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Reactions of Cyclopentadienylmetal–2-Alkenyl Carbonyl Complexes with Sulfur Dioxide. Isolation and Characterization of 2-Alkene-*S*-Sulfinato Products

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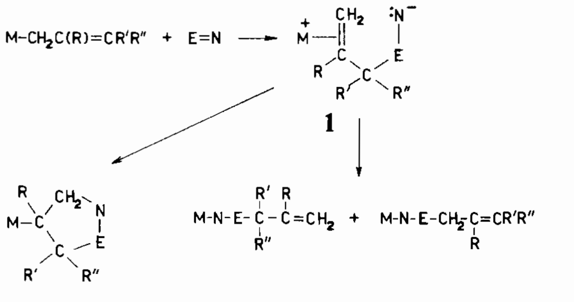
Transition metal–2-alkenyl complexes η^5-$C_5H_5Fe(CO)_2CH_2C(R)=CR'R''$ *(R, R', and R'' = H and/or* CH_3*) and* η^5-$C_5H_5Mo(CO)_3CH_2CH=CH_2$ *react rapidly with liquid* SO_2 *at –10 °C or below to afford the corresponding zwitterions,* η^5-$C_5H_5Fe^+(CO)_2(\eta^2$-$CH_2=C(R)C(R')(R'')SO_2^-)$ *and* η^5-$C_5H_5Mo^+(CO)_3(\eta^2$-$CH_2=CHCH_2SO_2^-)$*, respectively. These zwitterions were characterized by infrared and* ^1H *NMR spectroscopy and, in the case of* η^5-$C_5H_5Fe^+(CO)_2(\eta^2$-$CH_2=CHCH_2SO_2^-)$*, also by conductivity measurements and alkylation with* $(CH_3)_3OBF_4$ *and* $(C_6H_5)_3CCl$ *to give* $[\eta^5$-$C_5H_5Fe(CO)_2(\eta^2$-$CH_2=CHCH_2S(O)_2R]^+X^-$ *(R =* CH_3 *and* $(C_6H_5)_3C$*). Upon storage in liquid* SO_2 *the zwitterions were found by infrared and* ^1H *NMR spectroscopy to rearrange to the corresponding S-sulfinato complexes in the approximate order* η^5-$C_5H_5Fe^+(CO)_2(\eta^2$-$CH_2=CHC(CH_3)_2SO_2^-) \geqslant \eta^5$-$C_5H_5Fe^+(CO)_2(\eta^2$-$CH_2=C(CH_3)CH_2SO_2^-) > \eta^5$-$C_5H_5Fe^+(CO)_2(\eta^2$-$CH_2=CHCH(CH_3)SO_2^-) > \eta^5$-$C_5H_5Fe^+(CO)_2(\eta^2$-$CH_2=CHCH_2SO_2^-)$ *and* η^5-$C_5H_5Mo^+(CO)_3(\eta^2$-$CH_2=CHCH_2SO_2^-) > \eta^5$-$C_5H_5Fe^+(CO)_2(\eta^2$-$CH_2=CHCH_2SO_2^-)$*. The rearrangement of* η^5-$C_5H_5Fe^+(CO)_2(\eta^2$-$CH_2=CHCH_2SO_2^-)$ *to the S-sulfinate* η^5-$C_5H_5Fe(CO)_2S(O)_2CH_2CH=CH_2$ *occurs concomitantly with the formation of a cycloaddition product, formulated as* η^5-$C_5H_5Fe(CO)_2\overline{CHCH_2S(O)_2CH_2}$*. This cycloadduct is unstable toward dimerization and/or trimerization, especially in solution, yielding a readily isolable* $[\eta^5$-$C_5H_5Fe(CO)_2(C_3H_5SO_2)]_{2\ or\ 3}$*. The molybdenum zwitterion* η^5-$C_5H_5Mo^+(CO)_3(\eta^2$-$CH_2=CHCH_2SO_2^-)$ *displays a parallel behavior in rearrangement. Various factors that affect the formation of these products and possible mechanisms of these reactions are presented and discussed.*

Introduction

Transition metal–2-alkenyl complexes react with a host of unsaturated electrophilic molecules to afford products of (3 + 2) cycloaddition of the electrophile to the 2-alkenyl fragment with concomitant 1,2 metal migration (eq 1) [1–5]. A list of electrophiles (E=N) that cycloadd in this fashion includes, *inter alia*, $(CN)_2C=C(CN)_2$ [5–7], $F_3C(CN)C=C(CN)CF_3$ [2], $ClSO_2NCO$ [5, 8, 9], *p*-$CH_3C_6H_4SO_2NCO$ [5, 9], $(CF_3)_2CO$ [10], and CH_2SO_2 [5].



