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Cycloaddition and Insertion Reactions of *N*-Sulfinylmethanesulfonamide and Sulfur Bis(methanesulfonylimide) with Transition-Metal–Propargyl, –η^1-Allyl, and –Cyclopropylmethyl Complexes. Novel [3 + 3] Cycloaddition Products

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Reactions of the *N*-sulfinyl sulfonamides $R'S(O)_2NSO$ (R' = Me, Ph) and sulfur bis(methanesulfonylimide) ($[MeS(O)_2N]_2S$) with transition-metal–propargyl, –η^1-allyl, and –cyclopropylmethyl complexes have been investigated to complement previously reported studies of the corresponding reactions of SO_2. Metal–propargyl complexes react at ambient temperatures with $R'S(O)_2NSO$ and $[MeS(O)_2N]_2S$ to afford [3 + 2] cycloadducts $M\overline{C{=}C(R)S(O)N[S(O)_2R']C}H_2$ and $M\overline{C{=}C(R)S[NS(O)_2Me]N[S(O)_2Me]C}H_2$ (M = $CpFe(CO)_2$, $CpMo(CO)_3$, $CpW(CO)_3$, $CpCr(NO)_2$, $Mn(CO)_5$; R = Me, Ph), respectively. Metal–η^1-allyl complexes and $MeS(O)_2NSO$ at 25 °C also furnish [3 + 2] cycloaddition products $M\overline{CHCH_2S(O)N[S(O)_2Me]C}H_2$ (M = $CpFe(CO)_2$, $CpMo(CO)_3$, $Mn(CO)_5$); however, η^1-allyl complexes and $[MeS(O)_2N]_2S$ yield novel [3 + 3] cycloadducts, $M\overline{C(R)CH_2N[S(O)_2Me]SN[S(O)_2Me]C}H_2$ (M = $CpFe(CO)_2$, $CpMo(CO)_3$, $Mn(CO)_5$; R = H, Me). The structure of $CpFe(CO)_2\overline{CHCH_2N[S(O)_2Me]SN[S(O)_2Me]C}H_2$ was determined by X-ray diffraction analysis. The crystals are monoclinic of space group $P2_1/n$ with a = 8.500 (1) Å, b = 19.656 (1) Å, c = 10.380 (1) Å, β = 98.25 (1)°, and Z = 4. Least-squares refinement (on F^2) has resulted in a final value of R = 0.113 based on all the 5274 unique reflections. The six-membered heterocyclic ring adopts a chair conformation. The complex $CpFe(CO)_2CH_2\overline{CHCH_2C}H_2$ reacts at room temperature with $MeS(O)_2NSO$ and $[MeS(O)_2N]_2S$ to afford, in each case, products of insertion and cycloaddition. Thus, with the former, $CpFe(CO)_2\{N[S(O)_2Me]S(O)CH_2\overline{CHCH_2C}H_2\}$ (19%) and $CpFe(CO)_2\overline{CHCH_2CH_2S(O)N[S(O)_2Me]C}H_2$ (50%) are obtained, whereas with the latter, $CpFe(CO)_2\{N[S(O)_2Me]S(CH_2\overline{CHCH_2C}H_2NS(O)_2Me\}$ (52%) and $CpFe(CO)_2\overline{CHCH_2CH_2S[NS(O)_2Me]N[S(O)_2Me]C}H_2$ (28%) are isolated. There is no conversion of the insertion products into the corresponding cycloaddition products at room temperature in solution. Results of this study demonstrate that there are noticeable differences in the reaction of each of metal–η^1-allyl and –cyclopropylmethyl complexes with SO_2, $MeS(O)_2NSO$, and $[MeS(O)_2N]_2S$. These differences are discussed.

Introduction

Reactions of SO_2 with complexes containing transition-metal–carbon σ bonds have been the subject of considerable research activity.[1] With metal–alkyl and –η^1-allyl complexes, insertion is the general outcome of reaction.[1,2] In contrast, with metal–propargyl and –cyclopropylmethyl complexes, cycloaddition is the common pattern of interaction of SO_2.[3-5]

N-Sulfinyl sulfonamides ($R'S(O)_2NSO$)[6] and sulfur bis(sulfonylimide)s ($[R'S(O)_2N]_2S$),[7] containing the cumulated double bonds N=S=O and N=S=N, respectively, represent close electronic and structural analogues of SO_2. Analogy between SO_2 and the aforementioned unsaturated compounds extends to their chemistry; for example, all three cumulenes behave as dienophiles.[6-8] Such a similarity of behavior prompted us further to explore chemical analogy of these species in the general context of reactivity toward complexes with metal–carbon σ bonds.

We have already reported our studies on reactions of metal–alkyl complexes with $R'S(O)_2NSO$ and $[R'S(O)_2N]_2S$.[9,10] Corresponding reactions of metal–propargyl complexes have received limited attention. The *N*-sulfinyl sulfonamide p-$MeC_6H_4S(O)_2NSO$ reacts with $CpFe(CO)_2CH_2C{\equiv}CPh$ and $Mn(CO)_5CH_2C{\equiv}CPh$ to yield [3 + 2] cycloaddition products which were isolated in low purity.[11] The related, but less electrophilic, *N*-sulfinylaniline, PhNSO, undergoes similar [3 + 2] cycloaddition reactions with iron–propargyl complexes.[11,12] No studies have been reported on reactions of metal–η^1-allyl and –cyclopropylmethyl complexes with $R'S(O)_2NSO$ and $[R'S(O)_2N]_2S$.

This paper is concerned with an investigation of the behavior of metal–η^1-allyl, –propargyl, and –cyclopropylmethyl complexes toward $R'S(O)_2NSO$ (R' = Me, Ph) and $[MeS(O)_2N]_2S$. Reactions of metal–η^1-allyl complexes with

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$[MeS(O)_2N]_2S$ surprisingly afford a novel class of [3 + 3] cycloaddition products, one member of which was characterized by X-ray diffraction analysis. Reactions of $CpFe(CO)_2CH_2CHCH_2CH_2$ with each of $MeS(O)_2NSO$ and $[MeS(O)_2N]_2S$, unlike the corresponding reaction with SO_2, yield both insertion and cycloaddition products. Some aspects of this study were communicated earlier in a preliminary form.[13]

Experimental Section

General Procedures. Reactions were conducted under an atmosphere of dry nitrogen and, unless otherwise indicated, at room temperature. Sample preparation and various manipulations of air- and/or moisture-sensitive materials were performed in a drybox filled with argon or on a vacuum line. Chromatography was done on columns packed with 60–100 mesh Florisil or deactivated (5% H_2O) neutral alumina (Aldrich). Melting points were measured on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Elemental analysis was done by Galbraith Laboratories, Inc., Knoxville, TN.

Physical Measurements. IR spectra were recorded on a Perkin-Elmer Model 337 spectrophotometer and were calibrated with polystyrene. ^1H NMR spectra were measured on Varian Associates EM-360L and EM-390 and Bruker WM-300 spectrometers with use of Me_4Si as an internal reference. $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker HX-80 or HX-90 spectrometer at 22.625 MHz in the FT mode with the assistance of Dr. C. E. Cottrell. Chemical shifts are reported relative to Me_4Si at δ 0.

Materials. All solvents were reagent grade quality and were purified further by the methods described by Jolly[14] prior to use. Commercially procured reagents were used as received. Literature procedures were employed to synthesize $MeS(O)_2NSO$,[6] $PhS(O)_2NSO$,[6] and $[MeS(O)_2N]_2S$.[7]

The metal complexes $CpFe(CO)_2CH_2C{\equiv}CR$ (R = Me[3], Ph[15]), $CpMo(CO)_3CH_2C{\equiv}CR$ (R = Me,[16] Ph[16]), $CpW(CO)_3CH_2C{\equiv}CPh$,[17] $CpCr(NO)_2CH_2C{\equiv}CPh$,[18] $Mn(CO)_5CH_2C{\equiv}CPh$,[15] $CpFe(CO)_2CH_2C(R){=}CH_2$ (R = H,[19] and Me[20]), $CpFe(CO)_2CH_2H{=}CMe_2$,[2] $CpMo(CO)_3CH_2C(R){=}CH_2$ (R = H,[21] Me[20]), $Mn(CO)_5CH_2CH{=}CH_2$,[22] and $CpFe(CO)_2CH_2CHCH_2CH_2$[4] were prepared by established methods.

