full tables of bond lengths, bond angles, and selected torsion angles are available.[26]

Acknowledgment. Financial support from the National Science Foundation (E.P.K., Grant CHE81-13090), the Air Force Office of Scientific Research (R.B.K., Grants AFOSR-71-2000, -81-0051, and -84-0050), and the Robert A. Welch Foundation (E.P.K., Grant No. F573, and R.E.D., Grant No. F233). We also thank Professor Alan H. Cowley for a preprint of ref 16.

Registry No. 1, 57139-08-9; 4, 15321-51-4; 5, 89104-79-0; 6, 57139-05-6; 8, 89087-33-2; 9, 89210-02-6; 11, 95891-62-6; $Fe_3(CO)_{12}$, 17685-52-8.

Supplementary Material Available: Tables of observed and calculated structure factor amplitudes, fractional crystallographic coordinates, thermal parameters, and full listings of bond lengths and angles (137 pages). Ordering information is given on any current masthead page.

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(26) See note at the end of the paper regarding availability of supplementary material.

Proton-Initiated Opening of the Heterocyclic Ring in η^5-$C_5H_5(CO)_2Fe\overline{CHCH_2N(SO_2CH_3)SN(SO_2CH_3)C}H_2$ and η^5-$C_5H_5(CO)_2Fe\overline{CHCH_2N(SO_2CH_3)S(O)C}H_2$ and Deprotonation of Resultant Cationic Iron–η^2-Alkene Complexes†

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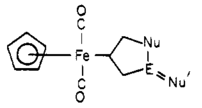
Reaction of η^5-$C_5H_5(CO)_2Fe\overline{CHCH_2N(SO_2CH_3)SN(SO_2CH_3)C}H_2$ (**3**) with $HPF_6\cdot(C_2H_5)_2O$ in CH_2Cl_2 results in the cleavage of the six-membered heterocyclic ring to afford the cationic complex $[\eta^5\text{-}C_5H_5(CO)_2Fe(\eta^2\text{-}CH_2{=}CHCH_2N(SO_2CH_3)SNH(SO_2CH_3))]^+PF_6^-$ (**4**) essentially quantitatively. Complex **4** was characterized by elemental analysis, ^1H and ^{13}C NMR and IR spectroscopy, and single-crystal X-ray diffraction techniques. Crystals of **4** are monoclinic of space group $P2_1/c$ with $a = 8.753$ (6) Å, $b = 23.74$ (1) Å, $c = 10.45$ (1) Å, $\beta = 98.56$ (5)°, and $Z = 4$. The structure was solved and refined to $R = 0.038$ and $R_w = 0.040$ by using 2317 independent reflections. The crystal structure of **4** consists of discrete iron–η^2-alkene complex cations and PF_6^- anions. Complex **4** reacts with 1,8-bis(dimethylamino)naphthalene (Proton Sponge) to regenerate **3** in 86% yield. There are no reactions between the oxonium salts $(CH_3)_3OBF_4$ and $(C_2H_5)_3OPF_6$ and **3** in CH_2Cl_2 solution at room temperature. The five-membered heterocyclic ring of η^5-$C_5H_5(CO)_2Fe\overline{CHCH_2N(SO_2CH_3)S(O)C}H_2$ (**5**) undergoes a similar protonation reaction with $HPF_6\cdot(C_2H_5)_2O$ to afford $[\eta^5\text{-}C_5H_5(CO)_2Fe(\eta^2\text{-}CH_2{=}CHCH_2S(O)NH(SO_2CH_3))]^+PF_6^-$ (**6**), which reacts with Proton Sponge to give back **5**.

Introduction

Complexes of the type **1** and **2** (E = electrophilic part; Nu and Nu′ = nucleophilic parts), obtained by cycloaddition reaction of η^5-$C_5H_5(CO)_2Fe(\eta^1\text{-}CH_2CH{=}CH_2)$ with the heterocumulenes Nu=E=Nu′ (i.e., RN=C=O[1,2] and RN=S=O[3]) and Nu=E=Nu (i.e., RN=S=NR[3]), respectively, present themselves as potential precursors of heterocyclic organic compounds.[4,5] In an attempt to ascertain possible applications of these cycloadducts to organic synthesis, we examined their reactions with protic acids. Cleavage of the Fe–C σ bond in η^5-$C_5H_5(CO)_2FeR$ on protonation generally is a facile process when R = alkyl, aryl, and cycloalkyl.[6-9]



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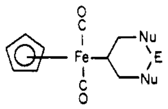

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Our previous, cursory, studies on reactions of **1** and related cycloadducts with acids led to the observation[1,10] that cleavage of the Fe–C σ bond therein occurs less readily than in the corresponding iron alkyls and cycloalkyls.

