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N-(Alkylsulfinyl)alkanesulfonamidato-*N*, *N*-[*S*-Alkyl-*N*'-(alkylsulfonyl)sulfinimidoyl]-alkanesulfonamidato-*N*, and Related Complexes of Dicarbonyl(η^5-cyclopentadienyl)iron(II) Derived by Insertion of *N*-Sulfinylsulfonamides and Disulfonylsulfur Diimides into Iron–Carbon σ Bonds[1]

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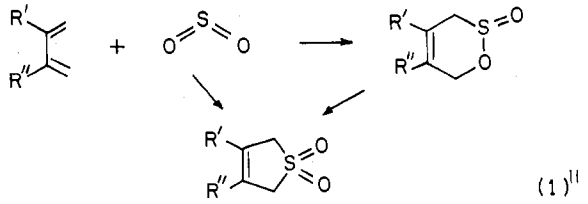
Reactions of the alkyl and aryl complexes η^5-$C_5H_5Fe(CO)_2R$ with some electronic and structural analogues of SO_2, viz., *N*-sulfinylamines, *N*-sulfinylsulfonamides, and disulfonylsulfur diimides, have been investigated. The *N*-sulfinylamines, $C_6H_{11}NSO$ and C_6H_5NSO, do not react with η^5-$C_5H_5Fe(CO)_2CH_3$ at ambient temperatures; $C_6H_{11}NSO$ reacts with η^5-$C_5H_5Fe(CO)_2CH_3$ in the presence of BF_3, but no stable product could be isolated and fully characterized. By contrast, under comparable conditions, more electrophilic *N*-sulfinylsulfonamides, $R'S(O)_2NSO$, insert into the Fe–R σ bond of η^5-$C_5H_5Fe(CO)_2R$ to yield N-bonded η^5-$C_5H_5Fe(CO)_2\{N[S(O)R][S(O)_2R']\}$ (**1**). Complexes **1** undergo ligand oxidation by *m*-$ClC_6H_4C(O)OOH$ to the corresponding η^5-$C_5H_5Fe(CO)_2\{N[S(O)_2R][S(O)_2R']\}$ (**2**) and linkage isomerization on heating in the solid or solution to η^5-$C_5H_5Fe(CO)_2\{S(O)(R)[NS(O)_2R']\}$ (**3**). Disulfonylsulfur diimides, $[R'S(O)_2N]_2S$, react at ambient temperatures with η^5-$C_5H_5Fe(CO)_2R$ to yield N-bonded insertion products η^5-$C_5H_5Fe(CO)_2\{N[S(O)_2R'][S(R)NS(O)_2R']\}$ (**4**). The new complexes **1**–**4** have been characterized by a combination of IR and ^1H and ^{13}C NMR spectroscopy, in addition to chemical analysis. By the use of *threo*-η^5-$C_5H_5Fe(CO)_2CHDCHDC_6H_5$ in conjunction with each of $C_6H_5S(O)_2NSO$ and $[p\text{-}XC_6H_4S(O)_2N]_2S$ (X = H, Cl), it was demonstrated that the formation of the appropriate **1** and **4** proceeds with inversion of configuration at the α carbon of $CHDCHDC_6H_5$. A mechanism similar to that proposed for the SO_2 insertion reaction of coordinatively saturated transition metal–alkyl carbonyl complexes appears likely.

Introduction

Insertion of SO_2 into transition metal–carbon σ bonds is a reasonably well-studied reaction, especially with coordinatively saturated metal–alkyl carbonyl complexes.[2-4] Although a viable reaction pathway has been proposed, several unusual features of the insertion still present somewhat of a mechanistic enigma. Particularly notable among them is the inversion of configuration at the α carbon of the alkyl ligand. This result, observed for several complexes of iron,[5-7] manganese,[7] and tungsten,[7,8] has been rationalized in terms of a backside electrophilic attack of SO_2 at the α carbon.[2]

To determine the scope of such an electrophilic insertion reaction, we turned attention to unsaturated molecules that are related to SO_2. The compounds with cumulated double bonds, *N*-sulfinylamines (RN=S=O)[9] and sulfur diimides (RN=S=NR),[10] may be regarded as close electronic and structural analogues of sulfur dioxide. Very similar to the foregoing, but more electrophilic, are the *N*-sulfinylsulfonamides ($RS(O)_2N$=S=O)[9] and disulfonylsulfur diimides ($RS(O)_2N$=S=$NS(O)_2R$).[10] Chemical analogy between SO_2 and the above cumulenes is reflected in several aspects of their organic chemistry, e.g., cycloaddition reactions (eq 1–3) as well as in their ability to form complexes with transition metals.[12-14]



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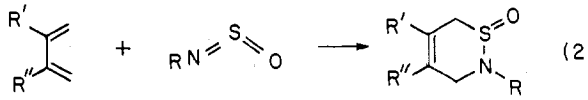

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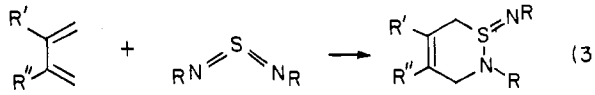

(3)[10]

Herein we report on reactions of *N*-sulfinylamines, *N*-sulfinylsulfonamides, and disulfonylsulfur diimides with the complexes η^5-$C_5H_5Fe(CO)_2R$ and, less extensively, η^5-$C_5H_5W(CO)_3R$, where R is alkyl or aryl. The results of this work further demonstrate striking similarities in the chemistry of the O=S=O, –N=S=O, and –N=S=N– cumulene systems. Certain aspects of this study were communicated earlier in a preliminary form.[15]

Results

Reactions of *N*-Sulfinylamines with M–C σ Bonds. Solutions containing η^5-$C_5H_5Fe(CO)_2CH_3$ or η^5-$C_5H_5W(CO)_3CH_3$ and a slight excess of $C_6H_{11}NSO$ or C_6H_5NSO were monitored by ^1H NMR spectroscopy at room temperature. No reaction was observed in 7 days between η^5-$C_5H_5Fe(CO)_2CH_3$ and $C_6H_{11}NSO$ in C_6D_6. Treatment of η^5-$C_5H_5Fe(CO)_2CH_3$ with neat C_6H_5NSO for 46 h led to some decomposition but produced no material exhibiting η^5-C_5H_5 and CH_3 proton reso-

(1) Presented in part at the XIX International Conference on Coordination Chemistry, Prague, Czechoslovakia, Sept 4–8, 1978. In the nomenclature employed in this paper, *alkyl* and *alkane* have a broad meaning and include *aryl* and *arene*, respectively.
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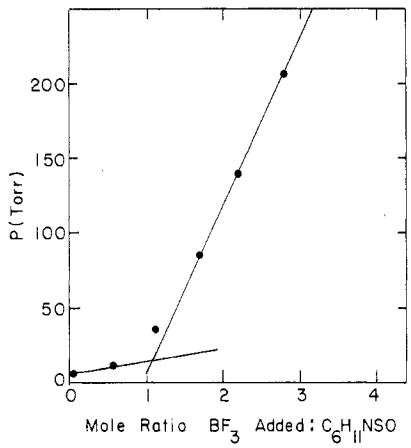


Figure 1. Tensimetric titration of $C_6H_{11}NSO$ with BF_3 in toluene at 1 °C. *P* is the total pressure over the reaction mixture.

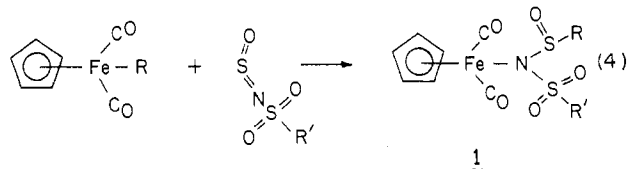
nances. When the same reaction was carried out at 80 °C for 1 h, the resulting solution showed IR ν(C≡O) absorptions of η^5-$C_5H_5Fe(CO)_2CH_3$ at 1990 and 1930 cm^{-1} as well as weaker absorptions of another dicarbonyl complex at 2050 and 2000 cm^{-1}. The latter frequencies are in the range expected for a product of insertion of C_6H_5NSO into the Fe–CH_3 bond. However, the observed material decomposed during an attempt at isolation. No reaction was noted between η^5-$C_5H_5W(CO)_3CH_3$ and each of $C_6H_{11}NSO$ and C_6H_5NSO.

It has recently been shown that the insertion of SO_2 into the W–C σ bond of η^5-$C_5H_5W(CO)_3R$ (R = CH_3, $CH_2C_6H_5$) is markedly promoted by the presence of BF_3.[16] Thus it seemed reasonable that the use of BF_3 would also enhance reactivity of *N*-sulfinylamines toward transition metal–carbon σ bonds.

Preliminary to such studies, tensimetric titrations were conducted of $C_6H_{11}NSO$, C_6H_5NSO, and *p*-$CH_3C_6H_4S(O)_2NSO$ with BF_3 to ascertain whether acid–base adducts are produced. The only Lewis acid–base adduct of BF_3 with an *N*-sulfinylamine known to us is $CH_3NSO{\cdot}BF_3$, in which BF_3 appears to be bonded to the nitrogen.[17] For the titration of C_6H_5NSO with BF_3 in benzene at 7 °C, we find that a plot of total pressure over the solution vs. mole ratio of added BF_3 to C_6H_5NSO yields a straight line. Thus, no adduct formation is indicated. The same type of behavior obtains for the more electrophilic *p*-$CH_3C_6H_4S(O)_2NSO$ and BF_3 in toluene at −23 °C. By contrast, a more basic *N*-sulfinylamine, $C_6H_{11}NSO$, and BF_3 interact in a 1:1 ratio in toluene at 1 °C as shown in Figure 1. The system $C_6H_{11}NSO$–BF_3 was therefore selected for an investigation of reactivity toward transition metal–carbon σ bonds.