Reactions of Metal–Propargyl and –η^1-Allyl Complexes with $R'S(O)_2NSO$ (R′ = Me, Ph) and $[MeS(O)_2N]_2S$. An equimolar amount or a slight excess of $R'S(O)_2NSO$ or $[MeS(O)_2N]_2S$ was added to the metal complex (2–13 mmol) dissolved in 25–30 mL of CH_2Cl_2, and the resulting mixture was stirred for 30 min. The reaction solution was then concentrated to ca. 5 mL and chromatographed on a 20 × 1-cm column of alumina or Florisil. The product was eluted with acetone, the effluent was evaporated to dryness, and the residue was redissolved in CH_2Cl_2 and crystallized by the addition of pentane. The resultant crystals were washed first with Et_2O and then with pentane and dried.

The chromatography step was omitted in all reactions of the manganese complexes and in the reactions of the metal–η^1-allyl complexes with $MeS(O)_2NSO$. Instead, pentane was added to the reaction solution after stirring to induce the precipitation of the product.

The reactions of $CpFe(CO)_2CH_2C(Me){=}CH_2$ and $CpMo(CO)_3CH_2C(Me){=}CH_2$ with $MeS(O)_2NSO$, and of $CpFe(CO)_2CH_2CH{=}CMe_2$ with $[MeS(O)_2N]_2S$, followed by workup as described above, resulted in the isolation of brown non-carbonyl decomposition materials. These reactions were not investigated further.

The products of reactions of metal–propargyl complexes with $R'S(O)_2NSO$ and $[MeS(O)_2N]_2S$, viz., $MC{=}C(R)S(O)N[S(O)_2R']CH_2$ (1) and $MC{=}C(R)S[NS(O)_2Me]N[S(O)_2Me]CH_2$ (3), respectively, and of metal–η^1-allyl complexes with $MeS(O)_2NSO$ and $[MeS(O)_2N]_2S$, viz., $MCHCH_2S(O)N[S(O)_2Me]CH_2$ (2) and $MC(R)CH_2N[S(O)_2Me]SN[S(O)_2Me]CH_2$ (4), respectively, are listed below together with their isolated yields, physical properties, spectroscopic data used for the characterization (^1H NMR, $^{13}C\{^1H\}$ NMR, and IR), and elemental analysis.

(i) $CpFe(CO)_2C{=}C(Ph)S(O)N[S(O)_2Me]CH_2$ (1a): 77%; yellow solid; mp 120 °C dec; ^1H NMR ($CDCl_3$) δ 7.37 (s, Ph), 4.74 (s, Cp, CH_2), 3.17 (s, Me); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 213.3 (2 CO), 158.2 (=CS), 150.3, 134.2, 131.0, 128.0 (Ph), 85.6 (Cp), 69.7 (CH_2), 42.3 (Me); IR ($CHCl_3$) ν(CO) 2030 (vs), 1985 (vs) cm^{-1}; IR (Nujol) $\nu(SO_2)$ 1345 (vs), 1160 (vs), ν(S=O) 1085 (s) cm^{-1}. Anal. Calcd for $C_{17}H_{15}FeNO_5S_2$: C, 47.13; H, 3.49. Found: C, 46.91; H, 3.17.

(ii) $CpFe(CO)_2C{=}C(Me)S(O)N[S(O)_2Ph]CH_2$ (1b): 70%; yellow solid; mp 123 °C dec; ^1H NMR ($CDCl_3$) δ 8.1–7.3 (m, Ph), 4.87 (Cp), 4.33 (s br, CH_2), 2.20 (s, Me); IR (Nujol) ν(CO) 2015 (vs), 1960 (vs), $\nu(SO_2)$ 1345 (vs), 1170 (vs), ν(S=O) 1085 (s) cm^{-1}.

(iii) $CpMo(CO)_3C{=}C(Ph)S(O)N[S(O)_2Me]CH_2$ (1c): 50%; yellow solid; mp 105 °C dec; ^1H NMR ($CDCl_3$) δ 7.39 (s, Ph), 5.30 (s, Cp), 4.85, 4.70 (AB q, $J_{H_A-H_B}$ = 14 Hz, CH_2), 3.19 (s, Me); IR (Nujol) ν(CO) 2015 (vs), 1960 (vs), $\nu(SO_2)$ 1345 (vs), 1170 (vs), ν(S=O) 1085 (s) cm^{-1}.

(iv) $CpFe(CO)_2CHCH_2S(O)N[S(O)_2Me]CH_2$ (2a): 66%; yellow solid; mp 143 °C dec; ^1H NMR ($CDCl_3$) δ 4.89, 4.88 (s × 2, Cp), 4.0–3.0 (m, 2 CH_2), 3.10 (s, Me), 2.9–2.7 (m, CH); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 215.2 (2 CO), 85.5 (Cp), 70.3 (SCH_2), 63.3 (NCH_2), 41.8 (Me), 9.8 (CH); IR ($CHCl_3$) ν(CO) 2015 (vs), 1970 (vs) cm^{-1}; IR (Nujol) $\nu(SO_2)$ 1335 (vs), 1155 (vs), ν(S=O) 1080 (s) cm^{-1}. Anal. Calcd for $C_{11}H_{13}FeNO_5S_2$: C, 36.78; H, 3.64. Found: C, 36.61; H, 3.61.

(v) $CpMo(CO)_3CHCH_2S(O)N[S(O)_2Me]CH_2$ (2b): 67%; yellow solid; mp 153 °C dec; ^1H NMR ($CDCl_3$) δ 5.42 (s, Cp), 4.2–3.0 (m, 2 CH_2), 3.10 (s, Me), 2.8–2.7 (m, CH); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 227.9 (3 CO), 93.0 (Cp), 69.7 (SCH_2), 63.1 (NCH_2), 41.8 (Me), 7.2 (CH); IR ($CHCl_3$) ν(CO) 2015 (vs), 1960 (vs), 1915 (vs) cm^{-1}; IR (Nujol) $\nu(SO_2)$ 1320 (vs), 1160 (vs), ν(S=O) 1080 (vs) cm^{-1}. Anal. Calcd for $C_{12}H_{13}MoNO_6S_2$: C, 33.73; H, 3.07. Found: C, 33.73; H, 3.14.

(vi) $Mn(CO)_5CHCH_2S(O)N[S(O)_2Me]CH_2$ (2c): 63%; white solid; mp 128 °C dec; ^1H NMR ($CDCl_3$) δ 4.3–3.3 (m, 2 CH_2), 3.13 (s, Me), 3.0–2.7 (m, CH); IR (Nujol) ν(CO) 2115 (m), 1990 (vs br), $\nu(SO_2)$ 1340 (vs), 1165 (vs), ν(S=O) 1105 (m) cm^{-1}.

(vii) $CpFe(CO)_2C{=}C(Ph)S[NS(O)_2Me]N[S(O)_2Me]CH_2$ (3a): 69%; yellow solid; mp 140 °C dec; ^1H NMR ($CDCl_3$) δ 7.65–7.2 (m, Ph), 4.96 (s, Cp), 4.74 (s br, CH_2), 3.24 (s, Me), 2.80 (s, Me); IR ($CHCl_3$) ν(CO) 2025 (vs), 1980 (vs) cm^{-1}; IR (Nujol) $\nu(SO_2)$ 1330 (s), 1275 (s), 1160 (s), 1130 (s), ν(S=N) 1010 (s br) cm^{-1}. Anal. Calcd for $C_{18}H_{18}FeN_2O_6S_3$: C, 42.36; H, 3.56. Found: C, 42.49; H, 3.78.

(viii) $CpMo(CO)_3C{=}C(Ph)S[NS(O)_2Me]N[S(O)_2Me]CH_2$ (3b): 55%; yellow solid; mp 150 °C dec; ^1H NMR ($CDCl_3$) δ 7.8–7.35 (m, Ph), 5.46 (s, Cp), 4.96, 4.83 (AB q, $J_{H_A-H_B}$ = 13 Hz, CH_2), 3.35 (s, Me), 2.90 (s, Me); IR ($CHCl_3$) ν(CO) 2040 (vs), 1970 (vs), 1950 (vs) cm^{-1}; IR (Nujol) $\nu(SO_2)$ 1340 (s), 1280 (s), 1165 (s), 1130 (s), ν(S=N) 1010 (s br) cm^{-1}. Anal. Calcd for $C_{19}H_{18}MoN_2O_7S_3$: C, 39.45; H, 3.14. Found: C, 39.29; H, 3.30.

(ix) $CpMo(CO)_3C{=}C(Me)S[NS(O)_2Me]N[S(O)_2Me]CH_2$ (3c): 57%; yellow solid; mp 150 °C dec; ^1H NMR ($CDCl_3$) δ 5.46 (s, Cp), 4.91 (s br, CH_2), 3.17 (s, SMe), 2.90 (s, SMe), 2.12 (s, CMe); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 93.3 (Cp), 69.7 (CH_2), 43.3, 41.9 (2 SMe), 16.6 (C*Me*); IR ($CHCl_3$) ν(CO) 2040 (vs), 1965 (vs), 1945 (vs) cm^{-1}; IR (Nujol) $\nu(SO_2)$ 1345 (s), 1280 (s), 1165 (s), 1130 (s), ν(S=N) 1000 (s br) cm^{-1}. Anal. Calcd for $C_{14}H_{16}MoN_2O_7S_3$: C, 32.56; H, 3.12. Found: C, 32.79; H, 3.21.