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† Inquiries concerning the X-ray crystallographic work should be directed to the Trieste address.

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Furthermore, in some cases, protonation appears to take place instead at the cyclic ligand. These observations prompted us to examine in some detail the reactions of η^5-$C_5H_5(CO)_2Fe\overline{CHCH_2N(SO_2CH_3)SN(SO_2CH_3)CH_2}$ (3) and η^5-$C_5H_5(CO)_2Fe\overline{CHCH_2N(SO_2CH_3)S(O)CH_2}$ (5) with $HPF_6{\cdot}(C_2H_5)_2O$. Our studies demonstrated that the addition of H^+ in these complexes occurs at the heterocyclic nitrogen and leads to ring opening with rearrangement to the appropriate iron–η^2-alkene complex cations. Results of these studies, including characterization by X-ray diffraction techniques of the complex derived from 3 and $HPF_6{\cdot}(C_2H_5)_2O$, as well as deprotonation reactions of the cationic products, are the subject of this paper.

Experimental Section

General Procedures and Measurements. All reactions were carried out under an atmosphere of purified nitrogen. Elemental analysis was done by Galbraith Laboratories, Inc., Knoxville, TN. Melting points were measured in vacuo on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared (IR) spectra were recorded on a Perkin-Elmer Model 283 spectrophotometer and were calibrated with polystyrene. ^1H NMR spectra were obtained on Varian Associates EM-390L and Bruker WM-300 spectrometers with use of Me_4Si as an internal reference. ^{13}C NMR spectra were recorded on the Bruker WM-300 at 75.430 MHz. Chemical shifts are reported relative to Me_4Si at δ 0.

Materials. Dichloromethane was distilled from P_4O_{10}. Tetrahydrofuran (THF) was purified by distillation from Na/K and benzophenone immediately before use. Pentane, hexane, and ether were distilled from sodium. Other solvents were of reagent grade quality and were used as received.

Commercially procured $HPF_6{\cdot}(C_2H_5)_2O$ (Columbia), $(C_2H_5)_3OPF_6$ (Columbia), $(CH_3)_3OBF_4$ (Alfa), and 1,8-bis(dimethylamino)naphthalene (trade name Proton Sponge, Aldrich) were used without further purification. The iron complexes η^5-$C_5H_5(CO)_2Fe\overline{CHCH_2N(SO_2CH_3)SN(SO_2CH_3)CH_2}$ (3) and η^5-$C_5H_5(CO)_2Fe\overline{CHCH_2N(SO_2CH_3)S(O)CH_2}$ (5) were synthesized as reported.[3]

Protonation of η^5-$C_5H_5(CO)_2Fe\overline{CHCH_2N(SO_2CH_3)SN(SO_2CH_3)CH_2}$ (3) with $HPF_6{\cdot}(C_2H_5)_2O$. Addition over 30 min with stirring of 1 mL of $HPF_6{\cdot}(C_2H_5)_2O$ in 40 mL of CH_2Cl_2 to a solution of 3 (1.23 g, 2.82 mmol) in 150 mL of CH_2Cl_2 at 0 °C resulted in the formation of a yellow precipitate. The reaction mixture was allowed to warm to room temperature, and the precipitate was collected and washed first with CH_2Cl_2 and then with pentane. The yield was 1.60 g (98%). The product was recrystallized from acetone–ether. Characterization of product 4: mp 129 °C dec; ^1H NMR (acetone-d_6, Bruker WM-300) δ 6.01 (s, C_5H_5), 5.62 (s, NH), 5.01 (m, $J_{H(c)H(a)} = 8.4$, $J_{H(c)H(b)} = 14.2$, $J_{H(c)H(d)} = 3.5$, $J_{H(c)H(e)} = 10.0$ Hz, H(c)), 4.75 (dd, $J_{H(d)H(c)} = 3.5$, $J_{H(d)H(e)} = 14.1$ Hz, H(d)), 4.28 (d, $J_{H(a)H(c)} = 8.4$ Hz, H(a)), 4.13 (d, $J_{H(b)H(c)} = 14.2$ Hz, H(b)), 3.56 (dd, $J_{H(e)H(c)} = 10.0$, $J_{H(e)H(d)} = 14.1$ Hz, H(e)), 3.23 (s, CH_3), 3.18 (s, CH_3); $^{13}C\{^1H\}$ NMR (acetone-d_6, Bruker WM-300) δ 40.84 (CH_3), 41.70 (CH_3), 56.50 (CH_2), 57.50 (CH_2), 76.87 (CH), 90.72 (C_5H_5), 207.86, 210.76 (2 CO); IR (Nujol) ν(NH) 3300 (m), ν(CO) 2080 (vs), 2040 (vs) cm^{-1}. Anal. Calcd for $C_{12}H_{17}F_6N_2O_6PS_3Fe$: C, 24.75; H, 2.94; S, 16.52. Found: C, 24.92; H, 2.85; S, 16.54.

