J(H_a, H_c) is larger than J(H_b, H_c). Proton H_c is coupled to protons H_a, H_b and H_d. The signal of H_d is split by H_c (J = 8.3 Hz). Based on the above analysis, the proton
Figure 8. Comparison of the $\nu$(NH) IR Absorption Bands of trans- and cis-$n^5$-C$_5$H$_5$(CO)$_2$FeCHCH(C$_6$H$_5$)C(O)N(S(O)$_2$NH)C$_6$H$_5$CH$_2$
Figure 9. The $^1$H NMR Spectrum of trans-$n^5$-C$_5$H$_5$(CO)$_2$Fe-
CHCH(C$_6$H$_5$)C(O)N(S(O)$_2$NHC$_6$H$_5$)$_2$CH$_2$ in CDCl$_3$ Solution
Figure 10. The $^1$H NMR spectrum of $\text{trans-}^5\text{C}_5\text{H}_5(\text{CO})_2\text{Fe-}$

$\text{CHCH(C}_6\text{H}_5)\text{C(O)N(S(O))}_2\text{NHC}_6\text{H}_5\text{)}\text{CH}_2$ in the region of

$\delta$ 2.40 - 4.10 ppm: (a) Without decoupling.

(b) Irradiation at the $\delta$ 3.90 signal. (c) Irradiation at the $\delta$ 3.46 signal. (d) Irradiation at the $\delta$ 3.25 signal (e) Irradiation at the $\delta$ 2.47 signal.
Figure 11. The $^1$H NMR Spectra of cis-$n^5$-C$_5$H$_5$(CO)$_2$Fe-
\[
\text{CHCH(C}_6\text{H}_5\text{)C(O)N(S(O)\text{)}_2\text{NHC}_6\text{H}_5\text{)CH}_2
\]
in CDCl$_3$ Solution.
Figure 12. The $^1$H NMR spectra of cis-$n^5$-C$_5$H$_5$(CO)$_2$Fe-
CHCH(C$_6$H$_5$)C(O)N(S(O)$_2$)NHC$_6$H$_5$CH$_2$ in the region of
the $\delta$ 2.90 - 4.10 ppm: (a) Without decoupling.
(b) Irradiation at the $\delta$ 3.96 signal. (c) Irradiation
at the $\delta$ 3.72 signal. (d) Irradiation at the $\delta$
3.48 signal. (e) Irradiation at the $\delta$ 3.04 signal.
resonance assignments of cis-11 are listed in Table 2 of Experimental Section.

\[
\text{cis-11}
\]

C. Extension to Related Complexes of the Conversion of trans Isomer to cis Isomer

As mentioned in the preceding sections, complexes trans-10, 11 were converted to cis-10, 11 through protonation-deprotonation. To determine the generality of this type of reaction, similar complexes trans-18, 19 were chosen to be studied. These complexes were also used in a mechanistic study to be described later. The complexes trans-18 and trans-19 were prepared by the method analogous to the
preparation of **trans-11**. In the preparations of both complexes, the *trans* isomer was the only product. It was recognized by the strong and sharp $\nu$(NH) band in the IR spectrum and the characteristic pattern of phenyl group resonances and a relatively highfield $\eta^5$-$C_5H_5$ signal in the $^1H$ NMR spectrum. Protonation of **trans-18** in a manner analogous to that of **trans-11** yielded a small amount of yellow precipitate at ca. -60°C. The reaction mixture turned red and became clear after being stored at room temperature for a few minutes. Continuous stirring for an additional 15 min suddenly resulted in the formation of a second precipitate. The second yellow precipitate is thought to be **cis-20**, the structure of which is strongly supported by the similarity of its IR spectrum to that of **cis-15**. In addition, two $\nu$(NH) absorptions at 3380 and 3230 cm$^{-1}$ were observed.
Deprotonation of cis-20 proceeded readily to give cis-18. The structure of the product was inferred from medium intensity and broad ν(NH) IR absorptions, as well as from the resonance pattern of the phenyl groups and a downfield $n^5$-C$_5$H$_5$ signal in its $^1$H NMR spectrum.

Protonation of trans-19 resulted in the formation of a metal-$\eta^2$-olefin complex, cis-21. Unlike the protonations of trans-11 and trans-18, there were only two observable stages for the protonation of trans-19. No precipitate formed at low temperature, and the yellow solution gradually changed to red at room temperature. After 20 min of stirring at room temperature, a yellow precipitate suddenly formed. The yellow precipitate was identified as cis-21 by IR spectroscopy.

When the complex cis-21 was treated with Proton Sponge, the reaction went readily at -60°C to generate cis-19 the identity of which was ascertained from its IR and $^1$H NMR spectroscopic data.
Both spectra showed characteristic features expected of the cis isomer. The results show the generality of the conversion of the trans isomer to the cis isomer via protonation-deprotonation of this type of organoiron complexes.

D. Mechanistic Study of the Protonation-Deprotonation Reaction

As mentioned in the preceding sections, the trans isomers of complexes $[M]CHCHR^1C(O)N(S(O)_{2}NHR^2)CH_2$ (when $[M] = n^5$-$C_5H_5(CO)_2Fe$, $R^1 = CH_3$, $C_6H_5$, $R^2 = C_6H_4CH_3-p$; when $[M] = (n^5$-$CH_3C_5H_4)(CO)_2Fe$, $R^1 = C_6H_5$, $R^2 = C_6H_4CH_3-p$) are converted to their cis isomers by the sequence protonation-deprotonation. In the absence of acid, it has been found that equilibrium between the cis and trans isomers is attained extremely slowly. As the protonation of the trans complex progresses, there are two different precipitates formed depending on the temperature (an exception is the protonation of trans-19). The trans metal-$n^2$-olefin complex in solution changes to a clear red solution, which then converts to the cis metal-$n^2$-olefin complex. Two mechanisms are considered for these changes as shown in Schemes V and IV.

The first mechanism involves enolization as the pathway for the transformation of the trans metal-$n^2$-olefin complex to its cis isomer. The carbonyl compound isomerizes to its enolate by transfer of the proton at the $\beta$-carbon bonded to the carbonyl group. When
Proposed Mechanism 1

\[ \text{(M)} = \eta^5-C_5H_5(CO)_2Fe, (\eta^5-CH_3C_5H_4)(CO)_2Fe \]
\[ R = CH_3, C_6H_5 \]
\[ Ar = C_6H_5, O-CH_3 \]
Proposed Mechanism 2

\[
(M) = \eta^5-C_5H_5\{CO\}_2Fe, (\eta^5-CH_3C_5H_4\{CO\}_2Fe
\]

\[R = CH_3, C_6H_5\]

\[Ar = C_6H_5, \bigcirc-CH_3\]
the enolate goes back to its carbonyl form, a proton from solution attaches to this β-carbon. Because a bulky [M] group may hinder the approach of the proton, the latter may return to the β-carbon atom from the opposite side. Hence, this mechanism results in the R group ending up cis to the [M] group. Of course, deprotonation of this cis metal-\( \eta^2 \)-olefin complex affords the cis metal-\( \gamma \)-lactam complex.

The second mechanism invokes metal-olefin dissociation in the process of trans-to-cis conversion. When the metal group reassociates with the olefin, it comes back from the opposite side, thus affording a cis metal-\( \eta^2 \)-olefin complex. To test these two proposed mechanisms, two experiments were carried out: isotope labelling and crossover.

If the hydrogen at the β-carbon bonded to the carbonyl group of trans-11 is replaced with deuterium, the sequence protonation-deprotonation of this deuterated complex provides an excellent method of testing the first mechanism. Should the reaction sequence follow the first mechanism, then this deuterium would be replaced with hydrogen from the solution. Otherwise, the first mechanism may be ruled out.

A multiple-step synthesis, which is shown in Scheme VII, was used to prepare deuterated trans-11. The structure of the deuterated trans-11 was verified by spectroscopic methods including
Scheme VII

\[
\text{PhC≡C-COOH} \xrightarrow{\text{MeOH}, \ H^+} \text{PhC≡C-COOH} \quad 83\% \quad \xrightarrow{\text{(1) LAH, (2) DCl-\ D}_2\text{O}} \text{D} = \text{C} = \text{C} - \text{CH}_2\text{OH} \quad 94\%
\]

\[
\xrightarrow{\text{SOCl}_2, \text{CHCl}_3, \text{Py}} \text{D} = \text{C} = \text{C} - \text{CH}_2\text{Cl} \quad 68\%
\]

\[
\xrightarrow{\text{(1)cis-2NCO, (2) PhNH}_2} \eta^5\text{-C}_5\text{H}_5\text{(CO)}_2\text{Fe} - \text{C} = \text{C} - \text{Ph} \quad 86\%
\]
Scheme VIII

Crossover Reaction

\[ \eta^5-C_5H_5(\text{CO})_2Fe + (\eta^5-\text{CH}_3C_5H_4)(\text{CO})_2Fe \rightarrow \text{M.wt. 492} \]

\[ \text{M.wt. 492} \rightarrow \eta^5-C_5H_5(\text{CO})_2Fe + \text{M.wt. 506} \]

\[ 520 \rightarrow (\eta^5-\text{CH}_3C_5H_4)(\text{CO})_2Fe + (\eta^5-\text{CH}_3C_5H_4)(\text{CO})_2Fe \]
Figure 13. The $^{1}H$ NMR Spectrum of $\text{trans-}n^5$-$C_5H_5(CO)_2Fe$-$CHCD(C_6H_5)C(O)N(S(O)_2NHC_6H_5)CH_2$ in CDCl$_2$ Solution.
Figure 14. The $^1$H NMR Spectrum of \([\text{cis-}n^5-\text{C}_5\text{H}_5(\text{CO})_2\text{Fe} \underline{\text{CHCD(C}_6\text{H}_5)\text{C}(\text{O})\text{N}(\text{S}(\text{O})_2\text{NH})_2\text{C}_6\text{H}_5})\text{CH}_2]\) in CDCl$_3$ Solution.
mass, IR, $^{1}$H NMR and $^{2}$H NMR. The IR spectrum revealed the $\nu$(NH) absorption of the trans isomer. The $^{1}$H NMR spectrum shown in Figure 13 is essentially identical with the spectrum of trans-11 except for the absence of the signal due to H at the $\beta$ carbon bonded to the carbonyl group. The $^{2}$H NMR spectrum shows a resonance at $\delta$ 3.26.