Reaction of η^5-$C_5H_5Fe(CO)_2CH_3$ with approximately threefold excess $C_6H_{11}NSO$ and equimolar BF_3 in toluene at −23 to +25 °C led to the isolation of an oil. The oil showed IR absorption bands (Experimental Section) that are in the range expected for an insertion product. However, this material could not be obtained in a sufficiently high purity for full characterization. A similar reaction of η^5-$C_5H_5W(CO)_3CH_3$ with equimolar $C_6H_{11}NSO$ and BF_3 in C_6D_6 was carried out at room temperature while being monitored by ^1H NMR spectroscopy. Considerable decomposition occurred and two new, very low-intensity signals appeared at τ 5.39 and 7.00. No attempt was made at isolation of this low-yield product.

Reactions of *N*-Sulfinylsulfonamides with Fe–C σ Bonds. Although organoiron complexes η^5-$C_5H_5Fe(CO)_2R$ do not react at ambient temperatures with *N*-sulfinylamines, they react readily (generally within 1 h) and cleanly under comparable conditions with more electrophilic *N*-sulfinylsulfonamides.[18]



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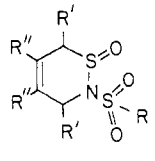
Several of these reactions were initially monitored in NMR tubes and later conducted on a larger, synthetic scale. Compared to η^5-$C_5H_5Fe(CO)_2R$, the tungsten complex η^5-$C_5H_5W(CO)_3CH_3$ was found to be much less reactive, affording on treatment with *p*-$CH_3C_6H_4S(O)_2NSO$ at 25 °C for 1 h only a very small amount (<5%) of a product with proton resonances at τ 4.05 (relative intensity 5) and 8.00 (relative intensity 3). This reaction was not studied further.

The iron–*N*-(alkylsulfinyl)alkanesulfonamidato-*N* products (**1**) are usually obtained as orange-red to red glasses by removal of the solvent either prior to or after chromatography on Florisil of the reaction mixture. They can be crystallized from CH_2Cl_2–hexane on cooling. A general method of synthesis and purification is described in the Experimental Section. Complexes **1** are very soluble in acetone, soluble in CH_2Cl_2 and $CHCl_3$, and insoluble in hydrocarbons. They are stable to air in the solid at least for a few hours (however, vide infra for isomerization).

Several products have been shown by elemental analysis to be 1:1 adducts of the iron alkyl or aryl complex and the *N*-sulfinylsulfonamide. This composition is confirmed by the observation of the molecular ion at *m/e* 333 in the mass spectrum of **1a**. However, mass spectra of other complexes **1** could not be obtained because of insufficient volatility and lack of thermal stability.

The IR and ^1H NMR spectroscopic data that serve to characterize these products are set out in Table I. Each complex displays two intense IR ν(C≡O) absorptions at frequencies appreciably higher than for the parent iron alkyl or aryl,[19] as well as a characteristic singlet proton resonance of the η^5-C_5H_5 ring. Furthermore, the products derived from the iron alkyl complexes show the resonance of the CH_3 or α-CH_2 group at a lower field than the precursor compounds.[20] Taken together, these data indicate that the η^5-$C_5H_5Fe(CO)_2$ fragment remains intact and that the R′S(O)$_2$NSO is inserted into the Fe–R bond. As illustrated in Figure 2, the IR spectra in the 1350–1000-cm^{-1} region of complexes **1** are remarkably similar, being all dominated by three strong $\nu(SO_2)$ and ν(SO) absorptions at 1315–1300, 1165–1135, and 1095–1065 cm^{-1}. The close similarity of the spectra attests to a common type of ligand formed by the insertion. Furthermore, the above bands compare well with those at 1350, 1165, and 1080 cm^{-1} reported by Kresze[9] for the organic cycloadducts of R′CH=C(R″)C(R″)=CHR′ and RS(O)$_2$NSO



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(18) No conformation of the *N*-sulfinylsulfonamide (syn or anti) is implied in eq 4.
(19) The alkyls and aryls η^5-$C_5H_5Fe(CO)_2R$ generally show ν(C≡O) absorptions in the ranges 2025–2000 and 1970–1950 cm^{-1}: Jacobson, S. E. Ph.D. thesis, The Ohio State University, 1972.
(20) Partial ^1H NMR spectra of η^5-$C_5H_5Fe(CO)_2R$: (a) R = CH_3, τ 9.89 (CH_3);[21] (b) R = $CH_2C_6H_5$, τ 7.23 (CH_2);[22] (c) R = $CH_2CH_2C_6H_5$, τ ~7.8 (α-CH_2).[23]
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Table I. IR and ^{1}H NMR Spectra of Iron-*N*-(Alkylsulfinyl)alkanesulfonamidato-*N* Complexes, **1**

complex			IR, cm^{-1}		
no.	R	R′	ν(C≡O)[a]	ν(SO$_2$), ν(SO)[b]	^{1}H NMR, τ[c]
1a[d]	CH_3	CH_3	2050, 2000	1300, 1135, 1080	4.77 (s, C_5H_5), 7.08 (s, O_2SCH_3), 7.49 (s, $OSCH_3$)
1b[e]	CH_3	p-$C_6H_4CH_3$	2060, 2015[h]	1300, 1146, 1080	2.63 (s, C_6H_4), 4.72 (s, C_5H_5), 7.42 (s, $OSCH_3$), 7.81 (s, CCH_3)[j]
1c	$CH_2C_6H_5$	CH_3	2055, 2010[i]	1300, 1140, 1080	2.65 (s, C_6H_5), 4.94 (s, C_5H_5), 5.72, 6.14 (AB q, J = 12.4 Hz, CH_2), 7.32 (s, CH_3)
1d	$CH_2C_6H_5$	p-$C_6H_4CH_3$	2045, 2000	1300, 1145, 1085	~2.5 (AA′BB′ m, C_6H_4), 2.71 (s, C_6H_5), 4.93 (s, C_5H_5), 6.22 (s, br, CH_2), 7.62 (s, CH_3)
1e	$CH_2CH_2C_6H_5$	CH_3	2045, 1998	1315, 1147, 1085, 1075, 1065	2.7 (s, C_6H_5), 4.75 (s, C_5H_5), ~7.0 (m, CH_2CH_2, CH_3)
1f	$CH_2CH_2C_6H_5$	C_6H_5	2047, 2000	1315, 1165, 1095	~2.4 (m, C_6H_5), 2.84 (s, C_6H_5), 4.92 (s, C_5H_5), 7.30 (s, CH_2CH_2)
1h	p-$C_6H_4CH_3$	CH_3	2047, 1999	1300, 1135, 1085, 1065	2.45 (AA′BB′ m, C_6H_4), 5.30 (s, C_5H_5), 6.90 (s, O_2SCH_3), 7.45 (s, CCH_3)
1i[f]	p-$C_6H_4CH_3$	p-C_6H_4Cl	2047, 2000	1300, 1150, 1085	2–3 (2 AA′BB′ m, 2 C_6H_4), 5.27 (s, C_5H_5), 7.55 (s, CH_3)
1j	p-C_6H_4Cl	p-C_6H_4Cl	2048, 2000	1310, 1150, 1090	2–3 (2 AA′BB′ m, 2 C_6H_4), 5.20 (s, C_5H_5)
1k[g]	p-C_6H_4F	p-C_6H_4Cl	2050, 2003	1300, 1150, 1090	1.8–3.0 (2 AA′BB′ m, 2 C_6H_4), 4.98 (s, C_5H_5)

[a] CH_2Cl_2 solution except as noted. All absorptions are strong. [b] Nujol mull. Only strong absorptions are listed. [c] $CDCl_3$ solution except as noted. Abbreviations: s, singlet; q, quartet; m, multiplet; br, broad. [d] Mp 105–106 °C (dec). Mass spectrum: molecular ion at *m/e* 333, also peaks corresponding to $(P-CH_3)^+$, $(P-CO)^+$, $(P-2CO)^+$, and $(P-2CO-CH_3)^+$. Anal. Calcd for $C_9H_{11}FeNO_5S_2$: C, 32.45; H, 3.33; S, 19.25. Found: C, 32.32; H, 3.23; S, 19.18. [e] Isolated as an oil. Anal. Calcd for $C_{15}H_{15}FeNO_5S_2$: C, 44.02; H, 3.69; S, 15.67. Found: C, 44.85; H, 4.18; S, 15.49. [f] Mp 140 °C (dec). Anal. Calcd for $C_{20}H_{16}ClFeNO_5S_2$: C, 47.50; H, 3.19. Found: C, 47.45; H, 3.36. [g] Mp 145–148 °C (dec). Anal. Calcd for $C_{19}H_{13}ClFFeNO_5S_2$: C, 44.77; H, 2.57. Found: C, 44.31; H, 2.63. [h] $CHCl_3$ solution. [i] Nujol mull: 2045, 1995 cm^{-1}. [j] C_6F_6 solution. $CDCl_3$ solution: 2.52 (AA′BB′ m, C_6H_4), 4.83 (s, C_5H_5), 7.60 (s, 2 CH_3).