Deprotonation of $[\eta^5$-$C_5H_5(CO)_2Fe(\eta^2$-$CH_2{=}CHCH_2N(SO_2CH_3)SNH(SO_2CH_3))]^+PF_6^-$ (4) 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 4 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 the mixture was filtered to remove the PF_6^- salt of protonated Proton Sponge. The filtrate was concentrated to 15 mL, and 30 mL of hexane was added with stirring. The resulting solution was cooled at ca. 0 °C for 12 h to yield 0.185 g (86%) of yellow crystals of η^5-$C_5H_5(CO)_2Fe\overline{CHCH_2N(SO_2CH_3)SN(SO_2CH_3)CH_2}$ (3) which were collected by filtration and identified by comparison of ^1H NMR spectrum with that of an authentic sample of 3.

Table I. Crystal Data for 4

formula	$FeC_{12}H_{17}F_6N_2O_6PS_3$	β, deg	98.56 (5)
mol wt	582.3	V, Å^3	2147.3
cryst class	monoclinic	Z	4
space group	$P2_1/c$	ρ_{calcd}, g cm^{-3}	1.80
a, Å	8.453 (6)		
b, Å	23.74 (1)	λ(Mo Kα), Å	0.7107
c, Å	10.45 (1)	μ(Mo Kα), cm^{-1}	4.4

Attempted Reaction of η^5-$C_5H_5(CO)_2Fe\overline{CHCH_2N(SO_2CH_3)SN(SO_2CH_3)CH_2}$ (3) with $(CH_3)_3OBF_4$. A solution of 3 (0.096 g, 0.22 mmol) in 20 mL of CH_2Cl_2 at −78 °C was added to a suspension of $(CH_3)_3OBF_4$ (0.070 g, 0.47 mmol) in 20 mL of CH_2Cl_2 also at −78 °C. The resulting mixture was stirred first at −78 °C for 30 min and then at room temperature for 2 h. The solvent was removed, and the residue was examined by ^1H NMR spectroscopy to show unreacted 3.

Attempted Reaction of η^5-$C_5H_5(CO)_2Fe\overline{CHCH_2N(SO_2CH_3)SN(SO_2CH_3)CH_2}$ (3) with $(C_2H_5)OPF_6$. To a solution of 0.81 g (1.9 mmol) of 3 in 75 mL of CH_2Cl_2 at −78 °C was added a solution of 0.48 g (1.9 mmol) of $(C_2H_5)_3OPF_6$ in 25 mL of CH_2Cl_2 also at −78 °C. The mixture was stirred first at −78 °C for 30 min and then at room temperature for 1.5 h. ^1H NMR spectrum showed unreacted 3.

Protonation of η^5-$C_5H_5(CO)_2Fe\overline{CHCH_2N(SO_2CH_3)S(O)CH_2}$ (5) with $HPF_6{\cdot}(C_2H_5)_2O$. A solution of 0.393 g (1.77 mmol) of $HPF_6{\cdot}(C_2H_5)_2O$ in 20 mL of CH_2Cl_2 at −78 °C was added to 0.500 g (1.39 mmol) of 5 (78:22 mixture of diastereomers) in 45 mL of CH_2Cl_2 also at −78 °C. A yellow precipitate formed immediately. The resulting mixture was then stirred at −78 °C for 10 min, 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_2Cl_2 (2 × 10 mL) to afford 0.610 g (87% yield) of product 6. Spectroscopic data: ^1H NMR (acetone-d_6) δ 6.03 (s, C_5H_5), 5.30–5.07 (m, $CH_2{=}CH$), 3.46–3.11 (m, CH_2), 3.08 (s, CH_3); IR (Nujol) ν(NH) 3295 (w, br), ν(CO) 2070 (vs), 2035 (vs), $\nu(SO_2)$ 1356 (vs), 1158 (vs), ν(SO) 1088 (vs, br) cm^{-1}.

Deprotonation of $[\eta^5$-$C_5H_5(CO)_2Fe(\eta^2$-$CH_2{=}CHCH_2S(O)NH(SO_2CH_3))]^+PF_6^-$ (6) with Proton Sponge. To 0.420 g (0.832 mmol) of 6 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. The residue was crystallized from 40 mL of 1:2 CH_2Cl_2–pentane to yield 0.170 g (57%) of η^5-$C_5H_5(CO)_2Fe\overline{CHCH_2N(SO_2CH_3)S(O)CH_2}$ (5) which was characterized by ^1H NMR spectroscopy as a 95:5 mixture of diastereomers.