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(x) $CpW(CO)_3\overline{C{=}C(Ph)S[NS(O)_2Me]N[S(O)_2Me]CH_2}$ (3d): 53%; yellow solid; mp 124 °C dec; ^1H NMR ($CDCl_3$) δ 7.8–7.4 (m, Ph), 5.49 (s, Cp), 5.04, 4.90 (AB q, $J_{H_A-H_B}$ = 15 Hz, CH_2), 3.34 (s, Me), 2.91 (s, Me); IR ($CHCl_3$) ν(CO) 2025 (vs), 1935 (vs br) cm^{-1}; IR (Nujol) ν(SO_2) 1335 (s), 1275 (s), 1165 (s), 1130 (s), ν(S=N) 1010 (s br) cm^{-1}.

(xi) $CpCr(NO)_2\overline{C{=}C(Ph)S[NS(O)_2Me]N[S(O)_2Me]CH_2}$ (3e): 58%; green solid; ^1H NMR ($CDCl_3$) δ 7.7–7.3 (m, Ph), 5.49 (s, Cp), 4.98 (s br, CH_2), 3.36 (s, Me), 2.92 (s, Me); IR ($CHCl_3$) ν(NO) 1800 (vs), 1700 (vs) cm^{-1}; IR (Nujol) ν(SO_2) 1340 (s), 1280 (s), 1150 (s), 1125 (s), ν(S=N) 1000 (s br) cm^{-1}.

(xii) $Mn(CO)_5\overline{C{=}C(Ph)S[NS(O)_2Me]N[S(O)_2Me]CH_2}$ (3f): 70%; white solid; mp 135 °C dec; ^1H NMR ($CDCl_3$) δ 7.9–7.4 (m, Ph), 5.01 (s br, CH_2), 3.44 (s, Me), 2.90 (s, Me); IR ($CHCl_3$) ν(CO) 2125 (m), 2065 (w), 2025 (vs br) cm^{-1}; IR (Nujol) ν(SO_2) 1345 (s), 1280 (s), 1150 (s), 1125 (s), ν(S=N) 1010 (s br) cm^{-1}. Anal. Calcd for $C_{16}H_{13}MnN_2O_9S_3$: C, 36.37; H, 2.48; N, 5.30. Found: C, 36.23; H, 2.53; N, 5.14.

(xiii) $CpFe(CO)_2\overline{CHCH_2N[S(O)_2Me]SN[S(O)_2Me]CH_2}$ (4a): 75%; yellow solid; mp 130 °C dec; ^1H NMR ($CDCl_3$) δ 4.80 (s, Cp), 4.4–3.5 (m, 2 CH_2), 3.03 (s, 2 Me), 2.85 (m, CH); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 215.6 (2 CO), 84.5 (Cp), 62.2 (2 CH_2), 40.8 (2 Me), 19.5 (CH); IR ($CHCl_3$) ν(CO) 1995 (vs), 1920 (vs) cm^{-1}; IR (Nujol) ν(SO_2) 1320 (s), 1155 (s) cm^{-1}. Anal. Calcd for $C_{12}H_{16}FeN_2O_6S_3$: C, 33.03; H, 3.70; N, 6.42. Found: C, 33.05; H, 3.74; N, 6.23.

(xiv) $CpFe(CO)_2\overline{C(Me)CH_2N[S(O)_2Me]SN[S(O)_2Me]CH_2}$ (4b): 63%; yellow solid; mp 80 °C dec; ^1H NMR ($CDCl_3$) δ 4.85 (s, Cp), 4.29, 4.04 (AB q, $J_{H_A-H_B}$ = 14.5 Hz, 2 CH_2), 3.14 (s, 2 SMe), 1.58 (s, CMe); IR ($CHCl_3$) ν(CO) 2005 (vs), 1950 (vs) cm^{-1}; IR (Nujol) ν(SO_2) 1325 (s), 1150 (s) cm^{-1}. Anal. Calcd for $C_{13}H_{18}FeN_2O_6S_3$: C, 34.67; H, 4.03; N, 6.22. Found: C, 34.54; H, 4.23; N, 6.11.

(xv) $CpMo(CO)_3\overline{CHCH_2N[S(O)_2Me]SN[S(O)_2Me]CH_2}$ (4c): 63%; yellow solid; mp 140 °C dec; ^1H NMR ($CDCl_3$) δ 5.47 (s, Cp), 4.48–3.75 (m, 2 CH_2), 3.14 (s, 2 Me); IR ($CHCl_3$) ν(CO) 2025 (vs), 1940 (vs br) cm^{-1}; IR (Nujol) ν(SO_2) 1350 (s), 1325 (s), 1160 (s), 1150 (s) cm^{-1}. Anal. Calcd for $C_{13}H_{16}MoN_2O_7S_3$: C, 30.96; H, 3.20. Found: C, 30.77; H, 3.26.

(xvi) $CpMo(CO)_3\overline{C(Me)CH_2([S(O)_2Me]SN[S(O)_2Me]CH_2}$ (4d): 15%; yellow solid; mp 70 °C dec; ^1H NMR ($CDCl_3$) δ 5.25 (s, Cp), 4.09 (s br, 2 CH_2), 2.93 (s, 2 SMe), 1.58 (s, CMe); IR (Nujol) ν(CO) 2020 (vs), 1950 (vs), 1920 (vs), ν(SO_2) 1320 (s), 1165 (s), 1155 (s) cm^{-1}.

(xvii) $Mn(CO)_5\overline{CHCH_2N[S(O)_2Me]SN[S(O)_2Me]CH_2}$ (4e): 60%; white solid; mp 140 °C dec; ^1H NMR ($CDCl_3$) δ 4.5–3.95 (m, 2 CH_2), 3.11 (s, 2 Me), 2.4 (m, CH); IR (Nujol) ν(CO) 2115 (m), 2000 (vs br), ν(SO_2) 1340 (s), 1330 (s), 1160 (s), 1155 (s) cm^{-1}.

Reaction of $CpFe(CO)_2CH_2\overline{CHCH_2CH_2}$ with $MeS(O)_2NSO$. A solution containing 1.0 g (4.3 mmol) of the title complex in 15 mL of CH_2Cl_2 was treated dropwise with 0.60 g (4.3 mmol) of $MeS(O)_2NSO$. The resulting solution was stirred for 30 min, during which time it changed color from yellow to red. It was then chromatographed on a 40 × 1-cm column of Florisil. Upon elution with 5:1 CH_2Cl_2–acetone, two bands developed. The faster moving yellow band was eluted with 5:1 CH_2Cl_2–acetone whereas the trailing red band was removed from the column with acetone. The latter solution was evaporated to dryness to afford a red solid (0.30 g, 19%), 5, which was further purified by recrystallization from 20 mL of 1:3 CH_2Cl_2–pentane: mp 112 °C dec; ^1H NMR ($CDCl_3$) δ 5.22 (s, Cp), 2.94 (s, Me), 2.58 (d, J_{H-H} = 7.0 Hz, SCH_2), 1.0–0.2 (m, $\overline{CHCH_2CH_2}$); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 85.7 (Cp), 63.8 (SCH_2), 42.1 (Me), 5.6 (CH), 5.0 (2 CCH_2C); IR ($CHCl_3$) ν(CO) 2030 (vs), 2000 (vs) cm^{-1}; IR (Nujol) ν(SO_2) 1330 (s), 1130 (s), ν(S=O) 1060 (s) cm^{-1}. Anal. Calcd for $C_{12}H_{15}FeNO_5S_2$: C, 38.62; H, 4.05. Found: C, 38.73; H, 4.12.