The sequence protonation-deprotonation on deuterated trans-11 yielded only deuterated cis-11, indicative of no deuterium exchange in the reaction. The $^{1}$H NMR of deuterated cis-11 is shown in Figure 14. The $^{2}$H NMR spectrum shows one signal at $\delta$ 3.51. The result of this experiment definitely rules out the first proposed mechanism.

Since the second proposed mechanism involves dissociation of a metal-olefin bond in the process of isomerization, it was thought that a crossover reaction would be helpful in this mechanistic study. This would entail use of a mixture containing two complexes: one consisting of a metal group M and a cycloalkyl group R, and the other consisting of a metal group M' and a cycloalkyl group R'. If the second mechanism is operative, scrambling of M and M' and R and R' would occur upon completion of the sequence protonation-deprotonation.

To carry out this study, the complexes trans-$n^{5}$C$_{6}$H$_{5}$(CO)$_{2}$FeCH-CH(C$_{6}$H$_{5}$)C(O)N(S(O)$_{2}$NCH$_{6}$H$_{5}$)CH$_{2}$, trans-11, and trans-($n^{5}$-CH$_{3}$C$_{5}$H$_{4}$)-(CO)$_{2}$FeCHCH(C$_{6}$H$_{5}$)C(O)N(S(O)$_{2}$NCH$_{6}$H$_{4}$CH$_{3}$-p)CH$_{2}$, trans-19, were selected. If dissociation of the metal-olefin bond takes place, a
Figure 15. The Mass Spectrum (FAB) of Product Mixture from the Crossover Reaction.
mixture of four products will be generated by the reaction protonation-deprotonation of trans-11 and trans-19. This possibility is shown in Scheme VIII. An analysis of the products of this reaction conducted on a mixture of trans-11 and trans-19 in a 1:1 ratio demonstrated that they are the cis isomers and that there was scrambling. The stereochemistry of the products was ascertained by $^1$H NMR spectroscopy. However, the $^1$H NMR spectrum did not allow the determination of the number of products in the mixture, owing to overlap of the signals of different components. The confirmation that the scrambling did occur in the reaction came from a mass spectrum obtained by use of the FAB technique.

The mass spectrum revealed three parent peaks each with the correct isotopic pattern at m/e 521, 507 and 493 as shown in Figure 15. Complexes cis-11 and cis-19 should have peaks at m/e 493 and 521, respectively. The peak at m/e 507 indicates the presence of the crossover products which have molecular weights of 506. It should be mentioned that the mass spectrum always shows the parent peak of a compound at the M + 1 position if the FAB technique is utilized. To exclude the possibility that the peak at m/e 507 derives from fragmentation in the mass spectrometer, a control experiment was carried out. The mass spectrum of a 1:1 mixture of cis-11 and cis-19 showed two parent peaks at m/e 521 and 493. The absence of a peak at m/e 507 in the spectrum rules out the
possibility of the scrambling through fragmentation in the mass spectrometer.

The intensities of the peaks at m/e 521 and 493 are approximately equal, but the intensity of the peak at m/e 507 is about one-fourth of each of the other two peaks. This suggests incomplete scrambling, possibly owing to little separation of the dissociated metal group and olefin compound which would favor recombination of these same species.

It is of interest to consider possible reasons for the conversion of the trans isomer of a metal-\(\eta^2\)-olefin complex to its cis isomer. Apparently, the relative stabilities of these two isomers play an important role in this transformation. It has been reported that when the allylic hydrogen eclipses the double bond in olefinic compounds, the molecule reaches its most stable conformation, shown below:\(^6^2\)

\[
\begin{align*}
\text{H} & \quad \text{H} \\
\text{R} & \quad \text{H} \\
\end{align*}
\]

Increasing steric requirements of the groups at the sp\(^3\) carbon increases the preference for the eclipsed conformation.

Application of these considerations to the metal-\(\eta^2\)-olefin complexes provides an explanation for the conversion of the trans to
the cis isomers of the metal-olefin complexes in the second
mechanism. A more detailed picture of this mechanism is depicted in
Scheme IX.

Protonation opens up the lactam ring to form a trans metal-\( \eta^2 \)-olefin complex. This complex then undergoes rotation about the C-C
bond of CHCHR to reach the most favorable conformation, i.e., the one
in which the allylic hydrogen eclipses the double bond. However, in
this conformation, steric repulsion between the iron group and the R
group at the \( \beta \) atom group increases. Therefore, dissociation of the
metal-olefin bond occurs. The iron group then reassociates with the
olefin from the less hindered side. Deprotonation of the rearranged
metal-\( \eta^2 \)-olefin complex leads to the formation of the cis isomer of
the metal-\( \gamma \)-lactam complexes.

The second mechanism is also supported by the results and
observations of other experiments of this investigation which are
summarized in Scheme X. In the protonation of 13, which has two
hydrogens at the \( \beta \) carbon bonded to the carbonyl group, a yellow
precipitate formed at \(-30^\circ\)C. The yellow precipitate remained
undissolved even when the mixture was warmed to room temperature.
The metal-\( \eta^2 \)-olefin complex survives at room temperature probably
owing to a stable metal-olefin bond. On the other hand, protonation
of 12, which has two methyl groups at the \( \beta \)-carbon bonded to the
carbonyl group, resulted in the formation of a yellow precipitate at
Scheme IX

\[
\begin{align*}
(M) &\xrightarrow{HPF_6} (M)^+ \xrightarrow{PF_6^-} (M)^+ \xrightarrow{PF_6^-} (M)^+ \\
\text{[{(M)}]} &\xrightarrow{\text{R} = \text{CH}_3, \text{C}_6\text{H}_5} \xrightarrow{\text{R'} = \text{C}_6\text{H}_5, \text{CH}_3} \xrightarrow{- \text{H}^+} \xrightarrow{\text{R} = \text{CH}_3, \text{C}_6\text{H}_5} \\
\end{align*}
\]

\[\text{[(M)]} = \eta^5-\text{C}_5\text{H}_5(\text{CO})_2\text{Fe}, (\eta^5-\text{CH}_3\text{C}_5\text{H}_4)(\text{CO})_2\text{Fe}\]

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

\[\text{R'} = \text{C}_6\text{H}_5, \text{CH}_3\]
Scheme X

-30 °C — -10 °C

\[ \text{trans: cis} = 90 : 10 \]

\[ \text{Yellow ppt.} \]

\[ \text{Red soln.} \rightarrow \text{Yellow ppt.} \]
Scheme X (continued)

-30 → -10°C R.T.

\[
\begin{align*}
\text{(M)} \begin{array}{c}
\text{N}^X \\
\text{H}^{\text{Ph}}
\end{array} + \text{H}^+ & \rightarrow \text{(M)} \begin{array}{c}
\text{N}^X \\
\text{H}^{\text{Ph}}
\end{array} \\
\text{(M)} \begin{array}{c}
\text{N}^X \\
\text{H}^{\text{Ph}}
\end{array} & \rightarrow \text{(M)} \begin{array}{c}
\text{N}^X \\
\text{H}^{\text{Ph}}
\end{array} \\
\text{(M)} \begin{array}{c}
\text{N}^X \\
\text{H}^{\text{Ph}}
\end{array} - \text{H}^+ & \rightarrow \text{(M)} \begin{array}{c}
\text{N}^X \\
\text{H}^{\text{Ph}}
\end{array}
\end{align*}
\]

Yellow ppt. Red soln. → Yellow ppt.

\[
\begin{align*}
\text{(M)} \begin{array}{c}
\text{N}^X \\
\text{H}^{\text{Ph}}
\end{array} + \text{H}^+ & \rightarrow \text{(M)} \begin{array}{c}
\text{N}^X \\
\text{H}^{\text{Ph}}
\end{array} \\
\text{(M)} \begin{array}{c}
\text{N}^X \\
\text{H}^{\text{Ph}}
\end{array} & \rightarrow \text{(M)} \begin{array}{c}
\text{N}^X \\
\text{H}^{\text{Ph}}
\end{array} \\
\text{(M)} \begin{array}{c}
\text{N}^X \\
\text{H}^{\text{Ph}}
\end{array} & \rightarrow \text{(M)} \begin{array}{c}
\text{N}^X \\
\text{H}^{\text{Ph}}
\end{array} + \text{H}^+
\end{align*}
\]

Yellow ppt. Acid = HF

\[
\begin{align*}
\text{(M)} \begin{array}{c}
\text{N}^X \\
\text{H}^{\text{Ph}}
\end{array} & \rightarrow \text{(M)} \begin{array}{c}
\text{N}^X \\
\text{H}^{\text{Ph}}
\end{array} \\
\text{(M)} \begin{array}{c}
\text{N}^X \\
\text{H}^{\text{Ph}}
\end{array} & \rightarrow \text{(M)} \begin{array}{c}
\text{N}^X \\
\text{H}^{\text{Ph}}
\end{array} \\
\text{(M)} \begin{array}{c}
\text{N}^X \\
\text{H}^{\text{Ph}}
\end{array} & \rightarrow \text{(M)} \begin{array}{c}
\text{N}^X \\
\text{H}^{\text{Ph}}
\end{array} + \text{H}^+
\end{align*}
\]

Red soln. → Yellow ppt.
-30°C but the yellow precipitate formed in the reaction decomposed when the mixture was warmed to room temperature. It is likely that interaction of the iron group with one of the methyl groups destabilizes the metal-olefin bond. As a result, the complex decomposes at room temperature.