X-ray Structural Determination of $[\eta^5$-$C_5H_5(CO)_2Fe(\eta^2$-$CH_2{=}CHCH_2N(SO_2CH_3)SNH(SO_2CH_3))]^+PF_6^-$ (4). Crystals suitable for X-ray diffraction were obtained by dissolving 4 (0.8 g) in 20 mL of acetone, adding 40 mL of ether, and cooling at 0 °C for ca. 12 h. They were washed with CH_2Cl_2 and pentane and dried under reduced pressure.

Crystal data are given in Table I. Cell parameters, determined from Weissenberg and precession photographs, were refined with the AED-Siemens automatic single-crystal diffractometer. Diffraction intensities were measured at room temperature by the θ–2θ scan technique with Mo Kα radiation. The intensity of one reflection was monitored after every 100 reflections, showing no significant variation throughout data collection.

A total of 2317 independent reflections were collected (7° $\leq 2\theta \leq$ 48°) with $I > 3\sigma(I)$. Intensity data were corrected for Lorentz and polarization effects. Absorption and extinction corrections were not applied. The structure was solved via Patterson and Fourier maps. Refinement by blocked full-matrix least-squares techniques converged at $R = 0.038$ and $R_w = 0.040$ with the weights

Table II. Fractional Coordinates ($\times 10^4$) of 4, with Estimated Standard Deviations in Parentheses

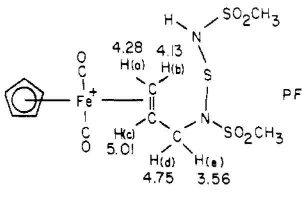
	x	*y*	*z*
Fe	-1540 (1)	6228 (0)	3810 (1)
S(1)	-3869 (2)	4968 (1)	7749 (1)
S(2)	-5714 (2)	5951 (1)	6837 (2)
S(3)	-4848 (2)	7090 (1)	7730 (2)
N(1)	-4122 (6)	5555 (2)	6857 (5)
N(2)	-5307 (7)	6426 (2)	8040 (5)
C(1)	-2563 (8)	6331 (3)	2209 (6)
C(2)	-1137 (8)	5503 (3)	3514 (7)
C(3)	-3887 (7)	6303 (3)	4263 (6)
C(4)	-3230 (7)	5822 (2)	4867 (6)
C(5)	-2758 (7)	5783 (3)	6310 (6)
C(6)	-6421 (9)	7373 (3)	6671 (9)
C(7)	-2815 (10)	5179 (3)	9235 (7)
O(1)	-3191 (7)	6411 (3)	1197 (5)
O(2)	-820 (7)	5047 (2)	3369 (7)
O(3)	-3534 (5)	7084 (2)	7063 (5)
O(4)	-4721 (7)	7366 (2)	8952 (5)
O(5)	-2941 (6)	4606 (2)	7087 (5)
O(6)	-5370 (6)	4781 (2)	7954 (5)
C(8)	-865 (10)	7069 (3)	4109 (11)
C(9)	-737 (9)	6815 (3)	5289 (8)
C(10)	237 (10)	6387 (3)	5334 (8)
C(11)	822 (10)	6359 (4)	4195 (12)
C(12)	144 (13)	6783 (5)	3419 (8)
P	9186 (2)	1384 (1)	5455 (2)
F(1)	9659 (6)	957 (2)	4418 (5)
F(2)	8717 (7)	1815 (2)	6501 (5)
F(3)	7395 (5)	1291 (2)	4908 (5)
F(4)	9110 (8)	880 (2)	6421 (5)
F(5)	954 (6)	1479 (2)	6035 (5)
F(6)	9297 (7)	1891 (2)	4495 (5)

$w = (\sigma^2(F) + 0.0229F^2)^{-1}$. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were located at the calculated positions, their contribution being held constant (B = 7 Å^2) during refinement. For the CH_3 groups, hydrogens were set in a staggered conformation with respect to the S–N bonds. All calculated positions occurred in regions of positive electron density in the difference Fourier map.