The yellow effluent was evaporated to dryness to furnish 0.8 g (50%) of 7 as a mixture of diastereomers, 7A and 7B, which were separated by fractional crystallization. A solution of 0.5 g of the yellow solid in 10 mL of CH_2Cl_2 was treated dropwise with pentane (26 mL) until precipitation just began. The volume of the solution was reduced in a stream of N_2 to induce the precipitation of 0.3 g of material which was collected by filtration and washed with 5 mL of pentane. It was shown by ^1H NMR spectroscopy to be ca. 85:15 **7B**/**7A**. Pentane (10 mL) was added to the filtrate to precipitate 0.15 g of spectroscopically (^1H NMR) pure **7A**. The 85:15 **7B**/**7A** was dissolved in CH_2Cl_2 and treated dropwise with pentane until crystallization just started. An additional 2 mL of pentane was introduced, and the yellow crystals were collected by filtration and characterized by ^1H NMR spectroscopy as pure **7B**. **7A**: mp 152 °C dec; ^1H NMR ($CDCl_3$) δ 4.88 (s, Cp), 3.10 (s, Me), 3.1–0.9 (m, $CH_2CHCH_2CH_2$); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 85.7 (Cp), 72.2 (SCH_2), 53.6 (NCH_2), 43.3 (Me), 30.4 (CCH_2C), 4.7 (CH); IR ($CHCl_3$) ν(CO) 2005 (vs), 1940 (vs) cm^{-1}; IR (Nujol) ν(SO_2) 1340 (s), 1150 (s), ν(S=O) 1115 (s) cm^{-1}. Anal. Calcd for $C_{12}H_{15}FeNO_5S_2$: C, 38.62; H, 4.05. Found (**7A,B** mixture): C, 38.36; H, 4.09. **7B**: mp 154 °C dec; ^1H NMR ($CDCl_3$) δ 4.87 (s, Cp), 3.23 (s, Me), 3.1–0.9 (m, $CH_2CHCH_2CH_2$); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 85.6 (Cp), 75.0 (SCH_2), 54.9 (NCH_2), 46.6 (Me), 33.4 (CCH_2C), 5.6 (CH); IR (low resolution) indistinguishable from that of **7A**.

Reaction of $CpFe(CO)_2CH_2\overline{CHCH_2CH_2}$ with $[MeS(O)_2N]_2S$. This reaction was carried out in a manner strictly analogous to that of the title complex with $MeS(O)_2NSO$. A similar workup procedure afforded a red insertion product, 6, in 52% yield and a yellow cycloaddition product as a mixture of diastereomers, 8A and 8B, in 28% yield. The diastereomers were separated by using the same procedure of fractional crystallization as for **7A,B**, with **8A** being designated as the less soluble isomer. 6: mp 140 °C dec; ^1H NMR ($CDCl_3$) δ 5.31 (Cp), 3.09 (s, Me) 2.99 (s, Me), 3.2–2.5 (m, SCH_2), 1.0–0.3 (m, $\overline{CHCH_2CH_2}$); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 85.8 (Cp), 60.0 (SCH_2), 43.0, 42.6 (2 Me), 5.9, 5.4, 5.0 ($\overline{CHCH_2CH_2}$); IR ($CHCl_3$) ν(CO) 2050 (vs), 2000 (vs) cm^{-1}; IR (Nujol) ν(SO_2) 1295 (s), 1285 (s), 1135 (s), 1125 (s), ν(S=N) 1005 (s) cm^{-1}. Anal. Calcd for $C_{13}H_{18}FeN_2O_6S_3$: C, 34.67; H, 4.03. Found: C, 34.55; H, 4.07. **8A**: mp 125 °C dec; ^1H NMR ($CDCl_3$) δ 4.89 (s, Cp), 3.41 (s, Me), 3.00 (s, Me), 3.4–2.3 (m, $CH_2CHCH_2CH_2$); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 86.0 (Cp), 75.9 (SCH_2), 53.3 (NCH_2), 44.1, 43.1 (2 Me), 35.7 (CCH_2C), 8.0 (CH); IR ($CHCl_3$) ν(CO) 2005 (vs), 1945 (vs) cm^{-1}; IR (Nujol) ν(SO_2) 1340 (s), 1285 (s), 1150 (s), 1130 (s), ν(S=N) 1020 (s) cm^{-1}. Anal. Calcd for $C_{13}H_{18}FeN_2O_6S_3$: C, 34.67; H, 4.03. Found: C, 34.47; H, 4.10. **8B**: mp 115 °C dec; ^1H NMR ($CDCl_3$) δ 4.87 (s, Cp), 3.40 (s, Me), 2.99 (s, Me), 3.4–2.2 (m, $CH_2CHCH_2CH_2$); IR (low resolution) indistinguishable from that of **8A**.

Crystallographic Analysis of $CpFe(CO)_2\overline{CHCH_2N[S(O)_2Me]SN[S(O)_2Me]CH_2}$ (4a). Crystals suitable for X-ray diffraction work were grown from a solution of CH_2Cl_2 and pentane by evaporation at low temperature. Preliminary examination of the diffraction pattern on a Syntex P$\bar{1}$ diffractometer equipped with graphite-monochromated Mo Kα radiation revealed a monoclinic cell with systematic absences $h0l$, $h + l = 2n + 1$ and $0k0$, $k = 2n + 1$. The space group is uniquely determined as $P2_1/n$.[23] Unit cell parameters were determined by the least-squares fit of the diffractometer setting angles for 35 reflections in the 2θ range 21–30°.

The crystal used in data collection was a rectangular prism approximately 0.15 × 0.15 × 0.40 mm in size. Intensity data were collected by the θ–2θ scan technique. Ten standard reflections were measured after every 100 reflections and indicated a small rate of crystal decay. The data were corrected for Lorentz and polarization effects and for the slight decay and were put on an approximately absolute scale by means of a Wilson plot.[24] An

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(23) The original unit cell reported for this structure in ref 13 was a = 10.380 (7) Å, b = 19.656 (1) Å, c = 12.437 (8) Å, and β = 137.446 (4)° with space group $P2_1/c$. In this work the cell has been transformed to an alternative setting $P2_1/n$ by the matrix

$$\begin{pmatrix} \bar{1} & 0 & \bar{1} \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix}$$

(24) CRYM crystallographic computing package: Duchamp, D. J.; Trus, B. L.; Westphal, B. J. (1964), California Institute of Technology, Pasadena, CA, and modified by G. G. Christoph at The Ohio State University.

Table I. Crystallographic Details for 4a

mol formula	$C_{12}H_{16}FeN_2O_6S_3$
mol wt	436.31
space group	$P2_1/n$
a, Å	8.500 (1)
b, Å	19.656 (1)
c, Å	10.380 (1)
β, deg	98.25 (1)
V, Å^3	1716
Z	4
ρ_{calcd}, g cm^{-3}	1.688
bounding planes	$\{12\bar{1}\}$, $(\bar{1}02)$, $(30\bar{1})$, (021)
crystal vol, mm^3	0.008 67
radiatn	graphite-monochromated Mo $K\alpha$ ($\lambda(K\alpha_1)$ = 0.709 26 Å)
linear abs coeff, cm^{-1}	12.57
transmissn factors	0.823–0.850
temp, °C	20 (1)
2θ limits, deg	4–61
scan speed	3–12°/min in 2θ
background time/scan time	0.5
scan range	1.0° below $K\alpha_1$ to 1.1° above $K\alpha_2$
data collected	$+h,+k,\pm l$
unique data	5274
unique data, with $F_o^2 > 3\sigma(F_o^2)$	2226
final no. of variables	217
$R(F)^a$	0.113
$R_w(F^2)$	0.100
error in observn of unit weight, e^2	1.26
R (for $F_o^2 > 3\sigma(F_o^2)$)	0.051

[a] Definitions of the R factors are $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w(F^2) = [\sum w^2(|F_o|^2 - |F_c|^2)^2/\sum w^2|F_o|^4]^{1/2}$ where $w = 1/\sigma(F_o^2)$.

Table II. Positional Parameters of Non-Hydrogen Atoms of 4a, with Estimated Standard Deviations in Parentheses

atom	x	y	z
Fe	0.44282 (6)	0.76394 (3)	0.87842 (6)
S(1)	0.41405 (12)	0.51311 (5)	0.68426 (10)
S(2)	0.27185 (11)	0.51855 (5)	0.92379 (10)
S(3)	−0.04136 (11)	0.57001 (5)	0.81889 (11)
O(1)	0.53500 (40)	0.72613 (17)	1.14795 (32)
O(2)	0.14578 (34)	0.82112 (14)	0.93421 (30)
O(3)	−0.13655 (29)	0.62229 (14)	0.86222 (32)
O(4)	−0.07959 (30)	0.50068 (13)	0.83869 (28)
O(5)	0.47648 (49)	0.56550 (15)	0.61236 (31)
O(6)	0.26495 (33)	0.48324 (17)	0.63588 (30)
N(1)	0.40959 (32)	0.54373 (13)	0.83260 (28)
N(2)	0.13883 (31)	0.58281 (14)	0.89514 (29)
C(1)	0.50067 (45)	0.74025 (20)	1.03921 (46)
C(2)	0.26028 (48)	0.79804 (18)	0.90991 (37)
C(3)	0.34288 (38)	0.66755 (17)	0.84210 (34)
C(4)	0.20635 (38)	0.65221 (17)	0.91995 (38)
C(5)	0.47384 (38)	0.61335 (17)	0.86715 (38)
C(6)	−0.03844 (49)	0.58133 (21)	0.65182 (44)
C(7)	0.55301 (46)	0.44742 (20)	0.71033 (43)
C(8)	0.50678 (67)	0.85537 (23)	0.79353 (68)
C(9)	0.45007 (59)	0.80915 (35)	0.69532 (55)
C(10)	0.54836 (79)	0.75219 (27)	0.70821 (57)
C(11)	0.66753 (55)	0.76337 (26)	0.81475 (62)
C(12)	0.63923 (62)	0.82785 (27)	0.86533 (55)

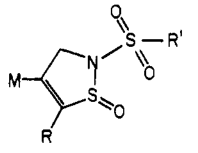
analytical absorption correction was also applied to the data. Crystallographic details appear in Table I.