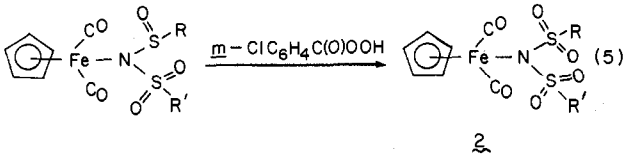
Table II. IR and ^{1}H NMR Spectra of Iron-*N*-(Alkylsulfonyl)alkanesulfonamidato-*N* Complexes, **2**, and Iron-*N*-(Alkylsulfonyl)alkanesulfinimidato-*S* Complexes, **3**

complex			IR, cm^{-1}		
no.	R	R′	ν(C≡O)[a]	ν(SO$_2$), ν(SO), ν(S=N)[b]	^{1}H NMR, τ[c]
2a[d]	CH_3	CH_3	2070, 2020	1321, 1315, 1295, 1135	4.84 (s, C_5H_5), 6.93 (s, 2 CH_3)
2b	CH_3	p-$C_6H_4CH_3$	2059, 2014[h]	1320, 1150, 1140	2.38 (AA′BB′ m, C_6H_4), 5.08 (s, C_5H_5), 6.90 (s, O_2SCH_3), 7.56 (s, CCH_3)
2c	$CH_2C_6H_5$	CH_3	2056, 2012[h]	1325, 1298, 1130	2.6 (m, C_6H_5), 5.29 (s, C_5H_5), 5.36 (s, CH_2), 6.95 (s, CH_3)
2e	$CH_2CH_2C_6H_5$	CH_3	2055, 2010	1325, 1270, 1145, 1110, 1080	2.85 (s, C_6H_5), 4.93 (s, C_5H_5), ~6.7 (m, CH_2CH_2), 6.96 (s, CH_3)
2f[e]	$CH_2CH_2C_6H_5$	C_6H_5	2055, 2010	1322, 1170, 1155, 1140, 1100	~2.1 (m, C_6H_5), 2.73 (s, C_6H_5), 4.83 (s, C_5H_5), 6.70 (AA′BB′ m, CH_2CH_2)
3a[f]	CH_3	CH_3	2070, 2020[i]	1275, 1130, 1110, 1000	4.70 (s, C_5H_5), 6.60 (s, $OSCH_3$), 7.00 (s, O_2SCH_3)
3b	CH_3	p-$C_6H_4CH_3$	2070, 2022[h]	1295, 1280, 1145, 1115, 1088, 1025, 1010	2.47 (AA′BB′ m, C_6H_4), 4.69 (s, C_5H_5), 6.65 (s, $OSCH_3$), 7.63 (s, CCH_3)
3c[g]	$CH_2C_6H_5$	CH_3	2065, 2005[i]	1275, 1130, 1105, 1030	2.52 (s, C_6H_5), 4.92 (s, C_5H_5), 5.33 (s, CH_2), 6.99 (s, CH_3)
3g	p-$C_6H_4CH_3$	CH_3	2055, 2008[i]	1285, 1160, 1140, 1125, 1085, 1025, 1005	2.4 (AA′BB′ m, C_6H_4), 4.90 (s, C_5H_5), 6.98 (s, O_2SCH_3), 7.38 (s, CCH_3)

[a] CH_2Cl_2 solution except as noted. All absorptions are strong. [b] Nujol mull. Only strong absorptions are listed. [c] $CDCl_3$ solution. See Table I for abbreviations. [d] Mp 129 °C (dec). Anal. Calcd for $C_9H_{11}FeNO_6S_2$: C, 30.96; H, 3.18; S, 18.36. Found: C, 30.85; H, 3.10; S, 18.12. [e] Anal. Calcd for $C_{21}H_{19}FeNO_6S_2$: C, 50.31; H, 3.82. Found: C, 50.54; H, 4.15. [f] Anal. Calcd for $C_9H_{11}FeNO_5S_2$: C, 32.45: H, 3.33. Found: C, 32.35; H, 3.24. [g] Mp 140–142 °C. Anal. Calcd for $C_{15}H_{15}FeNO_5S_2$: C, 44.02; H, 3.69. Found: C, 43.97; H, 3.90. [h] $CHCl_3$ solution. [i] Nujol mull.

thus suggesting similar features in the structures of **1** and the cycloadducts. However, the proposed *N*-(alkylsulfinyl)alkanesulfonamidato-*N* nature of the new ligand $R'S(O)_2NSO{\cdot}R$ receives its strongest support from studies on the oxidation of **1** with *m*-$ClC_6H_4C(O)OOH$.

Oxidation of *N*-(Alkylsulfinyl)alkanesulfonamidato-*N* Complexes. Complexes **1** react readily with *m*-chloroperoxybenzoic acid at room temperature to afford the corresponding *N*-(alkylsulfonyl)alkanesulfonamidato-*N* derivatives, **2**, in good yield.



2

These red crystalline oxidation products exhibit solubility properties and stability that are very similar to those of their precursors, **1**.

Structure **2** has been inferred with the aid of the spectroscopic IR and ^{1}H NMR data listed in Table II, as well as the ^{13}C NMR data contained in Table III. Thus, the IR spectra show two ν(C≡O) absorptions, generally at somewhat higher frequencies (up to 20 cm^{-1}) than those of the corresponding **1**. This shift very likely arises from a decreased σ-bonding ability of the ligand upon oxidation from $N[S(O)R][S(O)_2R']$ to $N[S(O)_2R][S(O)_2R']$. By comparison, the previously reported[24] η^5-$C_5H_5Fe(CO)_2\{N[S(O)_2F]_2\}$ displays ν(C≡O) bands at 2068 and 2033 cm^{-1}. The 1350–1000-cm^{-1} region of the IR spectra of **2** is characterized by two ranges of strong absorptions, 1330–1270 and 1170–1080 cm^{-1} (see Figure 3 for the spectrum of **2c**). These bands are often split, especially in unsymmetrical ligands, and are assigned to $\nu_{as}(SO_2)$ and $\nu_s(SO_2)$, respectively. In η^5-$C_5H_5Fe(CO)_2\{N[S(O)_2F]_2\}$, $\nu(SO_2)$ absorptions appear at 1418, 1398, 1221, and 1184 cm^{-1}.[24] In the region near 1080 cm^{-1}, where complexes **1** exhibit a strong ν(SO) band, no intense absorptions occur in the spectra of **2**. We infer accordingly that complexes **2** contain S=(O)$_2$ functionalities but no S=O.

The ^{1}H and ^{13}C NMR spectra of **2** accord with the assigned structure. Those of **1a** and **2a** are particularly informative with respect to the nature of the ligand formed by the insertion.

(24) Frobose, R.; Mews, R.; Glemser, O. *Z. Naturforsch., B* **1976**, *31*, 1497.

Table III. ^{13}C NMR Spectra of Iron Complexes

complex no.	R	R′	chemical shift, δ[a] CO	η^5-C_5H_5	CH_2	MS(O)-(O or NX)-CH_3[b,c]	XS-$(O)_2CH_3$[c]	XS-(O or NX)-CH_3[c]	other CH_3	aromatic
1a	CH_3	CH_3	212.2, 211.5	85.8			45.1	41.9[e]		
1c	$CH_2C_6H_5$	CH_3	212.2, 211.8	86.0	65.1 br		43.1			131.4, 130.5, 128.8, 128.0
2a	CH_3	CH_3	210.9	85.6			42.7			
2c	$CH_2C_6H_5$	CH_3	210.9	86.0	60.2		42.1			131.8, 130.5, 128.8
3b	CH_3	p-$C_6H_4CH_3$	208.8, 208.0	87.9		59.4			21.4	143.0, 141.5, 129.0, 126.5
3c	$CH_2C_6H_5$	CH_3	[d]	87.6	75.9		45.6			132.0, 130.2, 129.6, 129.0
4a	CH_3	CH_3	[d]	85.8			43.2, 42.4	39.1		
4c	$CH_2C_6H_5$	CH_3	212.0, 210.7	85.8	59.9		42.8, 42.0			131.2, 130.7, 128.9, 128.2
5a	CH_3		210.1	87.6		60.6				
5c	$CH_2C_6H_5$		209.7	87.2	78.0					131.6, 131.2, 128.6, 128.5

[a] $CDCl_3$ solution, ppm downfield from Me_4Si. [b] M $\equiv$ η^5-$C_5H_5Fe(CO)_2$. [c] X $\equiv$ remainder of ligand. [d] Signal too weak for accurate measurement. [e] Broad at ambient temperature, sharp at −50 °C.

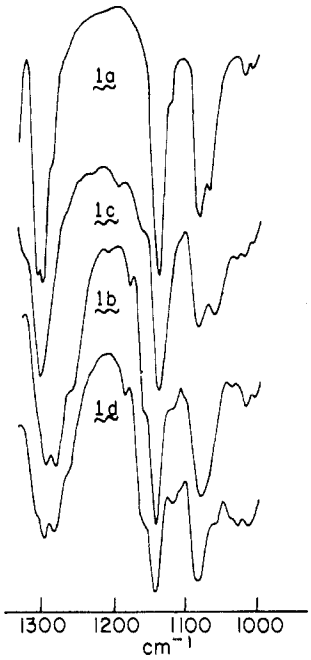


Figure 2. Infrared spectra in the 1350–1000-cm^{-1} region of some iron–*N*-(alkylsulfinyl)alkanesulfonamidato-*N* complexes, **1**, in Nujol mull.

Two CH_3 signals are observed in both the ^1H and ^{13}C NMR spectra of **1a**. However, upon oxidation of **1a** to **2a**, only one CH_3 resonance of combined relative intensities appears in each spectrum. The equivalence of the CH_3 groups in **2a** is consistent only with the assigned symmetrical *N*-(methylsulfonyl)methanesulfonamidato-*N* structure. Unless a rearrangement occurs during the oxidation, these data also corroborate the *N*-(methylsulfinyl)methanesulfonamidato-*N* structural assignment to the precursor **1a**. Such a rearrangement is, however, extremely improbable for the following reasons. To start, migration during reaction 5 of the methyl (or, generally, alkyl) group derived from the Fe–CH_3 fragment from the nitrogen or oxygen of a differently structured insertion complex to the sulfinyl sulfur of the *N*-(methylsulfinyl)methanesulfonamidato-*N* immediate precursor of **2a** must be considered very unlikely. This leaves for further consideration only one ligand, viz., $N[S(O)CH_3][S(O)_2CH_3]$, which may be bonded to the iron either through the nitrogen or the sulfinyl sulfur. However, as will be shown in the following subsection, such S-bonded linkage isomers of the N-$[S(O)R][S(O)_2R']$ ligand can be obtained irreversibly from the N-bonded complexes, **1**, and are therefore definitely not involved in the oxidation reaction with *m*-$ClC_6H_4C(O)OOH$.

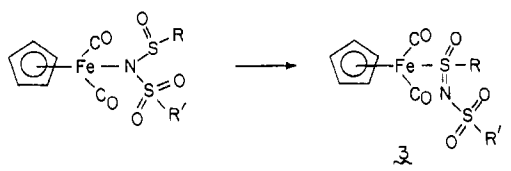
In the ^1H NMR spectrum of **1c**, the CH_2 signals appear as an AB quartet, owing to the presence of an asymmetric sulfinyl sulfur atom. As expected, on oxidation of **1c** to **2c**, this pattern changes to a singlet. These observations provide additional evidence for the assigned structures **1** and **2**.