Atomic scattering factors were those reported.[11] Data processing was performed by programs of the X-RAY 70 system,[12] and all other calculations were carried out with the SHELX 76 system.[13] Positional parameters of the non-hydrogen atoms are given in Table II together with their estimated standard deviations calculated from the inverse matrix of the final least-squares cycle. Listings of temperature factors, hydrogen atom coordinates, and structure factors are available as supplementary material.[14]

Results and Discussion

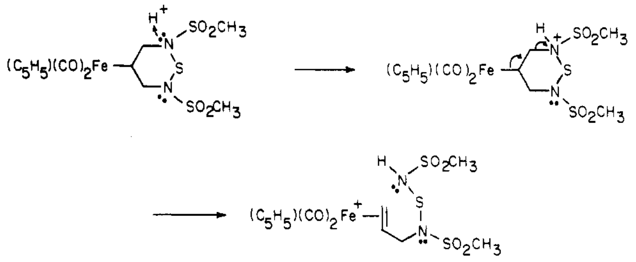
Protonation–Deprotonation Studies. Addition of $HPF_6\cdot(C_2H_5)_2O$ to a CH_2Cl_2 solution of η^5-C_5H_5-$(CO)_2FeCHCH_2N(SO_2CH_3)SN(SO_2CH_3)CH_2$ (3) at 0 °C results in the precipitation of a yellow solid in excellent (98%) yield. This solid is stable under nitrogen and was characterized by elemental analysis, IR and NMR spectroscopy, and X-ray crystallography (vide infra) as the ionic $[\eta^5\text{-}C_5H_5(CO)_2Fe(\eta^2\text{-}CH_2{=}CHCH_2N(SO_2CH_3)SNH(SO_2CH_3))]^+PF_6^-$ (4). The IR spectrum shows two ν(CO) absorptions at 2080 and 2040 cm^{-1}, the positions of which are indicative of a cationic nature of the iron complex.[2] The band at 3300 cm^{-1}, assigned to ν(NH), suggests that the protonation occurred at the nitrogen atom of one of the equivalent NSO_2CH_3 groups. The 300-MHz ^{1}H NMR spectrum exhibits a single resonance of the η^5-C_5H_5 protons at δ 6.01, two resonances of the CH_3 protons at δ 3.23 and 3.18, a sharp resonance of the NH proton at δ 5.62, and separate resonances for each of the remaining five protons of the $CH_2{=}CHCH_2$ fragment. The lettering scheme and the chemical shifts of those five protons are presented in Figure 1, whereas the coupling constants are listed in Experimental Section. The assignments were made with the aid of homonuclear decoupling experiments. Thus, irradiation at the frequency of the δ 3.56 signal collapses the δ 4.75 doublet of doublets to a doublet (J = 3.5 Hz). Similarly, irradiation at the δ 4.75 signal resulted in the collapse of the doublet of doublets at δ 3.56 to a doublet (J = 3.5 Hz). Irradiation at the δ 5.01 multiplet collapses the δ 4.75 signal to a doublet (J = 14.1 Hz), the δ 4.28 and 4.13 doublets to singlets, and the δ 3.56 signal to a doublet (J = 14.1 Hz). The assigned chemical shifts and coupling constants compare well with those reported[2] for a series of complexes $[\eta^5\text{-}C_5H_5(CO)_2Fe(\eta^2\text{-alkene})]^+BF_4^-$. Resonances in the $^{13}C\{^1H\}$ NMR spectrum, assigned with the help of the corresponding gated spectrum and given in Experimental Section, are also in complete accord with structure 4. A definite proof of the structure was provided by an X-ray crystallographic analysis, which is considered later in the paper.



4

Figure 1. The structure of 4, showing the lettering scheme for the protons (a)–(e) and their NMR chemical shifts.

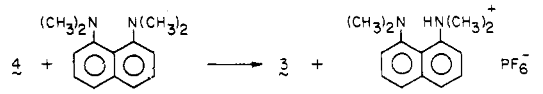
Scheme I



The formation of 4 proceeds by protonation of 3 at nitrogen followed by heterolytic cleavage of the CH_2–NH bond and rearrangement to an Fe–η^2-alkene structure. These steps are depicted in Scheme I.

Since 3 is readily converted to 4 by the action of $HPF_6\cdot(C_2H_5)_2O$, it was of interest to ascertain whether a similar reaction would occur on alkylation. However, attempts at alkylation of 3 with each of $(CH_3)_3OBF_4$ and $(C_2H_5)_3OPF_6$ in CH_2Cl_2 solution at room temperature gave no evidence of reaction.

Complex 4 reacts with a strong, noncoordinating base, 1,8-bis(dimethylamino)naphthalene (Proton Sponge) to regenerate 3 in 86% isolated yield. Deprotonation of



various complex cations $[\eta^5\text{-}C_5H_5(CO)_2Fe(\eta^2\text{-}CH_2{=}CHCH_2E)]^+$ (E = electrophilic fragment) with $(C_2H_5)_3N$ has been studied by Rosenblum and co-workers.[2] These

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[11] "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV.

[12] Stewart, J. M.; Kundal, F. A.; Baldwin, J. C. "The X-ray System"; University of Maryland: College Park, MD, 1970.