Protonation of trans-10 which has one methyl group at the β-carbon bonded to the carbonyl group resulted in the formation of a yellow precipitate at -30°C which then dissolved to give a clear red solution at room temperature. After an additional 15 min at 25°C, a second precipitate formed. It is proposed here that the first precipitate, the kinetic product, adopts the eclipsed conformation with the methyl group cis to the iron group. At room temperature, interaction of the methyl group and the iron group destabilizes the metal-olefin bond and accounts for the formation of the red solution. Since the methyl group is not very bulky, the iron group may reassociate with the olefin from either side; of course, the less hindered side leading to the cis product is favored. Hence, deprotonation of the resulting metal-η²-olefin complex gives a diastereomeric mixture which is 10:90 trans/cis.

Protonation of trans-11, which has a phenyl group at the β-carbon bonded to the carbonyl group, is analogous to the protonation of trans-10. However, the conversion from the trans isomer of the metal-η²-olefin complex derived from trans-11 to its cis isomer is
much faster and complete. Since the phenyl group is much larger than the methyl group, the interaction between the phenyl group and the iron group is stronger.

E. Extension of the Same Sequence to Analogous Tungsten Complexes

(i) Preparations

The success of the sequence protonation-deprotonation on iron-\(\gamma\)-lactam complexes prompted an extension of this chemistry to other analogous metal complexes. It has been reported that the reactions of molybdenum-\(\eta^1\)-allyl complexes with \(\text{ClSO}_2\text{NCO}\) gave \(\text{n}^5\text{-C}_5\text{H}_5\text{(CO)}_3\text{MoCl}\) rather than the expected [3 + 2] cycloadducts. In the same group of the periodic table, tungsten complexes generally are more stable than molybdenum complexes. Therefore, the same procedure as that for the preparation of iron-\(\gamma\)-lactam complexes was employed to synthesize tungsten-\(\gamma\)-lactam complexes. The reaction of \(\text{n}^5\text{-C}_5\text{H}_5\text{(CO)}_3\text{W(E-CH}_2\text{CH=CHCH}_3)\) with \(\text{ClSO}_2\text{NCO}\) readily gave a cycloaddition product which was further treated with aniline in situ to give its derivative, \(\text{trans-n}^5\text{-C}_5\text{H}_5\text{(CO)}_3\text{WCHCH(CH}_3)\text{C(O)N(S(O)}_2\text{HNCH}_6\text{H}_5)\text{CH}_2\), \(\text{trans-22}\). The reaction thus proceeded with the preservation of the \(\text{trans}\) geometrical relationship between the methyl group at the \(\gamma\)-carbon of the allyl ligand and the tungsten metal. This is also true when \(\text{trans-n}^5\text{-C}_5\text{H}_5\text{(CO)}_3\text{WCHCH(C}_6\text{H}_5)\text{C(O)N(S(O)}_2\text{HNCH}_6\text{H}_5)\text{CH}_2\), \(\text{trans-23}\), was prepared from \(\text{n}^5\text{-C}_5\text{H}_5\text{(CO)}_3\text{W(E-CH}_2\text{CH=CHCC}_6\text{H}_5)\) and \(\text{ClSO}_2\text{NCO}\),
and then aniline. In the preparation of trans-22, the replacement of chloride bonded to the sulfonyl group of the cycloadduct with C₆H₅NH proceeded relatively slowly; it required 6 hours at room temperature to complete the reaction. In contrast, in the preparations of 23 and n⁵-C₅H₅(CO)₃WCHC(CH₃)₂C(O)N(S(O)₂NH₆H₅)CH₂, 24, the replacement of chloride by C₆H₅NH went easily and completely in 1.5 hours. The reasons for this difference are not known at this point.

Complexes trans-22, 23, and trans-24 were characterized on the basis of elemental analysis and spectroscopic properties. Their IR and ¹H NMR data are listed in Tables 13 and 14, respectively, in Experimental Section. These IR and ¹H NMR data compare well with those reported for a series of iron-γ-lactam complexes which have been discussed in preceding sections. The stereochemical assignments of trans-23, and 24 were determined by their spectroscopic characteristics. The ¹H NMR spectrum of trans-22 shows a methyl doublet at δ 1.18, the position of which is close to that of the methyl doublet of its analogue, trans-n⁵-C₅H₅(CO)₃FeCHCH(CH₂)C(O)-N(S(O)₂NH₆H₅)CH₂. Its IR spectrum revealed a relatively sharp ν(NH) band at 3210 cm⁻¹ typical of the trans structure of this series of metal-γ-lactam complexes.

For complex 24, the stereochemical assignment is based on the IR spectrum which displays a weak and relatively sharp ν(NH) band at
3391 cm\(^{-1}\) (this \(v(\text{NH})\) band of its \textit{cis} isomer, which will be discussed in the following section, is much weaker and broad).

(ii) Protonation-Deprotonation

Protonation of \(\text{trans-22}\), was somewhat different from that of its iron analogue, \(\text{trans-10}\). A precipitate formed at ca. \(-30^\circ\text{C}\) and it did not dissolve even after 45 min at room temperature. Deprotonation of this yellow-green precipitate with Proton Sponge regenerated \textit{trans-22}. The IR spectrum of the yellow-green precipitate shows three strong \(v(\text{C}=\text{O})\) absorptions at 2108, 2055 and 2000 cm\(^{-1}\) and two \(v(\text{NH})\) bands at 3335 and 3241 cm\(^{-1}\). The shift of the frequencies of \(v(\text{C}=\text{O})\) bands from 2010, 1956, and 1912 cm\(^{-1}\) for the neutral \textit{trans-22} to the higher wavenumber for the protonated product indicates that the precipitate is a cationic species. The two \(v(\text{NH})\) bands and the result of the deprotonation suggests that the structure of the precipitate is \textit{trans-25}. Prolonged stirring at room temperature of \textit{trans-25} led to a slow conversion to \textit{cis-25}. There was no observable change for this transformation. Deprotonation of the resulting precipitate, which was obtained after 6 hours of stirring at room temperature, gave an isomeric mixture of \textit{22} in a 30:70 \textit{trans/cis} ratio. This ratio was estimated by measurement of the integrated intensities of
the appropriate $\eta^5$-$C_5H_5$ $^1H$ NMR signals. The stereochemical assignments of cis-22 are based on the methyl doublet at $\delta$ 0.80, analogous to that of cis-10, and the $\eta^5$-$C_5H_5$ signal at 0.05 ppm downfield from that of trans-22.

When trans-23 was treated with HPF$_6$·(C$_2$H$_5$)$_2$O, precipitate did not form until the temperature of the mixture reached room temperature. The IR spectrum of the precipitate, which was formed in the protonation, reveals two strong $\nu$(C=O) absorptions at 2115 and 2050 cm$^{-1}$ and two $\nu$(NH) bands at 3245 and 3185 cm$^{-1}$. As discussed earlier, the positive charge on the tungsten complex increases the frequency of the $\nu$(C=O) absorptions. Thus, it is reasonable to assign the structure of the precipitate as 26.
Complex 26 is relatively stable in acetone solution. Its $^1$H NMR spectrum taken in acetone-$d_6$ solution exhibits a signal of the $\eta^5$-C$_5$H$_5$ protons at $\delta$ 5.65, the resonances of the phenyl protons and the NH proton in the $\delta$ 7.24-7.77 region, and absorptions of the remaining protons of the allylic fragment in the $\delta$ 3.70-4.41 region.

Deprotonation of 26 readily occurred to give a yellow product. This yellow product is extremely air-sensitive and thermally rather unstable. It decomposed after 2 days of storage in a drybox. The $^1$H NMR spectrum showed that 26 was associated with one molecule of THF. Removal of the THF molecule by dissolving the compound in CH$_2$Cl$_2$ and then pumping off the solvent led to a decomposition of the complex. In the $^1$H NMR spectrum of the yellow product which contains a THF molecule, a sharp signal of the $\eta^5$-C$_5$H$_5$ protons is observed at $\delta$ 5.11, absorptions of the phenyl protons are found in the $\delta$ 7.05-7.63 region, and the peak of the NH proton occurs at $\delta$ 6.48. Therefore, the yellow product has a structure similar to trans-23. (It is not trans-23, since physical properties and resonance patterns in the $^1$H NMR spectra of the two species are different. Signals of the protons of the lactam ring are also found in the $\delta$ 2.58-3.13 and 3.80-4.48 regions.)

The IR spectrum of the deprotonated complex is similar to that of trans-23 but a broad $\nu$(NH) band at 3325 cm$^{-1}$ suggests that the structure is cis-23.
Protonation of 24, which has two methyl groups at the β carbon bonded to the carbonyl group of the lactam ring, led to the formation of a precipitate at 0°C. This precipitate decomposed on warming to room temperature. Because of a low yield and thermal instability of the product, deprotonation was not carried out. No spectroscopic data were obtained on protonated 24. From a similarity between the protonations of 24 and its iron analogue $\eta^5$-C$_5$H$_5$(CO)$_2$FeCHC(CH$_3$)$_2$C(O)N(S(O)$_2$NH)$_2$C$_6$H$_5$CH$_2$, the precipitate is assumed to be a tungsten-$\eta^2$-olefin complex 27.

27

The conversion of the trans isomers of the tungsten complexes to their cis isomers by the sequence protonation-deprotonation resembles closely the corresponding transformations of the iron complexes. The similarity between the two systems suggests that the reactions of the tungsten complexes proceed through the same mechanism as do the iron complexes. However, the transformation of
trans-22 to cis-22 appears to be much slower than that of the analogous iron complex.