Isomerization of *N*-(Alkylsulfinyl)alkanesulfonamidato-*N* Complexes. Storage of **1b** in the solid form at room temperature for 4 months resulted in the formation of a brown-black, somewhat gummy material. On treatment with $CHCl_3$ this material yielded a brown solution and a yellow solid. The solid is thought to be the corresponding *N*-(alkylsulfonyl)alkanesulfinimidato-*S* complex, **3b**, on the basis of the evidence presented later (vide infra).

An analogous complex, **3c**, was prepared during attempts at crystallization of **1c** from saturated $CHCl_3$ solutions at −10 °C over a period of several days. The mother liquor from these crystallizations contained both **1c** and **3c**, as determined by ^1H NMR spectroscopy.

A general preparative route to complexes **3** was subsequently developed; it entails heating the corresponding **1** for approximately 24 h either in CH_2Cl_2 solution at reflux or in the solid. Yields of 15–30% of yellow to yellow-orange air-stable solids have been realized. Complexes **3** are soluble in CH_2Cl_2, $CHCl_3$, and acetone, slightly soluble in ether, and insoluble in hydrocarbons. The isomeric nature of **1** and **3** is supported by elemental analysis.

The foregoing isomerization reactions may be represented by the equation



(6)

The proposed structure **3** is entirely compatible with the spectroscopic data collected in Table II. The two IR ν(C≡O) absorptions, characteristic of the η^5-$C_5H_5Fe(CO)_2$ fragment, occur in the same region as for the analogous, closely related *S*-sulfinato complexes, η^5-$C_5H_5Fe(CO)_2[S(O)_2R]$.[22] In the 1350–1000-cm^{-1} region, shown in Figure 3 for **3c**, bands are observed at 1295–1275, 1160–1125, 1115–1085, and 1030–1000 cm^{-1}. Those at 1295–1275 and 1160–1125 cm^{-1}

Table IV. IR and ^{1}H NMR Spectra of Iron-*N*-[*S*-Alkyl-*N'*-(alkylsulfonyl)sulfinimidoyl]alkanesulfonamidato-*N* Complexes, 4

complex			IR, cm^{-1}		
no.	R	R'	ν(C≡O)[a]	ν(SO$_2$), ν(S=N)[b]	^{1}H NMR, τ[c]
4a	CH_3	CH_3	2042, 2003, 1989[g]	1300, 1280, 1128, 1012	4.70 (s, C_5H_5), 6.91, 7.04, 7.39 (s, 3 CH_3)
4c[d]	$CH_2C_6H_5$	CH_3	2050, 2005[g]	1310, 1295, 1288, 1150, 1140, 1020, 1010	2.63 (s, C_6H_5), 4.73 (s, C_5H_5), 5.79, 5.91 (AB q, J = 12.1 Hz, CH_2), 6.90, 7.64 (s, 2 CH_3)
4e	$CH_2CH_2C_6H_5$	CH_3	2060, 2007	1280, 1250, 1140, 1010	2.74 (s, C_6H_5), 4.70 (s, C_5H_5), 6.85–7.10 (m, CH_2CH_2), 6.85, 7.10 (s, 2 CH_3)
4f	$CH_2CH_2C_6H_5$	C_6H_5	2045, 1997	1325, 1300, 1155, 1095, 990	1.9–3.3 (m, 3 C_6H_5), 4.85 (s, C_5H_5), 6.90–7.65 (m, CH_2CH_2)
4g[e]	$CH_2CH_2C_6H_5$	p-C_6H_4Cl	2048, 2000	1300, 1280, 1150, 1090, 990	2–3 (m, C_6H_5, 2 C_6H_4), 4.80 (s, C_5H_5), ~7.2 (m, CH_2CH_2)[h]
4h[f]	p-$C_6H_4CH_3$	CH_3	2045, 1994	1305, 1285, 1130, 1005	2.5 (AA'BB' m, C_6H_4), 4.98 (s, C_5H_5), 6.83, 6.98 (s, 2 O_2SCH_3), 7.63 (s, CCH_3)

[a] CH_2Cl_2 solution except as noted. All absorptions are strong. [b] Nujol mull. Only strong absorptions are listed. [c] $CDCl_3$ solution except as noted. See Table I for abbreviations. [d] Mp 148–149 °C (dec). Anal. Calcd for $C_{16}H_{18}FeN_2O_6S_3$: C, 39.51; H, 3.73; S, 19.78. Found: C, 39.55; H, 3.86; S, 18.92. [e] Mp 120 °C (dec). Anal. Calcd for $C_{27}H_{22}Cl_2FeN_2O_6S_3$: C, 45.57; H, 3.20. Found: C, 45.56; H, 3.47. [f] Mp 115 °C (dec). [g] Nujol mull. [h] CD_3CN solution.

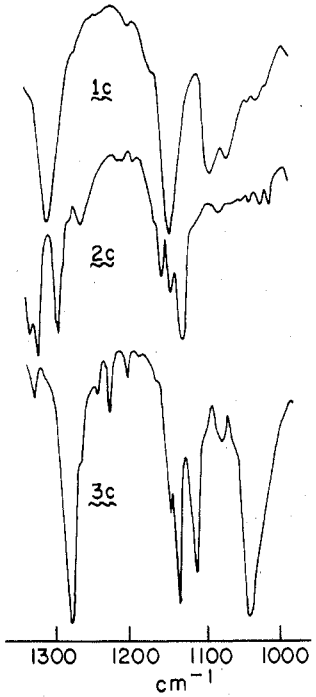
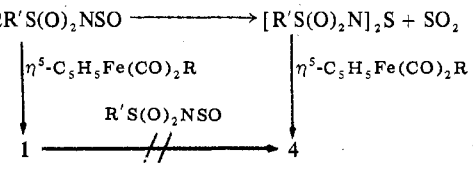


Figure 3. Infrared spectra in the 1350–1000-cm^{-1} region of η^5-$C_5H_5Fe(CO)_2$[N[S(O)$CH_2C_6H_5$][S(O)$_2CH_3$]] (**1c**), its oxidation product η^5-$C_5H_5Fe(CO)_2$[N[S(O)$_2CH_2C_6H_5$][S(O)$_2CH_3$]] (**2c**), and its S-bonded linkage isomer η^5-$C_5H_5Fe(CO)_2$[S(O)($CH_2C_6H_5$)[NS(O)$_2CH_3$]] (**3c**), in Nujol mull.

are assigned to $\nu_{as}(SO_2)$ and $\nu_s(SO_2)$, respectively. The absorptions at 1115–1085 and 1030–1000 cm^{-1} are thought to derive from ν(S=N) and ν(SO), possibly in that same order.[25]

The chemical shifts of the CH_2 and CH_3 protons of the group R also argue for Fe–S bonding in **3**. These resonances occur at τ 6.60 (CH_3, **3a**), 6.65 (CH_3, **3b**), and 5.36 (CH_2, **3c**), i.e., at considerably lower fields than the corresponding signals of the isomeric, Fe–N bonded **1**: 7.49 (CH_3, **1a**), 7.60 (CH_3, **1b**), and 5.93 (CH_2, **1c**). A comparable shift is observed on going from the hard O-bonded η^5-$C_5H_5Fe(CO)_2$[OS(O)R] to the isomeric, soft S-bonded η^5-$C_5H_5Fe(CO)_2$[S(O)$_2$R] (R = CH_3, $CH_2C_6H_5$): τ 6.95 to 7.85 (CH_3) and 6.49 to 5.79 (CH_2).[26]

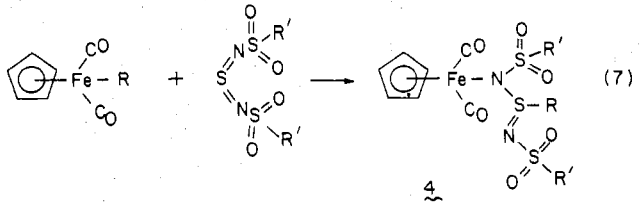
Scheme I



A further trend becomes apparent on examination of the ^{1}H NMR spectra of **1c**, **3c**, and related complexes containing R = $CH_2C_6H_5$ and a chiral sulfur atom. In those complexes that do not possess an M–S linkage, e.g., the *O*-sulfinates η^5-$C_5H_5Fe(CO)_2$[OS(O)$CH_2C_6H_5$],[26] η^5-$C_5H_5Mo(CO)_3$[OS(O)$CH_2C_6H_5$],[26] $Mn(CO)_5$[OS(O)$CH_2C_6H_5$],[26] η^5-$C_5H_5W(CO)_3$[OS(OBF$_3$)$CH_2C_6H_5$],[16] and η^5-$C_5H_5W(CO)_3$[OS(OSbF$_5$)$CH_2C_6H_5$],[16] as well as the N-bonded **1c** and **4c** (Table IV), the CH_2 proton resonances appear as an AB quartet. By contrast, when M–S bonding prevails, as in η^5-$C_5H_5W(CO)_3$[S(O)(OA)$CH_2C_6H_5$][16] (A = BF_3, SbF_5), the CH_2 resonance is a singlet. The observed singlet CH_2 resonance in the spectrum of **3c** would be consistent with Fe–S bonding on this basis.

Additional evidence for the proposed S-bonded structure of **3** rests on the ^{13}C NMR spectra (vide infra). An X-ray crystallographic study of a suitable **3** is planned.