The structure was solved by the direct methods program MULTAN74[25] by which the position of the iron atom was located. The whole molecule was elucidated by several cycles of structure factor and Fourier calculations. The structure was refined by the full-matrix least-squares procedure of the CRYM package,[24] with the following function minimized: $\sum w^2(|F_o|^2 - |F_c|^2)^2$ with $w = {}^1/\sigma(F_o^2)$. Hydrogen atoms were located on difference electron density maps and were included in the model as fixed contributions in calculated positions. All the 5274 unique reflections were used in the refinement. The final refinement cycle on the 217 variables (anisotropic non-hydrogen atoms, hydrogen atoms fixed) yielded $R(F)$ = 0.113 and $R_w(F^2)$ = 0.100. A structure factor calculation for the intensities with $F_o^2 > 3\ \sigma(F_o^2)$ yielded an $R(F)$ value of 0.051 at this point. The largest peak in the final difference electron density map is 1.1 e Å^{-3} and is located in the vicinity of the iron atom. Atomic scattering factors for the non-hydrogen atoms[26a] and for the hydrogen atoms[26b] are from the usual sources.

Positional parameters of the non-hydrogen atoms are given in Table II. Listings of temperature factors, hydrogen atom coordinates, and structure factors are available as supplementary material.[27]

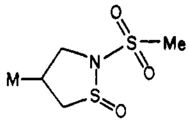
Results

Reactions of Metal–Propargyl and –η^1-Allyl Complexes with $R'S(O)_2NSO$ (R′ = Me, Ph). Propargyl and unsubstituted η^1-allyl complexes of (η^5-cyclopentadienyl)iron and -molybdenum carbonyls and manganese pentacarbonyl react at room temperature with $R'S(O)_2NSO$ to afford 50–77% isolated yields of [3 + 2] cycloaddition products **1a–c** and **2a–c**, respectively, as stable solids. However, corresponding reactions of the η^1-2-methylallyl complexes $CpFe(CO)_2CH_2C(Me){=}CH_2$ and $CpMo(CO)_3CH_2C(Me){=}CH_2$ resulted in the formation of brown non-carbonyl decomposition materials. Complexes **1** and **2** were characterized by elemental analysis and by a comparison of their spectroscopic properties (Experimental Section) with those of analogous [3 + 2] cycloaddition complexes and similar organic compounds.



1

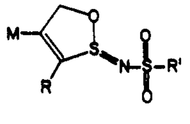
a M = CpFe(CO)$_2$, R = Ph, R′ = Me
b M = CpFe(CO)$_2$, R = Me, R′ = Ph
c M = CpMo(CO)$_3$, R = Ph, R′ = Me



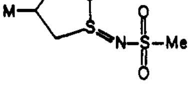
2

a M = CpFe(CO)$_2$
b M = CpMo(CO)$_3$
c M = Mn(CO)$_5$

In the IR spectra of complexes **1** and **2** the positions of the ν(CO) bands are very similar to those reported for related cycloaddition products.[3,4,11,18,28,29] Moreover, $\nu(SO_2)$ absorptions at 1345–1320 and 1165–1155 cm^{-1} and a ν(S=O) absorption at 1105–1080 cm^{-1} compare well with the corresponding absorptions in the spectra of various 3,6-dihydro-N-arenesulfonyl-1,2-thiazine 1-oxides, $CH(R)C(R'){=}C(R'')CH(R''')N[S(O)_2C_6H_4X\text{-}p]SO$.[30] No ν(S=N) band is observed around 1000 cm^{-1} [30] in the IR spectra of **1** and **2**, thus militating against the alternative structures **I** and **II**, respectively, in which the sulfinyl oxygen and the $NS(O)_2R'$ nitrogen have exchanged positions.



I



II

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[26] (a) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV. (b) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

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

[28] Cutler, A.; Ehntholt, D.; Giering, W. P.; Lennon, P.; Raghu, S.; Rosan, A.; Rosenblum, M.; Tancrede, J.; Wells, D. *J. Am. Chem. Soc.* **1976**, *98*, 3495.

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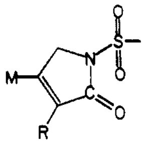
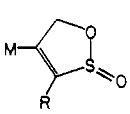
[30] Wucherpfennig, W.; Kresze, G. *Tetrahedron Lett.* **1966**, 1671.

Structure I for complexes 1 is also precluded by the appearance of ^1H NMR signals of the NCH_2 group at δ 4.85–4.33. This is in the range found[29] for similar γ-lactam cycloadducts III. By comparison, corresponding resonances of the OCH_2 group of IV occur at lower fields, δ 5.72–5.06.[3]



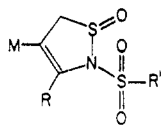
III



IV

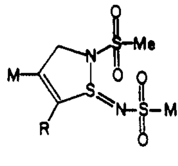
It is worthy of note that the ^1H NMR spectrum of **2a** shows two Cp resonances at δ 4.89 and 4.88 in the ratio 78:22, respectively. This may be attributed to the presence of diastereomers, since there are chiral centers at the CH carbon and SO sulfur. The other complexes **2** synthesized in this study do not reveal diastereomers in their NMR spectra.

$^{13}C\{^1H\}$ NMR spectra of **1a** and **2a**,**b** are entirely consistent with the proposed structures and rule out the possibility of insertion into the metal–carbon bond instead of cycloaddition of $R'S(O)_2NSO$. However, the combined available spectroscopic evidence cannot exclude a closely related cycloaddition structure V for complexes **1**. Nevertheless, we think that such a structure is unlikely for mechanistic reasons (see Discussion) which are backed by the X-ray diffraction results on $CpFe(CO)_2C{=}C(Me)S(O)OCH_2$[31] and *trans*-$CpFe(CO)_2CHCH(Ph)C(O)N[S(O)_2NHPh]CH_2$.[32] These two complexes, obtained by reaction of $CpFe(CO)_2CH_2C{\equiv}CMe$ with SO_2 and by successive treatment of $CpFe(CO)_2CH_2CH{=}CHPh$ with $ClS(O)_2NCO$ and $PhNH_2$, respectively, show ring structures that are derived by addition of the electrophilic atom of the unsaturated reagent to the multiple carbon–carbon bond of the propargyl and η^1-allyl ligand.

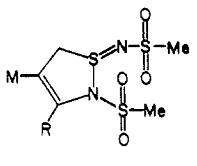


V

Reactions of Metal–Progargyl and -η^1-Allyl Complexes with $[MeS(O)_2N]_2S$. The propargyl complexes $CpFe(CO)_2CH_2C{\equiv}CPh$, $CpMo(CO)_3CH_2C{\equiv}CR$ (R = Me, Ph), $CpW(CO)_3CH_2C{\equiv}CPh$, $CpCr(NO)_2CH_2C{\equiv}CPh$, and $Mn(CO)_5CH_2C{\equiv}CPh$ react with $[MeS(O)_2N]_2S$ at ambient temperatures to afford stable solid products in 53–70% isolated yields. These products are formulated as the [3 + 2] cycloadducts **3a–f** from spectroscopic data and elemental analysis. Thus, the presence of an exocyclic $=NS(O)_2Me$ group is indicated by the appearance of a $\nu(S{=}N)$ band at 1010–1000 cm^{-1} in the IR spectra.[30] There are also four IR $\nu(SO_2)$ absorptions, supporting the existence of different environments for the two $S(O)_2Me$ groups. The ^1H and $^{13}C\{^1H\}$ NMR spectra are in complete accord with the assigned structures but, as for complexes **1**, do not unequivocally eliminate the alternative ring arrangement VI. The latter is, however, unlikely on mechanistic grounds.