[13] Sheldrick, G. M. "SHELX Crystallographic Program System"; University Chemical Laboratories, Cambridge, England, 1976.

[14] See paragraph at end of paper regarding supplementary material.

Table III. Bond Distances and Angles for 4, with Estimated Standard Deviations in Parentheses

(a) Bond Distances (Å)

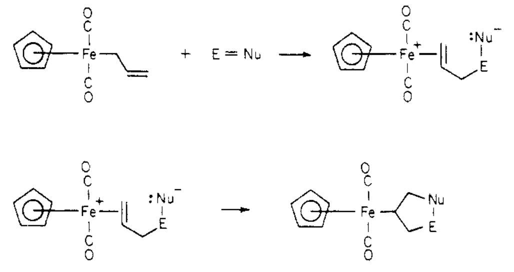
Fe-C(1)	1.793 (6)	S(1)-C(7)	1.757 (7)	C(8)-C(9)	1.362 (13)
Fe-C(2)	1.794 (7)	S(2)-N(1)	1.679 (5)	C(8)-C(12)	1.396 (15)
Fe-C(3)	2.183 (7)	S(2)-N(2)	1.686 (5)	C(9)-C(10)	1.322 (11)
Fe-C(4)	2.196 (6)	S(3)-O(3)	1.432 (5)	C(10)-C(11)	1.366 (16)
Fe-C(8)	2.093 (8)	S(3)-O(4)	1.425 (5)	C(11)-C(12)	1.372 (15)
Fe-C(9)	2.121 (8)	S(3)-N(2)	1.669 (5)	P-F(1)	1.583 (5)
Fe-C(10)	2.088 (8)	S(3)-C(6)	1.766 (8)	P-F(2)	1.594 (6)
Fe-C(11)	2.070 (8)	C(1)-O(1)	1.133 (8)	P-F(3)	1.602 (5)
Fe-C(12)	2.063 (12)	C(2)-O(2)	1.133 (9)	P-F(4)	1.574 (6)
S(1)-O(5)	1.430 (6)	C(3)-C(4)	1.388 (8)	P-F(5)	1.580 (5)
S(1)-O(6)	1.433 (5)	C(4)-C(5)	1.506 (8)	P-F(6)	1.592 (5)
S(1)-N(1)	1.674 (5)	C(5)-N(1)	1.499 (8)		

(b) Bond Angles (deg)

C(1)-Fe-C(2)	93.1 (3)	S(1)-N(1)-S(2)	120.9 (3)	F(1)-P-F(3)	90.6 (3)
O(5)-S(1)-O(6)	119.0 (3)	S(1)-N(1)-C(5)	117.8 (4)	F(1)-P-F(4)	89.5 (3)
O(5)-S(1)-N(1)	105.6 (3)	S(2)-N(1)-C(5)	120.0 (4)	F(1)-P-F(5)	90.8 (3)
O(5)-S(1)-C(7)	109.7 (4)	S(2)-N(2)-S(3)	121.1 (3)	F(1)-P-F(6)	90.4 (3)
O(6)-S(1)-N(1)	107.1 (3)	Fe-C(1)-O(1)	178.1 (6)	F(2)-P-F(3)	89.7 (3)
O(6)-S(1)-C(7)	107.2 (4)	Fe-C(2)-O(2)	176.7 (6)	F(2)-P-F(4)	90.5 (3)
N(1)-S(1)-C(7)	105.2 (3)	C(3)-C(4)-C(5)	122.6 (5)	F(2)-P-F(5)	89.0 (3)
N(1)-S(2)-N(2)	106.4 (3)	N(1)-C(5)-C(4)	106.8 (5)	F(2)-P-F(6)	89.6 (3)
O(3)-S(3)-O(4)	118.6 (3)	C(9)-C(8)-C(12)	106.2 (8)	F(3)-P-F(4)	89.5 (3)
O(3)-S(3)-N(2)	108.7 (3)	C(8)-C(9)-C(10)	109.8 (8)	F(3)-P-F(5)	178.5 (3)
O(3)-S(3)-C(6)	107.8 (4)	C(9)-C(10)-C(11)	109.3 (8)	F(3)-P-F(6)	91.6 (3)
O(4)-S(3)-N(2)	104.5 (3)	C(10)-C(11)-C(12)	107.0 (9)	F(4)-P-F(5)	89.7 (3)
O(4)-S(3)-C(6)	109.6 (4)	C(8)-C(12)-C(11)	107.7 (9)	F(4)-P-F(6)	178.9 (3)
N(2)-S(3)-C(6)	107.1 (3)	F(1)-P-F(2)	179.7 (3)	F(5)-P-F(6)	89.2 (3)

latter reactions proceed by loss of a CH_2 proton to yield η^5-$C_5H_5(CO)_2Fe(\eta^1$-$CH_2CH{=}CHE)$. In the present case, the NH proton is considerably more acidic than the CH_2 protons, and therefore the observed formation of **3** rather than η^5-$C_5H_5(CO)_2Fe(\eta^1$-$CH_2CH{=}CHN(SO_2CH_3)SNH(SO_2CH_3))$ is not unexpected.