(1) (2)

In contrast to the products of these cycloadditions, insertion derivatives are obtained when transition metal–2-alkenyl complexes react with SO_2 [11–13], $SnCl_2$ [14] or NC≡CCN [15] (eq 2). The observed insertion of SO_2 is particularly intriguing since the reaction of SO_2 with the corresponding transition metal–2-alkynyl complexes proceeds instead to (3 + 2) cycloadducts [16]. It has been proposed [7] that the cycloaddition and insertion reactions of the metal–2-alkenyl complexes in point occur via a common type of dipolar intermediate (**1**), but until recently direct evidence for such a species had been lacking. The combined detection and interception of the zwitterion **1** for E=N being SO_2, reported by us in a preliminary communication [17], has provided strong support to the above proposal.

Reported now is a full account of the characterization of the initially formed dipolar products of the reaction between some cyclopentadienylmetal–2-alkenyl carbonyl complexes and SO_2. Subsequent reactions of these zwitterionic intermediates to yield products other than the appropriate metal *S*-sulfinates are also considered here in detail. However, the characterization of the metal *S*-sulfinates derived from these reactions is the subject of the accompanying paper [18].

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TABLE I. Infrared ν(C≡O) Absorptions and ^{1}H NMR η^5-C_5H_5 Resonances of Zwitterionic Intermediates (3) and *S*-Sulfinato Products (4) of the Reaction of Iron–2-Alkenyl Complexes (2) with Liquid Sulfur Dioxide.[a]

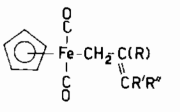
2-Alkenyl Complex	ν(C≡O), cm^{-1} [b]		η^5-C_5H_5 Resonance, τ [c]	
	Intermediate (3)	*S*-Sulfinate (4)	Intermediate (3)	*S*-Sulfinate (4)
2a	2085, 2050	2066, 2022	4.36	4.78
2b	2084, 2049	2065, 2022	4.36	4.75
2c	2079, 2041	2065, 2020	4.30	4.75
2d	2078, 2040	2066, 2022	4.40	4.77

[a] All measurements were made in liquid SO_2. [b] ±1 cm^{-1}. All absorptions are very strong. [c] ± 0.02 ppm. All resonances are singlets.

Results and Discussion

Reaction of η^5-$C_5H_5Fe(CO)_2CH_2C(R)=CR'R''$ where R, R′ and/or R″ = CH_3 with Sulfur Dioxide

The 2-alkenyl complexes **2b–d** react rapidly with neat SO_2 at –35 to –18 °C. Thus 5–10 min old solutions of **2b–d** in liquid SO_2 show two intense infrared ν(C≡O) absorptions at 2084–2078 and 2049–2040 cm^{-1}. They are listed in Table I. The frequencies of these bands are much too high to be ascribed to the parent 2-alkenyl complexes, which absorb in the ranges 2018–2005 and 1962–1945 cm^{-1} [6, 18, 19]. However, they are virtually identical with those of cationic complexes of the type $[\eta^5\text{-}C_5H_5Fe(CO)_2(\eta^2\text{-alkene})]^+X^-$ [5, 19] or $[\eta^5\text{-}C_5H_5Fe(CO)_2(\eta^2\text{-allene})]^+X^-$ [20, 21].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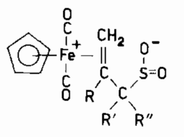
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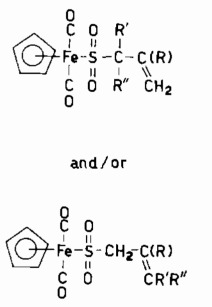
and/or

4

a R = R′ = R″ = H
b R = R′ = H, R″ = CH_3
c R = H, R′ = R″ = CH_3
d R = CH_3, R′ = R″ = H

The rapid reaction of **2b–d** with SO_2 is corroborated by the ^{1}H NMR measurements on freshly prepared solutions of these complexes in liquid SO_2 at –39 to –22 °C. In the η^5-C_5H_5 region (τ 4.0–5.5) a strong resonance is observed at τ 4.30–4.40 (Table I), whereas the corresponding resonance of the parent 2-alkenyl complex, expected at approximately τ 5.1–5.3 [6, 18, 19], is missing. The position of the signal at τ 4.30–4.40 accords with the positive charge on the iron as, *e.g.*, in $[\eta^5\text{-}C_5H_5Fe(CO)_2(\eta^2\text{-alkene})]^+X^-$ [5, 19].