II. Preparation and Reactions with Electrophilic Reagents of Platinum(II)-n^1-Allyl Complexes

(A) Preparation

In general, complexes trans-[(n^1-CH₂CH=CH₂)PtL₂Cl] (L = phosphine) can be prepared by two methods: (1) oxidative addition reaction of platinum(0) complexes PtLn (n = 3 or 4) with allyl chloride, and (2) reaction of [(C₃H₅)PtCl]₄ with appropriate phosphine. Although the first reaction proceeds readily to give a platinum(II)-n^1-allyl complex, complicated procedure in the preparation of the starting material PtLn, which is extremely air-sensitive in most cases, causes handling difficulties and significantly lowers the yield of product. On the other hand, the tetramer [(C₃H₅)PtCl]₄ is very air-stable and easily prepared. The reaction of the tetramer with appropriate phosphine usually affords a good yield of product. To synthesize different platinum(II)-n^1-allyl complexes, only one starting material is used, unlike in the first method. This is another advantage of this method.

Based on these considerations, the complex trans-[(n^1-CH₂CH=CH₂)Pt(P(C₂H₅)₃)₂Cl], 28, was made from one equiv of the tetramer and eight equiv of P(C₂H₅)₃ in diethyl ether solution. Its
IR and $^1$H NMR spectra are identical with those of an authentic sample prepared by the oxidative addition method, which was reported by R. G. Pearson.$^{40}$

The same procedure was employed to prepare trans-[$^1$-CH$_2$-CH=CH$_2$]Pt(P(i-C$_3$H$_7$)$_3$)$_2$Cl], 29. Reaction of one equiv of [(C$_3$H$_5$)Pt-Cl]$_4$ with eight equiv of P(i-C$_3$H$_7$)$_3$ gave 29 in 87% isolated yield.

Synthesis of the complex trans-[$^1$-CH$_2$CH=CH$_2$]Pt(P(CH$_3$)$_2$-C$_6$H$_5$)$_2$Cl], 30, required a modified procedure in which the addition of the phosphine to the tetramer was carried out in two stages. One equiv of the tetramer [(C$_3$H$_5$)PtCl]$_4$ was first treated with four equiv of P(CH$_3$)$_2$C$_6$H$_5$ in CH$_2$Cl$_2$ at low temperature. The addition had to be very slow. After one day, another four equiv of P(CH$_3$)$_2$C$_6$H$_5$ was slowly added. The spectroscopic data of the product were the same as those of the authentic sample prepared by G. Carturan.$^{63}$

A similar procedure was utilized in the synthesis of the complex trans-[$^1$-CH$_2$CH=CH$_2$]Pt(P(t-C$_4$H$_9$)$_3$)$_2$Cl], 31. Temperature control and the rate of phosphine addition are crucial in the preparation of the last two complexes.

All of these platinum(II)-$^1$-allyl complexes were characterized on the basis of elemental analysis and spectroscopic properties. Since one-third of naturally occurring platinum consists of the isotope platinum-195, which has a nuclear spin number 1/2, the
phosphorus atom attached to this platinum isotope is coupled. The magnitude of the coupling constant is a very sensitive tool in the characterization of platinum(II)-phosphine complexes. The $^{31}$P NMR spectra of the platinum complexes prepared in this study display a phosphorus signal surrounded symmetrically by two satellites. This type of coupling pattern also indicates the trans configuration of the two phosphines. The $^{195}$Pt-$^{31}$P coupling constants of about 2900 Hz are comparable to the coupling constant value of 2878 Hz for the previously reported complex trans-$\left(\eta^1\text{-CH}_2\text{CH}=\text{CH}_2\right)$Pt($\text{P}^\text{Q}$($\text{C}_6\text{H}_{11}$)$_3$)$_2\text{Cl}]$. The structures of these complexes are additionally supported by their IR spectra which reveal a $\nu$(C=C) absorption in the range 1600-1630 cm$^{-1}$ and a $\nu$(Pt-Cl) band around 260 cm$^{-1}$. The intensity of the $\nu$(C=C) absorption varies depending on the compound. Complex 28 shows a relatively strong and sharp $\nu$(C=C) band, whereas complex 31 exhibits a weak absorption for the C=C double bond stretch.

In the $^1$H NMR spectra, the $\eta^1$-CH$_2$CH=CH$_2$ fragment can be recognized by the presence of the signals of the olefinic protons in the $\delta$ 4-6 region and by the resonance of the methylene CH$_2$ protons around $\delta$ 2.20. The resonance of the protons of the CH$_2$ group bonded to the platinum metal is coupled to the olefinic CH proton and further coupled to $^{195}$Pt.
Interestingly, in complex 28 the signal of the CH$_3$ protons of the phosphine ethyl group appears as a quintet. The signal of the CH$_3$ protons of the isopropyl group in complex 29 is a quartet. In complex 30 the resonance of the CH$_3$ protons of the methyl group shows as a triplet which is further coupled to $^{195}$Pt. In complex 31 the CH$_3$ proton signal of the t-butyl group appears as a triplet.

To explain these unusual features in the spectra of the foregoing complexes, two modes of phosphorus-hydrogen coupling are considered. For the transition metal complexes containing two phosphines or phosphites, phosphorus-hydrogen coupling occurs not only within a ligand, but also between ligands. Therefore, the spectrum of the alkyl protons is treated as the X part of an XAA'X' system, where A and A' are two phosphorus atoms (one in each ligand), and X and X' are alkyl protons in different ligands. However, when the long range proton-proton coupling is zero ($J_{XX'} = 0$), this system can be simplified to X$_{12}$AA'. When the phosphine ligands are in mutually trans-positions, strong P-P coupling occurs. At the same time, if the values of the two P-H couplings are comparable, $J_{AA'} \gg |J_{AX} - J_{A'X}|$ results. Accordingly, a 1:2:1 triplet appearance for the proton spectrum is derived from calculations. When the two ligands are cis to each other, P-P coupling is weak and a simple doublet is observed.
On the basis of this analysis, the unusual appearance of the alkyl proton resonances of the platinum(II)-η^1-allyl complexes is rationalized. The first-order splitting pattern for the methyl protons of the ethyl group in complex 28 is the same as that for the methyl protons in trans-[PtX_2(P(C_3H_5)_3)] (X = monoanionic ligand). The analysis of the splitting is shown below:

The methyl proton signal is split by the methylene protons into a 1:2:1 triplet, and each of the peaks of this triplet is further coupled to the phosphorus atoms to yield another 1:2:1 triplet.

The same approach is applied to complex 27. The signal of the methyl protons of the isopropyl group is coupled to the CH proton. The resulting doublet is further split by the phosphorus atoms, and a quartet splitting pattern results. This analysis is shown below:
The splitting pattern for the methyl protons of complex 30 is very interesting. Phosphorus-hydrogen coupling leads to a 1:2:1 triplet. This major triplet is accompanied by two satellite triplets owing to $^{195}\text{Pt-H}$ coupling as shown below:

The $^1H$ NMR spectrum of complex 31 is simple by comparison. The resonance of the methyl protons is only coupled to the phosphorus atoms to form a 1:2:1 triplet.
Therefore, for complexes 28 - 31 the observed $^1$H NMR spectra of the alkyl protons of the phosphines are consistent with their predicted appearance based on the trans configuration of the molecules.

The crotyl complex trans-[$(\eta^1\text{-CH}_2\text{CH}=\text{CHCH}_3)\text{Pt}(\text{P(C}_2\text{H}_5)_3)_2\text{Cl}]$ reported by R. G. Pearson$^{40}$ was prepared by the oxidative addition reaction of Pt(P(C$_2$H$_5$)$_3$)$_4$ with crotyl chloride. However, the product is an isomeric mixture not a single complex as reported. The $^{31}\text{P}$ NMR spectrum of the product showed that there were two sets of peaks at $\delta$ 13.65 ppm with a $J(195\text{Pt-P})$ value of 2944 Hz and at $\delta$ 13.48 ppm with a $J(195\text{Pt-P})$ value of 2925 Hz, indicative of a small structural difference between the two isomers. From a comparison of the intensities of the two phosphine signals, the ratio of the two isomers was estimated to be about 7 to 1.

The 500-MHz $^1$H NMR spectrum of the product is shown in Figure 16. The assignments of the olefinic resonances for the CH$_2$CH$_b$=CH$_a$-CH$_3$ fragment were made with the aid of a decoupling experiment as shown in Figure 17. Four sets of these protons absorptions are observed in the region $\delta$ 5.30 to 6.10 ppm. Irradiation at the frequency of the $\delta$ 1.73 CH$_3$ signal collapses the $\delta$ 5.45 multiplet to a doublet ($J = 14.7$ Hz) and the $\delta$ 5.33 multiplet to an unsymmetrical doublet ($J = 11.0$ Hz) owing to off-resonance effects. Two other multiplets at $\delta$ 5.99 and 5.82 belong to $H_a$ and $H_b$, respectively, of
Figure 16. 500-MHz $^1$H NMR Spectrum of trans-[$(n^1-CH_2CH=CHCH_3)$-Pt($P(C_2H_5)_3$)$_2$Cl] in C$_6$D$_6$ Solution.
Figure 17. (a) 500-MHz $^1$H NMR Spectrum of trans-[$(n^1-\text{CH}_2\text{CH}=$CHCH$_3$)-Pt(P(C$_2$H$_5$)$_3$)$_2$Cl] in the $\delta$ 5.30 to 6.10 Region.