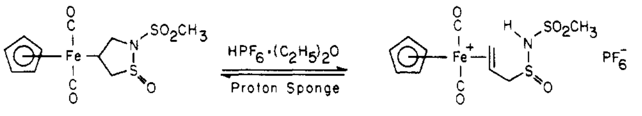
The facile formation of **3** from **4** on removal of the NH proton is relevant to the two-step polar mechanism proposed for the cycloaddition reactions of η^5-$C_5H_5(CO)_2Fe(\eta^1$-$CH_2CH{=}CH_2)$ with various unsaturated molecules E = Nu,[4,5] viz.



The second step of this mechanism is mimicked by the conversion of deprotonated **4** to **3**. The observation that the latter reaction proceeds readily and cleanly at room temperature accords with the proposed pathway for cycloaddition.

The successful protonation–deprotonation reaction sequence on the six-membered ring of **3** suggested an extension of this study to the five-membered ring of a similar cycloadduct, η^5-$C_5H_5(CO)_2FeCHCH_2N(SO_2CH_3)S(O)CH_2$ (**5**). Reaction of **5** with $HPF_6 \cdot (C_2H_5)_2O$ in CH_2Cl_2 proceeds rapidly at −78 °C to give yellow crystalline $[\eta^5$-$C_5H_5(CO)_2Fe(\eta^2$-$CH_2{=}CHCH_2S(O)NH(SO_2CH_3))]^+PF_6^-$ (**6**) in 87% isolated yield. The structure of **6** was assigned from IR and ^1H NMR spectroscopic data. The IR spectrum revealed $\nu(CO)$ absorptions typical of complex cations $[\eta^5$-$C_5H_5(CO)_2Fe(\eta^2$-alkene$)]^+$ [2] and a $\nu(NH)$ band at 3295 cm^{-1}. The ^1H NMR spectra showed η^5-C_5H_5 and $CH_2{=}CHCH_2$ resonances in the range reported for $[\eta^5$-$C_5H_5(CO)_2Fe(\eta^2$-alkene$)]^+$;[2] however, the signals were rather broad possibly owing to a much lower stability of **6** compared to **4** 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** to regenerate **5** was effected in 57% isolated yield by using Proton Sponge. It is of interest that the sequence protonation–deprotonation leads to what appears to be a change in the diastereomeric composition of **5** (chiral centers at the CH carbon and SO sulfur). Complex **5** was obtained from η^5-$C_5H_5(CO)_2Fe(\eta^1$-$CH_2CH{=}CH_2)$ and $CH_3SO_2N{=}S{=}O$ as a 78:22 mixture of diastereomers as evidenced by the presence of two η^5-C_5H_5 ^1H NMR signals.[15] After protonation–deprotonation, this ratio changes to 95:5. We cannot tell at this time whether the observed enrichment of **5** in the predominant diastereomer results from some loss of stereospecificity in the two-step reaction sequence or from epimerization of either **5** or, more likely, **6** during the reactions or whether it simply reflects greater decomposition of the less abundant isomer of **5** or **6** (cf. isolated yield of **5** from **6**).



5 **6**

Investigations are in progress on protonation–deprotonation reactions involving various complexes η^5-$C_5H_5(CO)_2FeCHCH_2N(R)C(O)CHR'$ with a particular view to elucidating stereochemistry of these processes.

Crystal and Molecular Structure of $[\eta^5$-$C_5H_5(CO)_2Fe(\eta^2$-$CH_2{=}CHCH_2N(SO_2CH_3)SNH(SO_2CH_3))]^+PF_6^-$ (4). The crystal structure of **4** consists of discrete PF_6^- anions and $[\eta^5$-$C_5H_5(CO)_2Fe(\eta^2$-$CH_2{=}CHCH_2N(SO_2CH_3)SNH(SO_2CH_3))]^+$ cations, with no unusually close contacts. Bond distances and angles are

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[15] Leung, T. W. Ph.D. Thesis, The Ohio State University, 1980.