The above infrared and ^{1}H NMR spectral data suggest the presence of the zwitterionic species **3b–d** in these solutions. The proposed formulation receives strong support from the strictly parallel behavior of **2a** in liquid SO_2 in conjunction with the trapping of the zwitterion **3a** in these solutions by methylation with $(CH_3)_3OBF_4$ (*vide infra*). Attempts to isolate **3b–d** by rapid removal of the solvent from freshly prepared (as well as aged) solutions of **2b–d** in liquid SO_2 afforded only the corresponding *S*-sulfinato complexes, **4b–d**.*

Storage of solutions of **2b–d** in liquid SO_2 at –39 to –18 °C also gives rise to the formation of **4b–d**. This transformation was followed by monitoring the ν(C≡O) region in the infrared spectrum and the η^5-C_5H_5 resonance region** in the ^{1}H NMR spectrum. In the former, ν(C≡O) absorptions of **4b–d** appear and grow at 2066–2065 and 2022–2020 cm^{-1} (Table I) as the intensities of the corresponding bands of **3b–d** decrease. The two sets of the ν(C≡O) absorptions attain comparable intensities*** as a function of the allyl fragment in the order **3c** ~ **3d** > **3b**. The approximate times required to obtain such spectra are provided in Table II.

In the ^{1}H NMR spectra of **2b–d** in liquid SO_2 new η^5-C_5H_5 resonances grow in at τ 4.75–4.77 as the intensities of the signals at τ 4.30–4.40 decrease. The relative rates of the conversion of **3** to **4** follow the order **3c** ⩾ **3d** > **3b** which is essentially that observed by infrared spectroscopy. However, as may be seen in Table II, the rates of the conversion appear to be faster under the conditions of the NMR measurements than under the conditions of the infrared measurements.

This apparent discrepancy is most likely a consequence of the different concentrations of **2b–d**

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*The isomerism of the allyl fragment in these complexes (*i.e.* structures 4) is discussed in the following paper (ref. 18).

**The rest of the ^{1}H NMR spectrum is much less informative because of its complexity and/or poor resolution. Accordingly it is not considered in the paper.

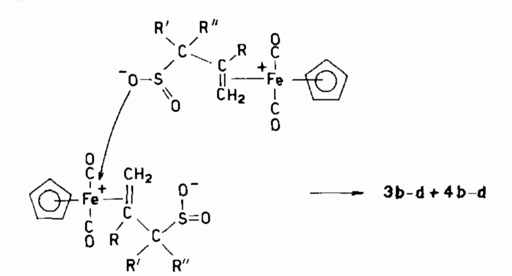
***At this point the concentrations of the two species are not equal, since specific intensities increase as the frequencies decrease for the CO stretching of a series of isoelectronic and isostructural compounds. Accordingly the concentration of 4b–d is still lower than that of 3b–d. For a review of and references to intensities of ν(C≡O) bands see ref. 22.

TABLE II. Approximate Half-Lives for Rearrangement of Zwitterionic Intermediates (3) to *S*-Sulfinato Products (4) in Liquid Sulfur Dioxide.

Zwitterionic Intermediate^a	Infrared Measurements		^{1}H NMR Measurements	
	Temp, °C	Approx. half-life, min^{b,c}	Temp, °C	Approx. half-life, min^b
3a	−18	200		d
3b	−18	120	−22	100
3c	−35	100	−39	45
3d	−35	110	−39	60

^{a}Concentration ~7 × 10^{-3} *M* for the infrared measurements and ⩾0.2 *M* for the ^{1}H NMR measurements. ^{b}±10 min. ^{c}Actually the times given are those required for the ν(C≡O) absorptions of 3 and 4 to reach comparable intensities and are less than the true half-lives for the reaction; see a footnote in the text. However, the error introduced in making this approximation is thought to be uniform for all four zwitterions, 3a–d. ^{d}Not applicable since the rearrangement 3a to 4a is a relatively minor reaction under these conditions; see the text.

employed in the two experiments. The faster rates observed in the NMR experiments, where concentrations of **2b–d** were at least 30 times as high as those in the infrared experiments, suggest that the rearrangement in question is at least in part bimolecular (or of a higher molecularity), becoming more so at the higher concentrations. This somewhat surprising result of an associative pathway for the decomposition of **3b–d** would be consistent with nucleophilic attack of the negative pole of one zwitterion **3b–d** at the positive iron of another **3b–d** to displace the *dihapto*coordinated alkenesulfinate anion as shown in eq (3). The generated ions would then combine to give rise to the observed apparent insertion. It is further significant that the relative rates of this rearrangement of **3b–d** follow approximately a decreasing order of stability of the iron–η^2-alkenesulfinate bonds expected on the basis of the increasing extent of methyl substitution in the allyl fragment [5, 23].