Reactions of Disulfonylsulfur Diimides with Fe–C σ Bonds. Reactions between η^5-$C_5H_5Fe(CO)_2R$ and [R'S(O)$_2$N]$_2$S in CH_2Cl_2 or $CHCl_3$ proceed readily at room temperature according to the equation[27]



(7)

Complexes **4** also result when η^5-$C_5H_5Fe(CO)_2R$ is allowed to react with neat or very concentrated R'S(O)$_2$NSO at ambient temperatures. Thus, **4c** and **4h** were isolated as byproducts of the reactions of η^5-$C_5H_5Fe(CO)_2CH_2C_6H_5$ and η^5-$C_5H_5Fe(CO)_2C_6H_4CH_3$-*p*, respectively, with concentrated $CH_3S(O)_2NSO$. In view of these unexpected results, it became of interest to ascertain whether the byproducts arose from the disproportionation of the R'S(O)$_2$NSO to [R'S(O)$_2$N]$_2$S and

(25) Unequivocal assignments cannot be made without the aid of isotopic labeling (^{15}N or ^{18}O). For C_6H_5NSO, ν(SN) and ν(SO) occur at 1284 and 1154 cm^{-1}, respectively, with hardly any coupling between them. Similar assignments were made for other *N*-sulfinylanilines: Meij, R.; Oskam, A.; Stufkens, D. J. *J. Mol. Struct.* **1979**, *51*, 37.

(26) Jacobson, S. E.; Reich-Rohrwig, P.; Wojcicki, A. *Inorg. Chem.* **1973**, *12*, 717.

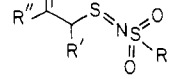
(27) No conformation of the disulfonylsulfur diimide (trans–trans or cis–trans) or of product **4** is implied in eq 7.

SO_2, which is known to be catalyzed by bases,[28] followed by reaction 7, or whether they resulted from reaction of the initially formed **1** with excess $R'S(O)_2NSO$.

To resolve this point, we treated complex **1h** with concentrated $CH_3S(O)_2NSO$ in CH_2Cl_2 at 25 °C for 1 h. No **4h** was detected in the reaction mixture. Therefore, this result supports the disproportionation of $R'S(O)_2NSO$ as the pathway for the formation of **4** (Scheme I).

Complexes **4** were isolated as red or orange-red solids. Their solubility properties and stability to air are comparable to those of the corresponding **1** and **2**. The assigned formulation of **4** as 1:1 adducts of the reactants in eq 7 rests on chemical analysis, and the structure derives from the spectroscopic data set out in Tables III and IV.

The IR spectra (Table IV) show two strong $\nu(C{\equiv}O)$ bands positioned very closely to those of the corresponding **1** and/or **2**. In the 1350–950-cm^{-1} region, strong stretching absorptions of the SO_2 and SN groups occur which are very similar to those at 1370–1345, 1180–1160 ($\nu(SO_2)$ of NSO_2), 1310–1280, 1160–1120 ($\nu(SO_2)$ of $=NSO_2$), and 1010–975 cm^{-1} ($\nu(SN)$) reported by Kresze[28] for the organic cycloadducts of $R'CH{=}C(R'')C(R''){=}CHR'$ and $[RS(O)_2N]_2S$.



That the new ligand $[R'S(O)_2N]_2SR$ is bonded to iron via one of its nitrogen atoms rather than the sulfur is convincingly demonstrated by the NMR spectra of **4a**, **4c**, **4e**, and **4h**. Each of the ^1H (Table IV) and ^{13}C (Table III) NMR spectra shows two signals of the CH_3 groups bonded to the sulfonyl sulfur atoms. The ^1H NMR spectrum of **4a** in $CDCl_3$ remains unaltered from 25 to 50 °C, indicating the compound to be nonfluxional over this relatively narrow temperature range.

Unlike **1e**, complex **4e** does not undergo ligand oxidation to a tractable product on treatment with *m*-$ClC_6H_4C(O)OOH$ under comparable conditions. An unidentified decomposition material was obtained and considerable unreacted **4e** was recovered.

^{13}C NMR Spectra. The spectra of some representative complexes **1**, **2**, **3**, **4**, and η^5-$C_5H_5Fe(CO)_2[S(O)_2R]$ (**5**) are compiled in Table III. In addition to helping establish the identity of new complexes, these spectra reveal several interesting relationships with respect to the chemical shift of the various kinds of carbons.

The chemical shifts of the CO carbons vary depending on whether Fe–S bonding or Fe–N bonding occurs in the complex. Accordingly, **1**, **2**, and **4**, all N bonded, show ^{13}C resonances of the carbonyl groups in the region 210.7–212.2 ppm. However, **3** and **5**, which are S bonded, exhibit the corresponding signals with smaller chemical shifts, 208.0–210.1 ppm. The IR CO stretching frequencies show just the opposite relationship: complexes **1b** and **1c** have lower $\nu(C{\equiv}O)$ than the S-bonded linkage isomers **3b** and **3c**, respectively (Tables I and II). Inverse linear relationships between ^{13}C chemical shifts of CO carbons and Cotton–Kraihanzel force constants have been noted for series of analogous complexes.[29,30] It is further noteworthy that the complexes containing asymmetric sulfur, i.e., **1**, **3**, and **4**, show a magnetic nonequivalence of the two CO groups in the spectra. However, **2** and **5**, which lack an asymmetric sulfur atom, exhibit only one resonance.

A similar, but opposite, relationship exists for the η^5-C_5H_5 ^{13}C chemical shifts. The N-bonded **1**, **2**, and **4** absorb at 85.6–86.0 ppm, whereas the S-bonded **3** and **5** absorb at 87.2–87.9 ppm. These observations are in a qualitative agreement with the results of Gansow et al.[29] They examined ^{13}C NMR spectra of a series of complexes η^5-$C_5H_5Fe(CO)_2X$ and concluded that the trend of the η^5-C_5H_5 resonances is to high field with increased electron withdrawal from iron.

In all of the complexes **1**–**5**, derived by insertion of $R'S(O)_2NSO$, $[R'S(O)_2N]_2S$, or SO_2 into the Fe–R bond of η^5-$C_5H_5Fe(CO)_2R$, the group R is either known or thought to be bonded to the electrophilic sulfur. The chemical shift of the α carbon of a given alkyl is, nevertheless, dependent on the coordination mode of the product ligand to the metal. Focusing first on the complexes containing $CH_2C_6H_5$, the N-bonded **1c**, **2c**, and **4c** show a resonance of the CH_2 carbon at 59.9–65.1 ppm, whereas the S-bonded **3c** and **5c** display the corresponding signal at 75.9–78.0 ppm. For the complexes containing a CH_3 group, the chemical shift of a methyl carbon bonded to a metal-coordinated sulfur ranges from 59.4 to 60.6 ppm (complexes **3b** and **5a**). By contrast, the resonances of the other methyl carbons that are bonded to sulfur occur at 39.1–45.6 ppm (complexes **1a**, **1c**, **2a**, **2c**, **3c**, **4a**, and **4c**). The reason for such a relatively large deshielding of the CH_2 and CH_3 carbons attached to iron via an intervening sulfur atom is not clear to us at present.

The foregoing ranges of the ^{13}C chemical shifts, especially the well-separated ones for the SR groups, serve to reinforce our assignment of the *N*-(alkylsulfonyl)alkanesulfinimidato-*S* structure to the ligand in complexes **3**. They may also provide useful empirical rules for the characterization of related compounds.

Stereochemistry at α C of Reaction 4. In order to obtain some basis for a mechanistic comparison of the insertion reactions of SO_2 and *N*-sulfinylsulfonamides, we studied the stereochemistry at the α carbon of the Fe–R of reaction 4. For these investigations we selected the complex η^5-$C_5H_5Fe(CO)_2CHDCHDC_6H_5$,[31] which can be prepared more easily and conveniently as a single diastereomer, threo or erythro, than the analogous η^5-$C_5H_5Fe(CO)_2CHDCHDC(CH_3)_3$.[5] The usefulness of the α,β-dideuteriophenethyl group as a stereochemical probe rests on the observations[6,7,31,32] that the vicinal coupling constants for its threo and erythro diastereomers are not equal, $^3J_{HH}(\text{threo}) < {}^3J_{HH}(\text{erythro})$. The stereochemistry of the insertion reaction of *threo*-η^5-$C_5H_5Fe(CO)_2CHDCHDC_6H_5$ with SO_2 was elucidated in this fashion.[7]

Our initial efforts focused on the reaction between *threo*-η^5-$C_5H_5Fe(CO)_2CHDCHDC_6H_5$ and $CH_3S(O)_2NSO$, which was conducted in the usual fashion to yield η^5-$C_5H_5Fe(CO)_2\{N[S(O)CHDCHDC_6H_5][S(O)_2CH_3]\}$, **1e**-$d_2$. The product was characterized spectroscopically by comparison of its IR and ^1H NMR data with those for the all-H **1e**. However, the elucidation of the diastereomeric nature of **1e**-d_2 was precluded by the overlap of the ^1H NMR signals of the α and β hydrogens of the $CHDCHDC_6H_5$ with the signal of the CH_3 group at τ 7.00.

In an attempt to obviate this problem, **1e**-d_2 was oxidized with *m*-$ClC_6H_4C(O)OOH$ according to eq 5, and the resulting product, characterized spectroscopically as **2e**-d_2, was investigated by ^1H NMR spectroscopy with respect to the stereochemistry. As may be seen in Tables I and II, on oxidation of **1** to the corresponding **2**, the resonance due to the protons on the α carbon of R moves downfield. Accordingly, the signal of the α hydrogen of the $CHDCHDC_6H_5$ of **2e**-d_2 is now discernible as a two-peak half of the presumed AB quartet,

(28) Wucherpfennig, W.; Kresze, G. *Tetrahedron Lett.* **1966**, 1671.
(29) Gansow, O. A.; Schexnayder, D. A.; Kimura, B. Y. *J. Am. Chem. Soc.* **1972**, *94*, 3406.
(30) Mann, B. E. *Adv. Organomet. Chem.* **1974**, *12*, 135.
(31) Slack, D. A.; Baird, M. C. *J. Am. Chem. Soc.* **1976**, *98*, 5539.
(32) Dong, D.; Slack, D. A.; Baird, M. C. *Inorg. Chem.* **1979**, *18*, 188.