(b) The Resulting Spectrum in the Same Region when the Signal at $\delta$ 1.73 is Irradiated.
one isomer. The absorptions at $\delta$ 5.33 and 5.99 are attributed to $H_a$ and $H_b$ of the other isomer. Since H-H coupling between two trans-olefinic hydrogens is larger than that between two cis olefinic hydrogens,\textsuperscript{68} the major product is trans-[(n\textsuperscript{1}-E-CH\textsubscript{2}CH=CHCH\textsubscript{3})Pt(P(C\textsubscript{2}H\textsubscript{5})\textsubscript{3})\textsubscript{2}Cl], and the minor product is trans-[(n\textsuperscript{1}-Z-CH\textsubscript{2}CH=CHCH\textsubscript{3})Pt(P(C\textsubscript{2}H\textsubscript{5})\textsubscript{3})\textsubscript{2}Cl]. The deuterated crotyl complex trans-[(n\textsuperscript{1}-CH\textsubscript{2}CH=CD-CH\textsubscript{3})Pt(P(C\textsubscript{2}H\textsubscript{5})\textsubscript{3})\textsubscript{2}Cl] prepared from Pt(P(C\textsubscript{2}H\textsubscript{5})\textsubscript{3})\textsubscript{4} and Z-ClCH\textsubscript{2}CHCDCH\textsubscript{3} also contained two isomers in a 7:1 E/Z ratio as estimated from its $^{31}$P NMR phosphine signals.

(b) Reactions of Platinum(II)-n\textsuperscript{1}-Allyl Complexes with Sulfur Dioxide

Complexes (CH\textsubscript{2}CH=CHR)PtL\textsubscript{2}Cl afford an equilibrium mixture of n\textsuperscript{1}-allyl species and n\textsuperscript{3}-allyl species in solution (eq 11). Relative concentration of each species depends on the polarity of the solvent as well as the nature of ligand L. Generally speaking, n\textsuperscript{3}-allyl species predominate in polar solvents, whereas electron-releasing phosphines favor the presence of n\textsuperscript{1}-allyl species.\textsuperscript{40,69-74}

\[
\text{L}_2\text{ClPt} - \text{R} \rightleftharpoons \left[ \begin{array}{c} \text{Pt} \\ \text{R} \\ \text{L} \end{array} \right]^{+} \text{Cl}^{-} \quad (11)
\]
Hence, use of a nonpolar solvent and a proper ligand L for these complexes is important in obtaining a high concentration of an $n^1$-allyl species. $^{31}\text{P}$ NMR spectra of the complexes trans-$[(\text{CH}_2\text{CH}=\text{CHR})\text{PtL}_2\text{Cl}]$ (L = $\text{P(C}_2\text{H}_5)_3$, $\text{P(CH}_3\text{)}_2\text{C}_6\text{H}_5$, $\text{P(1-C}_3\text{H}_7)_3$, $\text{P(t-C}_4\text{H}_7)_3$, and $\text{P(C}_6\text{H}_{11})_3$) in a nonpolar solvent, such as benzene, toluene, diethyl ether, show that only the $n^1$-allyl species is present in solution.

For the iron-$n^1$-allyl complexes $\eta^5$-$\text{C}_5\text{H}_5(\text{CO})_2\text{FeCH}_2\text{CR}^1=\text{CR}^2\text{R}^3$ two methods have been used to conduct reactions with sulfur dioxide. Either the metal complex was dissolved in liquid $\text{SO}_2$ or $\text{SO}_2$ was bubbled into the solution of the complex in an organic solvent. However, because of the presence of a high concentration of the $n^3$-allyl species in polar $\text{SO}_2$ solutions, reaction of platinum(II)-$n^1$-allyl complexes with liquid $\text{SO}_2$ was found to be complicated and was not pursued further.

Bubbling anhydrous sulfur dioxide through a benzene solution of trans-$[(\eta^1$-$\text{CH}_2\text{CH}=\text{CH}_2)\text{Pt(P(C}_2\text{H}_5)_3)_2\text{Cl}]$ afforded a quantitative yield of a light yellow solid product. The reaction proceeded rapidly and was completed in 20 min. Two possible structures of the product deserve particular consideration. One results from cycloaddition, and the other one from insertion of $\text{SO}_2$ (eq 12).

The $^{31}\text{P}$ NMR spectrum of the product exhibits only one signal at $\delta 20.02$ with a $^{195}\text{Pt-P}$ coupling constant value of 2705 Hz,
indicative of the presence of only one species. In the IR spectrum, the low value for the \( \nu(\text{Pt-Cl}) \) band is consistent with a trans- \( P_2X\text{PtR} \) configuration.\(^7\) Two strong \( \nu(\text{SO}_2) \) absorptions at 1212 and 1076 cm\(^{-1}\) are comparable to those reported for the \( \text{SO}_2 \) insertion products of 18-electron metal-\( \eta^1\)-allyl complexes.\(^8\) A sharp band at 1639 cm\(^{-1}\) is assigned to a carbon-carbon double bond stretch. This evidence points to the product being trans-\[ \text{[(CH}_2\text{CH}=\text{CH}_2\text{SO}_2)\text{Pt}(\text{P-} (\text{C}_2\text{H}_5)_3)_2\text{Cl}] \].

This structure is further supported by \(^1\)H NMR spectroscopy. The resonances of the olefinic protons are observed at \( \delta \) 6.22 (1H) and 5.32 (2H). The presence of a doublet \( (J = 7.7 \text{ Hz}) \) at \( \delta \) 3.84, assigned to the two protons of the methylene group bonded to \( \text{SO}_2 \), is similar to the corresponding resonance for the complex \( \text{(CO)}_5\text{MnSO}_2\text{-C}_3\text{H}_5 \).\(^7\) The \(^1\)H NMR spectra of the starting platinum complex and the product are compared in Figure 18.

Similarly, reaction of trans-\[ \text{[(n}^1\text{-CH}_2\text{CH}=\text{CH}_2)\text{PtP(CH}_3)_2\text{-C}_6\text{H}_5 \text{]}_2\text{Cl}] \) with sulfur dioxide in benzene rapidly gave a light yellow
Figure 18. Comparison of the $^1$H NMR Spectra of (a) trans-
$[(n^1\text{-CH}_2\text{CH}=\text{CH}_2)\text{Pt}(\text{P(C}_2\text{H}_5)_3)_2\text{Cl}]$ and (b) trans-
$[(\text{CH}_2\text{CH}=\text{CH}_2\text{SO}_2)\text{Pt}(\text{P(C}_2\text{H}_5)_3)_2\text{Cl}]$ in C$_6$D$_6$ Solution.
Figure 19. The Molecular Structure of $\text{trans-}[(\text{CH}_2\text{CH}=\text{CH}_2\text{SO}_2)-\text{Pt}(\text{P(CH}_3)_2\text{C}_6\text{H}_5)_2\text{Cl}]$. 
P1 - Pt - Cl 88.1°
P2 - Pt - Cl 88.8°
P1 - Pt - S 91.7°
P2 - Pt - S 94.6°
solid in quantitative yield. The $^{31}$P NMR spectrum of the product reveals that the $J(^{195}$Pt-P) value of 2780 Hz is close to that for the complex trans-[(CH$_2$CH=CH$_2$SO$_2$)Pt(P(C$_2$H$_5$)$_3$)$_2$Cl]. The IR spectrum shows a $\nu$(C=C) band at 1634 cm$^{-1}$, $\nu$(SO$_2$) absorptions at 1223 and 1065 cm$^{-1}$, and a $\nu$(Pt-Cl) band at 299 cm$^{-1}$. In the $^1$H NMR spectrum, a doublet at $\delta$ 3.10 ($J = 6.8$ Hz) is consistent with that expected for the CH$_2$ protons bonded to SO$_2$. These data present strong evidence for the structure of the product being trans-[(CH$_2$CH=CH$_2$SO$_2$)Pt(P(CH$_3$)$_2$C$_6$H$_5$)$_2$Cl].

A definite proof of the structure was provided by an X-ray crystallographic analysis. Crystals for X-ray diffraction were grown by the method of slow solvent diffusion in which the sample was crystallized from a 1:2 benzene-n-pentane mixture. This structure determination was performed by Dr. M. Calligaris at the University of Trieste, Italy. The molecular structure is shown in Figure 19.

In contrast to the previously mentioned insertion reactions of SO$_2$, the reaction of trans-[(n$^1$-CH$_2$CH=CH$_2$)Pt(P(i-C$_3$H$_7$)$_3$)$_2$Cl] with SO$_2$ proceeded slowly. After 1 hour of bubbling SO$_2$, half of the starting material was converted to a product. Continuous bubbling for an additional 3 hours produced more product, as shown by $^{31}$P NMR spectroscopy. The $^{31}$P NMR spectrum also revealed that this prolonged bubbling led to the formation of other materials. These side
products or decomposition materials of the major product were not characterized. On the basis of a comparison of $^{31}$P NMR data of the major product (e.g., the $^{195}$Pt-P coupling constant value of 2766 Hz) with the data of other insertion products in this series, an insertion structure is assigned to the former. Because of the inability to separate impurities, no $^1$H NMR spectrum was recorded. In the IR spectrum, a $\nu$(C=C) absorption at 1635 cm$^{-1}$ and a $\nu$(Pt-Cl) band at 280 cm$^{-1}$ provide further evidence for the proposed structure. Interference of bands due to impurities prevents making an assignment of SO$\textsubscript{2}$ stretching bands.

When the size of ligand L increases, the reaction rate decreases significantly. For the complex trans-[(n$^1$-CH$_2$CH=CH$_2$)Pt-(P(t-C$_4$H$_9$)$_3$)$_2$Cl], no reaction was detected by $^{31}$P NMR spectroscopy even after the mixture was maintained under a slightly positive pressure of SO$\textsubscript{2}$ for 18 hours. The bulky ligand P(t-C$_4$H$_9$)$_3$ apparently hinders the reaction.