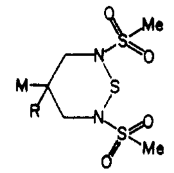
3



VI

a M = $CpFe(CO)_2$, R = Ph
b M = $CpMo(CO)_3$, R = Ph
c M = $CpMo(CO)_3$, R = Me
d M = $CpW(CO)_3$, R = Ph
e M = $CpCr(NO)_2$, R = Ph
f M = $Mn(CO)_5$, R = Ph

Reactions of η^1-allyl, including η^1-2-methylallyl, complexes of (η^5-cyclopentadienyl)iron and -molybdenum carbonyls and manganese pentacarbonyl with $[MeS(O)_2N]_2S$ occur readily at room temperature and lead to the isolation of stable solid products **4a–e** generally in 60–75% yields. The IR spectra of **4** show $\nu(SO_2)$ absorptions at 1350–1320 and 1165–1150 cm^{-1} but no absorption attributable to $\nu(S{=}N)$ around 1000 cm^{-1}.[30] The absence of an exocyclic $=NS(O)_2Me$ group in the structure of **4** is also indicated by the ^1H and $^{13}C\{^1H\}$ NMR spectra. The two $S(O)_2Me$ groups appear equivalent, and their proton chemical shifts are almost identical with those of **2**, where the nitrogen of the $-NS(O)_2Me$ fragment is also endocyclic.



4

a M = $CpFe(CO)_2$, R=H
b M = $CpFe(CO)_2$, R=Me
c M = $CpMo(CO)_3$, R=H
d M = $CpMo(CO)_3$, R=Me
e M = $Mn(CO)_5$, R=H

Besides indicating the equivalence of the $S(O)_2Me$ groups, the ^1H and $^{13}C\{^1H\}$ NMR spectra of **4** demonstrate that the two CH_2 groups are equivalent. Accordingly, the ^1H NMR spectrum of **4b** shows the signal of the CH_2 groups as an AB quartet, with $J_{H_A-H_B}$ = 14.5 Hz. For the related complex **4d**, this resonance appears as a broad singlet. In the spectrum of **4a**, the signals of CH_2CHCH_2 are seen as multiplets at δ 4.4–3.5 (4 H) and 2.85 (center, 1 H). Upon irradiation at the frequency of the CH proton at δ 2.85, the multiplet at δ 4.4–3.5 collapses to an AB pattern (δ 4.25, 3.83; $J_{H_A-H_B}$ = 14 Hz). In agreement with these results, the $^{13}C\{^1H\}$ NMR spectrum of **4a** shows only one signal for the CH_2 groups. The aforementioned data strongly support structure **4** for these cycloaddition products. Final proof of the structure was provided by a single-crystal X-ray analysis of **4a** which is considered later in the paper.

Reactions of $CpFe(CO)_2CH_2CHCH_2CH_2$ with $MeS(O)_2NSO$ and $[MeS(O)_2N]_2S$. Reaction of the title iron complex with $MeS(O)_2NSO$ at room temperature affords the red insertion product **5** and the yellow cycloaddition product **7** in 19 and 50% yields, respectively. The corresponding reaction with $[MeS(O)_2N]_2S$ also gives insertion and cycloaddition products, **6** and **8**, in 52 and 28% yields, respectively. Solutions of **5** and **6** in $CDCl_3$ show no change

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(31) Churchill, M. R.; Wormald, J. *J. Am. Chem. Soc.* **1971**, *93*, 354.
(32) Hu, Y.-R.; Calligaris, M.; Nardin, G.; Wojcicki, A., to be submitted for publication.

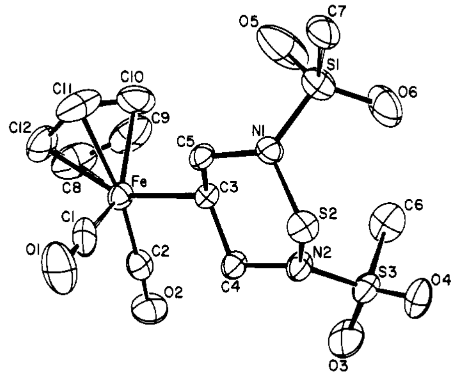
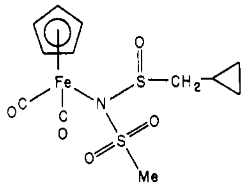


Figure 1. ORTEP drawing of **4a**, showing atom numbering scheme. Non-hydrogen atoms are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

in their ^1H NMR spectra after storage for 24 h to rule out partial conversion of these insertion products to the corresponding cycloadducts **7** and **8** during the reaction.



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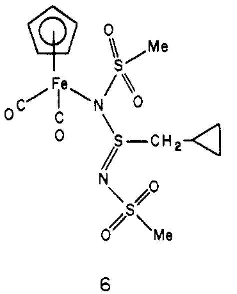
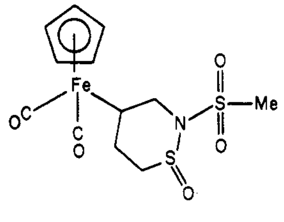


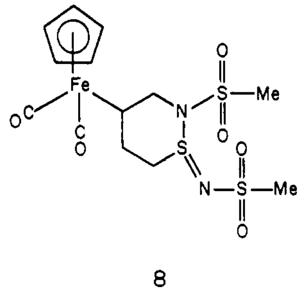
6

The insertion complexes **5** and **6** are strictly analogous to other complexes $CpFe(CO)_2\{N[S(O)_2Me]S(O)R\}$ and $CpFe(CO)_2\{N(S(O)_2Me]S(R)NS(O)_2Me\}$, obtained by the respective reactions of $CpFe(CO)_2R$ with $MeS(O)_2NSO$ and $[MeS(O)_2N]_2S$.[9] They were characterized by use of the appropriate IR and ^1H and $^{13}C\{^1H\}$ NMR data, as detailed elsewhere,[9] in conjunction with elemental analysis. The presence of a characteristic multiplet at δ 1.0–0.2 in the ^1H NMR spectra[33] and of the resonance at δ 6–5 in the $^{13}C\{^1H\}$ NMR spectra[34] shows that the cyclopropyl ring remains intact in **5** and **6**.

The cycloaddition complexes **7** and **8** were obtained as mixtures of diastereomers (chiral centers at the CH carbon and the endocyclic sulfur), which differ slightly in their ^1H and $^{13}C\{^1H\}$ NMR spectra. The diastereomers were completely separated in each case by fractional crystallization from CH_2Cl_2–pentane.



7



8

The infrared spectra of the diastereomers **7a** and **7b** show ν(CO), $\nu(SO_2)$, and ν(S=O) absorptions that are very similar to those of complexes **2**. They thus suggest the presence of a similar heterocyclic ring. Likewise, the spectra of the diastereomers **8a** and **8b** reveal $\nu(SO_2)$ and ν(S=N) bands that are comparable to those found for complexes **3**, again suggesting similarities in structure. The ^1H and $^{13}C\{^1H\}$ NMR spectra of the diastereomers of **7** and **8** are consistent with the presence of a $CH_2CHCH_2CH_2$ fragment and indicate the absence of a cyclopropyl ring. The heterocyclic structures $FeCHCH_2CH_2S(X)N[S(O)_2Me]CH_2$, rather than $FeCHCH_2CH_2N[S(O)_2Me]S(X)CH_2$ (X = O, $NS(O)_2Me$), are suggested on the basis of the mechanism proposed[4] for the related reactions of $CpFe(CO)_2CH_2CHCH_2CH_2$ with SO_2 and tetracyanoethylene. However, the heterocyclic arrangement alternative to that present in **7** and **8** cannot be ruled out from the available spectroscopic data.

Table III. Bond Distances (Å) for 4a, with Estimated Standard Deviations in Parentheses

Fe–C(1)	1.735 (5)	S(3)–C(6)	1.752 (5)
Fe–C(2)	1.763 (4)	S(2)–N(1)	1.682 (3)
Fe–C(3)	2.089 (7)	S(2)–N(2)	1.693 (3)
Fe–C(8)	2.107 (5)	N(1)–C(5)	1.498 (4)
Fe–C(9)	2.107 (6)	N(2)–C(4)	1.488 (4)
Fe–C(10)	2.106 (6)	C(3)–C(4)	1.536 (5)
Fe–C(11)	2.109 (4)	C(3)–C(5)	1.536 (7)
Fe–C(12)	2.109 (5)	C(1)–O(1)	1.158 (6)
S(1)–N(1)	1.659 (3)	C(2)–O(2)	1.135 (4)
S(1)–O(5)	1.419 (3)	C(8)–C(9)	1.399 (9)
S(1)–O(6)	1.421 (3)	C(9)–C(10)	1.392 (8)
S(1)–C(7)	1.745 (4)	C(10)–C(11)	1.406 (8)
S(3)–N(2)	1.639 (3)	C(11)–C(12)	1.406 (7)
S(3)–O(3)	1.420 (3)	C(8)–C(12)	1.369 (7)
S(3)–O(4)	1.423 (3)		

Molecular Structure of $CpFe(CO)_2CHCH_2N[S(O)_2Me]SN[S(O)_2Me]CH_2$ (4a). Figure 1 shows the molecular structure of **4a**. The six-membered heterocyclic ring is derived by [3 + 3] cycloaddition of the N=S=N fragment of $[MeS(O)_2N]_2S$ to carbons 1 and 3 of the η^1-allyl ligand of $CpFe(CO)_2CH_2CH=CH_2$ with 1,2 metal migration.