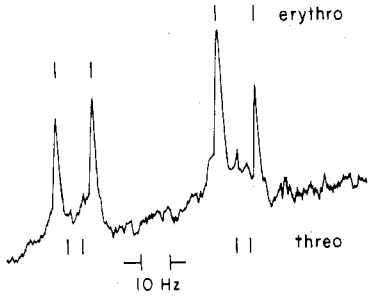


Figure 4. Deuterium-decoupled 100-MHz NMR spectrum of the CHDCHD protons of η^5-$C_5H_5Fe(CO)_2\{N[S(O)_2CHDCHDC_6H_5][S(O)_2C_6H_5]\}$ (**2f**-d_2), resulting from insertion of $C_6H_5S(O)_2NSO$ into the Fe–C σ bond of *threo*-η^5-$C_5H_5Fe(CO)_2CHDCHDC_6H_5$ and subsequent oxidation of the reaction product **1f**-d_2 with *m*-$ClC_6H_4C(O)OOH$; in $CDCl_3$.

broadened somewhat by the interaction with deuterium. However, the remaining half of the AB pattern still appears hidden under the CH_3 resonance, now at τ 6.96. By using the two discernible peaks in the spectrum without deuterium decoupling, we obtained an approximate value of $^3J_{HH} \sim 13.5$ Hz. The chemical shift of the α H is estimated as ca. τ 6.5. The above value of $^3J_{HH}$ points to the erythro structure of **2e**-d_2.

Because of the aforementioned problems with the ^1H NMR spectra, we turned to another *N*-sulfinylsulfonamide, $C_6H_5S(O)_2NSO$, with a view to corroborating our first stereochemical result. Reaction of *threo*-η^5-$C_5H_5Fe(CO)_2CHDCHDC_6H_5$ with $C_6H_5S(O)_2NSO$ led to the isolation of η^5-$C_5H_5Fe(CO)_2\{N[S(O)CHDCHDC_6H_5][S(O)_2C_6H_5]\}$, **1f**-$d_2$. This complex exhibited an ^1H NMR spectrum identical with that of the all-H **1f**, except for the signals of the α and β hydrogens of the $CHDCHDC_6H_5$ which overlapped at ca. τ 7.3. However, oxidation of **1f**-d_2 with *m*-$ClC_6H_4C(O)OOH$ yielded **2f**-d_2, which showed nondegenerate resonances for the two ethylene protons of the dideuteriated alkyl group. A deuterium-decoupled NMR spectrum of these protons is depicted in Figure 4. Analysis of the four intense peaks yields chemical shifts of τ 6.40 and 6.97 and a $^3J_{HH}$ = 12.9 Hz. Therefore, an erythro structure is implicated again. Two much weaker signals are, however, present between each pair of the outer components of the dominant AB quartet. The observed pattern would have a right value of $^3J_{HH}$, ca. 4.5 Hz, to originate from the presence of a small amount of the threo diastereomer of **2f**-d_2.

To check on the aforementioned extraneous peaks and to make the result of this study completely unequivocal, we prepared a mixture of *threo*- and *erythro*-η^5-$C_5H_5Fe(CO)_2CHDCHDC_6H_5$ from epimerized $C_6H_5CHDCHDCl$. This mixture was then converted to **2f**-d_2 by reactions 4 and 5. An exmination of the deuterium-decoupled ^1H NMR spectrum of the isolated **2f**-d_2 revealed two AB quartets of comparable intensities, one of which was identical with that observed for the **2f**-d_2 obtained from *threo*-η^5-$C_5H_5Fe(CO)_2CHDCHDC_6H_5$ and $C_6H_5S(O)_2NSO$. The other AB quartet gave a $^3J_{HH}$ = 4.6 Hz, indicative of a threo diastereomeric structure.

Since threo diastereomers involving the $CHDCHDC_6H_5$ group *never* show a larger $^3J_{HH}$ than their erythro counterparts,[6,7,31,32] the foregoing results establish convincingly that the **2e**-d_2 obtained from *threo*-η^5-$C_5H_5Fe(CO)_2CHDCHDC_6H_5$ is largely erythro. As no bond breaking occurred during the conversion of **1e**-d_2 to **2e**-d_2, the insertion of $C_6H_5S(O)_2NSO$ into the Fe–C bond of η^5-$C_5H_5Fe(CO)_2CHDCHDC_6H_5$ must proceed with a high degree of *inversion of configuration at α carbon* (Scheme II).

Stereochemistry at α C of Reaction 7. The stereochemistry at the α carbon of η^5-$C_5H_5Fe(CO)_2CHDCHDC_6H_5$ was investigated also for the insertion of disulfonylsulfur diimides (eq 7). Our initial studies were concerned with the reaction between *threo*-η^5-$C_5H_5Fe(CO)_2CHDCHDC_6H_5$ and $[CH_3S(O)_2N]_2S$, which afforded η^5-$C_5H_5Fe(CO)_2\{N[S(O)_2CH_3][S(CHDCHDC_6H_5)NS(O)_2CH_3]\}$, **4e**-$d_2$. However, the NMR spectrum of the CHDCHD protons of the product was masked in part by the signals of the CH_3 groups at τ 6.85 and 7.10, thus precluding the elucidation of the coupling constant, $^3J_{HH}$. In an attempt to circumvent this problem, an NMR shift reagent, Pr(fod)$_3$,[33] was employed. Although the resultant spectra spread out considerably, the signals were broad, even after deuterium decoupling. Unequivocal assignments, necessary for the calculation of $^3J_{HH}$, were thus not possible.

In a further effort to prepare a suitable **4**-d_2, η^5-$C_5H_5Fe(CO)_2CHDCHDC_6H_5$ was treated with $[C_6H_5S(O)_2N]_2S$ under typical conditions for reaction 7. The isolated **4f**-d_2 showed a seven-peak deuterium-decoupled NMR spectrum of the CHDCHD protons. This pattern may be interpreted in terms of two overlapping, similar in appearance, AB quartets. The appearance of *two* AB quartets no doubt derives from the presence of an asymmetric sulfur atom. The chemical shifts of the CHDCHD protons of one diastereomer of **4f**-d_2 are τ 7.02 and 7.44, and of the other 7.12 and 7.62. The value of $^3J_{HH}$, 10.0 Hz, for each species is indicative of an erythro diastereomeric structure.

To corroborate the above stereochemical finding, we synthesized **4g**-d_2 from η^5-$C_5H_5Fe(CO)_2CHDCHDC_6H_5$ and $[p\text{-}ClC_6H_4S(O)_2N]_2S$ at ambient temperatures. The product, characterized spectroscopically by comparison with the corresponding IR and ^1H NMR data for the all-H **4g**, exhibits a deuterium-decoupled NMR spectrum of the CHDCHD protons which is shown in Figure 5. Again the spectrum consists of two very similar, overlapping AB quartets. Each quartet yields a $^3J_{HH}$ = 8.5 Hz; the chemical shifts of the

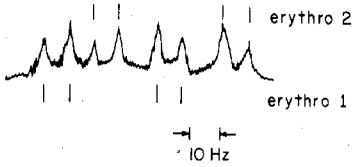
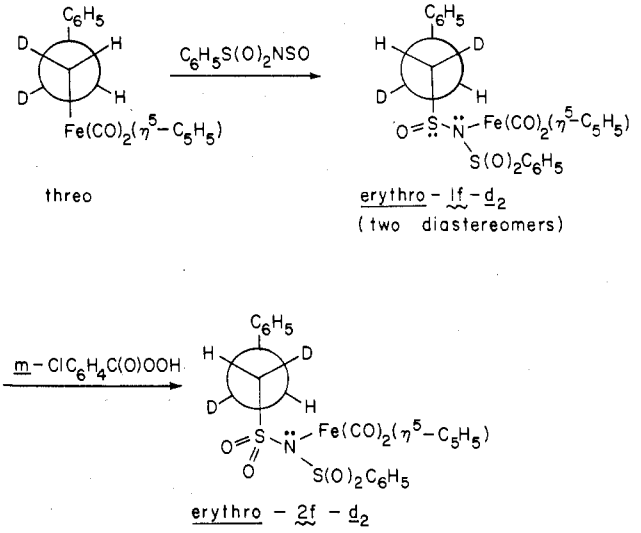


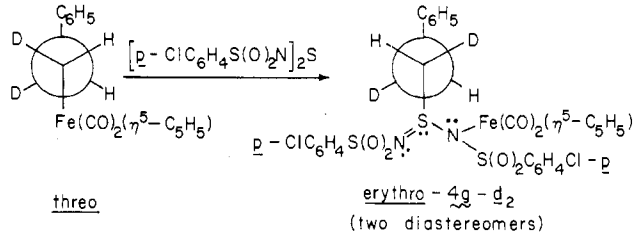
Figure 5. Deuterium-decoupled 100-MHz NMR spectrum of the CHDCHD protons of η^5-$C_5H_5Fe(CO)_2\{N[S(O)_2C_6H_4Cl\text{-}p][S(CHDCHDC_6H_5)NS(O)_2C_6H_4Cl\text{-}p]\}$ (**4g**-d_2), resulting from insertion of $[p\text{-}ClC_6H_4S(O)_2N]_2S$ into the Fe–C σ bond of *threo*-η^5-$C_5H_5Fe(CO)_2CHDCHDC_6H_5$, in $CDCl_3$.

Scheme II



(33) fod = 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione.

Scheme III



CHDCHD protons of one diastereomer are τ 6.91 and 7.28 and of the other are τ 7.11 and 7.53.

The coupling constants of 8.5 Hz are well within a range of 7.4–12.6 Hz for erythro diastereomers of $CHDCHDC_6H_5$.[31] This notwithstanding, an attempt was made to determine the $^3J_{HH}$ of the threo diastereomers of **4g**-d_2 by synthesizing *threo,erythro*-**4g**-d_2 and obtaining its $^1H\{^2H\}$ NMR spectrum. The recorded spectra of the CHDCHD protons were, however, of an unexpectedly low resolution, thus precluding the elucidation of $^3J_{HH}$.