In order to obtain a better mechanistic understanding of this type of reaction, SO$\textsubscript{2}$ gas was bubbled through a benzene solution of trans-[(n$^1$-CH$_2$CH=CHCH$_3$)Pt(P(C$_2$H$_5$)$_3$)$_2$Cl] and quantitatively yielded an insertion product, trans-[(CH$_2$=CHCH(CH$_3$)SO$_2$Pt(P(C$_2$H$_5$)$_3$)$_2$Cl], with a rearranged allylic fragment. The product was characterized on the basis of elemental analysis and spectroscopic properties.
It is known that the \( \text{C} = \text{C} \) stretching mode of terminal double bonds generally gives a much stronger IR absorption band than that of internal double bonds because of lack of symmetry.\(^{77}\)

Accordingly, the starting material containing an internal double bond shows a broad and weak absorption for the \( \text{C} = \text{C} \) stretch. On the other hand, the product exhibits a relatively strong and sharp peak at 1634 cm\(^{-1}\), typical of a terminal double bond. In addition to the \( \text{C} = \text{C} \) stretching vibration, \( \nu(\text{SO}_2) \) bands at 1213 and 1065 cm\(^{-1}\) as well as a \( \nu(\text{Pt-Cl}) \) absorption at 291 cm\(^{-1}\) are observed.

The \(^1\text{H} \text{NMR} \) spectrum of the product is shown in Figure 20. The prominent features of this spectrum are a doublet at \( \delta \) 1.48 for the methyl protons of the allylic fragment and the absence of a signal for the CH\(_2\) protons bonded to platinum. If there was no rearrangement, the spectrum would be expected to exhibit one doublet for the methyl protons at ca. \( \delta \) 1.7 and another doublet in the \( \delta \) 3-5 region with the relative intensity corresponding to two methylene protons.\(^{76}\)

The \(^{31}\text{P} \text{NMR} \) spectrum affords another evidence for this rearranged insertion product. The \(^{195}\text{Pt-P} \) coupling constant value of 2726 Hz is consistent with the values for the SO\(_2\) insertion complexes discussed earlier. The \(^{31}\text{P} \text{NMR} \) spectra of the starting material and the insertion product are shown in Figure 21. There are two sets of peaks for the starting material owing to the
presence of two geometrical isomers, trans-[(\(\eta^1-E-CH_2CH=CHCH_3\))Pt(P(C_2H_5)_3)_2Cl] and trans-[(\(\eta^1-Z-CH_2CH=CHCH_3\))Pt(P(C_2H_5)_3)_2Cl]. After completion of the reaction, only one set of peaks is found for the insertion product. This result suggests that the product contains two enantiomers which cannot be distinguished by NMR techniques under these conditions. According to this result, the insertion reaction must proceed with rearrangement of the crotyl moiety (eq 13).

\[
\begin{align*}
 &\text{E} \\ &\text{Z} \\ &\xrightarrow{\text{SO}_2} \\
\end{align*}
\]

A similar reaction of trans-[(\(\eta^1-CH_2CH=CDCH_3\))Pt(P(C_2H_5)_3)_2Cl] with SO\(_2\) also gave a rearranged insertion product, trans-[(\(CH_2=CHCD-(CH_3)SO_2\))Pt(P(C_2H_5)_3)_2Cl]. The signal at \(\delta 3.43\) in the \(^2\text{H}\) NMR spectrum is assigned to deuterium on the carbon bonded to SO\(_2\).

In summary, reactions platinum(II)-\(\eta^1\)-allyl complexes with sulfur dioxide lead to the formation of the insertion products rather than cycloaddition products when the phosphine ligands are not too bulky. Polarity of the solvent and basicity of the ligand \(L\) are two factors which influence success of these reactions. Hence,
Figure 20. The $^1$H NMR Spectrum of trans-[$(\text{CH}_2=\text{CHCH}_2\text{SO}_2)$-Pt(P(C_2H_5)_3)_2Cl] in C_6D_6 Solution.
Figure 21. The $^{31}$P NMR Spectra of (a) $\text{trans-}[(\text{n}^1\text{-E-CH}_2\text{CH}=\text{CHCH}_3)\text{-Pt(P(C}_2\text{H}_5)_3\text{Cl)}], (X)$, and $\text{trans-}[(\text{n}^1\text{-Z-CH}_2\text{CH}=\text{CHCH}_3)\text{-Pt(P(C}_2\text{H}_5)_3\text{Cl)}]$, (o) in $\text{C}_6\text{H}_6$ Solution. (b) $\text{trans-}[\text{(CH}_2=\text{CHCH(CH}_3\text{)SO}_2\text{Pt(P(C}_2\text{H}_5)_3\text{Cl)}]}$ in $\text{C}_6\text{H}_6$ Solution.
nonpolar solvents were used for all of the reactions and electron-releasing phosphines were chosen as ligands for these platinum complexes. Influence of the size of ligand on reactivity is demonstrated by the decreasing reaction rates with the increasing size of ligand $L$, i.e., $P(C_2H_5)_3 \succ P(CH_3)_2C_6H_5 > P(i-C_3H_7)_3 \succ P(t-\text{C}_4\text{H}_9)_3$. A rearranged insertion product was obtained from the reaction of trans-$[(n^1-\text{CH}_2\text{CH}=\text{CHCH}_2)\text{Pt}(P(C_2\text{H}_5)_3)_2\text{Cl}]$ with $\text{SO}_2$.

Mechanism for this series of reactions will be discussed later.

(C) Reactions of Platinum(II)-$n^1$-Allyl Complexes with CISO$_2$NCO

When platinum(II)-$n^1$-allyl complexes reacted with CISO$_2$NCO in a nonpolar solvent at room temperature, the colorless reaction mixture changed to light yellow immediately. From the reaction of trans-$[(n^1-\text{CH}_2\text{CH}=\text{CHCH}_2)\text{Pt}(P(C_2\text{H}_5)_3)_2\text{Cl}]$, 28, with CISO$_2$NCO, only trans-$[(C_2\text{H}_5)_3\text{PtCl}_2]$ was isolated and characterized by comparison of its $3^1\text{P}$ NMR spectrum with the data reported for an authentic sample. 53

Reaction of trans-$[(n^1-\text{CH}_2\text{CH}=\text{CH}_2)\text{Pt}(P(C_6\text{H}_{11})}_3)_2\text{Cl}]$, 32, with CISO$_2$NCO at room temperature led to the formation of trans-$[P(C_6\text{H}_{11})_3\text{PtCl}_2]$. The identical $3^1\text{P}$ NMR spectra of an independently synthesized trans-$[P(C_6\text{H}_{11})_3\text{PtCl}_2]$ and the present reaction product confirmed the structure of the latter. Similarly, trans-$[(n^1-\text{CH}_2\text{CH}=\text{CH}_2)\text{Pt}(i-\text{C}_3\text{H}_7)_3\text{Cl}]$, 29, reacted with CISO$_2$NCO to give trans-$[(P(i-\text{C}_3\text{H}_7)_3\text{PtCl}_2]$. The $3^1\text{P}$ NMR spectrum of an
independently prepared trans-[(P(i-Pr)₃)₂PtCl₂] reveals a signal at δ 26.96 with a $^{195}$Pt-P coupling constant value of 2441 Hz. These data match those recorded for 29. Thus, the structure of the reaction product is confirmed by $^{31}$P NMR spectroscopy.

However, when the foregoing reactions were carried out at low temperature, a different reaction pathway was observed depending on the control of temperature. Progress of these reactions was followed at low temperature by $^{31}$P NMR spectroscopy.

The reaction of 28 with ClSO₂NCO in a 10-mm NMR tube readily generated three species at -75°C. These products showed three sets of peaks in the $^{31}$P NMR spectrum at δ 19.9 with a J($^{195}$Pt, P) value of 2680 Hz, 11.9 with a J($^{195}$Pt, P) value of 2430 Hz, and -3.9 with a J($^{195}$Pt, P) value of 1700 Hz. In the process of warming to room temperature, the spectrum underwent the following changes. The signal at δ 19.9 remained intact, but the intensity of the signal at δ 11.9 increased as that of the signal at δ -3.9 gradually decreased. When the temperature reached 25°C, only two absorptions at δ 20.0 and 11.6 in a 1:3 intensity ratio were observed. $^{31}$P NMR spectra of this variable temperature study are shown in Figure 22. The signal at δ 11.6 with a J($^{195}$Pt, P) value of 2434 Hz is identical with the $^{31}$P NMR resonance of trans-[(P(C₂H₅)₃)₂PtCl₂].

The above observations are consistent with the reaction proceeding by two pathways. The formation of trans-[(P(C₂H₅)₃)₂PtCl]
Figure 22. $^{31}$P NMR Spectra of a Variable Temperature Study of Reaction of trans-[$(n^1-CH_2CH=CH_2)Pt(P(C_2H_5)_3)_2Cl$] with ClSO$_2$NCO in Toluene Solution.

x: trans-[$(P(C_2H_5)_3)_2ClPtCHCH_2(C(O)N(S(O)_2Cl)CH_2$

Δ: trans-[$(P(C_2H_5)_3)_2PtCl_2$]

o: Intermediate
occurred via an intermediate displaying a signal at $\delta$ -3.9 with a $J^{(195\text{Pt}, \text{P})}$ value of 1700 Hz. In general, $^{195}\text{Pt}-\text{P}$ coupling constants of Pt(IV) complexes of the type $\text{PtR}_2^2\text{X}_2\text{L}_2$ ($\text{X} = \text{halogen}, \text{L} = \text{phosphine}$) are in the range of 1500 - 1900 Hz.\textsuperscript{78} The magnitude of the coupling constant of the intermediate suggests that the starting Pt(II) complex undergoes an oxidative addition reaction to yield a Pt(IV) species. This intermediate is then converted to \textit{trans-}[$(\text{P(C}_2\text{H}_5)_3\text{Cl})_2\text{PtCl}_2]$ by reductive elimination (eq 14). This result is not unexpected since reagents RSO$_2$Cl are known to undergo oxidative addition to coordinately unsaturated $d^8$ complexes.\textsuperscript{79}

The other product displaying a signal at $\delta$ 20.02 with a $J^{(195\text{Pt}, \text{P})}$ value of 2676 Hz is presumed to be the cycloadduct \textit{trans-}[$(\text{P(C}_2\text{H}_5)_3\text{Cl})_2\text{PtCHCH}_2\text{C}(\text{O})\text{N(SO}_2\text{Cl})\text{CH}_2$]. A comparison of the $^{31}\text{P}$ NMR data of this complex with the reported $J^{(195\text{Pt}, \text{P})}$ value of
2677 Hz for an analogous complex,\(^{28}\) \text{trans-}[\{(P(C_6H_{11})_3)_2Cl\text{PtCH}_2\text{CH}_2C(CN)_2C(N)\text{CH}_2\text{Cl}\}], supports the assigned structure.