The bond distances and angles within the $CpFe(CO)_2$ moiety are similar to those reported[10,31,32,35–39] for various neutral complexes containing this fragment. The Fe–C(3) bond length of 2.089 (7) Å may be compared with the mean value of 2.098 (2) Å for the Fe–C(sp^3) distance in $CpFe(CO)_2C(Me)CH_2C(CN)_2C(CN)_2CH_2$.[38] The angles about the two nitrogen atoms, viz., C(5)–N(1)–S(2), C(5)–N(1)–S(1), S(2)–N(1)–S(1), C(4)–N(2)–S(2), C(4)–N(2)–S(3), and S(2)–N(2)–S(3), are 113.2 (2), 119.9 (2), 121.7 (2), 115.0 (2), 122.3 (2), and 121.6 (2)°, respectively. They indicate that the geometry at each nitrogen is approaching planarity. The flattening of the nitrogen pyramids is likely due to steric effects of the $S(O)_2Me$ groups and to the constraint of the six-membered ring. The S(2)–N(1) and S(2)–N(2) distances of 1.682 (3) and 1.693 (3) Å, respectively, are shorter than the S–N single bond of 1.77 Å in sulfamic acid.[40] However, the average S(2)–N distance is between the values of 1.633 (5) and 1.692 (5) Å found in tertiary mesylamines $(R)(R')NS(O)_2Me$, where multiple bonds are present.[41,42] The angle N(1)–S(2)–N(2) of 100.5

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Table IV. Bond Angles (deg) for 4a, with Estimated Standard Deviations in Parentheses

Fe–C(1)–O(1)	177.4 (3)	C(8)–Fe–C(12)	37.9 (2)
Fe–C(2)–O(2)	177.4 (3)	C(9)–Fe–C(10)	38.6 (2)
Fe–C(3)–C(4)	113.7 (3)	C(9)–Fe–C(11)	64.8 (2)
Fe–C(3)–C(5)	109.4 (2)	C(9)–Fe–C(12)	64.2 (2)
Fe–C(8)–C(9)	70.6 (3)	C(10)–Fe–C(11)	39.0 (2)
Fe–C(8)–C(12)	71.1 (3)	C(10)–Fe–C(12)	64.8 (2)
Fe–C(9)–C(8)	70.6 (3)	C(11)–Fe–C(12)	38.9 (2)
Fe–C(9)–C(10)	70.7 (3)	C(3)–C(5)–N(1)	111.3 (3)
Fe–C(10)–C(9)	70.7 (3)	C(3)–C(4)–N(2)	113.0 (4)
Fe–C(10)–C(11)	70.6 (3)	C(5)–N(1)–S(2)	113.2 (2)
Fe–C(11)–C(10)	70.4 (3)	C(4)–N(2)–S(2)	115.0 (2)
Fe–C(11)–C(12)	70.5 (3)	N(1)–S(2)–N(2)	100.5 (1)
Fe–C(12)–C(8)	71.0 (3)	C(4)–C(3)–C(5)	111.0 (4)
Fe–C(12)–C(11)	70.5 (3)	C(5)–N(1)–S(1)	119.9 (2)
C(1)–Fe–C(2)	93.4 (2)	C(4)–N(2)–S(3)	122.3 (2)
C(1)–Fe–C(3)	89.0 (2)	S(2)–N(1)–S(1)	121.7 (2)
C(1)–Fe–C(8)	125.2 (2)	S(2)–N(2)–S(3)	121.6 (2)
C(1)–Fe–C(9)	160.1 (2)	N(1)–S(1)–O(5)	106.6 (2)
C(1)–Fe–C(10)	133.0 (2)	N(1)–S(1)–O(6)	109.9 (1)
C(1)–Fe–C(11)	99.0 (2)	N(1)–S(1)–C(7)	103.3 (2)
C(1)–Fe–C(12)	96.0 (2)	N(2)–S(3)–O(3)	105.7 (1)
C(2)–Fe–C(3)	91.9 (2)	N(2)–S(3)–O(4)	107.1 (1)
C(2)–Fe–C(8)	92.3 (2)	N(2)–S(3)–C(6)	108.3 (2)
C(2)–Fe–C(9)	98.5 (2)	O(5)–S(1)–O(6)	119.7 (2)
C(2)–Fe–C(10)	133.6 (2)	O(5)–S(1)–C(7)	108.8 (2)
C(2)–Fe–C(11)	157.0 (2)	O(6)–S(1)–C(7)	107.4 (2)
C(2)–Fe–C(12)	120.7 (2)	O(3)–S(3)–O(4)	119.7 (2)
C(3)–Fe–C(8)	145.2 (2)	O(3)–S(3)–C(6)	108.1 (2)
C(3)–Fe–C(9)	106.5 (2)	O(4)–S(3)–C(6)	107.5 (2)
C(3)–Fe–C(10)	87.7 (2)	C(8)–C(9)–C(10)	108.2 (5)
C(3)–Fe–C(11)	107.6 (2)	C(9)–C(10)–C(11)	107.7 (5)
C(3)–Fe–C(12)	146.5 (2)	C(10)–C(11)–C(12)	107.0 (4)
C(8)–Fe–C(9)	38.8 (3)	C(11)–C(12)–C(8)	108.9 (5)
C(8)–Fe–C(10)	64.9 (2)	C(12)–C(8)–C(9)	108.0 (5)
C(8)–Fe–C(11)	64.8 (2)		

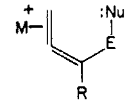
(1)° is somewhat smaller than the N–S–N angles of 104° in the cyclic compound S_4N_4, where extensive delocalization of valence electrons takes place.[43] These and other bond distances and angles are listed in Tables III and IV, respectively.

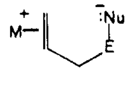
The heterocyclic ligand adopts a chair conformation. The ring is tilted so that the molecule in the crystal does not possess a plane of symmetry. This has also been observed for $CpFe(CO)_2C(Me)CH_2C(CN)_2C(CN)_2CH_2$.[38]

Discussion

At this point we wish to compare the reactions of transition-metal–propargyl, –η^1-allyl, and –cyclopropylmethyl complexes with each of the three related electrophilic reagents E=Nu (E = electrophilic part, Nu = nucleophilic part): SO_2, $MeS(O)_2NSO$, and $[MeS(O)_2N]_2S$. These reactions proceed to the products listed in Table V.

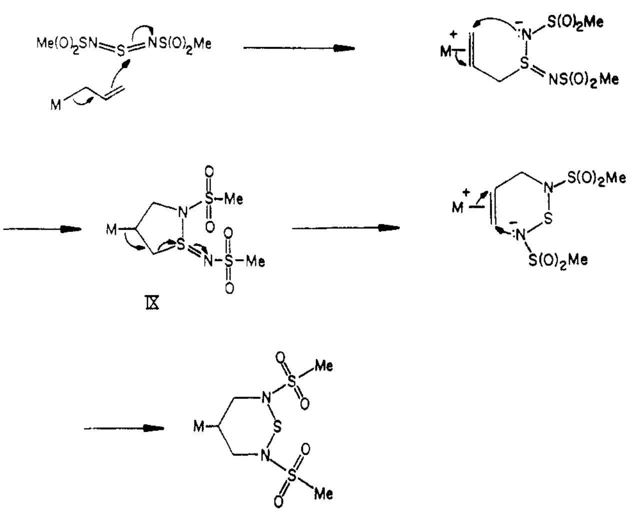
Metal–propargyl complexes uniformly afford [3 + 2] cycloadducts, IV,[1,3,5] 1, and 3 via the probable intermediacy of the corresponding zwitterionic metal–η^2-allene compounds VII. The mechanism of such cycloaddition reactions was elaborated elsewhere.[5,28]


VII


VIII

Metal–η^1-allyl complexes behave differently toward each of the three electrophiles. "Normal", [3 + 2] cycloaddition has been observed only with $MeS(O)_2NSO$. In this case, the reaction very likely proceeds via a dipolar metal–η^2-alkene intermediate, VIII, which collapses to 2 by nucleophilic attack of Nu at the η^2-alkene terminus. In contrast, reactions of metal–η^1-allyl complexes with SO_2 almost invariably afford sulfinato-*S* insertion products.[1,2,5] This behavior probably results from the lesser stability of the metal–η^2-alkene bond than of the metal–η^2-allene bond[44] in intermediates VIII and VII, respectively, and from the poor nucleophilic properties of the sulfinate oxygen. Accordingly, the appropriate zwitterions VIII (E= Nu = SO_2), a few of which have been observed in solution and isolated after alkylation,[45,46] undergo metal–η^2-alkene bond dissociation before ring closure can occur. Recombination of the ions results in the formation of the sulfinato-*S* complexes as apparent insertion products. Since the metal–η^2-allene bond in VII is presumably stronger than the metal–η^2-alkene bond in VIII, the η^2-allene may be better activated toward nucleophilic addition than the η^2-alkene. As a result, cycloaddition products IV are formed when metal–propargyl complexes react with SO_2. The formation of cycloadducts 2 from metal–η^1-allyl complexes and $MeS(O)_2NSO$ is probably due to the nitrogen atom in their precursor zwitterions VIII being a better nucleophile than the oxygen atom in VIII containing SO_2.