On the basis of the foregoing stereochemical results we conclude that the insertion of $[C_6H_5S(O)_2N]_2S$ and $[p\text{-}ClC_6H_4S(O)_2N]_2S$ into the Fe–C bond of η^5-$C_5H_5Fe(CO)_2CHDCHDC_6H_5$ proceeds with a high degree of *inversion of configuration at* α *carbon* (Scheme III).

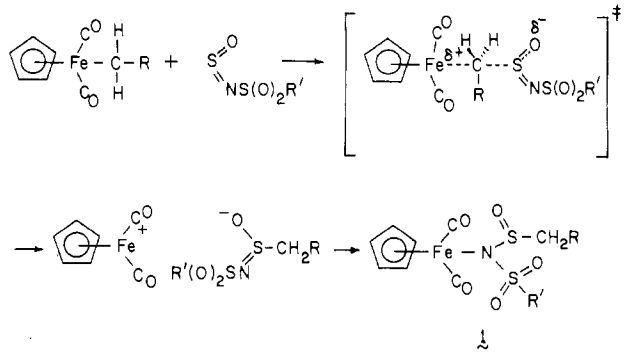
Discussion

Striking similarities may be noted between the insertions of SO_2 and *N*-sulfinylamines or -amides into iron–carbon σ bonds. First, the insertion of the *N*-sulfinyl compounds, like that of SO_2,[2] appears to be an electrophilic cleavage process. This is supported by the qualitative observations on relative reactivity toward a given η^5-$C_5H_5Fe(CO)_2R$ of R′NSO as a function of R′. When R′ is alkyl and aryl, as in $C_6H_{11}NSO$ and C_6H_5NSO, respectively, no insertion reaction occurs with η^5-$C_5H_5Fe(CO)_2CH_3$ at ambient temperatures. However, when R′ is a more electron-withdrawing alkanesulfonyl and arenesulfonyl group as, e.g., in $CH_3S(O)_2NSO$ and $C_6H_5S(O)_2NSO$, respectively, a facile insertion takes place at room temperature. Furthermore, the Lewis acid BF_3 considerably enhances reactivity of $C_6H_{11}NSO$ toward η^5-$C_5H_5Fe(CO)_2CH_3$, although the reaction does not proceed cleanly and the product was not fully characterized. An enhancement of the SO_2 insertion into the W–R bond of η^5-$C_5H_5W(CO)_3R$ by BF_3, presumably by increasing the electrophilic power of SO_2 through coordination, has been reported.[16]

Second, the stereochemistry at the α carbon of η^5-$C_5H_5Fe(CO)_2CHDCHDC_6H_5$ of the insertion of $C_6H_5S(O)_2NSO$ is inversion. Since the stereochemistry of the analogous SO_2 insertion is also inversion,[7] the two reactions may well proceed by similar pathways. On the basis of the generally accepted mechanism of the SO_2 insertion of coordinatively saturated transition metal–alkyl complexes,[2-4] we suggest that the *N*-sulfinylsulfonamide, $R'S(O)_2NSO$, attacks the α carbon of the Fe–CH_2R from the backside. This is depicted in Scheme IV. The resultant ion pair $[\eta^5\text{-}C_5H_5Fe(CO)_2]^+[OS(CH_2R)NS(O)_2R']^-$ then combines to yield the neutral product η^5-$C_5H_5Fe(CO)_2\{N[S(O)CH_2R][S(O)_2R']\}$ (**1**) directly, or via an intermediacy of O-bonded η^5-$C_5H_5Fe(CO)_2[OS(CH_2R)NS(O)_2R']$. Anions $R'NS(R)O^-$, strictly analogous to that proposed in the aforementioned ion pair, can be obtained by treatment of R′NSO with LiR or RMgX.[9]

As with SO_2,[26] the initial product of the insertion contains the harder, in this case nitrogen, donor atom bonded to the metal. A salient difference between the two types of insertion is a much higher stability of this N-bonded product, compared to the O-bonded sulfinato product from SO_2, with respect to linkage isomerization to the corresponding Fe–S bonded species. In the SO_2 insertion, the *O*-sulfinate is too unstable

Scheme IV



to be isolated;[26] in the *N*-sulfinylsulfonamide insertion, the S-bonded product, **3**, is obtained only after prolonged crystallization or storage of the isolated N-bonded isomer. This behavior accords with a generally higher stability of η^5-$C_5H_5Fe(CO)_2X$ complexes where X is an N-donor ligand compared to those with an O-donor ligand.[34]

The insertion reaction of η^5-$C_5H_5Fe(CO)_2CHDCHDC_6H_5$ with $[C_6H_5S(O)_2N]_2S$ and $[p\text{-}ClC_6H_4S(O)_2N]_2S$ also proceeds with inversion at α carbon and therefore may be considered to involve a mechanism similar to that shown in Scheme IV for $R'S(O)_2NSO$. The N-bonded products η^5-$C_5H_5Fe(CO)_2\{N[S(O)_2C_6H_4X\text{-}p][S(CHDCHDC_6H_5)NS(O)_2C_6H_4X\text{-}p]\}$ (X = H, Cl), as well as other complexes **4**, appear even more stable than **1** with respect to isomerization to the corresponding S-bonded species. So far, all attempts at inducing such a rearrangement of **4** to η^5-$C_5H_5Fe(CO)_2\{S(R)[NS(O)_2R']_2\}$ have been unsuccessful.

Experimental Section

General Procedures. Reactions were conducted under an atmosphere of dry nitrogen. Sample preparation and various manipulations of air- and/or moisture-sensitive materials were performed in a drybox filled with argon. All reactions involving BF_3 were carried out in a grease-free vacuum line.

Chromatography was performed by using columns packed either with neutral alumina (Ventron) deactivated by the addition of H_2O (generally 4–5%) or with 60–100 mesh Florisil. Melting points were measured in vacuo or under argon or nitrogen on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Elemental analyses were done by Galbraith Laboratories, Inc., Knoxville, Tenn.

Physical Measurements. ^1H NMR spectra were recorded on Varian Associates A-60A and EM360L spectrometers using Me_4Si as an internal reference. $^1H\{^2H\}$ NMR spectra were measured on a Varian Associates HA-100 spectrometer using a decoupling frequency of 7.676076 MHz with the assistance of Dr. C. E. Cottrell. ^{13}C NMR spectra were obtained on a Brucker HX-90 spectrometer at 22.625 MHz in a Fourier transform mode, also with the help of Dr. Cottrell.

IR spectra were recorded on Beckman IR-9 and Perkin-Elmer Model 337 spectrophotometers. Mass spectra were obtained at 70 eV on an A.E.I. Model MS-9 spectrometer by Mr. C. R. Weisenberger.

Materials. All commercially procured solvents were of reagent grade quality; the following were purified further by reflux over and distillation from the indicated materials: THF, pentane, and toluene ($LiAlH_4$); benzene (CaH_2); $CHCl_3$ and CH_2Cl_2 (P_4O_{10}). Other solvents were used as received. They were deaerated by three freeze–thaw cycles or by purging with argon or nitrogen.

Boron(III) fluoride (Matheson) was treated with NaF and then fractionally distilled. All other chemicals were procured in reagent grade or equivalent quality and were used as received.

The *N*-sulfinylamines, C_6H_5NSO[35] and $C_6H_{11}NSO$,[36] were prepared by literature methods. Literature procedures were also used to synthesize the *N*-sulfinylsulfonamides,[9,10] $CH_3S(O)_2NSO$, $C_6H_5S(O)_2NSO$, p-$CH_3C_6H_4S(O)_2NSO$, and p-$ClC_6H_4S(O)_2NSO$, and the

(34) Kilner, M. *Adv. Organomet. Chem.* **1972**, *10*, 115 and references cited therein.
(35) Michaelis, A.; Hertz, R. *Ber. Dtsch. Chem. Ges.* **1891**, *24*, 746.
(36) Klamann, D.; Sass, Chr.; Zelenka, M. *Chem. Ber.* **1959**, *92*, 1910.

disulfonylsulfur diimides,[10,28] $[CH_3S(O)_2N]_2S$, $[C_6H_5S(O)_2N]_2S$, and $[p\text{-}ClC_6H_4S(O)_2N]_2S$.

The iron complexes $\eta^5\text{-}C_5H_5Fe(CO)_2R$, where R = CH_3,[37] $CH_2CH_2C_6H_5$,[23] $CH_2C_6H_5$,[22] $p\text{-}C_6H_4CH_3$,[26] $p\text{-}C_6H_4Cl$,[23] and $p\text{-}C_6H_4F$,[21] were prepared by known procedures. The α,β-dideuterated $\eta^5\text{-}C_5H_5Fe(CO)_2CHDCHDC_6H_5$ was obtained both as the threo diastereomer and as a threo–erythro mixture according to Slack and Baird.[31] The organotungsten complex $\eta^5\text{-}C_5H_5W(CO)_3CH_3$ was synthesized[37] and purified[38] as described in the literature. The *S*-sulfinates $\eta^5\text{-}C_5H_5Fe(CO)_2[S(O)_2R]$, where R = CH_3 and $CH_2C_6H_5$, were synthesized by standard procedures.[22]

Tensimetric Titrations with BF_3. A. C_6H_5NSO. *N*-Sulfinylaniline (0.305 g, 2.19 mmol) was transferred in vacuo to a reaction flask at −196 °C, benzene (ca. 3 mL) was added, and the contents of the flask were allowed to warm to 7.0 °C for a measurement of the pressure. The solution was then cooled to −196 °C, treated with ca. 0.6 mmol of BF_3, and allowed to warm back to 7.0 °C in ca. 45 min. A pressure reading was taken after allowing 10 min for equilibration at 7.0 °C. This procedure was repeated several times until 2.484 mmol of BF_3 was introduced.

B. $C_6H_{11}NSO$. *N*-Sulfinylcyclohexylamine (0.077 g, 0.53 mmol) was transferred in vacuo to a reaction flask at −196 °C. Following the addition of 1 mL of toluene, the flask was warmed to and maintained at 1.0 ± 0.2 °C. The solution was treated with 2.215 mmol of BF_3 in ca. 0.3-mmol aliquots. Pressure readings were taken after allowing 30 min for equilibration following each addition.