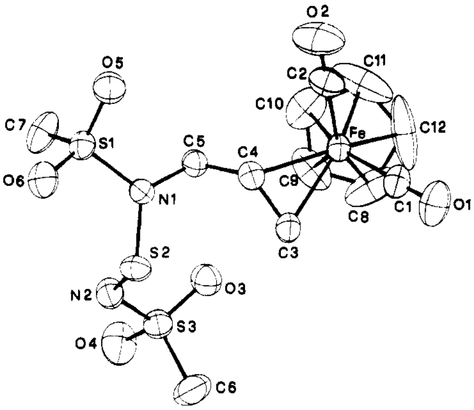

Figure 2. ORTEP drawing of the cation of 4, $[\eta^5\text{-}C_5H_5(CO)_2Fe(\eta^2\text{-}CH_2{=}CHCH_2N(SO_2CH_3)SNH(SO_2CH_3))]^+$, with labeling scheme. Hydrogen atoms have been omitted.

reported in Table III. The structure of the cation is shown in Figure 2.

The iron atom is η^5-bonded to the cyclopentadienyl ring and η^2-bonded to the alkene group in such a way that the dihedral angle between the planes defined by η^5-C_5H_5 and C(3)C(4)C(5) is 34°, with the Fe atom being displaced 1.97 and 1.73 Å, respectively, from the two planes. If the centroids of the cyclopentadienyl and alkene groups are labeled as cp and alk, then the Fe–cp and Fe–alk distances are 2.08 and 1.71 Å, respectively. The arrangement of ligands around Fe is quite symmetrical as shown by the following angles: cp–Fe–alk = 125.1, cp–Fe–C(1) = 121.4, cp–Fe–C(2) = 121.6, alk–Fe–C(1) = 92.6, alk–Fe–C(2) = 94.9, and C(1)–Fe–C(2) = 93.1°.

The average Fe–C(η^5-C_5H_5) bond distance of 2.09 (2) Å is comparable, within experimental error, to that of 2.108 (2) Å found in the parent compound 3.[3,15] The C–C distances of the η^5-C_5H_5 ring (planar within ±0.01 Å) range from 1.32 (1) to 1.40 (2) Å, averaging to 1.36 (3) Å. The shortening of the distances with respect to the normal value of 1.40 Å may be attributed to the thermal motion of the group.

The alkene axis C(3)–C(4) of 1.388 (8) Å is parallel to the C(11)–C(12) bond of the cyclopentadienyl group, with an average Fe–C distance of 2.190 (9) Å.

The average distances Fe–C and C–O for the carbonyl ligands are 1.794 (7) and 1.133 (9) Å, respectively, whereas in the parent complex 3 they are 1.748 (4) and 1.148 (4) Å.[3,15] The foregoing data reflect less π back-donation from Fe to CO in 4 compared to 3; this is supported also by the values of ν(CO) of the two complexes.

The most interesting structural feature of the disulfonylsulfur diimide fragment is the trigonal nature of the two nitrogen atoms, whose bond angles are close to 120°. This geometry, together with the values of the S–N bond distances, suggests the presence of a partial π-bonding contribution along the S–N bonds. In fact, the average value of 1.677 (7) Å is significantly shorter than 1.76 (2) Å, expected for a single S–N bond,[16] and between the values of 1.633 (5) and 1.692 (5) Å found in tertiary mesyl amines $RR'NSO_2CH_3$, where multiple bonds are present.[17,18] Furthermore, it is comparable to the value of 1.662 (5) Å found in the iminodisulfonate ion, where a partial double bond has been demonstrated.[19] The mean bond lengths and angles involving the NSO_2CH_3 tetrahedra are S–N = 1.672, S–O = 1.430, and S–C = 1.762 Å and O–S–O = 118.8, O–S–N = 106.5, O–S–C = 109.1, and N–S–C = 106.2°. These values are close to those found in several *N*-mesyl compounds.[18-20] In the parent complex 3, where the disulfonylsulfur diimide fragment is part of a six-membered ring, the nitrogen atoms are still essentially planar.[3,15] The observed distortions probably result from ring closure constraints. The average exo- and endocyclic S–N bond distances are 1.65 (1) and 1.69 (1) Å, respectively, showing that also in this complex there is a partial π-bonding contribution.

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Registry No. 3, 86750-93-8; 4, 96109-52-3; 5 (isomer I), 96192-43-7; 5 (isomer II), 96192-44-8; 6, 96109-54-5; 1,8-bis(dimethylamino)naphthalene, 20734-58-1; 1-(dimethylamonium)-8-(dimethylamino)naphthalene hexafluorophosphate, 96095-84-0.

Supplementary Material Available: Listings of temperature factors (Table IV), hydrogen atom coordinates (Table V), and structure factors (Table VI) for complex 4 (12 pages). Ordering information is given on any current masthead page.

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