Scheme I



It is very unlikely that the formation of the [3 + 3] cycloadducts 4 from metal–η^1-allyl complexes and $[MeS(O)_2N]_2S$ proceeds directly by a two-step pathway analogous to that for the [3 + 2] cycloadducts. This is because the nitrogen atoms of $[MeS(O)_2N]_2S$ lack the necessary electrophilic properties to provide a driving force toward the appropriate zwitterion. However, the formation of 4 may occur by a route depicted in Scheme I. Initially, a normal [3 + 2] cycloadduct, IX, obtains which undergoes ring opening to yield a different metal–η^2-alkene zwitterion. The latter then collapses as expected to furnish 4. Our attempts to observe the proposed [3 + 2] cycloaddition intermediates IX at low temperatures by ^1H NMR spectroscopy were thwarted by unfavorable solubility properties of $[MeS(O)_2N]_2S$.

If complexes IX are indeed reaction intermediates in the synthesis of 4 according to Scheme I, then their facile

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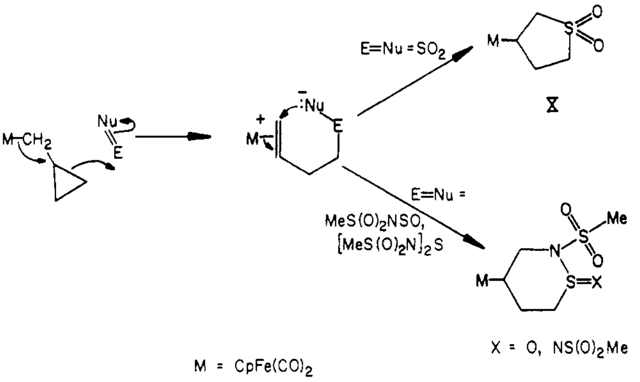
Table V. Comparison of Products of Reactions of Some Organometallic Complexes with SO_2, $MeS(O)_2NSO$, and $[MeS(O)_2N]_2S$

complex	product with different E=Nu: SO_2	$MeS(O)_2NSO$	$[MeS(O)_2N]_2S$
propargyl	5-membered ring[a]	5-membered ring	5-membered ring
η^1-allyl	insertion[b,c]	5-membered ring	6-membered ring
cyclopropylmethyl	5-membered ring[d]	6-membered ring[e] insertion[f]	insertion[e] 6-membered ring[f]

[a] Reference 3. [b] Reference 2. [c] For exceptions, see ref 46. [d] Reference 4. [e] Major product. [f] Minor product.

Scheme II



rearrangement must be related to a lack of stability of the five-membered heterocyclic ring. The structurally characterized complexes **4a** and $CpFe(CO)_2C(Me)CH_2C(CN)_2C(CN)_2CH_2$[38] show markedly nonplanar six- and five-membered cycloaddition rings. If a related nonplanar conformation is adopted by IX, repulsive interactions between the $S(O)_2Me$ and $=NS(O)_2Me$ substituents on adjacent atoms in the heterocyclic ring would be substantial. Thus, it is possible that the proposed ring opening in IX occurs readily to relieve such a steric crowding. In the related five-membered cycloaddition complexes **3** derived from metal propargyls and $[MeS(O)_2N]_2S$, steric interaction between $S(O)_2Me$ and $=NS(O)_2Me$ may not be as large as in IX. This is inferred by assuming that the structure of **3** is similar to that of IV, in which the five-membered sultine ring is nearly planar (when M = $CpFe(CO)_2$ and R = Me).[31] Furthermore, complexes **3** may also derive stability from C=C—S=N conjugation. As a result, there is no apparent tendency for **3** to undergo rearrangement.

Finally, we wish to consider the reactions of $CpFe(CO)_2CH_2CHCH_2CH_2$ with SO_2 and its two analogues. The reaction of the iron complex with SO_2 was reported[4] to proceed to the cyclic sulfone product X as shown in Scheme II. We find in this study that the corresponding reactions with $MeS(O)_2NSO$ and $[MeS(O)_2N]_2S$ in place of SO_2 result in the formation of both cycloaddition and insertion products. Moreover, the amount of the insertion product increases and that of the cycloaddition product decreases on going from $MeS(O)_2Me$ to $[MeS(O)_2N]_2S$. Control experiments showed that there is no conversion of the insertion complexes to the cycloaddition complexes under the conditions of these reactions. Thus, the two processes proceed by independent, parallel paths.

The formation of a five-membered ring for X and of six-membered rings for **7** and **8** may be rationalized again on the basis of the most facile mode of cyclization of the iron–η^2-alkene intermediate in Scheme II. Accordingly, with SO_2, addition to the η^2-alkene of the more nucleophilic sulfur (rather than oxygen) is preferred. In contrast, with $MeS(O)_2NSO$ and $[MeS(O)_2N]_2S$, the nitrogen, a more effective nucleophile than oxygen, competes favorably with sulfur for the addition to the η^2-alkene to yield a six-membered ring.

The increasing amount of insertion product at the expense of cycloaddition product on going from SO_2 to $MeS(O)_2NSO$ and to $[MeS(O)_2N]_2S$ is more difficult to rationalize. Both insertion and cycloaddition are thought to be electrophilic addition processes: the former to the α-carbon atom of the $CH_2CHCH_2CH_2$ ligand,[9] and the latter to the cyclopropyl group.[4] It is not obvious to us why the relatively small SO_2 prefers attack at the cyclopropyl group, whereas the larger $[MeS(O)_2N]_2S$ prefers interaction with α carbon. The more crowded environment about the α-carbon atom compared to the cyclopropyl group suggests that the observed selectivities are more electronic than steric in origin.

Acknowledgment. We are grateful to the National Science Foundation for support of this research through Grant CHE-7911882. We thank Dr. Dennis Kountz for his help with crystallographic calculations.

Registry No. **1a**, 100946-37-0; **1b**, 100946-38-1; **1c**, 100946-39-2; **2a**, 86638-04-2; **2b**, 100946-40-5; **2c**, 100946-41-6; **3a**, 100946-42-7; **3b**, 100946-43-8; **3c**, 100946-44-9; **3d**, 100946-45-0; **3e**, 100946-46-1; **3f**, 100993-30-4; **4a**, 86750-93-8; **4b**, 100946-47-2; **4c**, 100946-48-3; **4d**, 100946-49-4; **4e**, 100993-31-5; **5**, 100946-50-7; **6**, 100946-52-9; **7A**, 100946-51-8; **7B**, 101052-86-2; **8A**, 100946-53-0; **8B**, 101052-87-3; $CpFe(CO)_2CH_2C{\equiv}CPh$, 33114-75-9; $CpMo(CO)_3CH_2C{\equiv}CMe$, 32877-62-6; $CpMo(CO)_3CH_2C{\equiv}CPh$, 32877-61-5; $CpW(CO)_3CH_2C{\equiv}CPh$, 32993-03-6; $CpCr(NO)_2CH_2C{\equiv}CPh$, 76498-84-5; $Mn(CO)_2CH_2C{\equiv}CPh$, 23626-46-2; $CpFe(CO)_2CH_2CH{=}CH_2$, 38960-10-0; $CpFe(CO)_2CH_2C(Me){=}CH_2$, 31781-60-9; $CpMo(CO)_3CH_2CH{=}CH_2$, 33057-54-4; $CpMo(CO)_3CH_2C(Me){=}CH_2$, 53320-42-6; $Mn(CO)_5CH_2CH{=}CH_2$, 14057-83-1; $CpFe(CO)_2CH_2CHCH_2CH_2$, 34788-98-2; $MeS(O)_2NSO$, 40866-96-4; $PhS(O)_2NSO$, 6536-23-8; $[MeS(O)_2N]_2S$, 5636-09-9.

Supplementary Material Available: Listings of temperature factors, hydrogen atom coordinates, and structure factors for complex **4a** (28 pages). Ordering information is given on any current masthead page.