C. $p\text{-}CH_3C_6H_4S(O)_2NSO$. A degassed solution of *N*-sulfinyl-*p*-toluenesulfonamide (0.211 g, 0.971 mmol) in toluene (ca. 3 mL) at −23 °C (CCl_4 slush bath) was treated with 4.55 mmol of BF_3 in 11 portions. Pressure readings were taken after allowing 30 min for equilibration following each addition.

Reaction of $\eta^5\text{-}C_5H_5Fe(CO)_2CH_3$ with $C_6H_{11}NSO$ and BF_3. *N*-Sulfinylcyclohexylamine (0.394 g, 2.71 mmol) was transferred in vacuo onto 0.191 g (0.995 mmol) of $\eta^5\text{-}C_5H_5Fe(CO)_2CH_3$ in a round-bottom flask at −78 °C, and to the resulting mixture was added 10 mL of toluene. The flask was then placed in a CCl_4 slush bath (−23 °C) and charged with 0.990 mmol of BF_3 (three 59.53-mL aliquots: 86.5 torr, 23.5 °C; 106.8 torr, 23.5 °C; 114.1 torr, 22.7 °C). A very fast reaction occurred upon the addition of BF_3, as evidenced by the precipitation of a dark, poorly formed, crystalline-appearing substance. The mixture was stirred for 1 h and allowed to warm to 25 °C, causing the precipitate to turn into an oil. Volatile matter was removed under reduced pressure at 40 °C, and the residual oil was examined by IR spectroscopy (2075 (s), 2020 (s), 1955 (s), 1150–1000 (vs, br) cm^{-1}, neat between KBr plates). A portion of the oil was dissolved in CH_2Cl_2 and the resulting solution was passed through 1 cm of Florisil on a frit. Dichloromethane eluted off unreacted $\eta^5\text{-}C_5H_5Fe(CO)_2CH_3$, and then acetone removed an orange band which after rotary evaporation yielded a yellow-brown oil, $\nu(C{\equiv}O)$ 2060, 2015 cm^{-1} (CH_2Cl_2 solution). A satisfactory ^1H NMR spectrum could not be obtained, and further attempts at purification and characterization of the oil proved unsuccessful.

Reaction of $\eta^5\text{-}C_5H_5Fe(CO)_2R$ with $R'S(O)_2NSO$. Preparation of $\eta^5\text{-}C_5H_5Fe(CO)_2\{N[S(O)R][S(O)R']\}$ (1). A slight excess of the *N*-sulfinylsulfonamide in 20 mL of $CHCl_3$ or CH_2Cl_2 was added dropwise to a stirred solution of ca. 1.5 mmol of $\eta^5\text{-}C_5H_5Fe(CO)_2R$ in 10 mL of the same solvent. (The use of at least the indicated volume of solvent is important, as it retards the disproportionation of $R'S(O)_2NSO$ to $[R'S(O)_2N]_2S$ and SO_2.) The reaction was generally complete within 1 h to afford a deep red solution. The solvent was removed on a rotary evaporator and the residue was treated with 5 mL of 10% H_2O in acetone to destroy excess *N*-sulfinylsulfonamide. The solvent was again evaporated, the residue was dissolved in $CHCl_3$, and the solution was dried over $MgSO_4$ and filtered. The filtrate was concentrated and cooled at 0 °C. Generally, crystallization could not be effected in this fashion, and the insertion product $\eta^5\text{-}C_5H_5Fe(CO)_2\{N[S(O)R][S(O)_2R']\}$ (1) was isolated as an orange-red glass by evaporation of the solvent. Alternatively (especially when R = aryl), the solution was chromatographed on a Florisil column (alumina causes extensive decomposition) eluting first with CH_2Cl_2 to remove any unreacted $\eta^5\text{-}C_5H_5Fe(CO)_2R$, and then with acetone or acetone–CH_2Cl_2 to remove the product. Analytical samples can be obtained by dissolution in CH_2Cl_2 and addition of hexane with cooling to precipitate orange-red to red solids. Yields of **1** from the iron–alkyl complexes were almost quantitative; those from the less reactive iron–aryl complexes were 50–80%.

Oxidation of $\eta^5\text{-}C_5H_5Fe(CO)_2\{N[S(O)R][S(O)_2R']\}$ (1) with *m*-$ClC_6H_4C(O)OOH$. Preparation of $\eta^5\text{-}C_5H_5Fe(CO)_2\{N[S(O)_2R][S(O)_2R']\}$ (2). Approximately 1.5 mmol of $\eta^5\text{-}C_5H_5Fe(CO)_2\{N[S(O)R][S(O)_2R']\}$ (1) in 5 mL of CH_2Cl_2 was treated with a slight excess of *m*-$ClC_6H_4C(O)OOH$ in 15 mL of CH_2Cl_2. The resulting red solution was stirred at 25 °C for 1 h, after which time the solvent was removed on a rotary evaporator. The residue was treated with 5 mL of methanol and a large excess (2.0 g) of $NaHCO_3$, and the resulting slurry was stirred for 1 h. Excess $NaHCO_3$ was filtered off and washed with 2 mL of methanol. The filtrate and the wash were combined, and the solvent was evaporated. The residue was dissolved in CH_2Cl_2, and the solution was dried over $MgSO_4$ and filtered. Removal of the solvent from the filtrate afforded the product as a red solid, which can be crystallized from 1:1 CH_2Cl_2–hexane at low temperature (ca. −78 °C). Yields before crystallization were at least 70%.

Isomerization of $\eta^5\text{-}C_5H_5Fe(CO)_2\{N[S(O)R][S(O)_2R']\}$ (1) to $\eta^5\text{-}C_5H_5Fe(CO)_2\{S(O)(R)[NS(O)_2R']\}$ (3). A solution of 2.5–3.0 mmol of $\eta^5\text{-}C_5H_5Fe(CO)_2\{N[S(O)R][S(O)_2R']\}$ (1) in 80 mL of CH_2Cl_2 was maintained at reflux for approximately 24 h. It was then cooled to 25 °C, concentrated to 10 mL, and chromatographed on Florisil eluting with acetone to remove an orange band of the starting material and a yellow band of the product in that order. The yellow effluent was evaporated to dryness, the solid residue was dissolved in 5 mL of CH_2Cl_2, and the resulting solution was treated with 25 mL of ether or cyclohexane to effect precipitation of the product. Yields were 15–20%.

The isomerization has also been effected, in 30% yields, in the solid at 50 °C within 24 h.

Reaction of $\eta^5\text{-}C_5H_5Fe(CO)_2R$ with $[R'S(O)_2N]_2S$. Preparation of $\eta^5\text{-}C_5H_5Fe(CO)_2\{N[S(O)_2R'][S(R)NS(O)_2R']\}$ (4). A solution of 1–2 mmol of $\eta^5\text{-}C_5H_5Fe(CO)_2R$ in 5–10 mL of $CHCl_3$ or CH_2Cl_2 was treated with a slight excess of solid $[R'S(O)_2N]_2S$. The reaction mixture was stirred at 25 °C for 1–2 h or until dissolution of the sparingly soluble $[R'S(O)_2N]_2S$ ceased. Excess disulfonylsulfur diimide was filtered off, and solvent was evaporated from the red filtrate. The residue was crystallized at low temperature from $CHCl_3$ or, alternatively, chromatographed on Florisil eluting first with CH_2Cl_2 or $CHCl_3$ to remove unreacted $\eta^5\text{-}C_5H_5Fe(CO)_2R$ and then with acetone to remove the insertion product. Yields were around 50%.

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Registry No. **1a**, 66973-81-7; **1b**, 66973-82-8; **1c**, 66973-83-9; **1d**, 72659-03-1; **1e**, 72659-04-2; **1f**, 72659-05-3; **1h**, 72659-06-4; **1i**, 72659-07-5; **1j**, 72659-08-6; **1k**, 72659-09-7; **2a**, 66973-84-0; **2b**, 66973-85-1; **2c**, 66973-86-2; **2e**, 72659-10-0; **2f**, 72659-11-1; **3a**, 66868-27-7; **3b**, 66868-28-8; **3c**, 66868-29-9; **3g**, 72658-86-7; **4a**, 66973-87-3; **4c**, 66973-88-4; **4e**, 72659-12-2; **4f**, 72659-13-3; **4g**, 72659-14-4; **4h**, 72659-15-5; **5a**, 12080-26-1; **5c**, 12087-32-0; **1f**-d_2, 72659-16-6; **2f**-d_2, 72659-17-7; **4f**-d_2, 72659-18-8; **4g**-d_2, 72659-19-9; *threo*-$\eta^5\text{-}C_5H_5Fe(CO)_2CHDCHDC_6H_5$, 55102-02-8; $CH_3S(O)_2NSO$, 40866-96-4; $C_6H_5S(O)_2NSO$, 6536-23-8; $p\text{-}CH_3C_6H_4S(O)_2NSO$, 4104-47-6; $p\text{-}ClC_6H_4S(O)_2NSO$, 52867-26-2; $[CH_3S(O)_2N]_2S$, 5636-09-9; $[C_6H_5S(O)_2N]_2S$, 667-20-9; $[p\text{-}ClC_6H_4S(O)_2N]_2S$, 851-07-0; $\eta^5\text{-}C_5H_5Fe(CO)_2CH_3$, 12080-06-7; $\eta^5\text{-}C_5H_5Fe(CO)_2CH_2CH_2C_6H_5$, 32760-31-9; $\eta^5\text{-}C_5H_5Fe(CO)_2CH_2C_6H_5$, 12093-91-3; $\eta^5\text{-}C_5H_5Fe(CO)_2\text{-}p\text{-}C_6H_4CH_3$, 12093-90-2; $\eta^5\text{-}C_5H_5Fe(CO)_2\text{-}p\text{-}C_6H_4Cl$, 12282-67-6; $\eta^5\text{-}C_5H_5Fe(CO)_2\text{-}p\text{-}C_6H_4F$, 31781-18-7; $\eta^5\text{-}C_5H_5W(CO)_3CH_3$, 12082-27-8.

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