Complex 32 reacted with ClSO_2NCO in a 10-mm NMR tube at -75°C but not as rapidly as did complex 28. This may be due to the presence of the somewhat bulky P(C_6H_{11})_3 ligands. The \(^{31}\text{P}\) NMR spectrum of the mixture at -75°C showed the signal of the starting material and a new resonance at \(\delta\) 15.66 with a \(J(^{195}\text{Pt}, P)\) value of ca. 2700 Hz. The intensity of this new signal increased at -55°C. When the temperature reached -30°C, all of the starting material was converted to the new product. The \(^{195}\text{Pt-P}\) coupling constant value of 2706 Hz for the product implicates a cycloadduct, \text{trans-}[\{(P(C_6H_{11})_3)_2Cl\text{PtCH}_2\text{C(O)N(S(O)Cl)CH}_2\}].

However, when the same reaction was carried out in a Schlenk flask instead of a 10-mm NMR tube first at -78°C and then with slow warming to room temperature over 1.5 hours, it yielded a mixture of the cycloaddition complex and \text{trans-}[\{(P(C_6H_{11})_3)_2\text{Cl}\}] detected by \(^{31}\text{P}\) NMR spectroscopy of the products. An attempt to separate these two products by chromatography led to decomposition of the cycloadduct. It is thought that \text{trans-}[\{(P(C_6H_{11})_3)_2\text{Cl}\}] was formed via an oxidative addition-reductive elimination pathway as observed for the generation of \text{trans-}[\{(P(C_5H_5)_3)_2\text{Cl}\}] from complex 28.
The reason for the difference between the reactions in an NMR tube and those in a Schlenk flask is not clear. A possible explanation may be that the temperature difference for the two pathways is small. The temperature of the reaction mixture can be controlled relatively accurately in an NMR probe. Therefore, only the cycloaddition product formed as the temperature increased slowly in a probe of the NMR spectrophotometer.

The reaction of complex 29 with ClSO₂NCO in a 10-mm NMR tube proceeded somewhat differently. The $^{31}$P NMR spectrum showed that it did not occur until a temperature of -25°C was reached. Raising the temperature further led to the formation of more product which exhibited a $^{31}$P NMR signal at δ 27.16 with a $J^{(195}Pt, P)$ value of 2782 Hz. When the temperature reached -15°C, another resonance, corresponding to trans-[(P(i-C₃H₇)₃)₂PtCl₂], was observed in the spectrum. The intensity of the second signal rapidly increased with increasing temperature. The first product formed at low temperature is believed to be a cycloaddition product. This structural assignment is based on a comparison of its $J^{(195}Pt, P)$ value with the values of other cycloaddition products in this series.

When the same reaction was run in a Schlenk flask first at -78°C and then with slow warming to room temperature over 2 hours (this included 30 min of stirring at -20°C), it generated a mixture of the cycloaddition complex and trans-[(P(i-C₃H₇)₃)₂PtCl₂] detected
by their $^{31}$P NMR spectra. An attempt to separate these two products by chromatography led to decomposition of the cycloadduct. The mass spectrum of a mixture of the two products which was done by use of the FAB technique showed a parent peak at m/e 664. The M + 1 peak agrees with the formula weight of trans-[(P(i-C$_7$H$_7$)$_3$)$_2$ClPtCHCH$_2$C(O)-N(S(0)$_2$Cl)CH$_2$].

For this series of reactions, no IR and $^1$H NMR spectra were obtained since the cycloaddition products were not pure.

Reactions of platinum(II)-n'-allyl complexes with CISO$_2$NCO are significantly affected by temperature. The oxidative addition-reductive elimination reaction pathway is dominant at higher temperature. Lower temperature favors the formation of a cycloadduct. However, the difference in temperature at which the two types of reactions occur is not large. The size of ligand L apparently influences the rate of both reactions. The reaction mechanism will be discussed later.

(D) Reactions of trans-[(n'-CH$_2$CH=CH$_2$)PtL$_2$Cl] (L = P(C$_2$H$_5$)$_3$, P(C$_6$H$_{11}$)$_3$) with HPF$_6$*(C$_2$H$_5$)$_2$O

Addition of HPF$_6$*(C$_2$H$_5$)$_2$O to a THF solution of trans-[(n'-CH$_2$CH=CH$_2$)Pt(P(C$_2$H$_5$)$_3$)$_2$Cl], 28, in an NMR tube at -78°C resulted in no apparent reaction. Reaction did not occur until the temperature reached -25°C. The $^{31}$P NMR spectrum of the reaction mixture showed one signal at $\delta$ 20.76 with a J($^{195}$Pt, P) value of 2067 Hz and
another signal at $\delta$ 11.17 with a $\text{J}^{195}\text{Pt}, \text{P}$ value of 3716 Hz, corresponding to $[(\eta^3-\text{C}_3\text{H}_5)\text{Pt}(\text{P}(\text{C}_2\text{H}_5)_3)_2]^{+}\text{PF}_6^{-}$, which was prepared independently from trans-$[(\eta^1-\text{CH}_2\text{CH}=\text{CH}_2)\text{Pt}(\text{P}(\text{C}_2\text{H}_5)_3)_2\text{Cl}]$ and AgPF$_6$ in THF.

Although this reaction gave an almost quantitative isolated yield of the product with the $\delta$ 20.76 $\text{^31P}$ NMR signal, the THF molecule associated with this complex, which was indicated by $\text{^1H}$ NMR spectroscopy, caused difficulties in the characterization by other methods.

To overcome this difficulty, diethyl ether was used as the medium for the reaction. This reduces the possibility of association between solvent and the product.

Addition of HPF$_6$·(C$_2$H$_5$)$_2$O to a diethyl ether solution of 28 in a Schlenk flask at $-78^\circ$C resulted in the formation of a white precipitate. The temperature of the reaction mixture was then allowed to rise to room temperature over 1.5 hours. During this period more of the white precipitate formed. The $\text{^31P}$ NMR spectrum of the white precipitate showed that a single product was present. However, the temperature of the mixture must increase very slowly during reaction; otherwise, a small amount of $[(\eta^3-\text{C}_3\text{H}_5)\text{Pt}-(\text{P}(\text{C}_2\text{H}_5)_3)_2]^{+}\text{PF}_6^{-}$ will be produced along with the major product.
The mass spectrum of the white precipitate which was obtained by use of the FAB technique showed a parent peak (M + H) at m/e 655. Taking into account the results of elemental analysis and the mass spectrum, there are two possibilities for structure of the product, i.e.:

\[
\text{\text{PEt}_3} \quad \text{Cl} \quad \text{Pt} \quad \text{PEt}_3
\]

\[
\text{PF}_5
\]

Since no hydride signal was found in the $^1$H NMR spectrum, the possibility of the product being a metal hydride is very small. On the other hand, the $^1$H NMR spectrum reveals a doublet at $\delta 1.89$ with a $J(\text{CH}_3, \text{H})$ value of 5.9 Hz suggestive of structure 34. This signal is further coupled to $^{195}\text{Pt}$. A 500-MHz $^1$H NMR spectrum of the product is shown in Figure 23.

In order to facilitate discussion of the analysis of the spectrum, a lettering scheme for the different hydrogens is presented as follows:
The assignments for the olefinic protons were made with the aid of homonuclear decoupling experiments as illustrated in Figure 24. Irradiation at the frequency of the δ 5.42 signal collapses the δ 1.89 doublet to a singlet. Irradiation at the δ 4.08 and 3.90 resonances has no significant effect on the other signals. On the basis of these experiments and the values of the coupling constants (in Table 27), each absorption of the olefinic protons is assigned: the resonance of H_c at δ 5.42, the resonance of H_a at δ 4.08, and the resonance of H_b at δ 3.90. For the triethylphosphine ligand, two signals at δ 2.12 and 2.00 for the methylene protons and two absorptions at δ 1.21 and 1.18 for the methyl protons indicate two inequivalent phosphines.

The 13C NMR spectrum of the product shown in Figure 25 is consistent with the proposed structure. The signals at δ 93.00 (J(^{195}Pt, C) = 73.8 Hz) and 63.43 (J(^{195}Pt, C) = 79.6 Hz) are
Figure 23. The 500-MHz $^1\text{H}$ NMR Spectrum of trans-[$(\eta^2-\text{CH}_2=\text{CHCH}_3)$-Pt($\text{P}($\text{C}_2\text{H}_5)_3$)$\text{Cl}$]$^+\text{PF}_6^-$ in CDC$_3$ Solution.
Figure 24. The 500-MHz $^1$H NMR Spectrum of trans-$[\left(\pi^2\text{-CH}_2=\text{CHCH}_3\right)\text{-Pt(}\text{P(C}_2\text{H}_5)_3\text{)Cl}]/\text{PF}_6^-$ in CDCl$_3$ Solution: (a) Without Irradiation. (b) Irradiation at the $\delta$ 5.42 Signal. (c) Irradiation at the $\delta$ 4.08 Signal. (d) Irradiation at the $\delta$ 3.90 Signal.
attributed to the olefinic carbons. The absorption at δ 22.35 is assigned to the methyl carbon of the allylic fragment. The signals of the carbon nuclei of two inequivalent ethyl groups are observed at δ 14.40, 12.20, 7.99 and 7.70.

The 500-MHz $^{31}$P NMR spectrum of the product shown in Figure 26 exhibits two phosphine signals at δ 18.80 and 18.66 with $J(^{195}$Pt, P) values of 2056 and 2086 Hz, respectively. This spectrum agrees with the structure of 34.

The IR spectrum reveals a weak $\nu$(C=O) absorption at 1509 cm$^{-1}$ typical of complexes with M($n^2$-alkene) bonding$^{80}$ and a $\nu$(Pt-Cl) band at 326 cm$^{-1}$.

Hence, the above discussed spectroscopic data confirm the structure of 34. The olefin is perpendicular to the PtP$_2$Cl plane, and the methyl group of the allylic fragment is on the same side as one of the phosphine ligands.

When the analogous complex with the P($C_6H_{11}$)$_3$ ligands was allowed to react with HPF$_6$·($C_2H_5$)$_2$O, the protonation occurred at ca. -30°C as indicated by the formation of a white precipitate. The reaction gave a quantitative yield of trans-$[($n$^2$-CH=CHCH$_3$)(P-$\cdot(C_6H_{11})_3$)$_2$ClPt]$^+$PF$_6^-$, characterized by elemental analysis and spectroscopic methods. The IR spectrum shows a weak $\nu$(C=C) absorption at 1510 cm$^{-1}$, the position of which is similar to the C=C
Figure 25. The $^{13}$C NMR Spectrum of trans-[$(\eta^2-\text{CH}_2=\text{CHCH}_2)$-Pt($\text{P(C}_2\text{H}_5)_3\text{Cl}$)]$^+$PF$_6^-$ in CDCl$_3$ Solution.
Figure 26. The 500-MHz $^{31}$P NMR Spectrum of trans-[$(\eta^1-\text{CH}_2=\text{CHCH}_3)$-Pt($\text{P}$(C$_2$H$_5$)$_3$)$_2$Cl]$^+$PF$_6^-$ in CH$_2$Cl$_2$ Solution.
stretching frequency of the preceding protonation product. The band at 325 cm\(^{-1}\) is assigned to the \(\nu(\text{Pt-Cl})\) absorption.

The \(^{31}\text{P}\) NMR spectrum showed two signals, one at \(\delta 20.92\) \((J(^{195}\text{Pt}, \text{P}) = 2017 \text{ Hz})\) and the other one at \(\delta 20.69\) \((J(^{195}\text{Pt}, \text{P}) = 1998 \text{ Hz})\), indicative of two inequivalent phosphines. The results of these spectroscopic data suggest that the structure of the protonation product is \(\text{trans-}[\left(\eta^2-\text{CH}_2=\text{CHCH}_3\right)\text{PF}_6\text{CH}_3\text{PCy}_3]^+\) as shown below:

This protonation product is less stable than 34 and must be stored in a freezer.

(E) **Mechanisms of Reactions of Platinum(II)-\(\eta^1\)-Allyl Complexes with Electrophilic Reagents**

(i) **Protonation**

In the study of mechanisms of reactions of platinum(II)-\(\eta^1\)-allyl complexes with electrophilic reagents, an important consideration is whether the electrophile first attacks the platinum or the allylic double bond. Protonation of these \(\eta^1\)-allyl complexes
provides a simple and an effective method in ascertaining which of these two sites is attacked.

Belluco et al. have reported that on treatment with HCl complexes trans-[(P(C₂H₅)₃)₂PtMeX] (X = Cl or I) undergo a two-step reaction involving oxidative addition and reductive elimination to give trans-[(P(C₂H₅)₃)₂PtClX] products (eq 15).⁸¹

\[
\begin{align*}
\text{Cl} & \quad \text{PEt₃} & \quad \text{Me} & \quad \text{Pt} & \quad \text{H} & \quad \text{PEt₃} & \quad \text{Me} \\
\text{Cl} & \quad \text{PEt₃} & \quad \text{Cl} & \quad \text{Pt} & \quad \text{Cl} & \quad \text{PEt₃} \\
\text{Cl} & \quad \text{PEt₃} & \quad \text{Cl} & \quad \text{Pt} & \quad \text{PEt₃} & \quad \text{CH₄}
\end{align*}
\]

Therefore, the possibility of the protonation occurring at the metal center to form a metal hydride complex cannot be ruled out for the platinum(II)-η¹-allyl complexes. The resultant metal hydride may further react by reductive elimination to give a platinum(II) complex.

On the other hand, it has been well established that the reactions of the 18-electron transition metal-η¹-allyl complexes with electrophiles, including HCl,³³ HgCl₂,⁸² and SO₂,¹¹,¹⁸ occur at
the allylic double bond. Accordingly, the protonation of the 16-electron transition metal-\(\eta^1\)-allyl complexes may proceed similarly to form a trans-\([(\eta^2-\mathrm{CH}_2=\mathrm{CHCH}_3)\mathrm{PtL}_2\mathrm{Cl}]^+\) species.

In this research, when the complexes trans-\([(\eta^2-\mathrm{CH}_2\mathrm{CH}=\mathrm{CH}_2)\mathrm{PtL}_2\mathrm{Cl}]\) (L = \(\mathrm{P(C}_2\mathrm{H}_5)_3\), \(\mathrm{P(C}_6\mathrm{H}_{11})_3\)) were treated with \(\mathrm{HPF}_6\cdot(\mathrm{C}_2\mathrm{H}_5)_2\mathrm{O}\), trans-\([(\eta^2-\mathrm{CH}_2=\mathrm{CHCH}_3)\mathrm{PtL}_2\mathrm{Cl}]^+\mathrm{PF}_6^-\) were produced. This result clearly indicates that the proton attacks at the terminal carbon of the allylic double bond. The reaction proceeds readily when the ligand L is relatively small, viz. \(\mathrm{P(C}_2\mathrm{H}_5)_3\). In contrast, protonation of trans-\([(\eta^1-\mathrm{CH}_2=\mathrm{CHCH}_2)\mathrm{Pt}(\mathrm{P(C}_6\mathrm{H}_{11})_3)_2\mathrm{Cl}]\) takes place at a higher temperature. Hence, the size of ligand L apparently influences the rate of reaction.

(ii) \(\text{SO}_2\) Insertion Reactions

The \(\text{SO}_2\) insertion reactions of platinum(II)-alkyl complexes have been known for a long time.\(^{29}\) For example, trans-\([\mathrm{P(C}_2\mathrm{H}_5)_3\mathrm{Cl}\mathrm{Pt}(\mathrm{C}_6\mathrm{H}_5)\mathrm{Cl}]\) can be converted by \(\text{SO}_2\) to the corresponding S-sulfinate.\(^{30}\) The mechanism is thought to consist first of coordination of \(\text{SO}_2\) to the metal, followed by migration of the alkyl group to \(\text{SO}_2\) to form the insertion product.\(^{30}\) In this research, reactions of platinum(II)-\(\eta^1\)-allyl complexes with \(\text{SO}_2\) also give analogous insertion products. If \(\text{SO}_2\) first attacked the metal center followed by allyl group migration (eq 16), it would be
difficult to explain the rearranged nature of the product from the reaction of trans-[(n\(^1\)-CH\(_2\)CH=CHCH\(_3\))Pt(P(C\(_2\)H\(_5\))\(_3\)]Cl].

![Chemical reaction diagram](image)

The SO\(_2\) insertion reactions of 18-electron transition metal-\(\pi^2\)-allyl complexes have been extensively studied.\(^{17,18,83}\) The mechanism is thought to be attack of SO\(_2\) at the double bond of the allylic fragment. Dissociation of the resultant metal-olefin bond followed by recombination of the ions yields the sulfinato-S product.\(^{18}\)

Protonation of the platinum(II)-\(\pi^1\)-allyl complexes under study demonstrates that H\(^+\) is transferred to the terminal carbon of the allylic double bond. As mentioned earlier, the reaction of trans-[(n\(^1\)-CH\(_2\)CH=CHCH\(_3\))Pt(P(C\(_2\)H\(_5\))\(_3\)]Cl] with SO\(_2\) gives a rearranged sulfinato-S product. These facts suggest that the reactions of the 16-electron transition metal-\(\pi^2\)-allyl complexes with SO\(_2\) are mechanistically analogous to those of the 18-electron complexes (eq 17). However, since the Pt center is coordinately unsaturated, dissociation into ions need not be invoked. The olefin complex may directly rearrange to the final sulfinato-S product.
(iii) Reactions with ClSO₂NCO

There are two competing pathways in the reactions of platinum(II)-n⁵-allyl complexes with ClSO₂NCO. One pathway consists of two steps involving oxidative addition and reductive elimination (eq 14), whereas the other pathway consists of the formation of a cycloadduct probably via a dipolar intermediate (eq 18).
The intermediate for the first reaction pathway when \( L = P(C_2H_5)_3 \) has been detected by \(^{31}\text{P} \) NMR spectroscopy at low temperature. The second reaction pathway may be similar to that proposed for \([3 + 2]\) cycloaddition of the 18-electron transition metal-\( \eta^2 \)-allyl complexes. It is supported by the protonation experiments on platinum(II)-\( \eta^1 \)-allyl complexes mentioned earlier. When ligand \( L \) is small, the reaction proceeds readily at very low temperature. Reaction takes place at higher temperature for complexes with bulkier ligands. For the same ligand \( L \), cycloaddition reaction is favored at low temperature, but the difference in the temperature required for the two reaction pathways is not large.
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