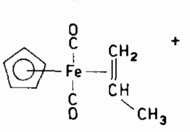
Reaction of η^5-$C_5H_5Fe(CO)_2CH_2CH{=}CH_2$ with Sulfur Dioxide

Dissolution of **2a** in liquid SO_2 initially leads to a behavior which is very similar to that described above for the methyl-substituted iron–2-alkenyl compounds **2b–d**. However, the generated zwitterion **3a** displays a more complex chemistry than **3b–d** and hence the entire reaction is treated separately.

The infrared spectrum of a freshly prepared solution of **2a** in liquid SO_2 shows that the starting material has been completely converted to a species with two ν(C≡O) bands at higher frequencies. Likewise, only one η^5-C_5H_5 resonance is detectable in the ^{1}H NMR spectrum, and it occurs at a considerably lower field compared to that of **2a** [19]. These data are included in Table I. Both changes are consistent with the formation of the zwitterion **3a** as already discussed for the other complexes. In further support of the formulation **3a** is a virtual lack of conductivity of a freshly prepared solution (1.2 × 10^{-2} *M*) of **2a** in liquid SO_2 at −70 °C. The measured value, Λ_M = 2.24 ohm^{-1} cm^2, contrasts with a Λ_M of 84 ohm^{-1} cm^2 for $[\eta^5\text{-}C_5H_5Fe(CO)_2P(C_6H_5)_3]^+PF_6^-$ [24] which is in the region expected for 1:1 electrolytes [25] Hence ionic structures such as $[\eta^5\text{-}C_5H_5Fe(CO)_2SO_2]^+O_2SC_3H_5^-$, equally consistent with the infrared and ^{1}H NMR data as **3a**, are precluded on this basis.

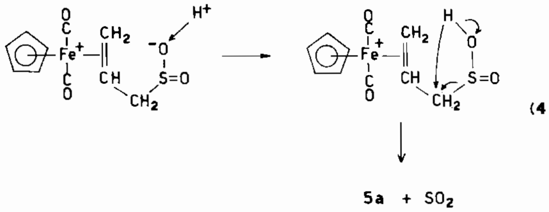
A number of reactions have been carried out with the freshly generated **3a** in liquid SO_2. Addition of a large excess of KI afforded after work-up η^5-$C_5H_5Fe(CO)_2I$ and the *S*-sulfinate **4a** as the principal and minor products, respectively. The complex η^5-$C_5H_5Fe(CO)_2I$ no doubt arises through replacement of the *dihapto*coordinated alkenesulfinate anion by iodide. Similar substitution of the alkene ligand in $[\eta^5\text{-}C_5H_5Fe(CO)_2(\eta^2\text{-alkene})]^+X^-$ by iodide has been reported [26]. Complex **4a** is formed by rearrangement of **3a** as will be discussed later.

Treatment of **3a** in liquid SO_2 with gaseous HCl led to the formation of the known cation **5a**, isolated as the PF_6^- salt, and of a trace amount of η^5-$C_5H_5Fe(CO)_2Cl$. The cation **5a** likely arises through initial protonation of the sulfinate terminus of **3a**, probably



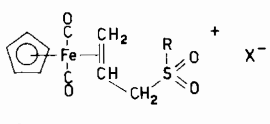
5a

at oxygen, followed by loss of SO_2 as shown in eq (4). Surprisingly, the same compound was isolated when **3a** was treated with CH_3SO_3F followed by NH_4PF_6. This result can be rationalized only on the assumption that the added CH_3SO_3F contained a more reactive acid impurity.



(4)

Methylation of **3a** in liquid SO_2 with $(CH_3)_3OBF_4$ afforded the iron–η^2-(allyl methyl sulfone) cation isolated as the yellow BF_4^- and PF_6^- salts, **6a–a'**, respectively. These compounds are readily soluble in acetone, sparingly soluble in $CHCl_3$, and insoluble in benzene and pentane. They are somewhat air-sensitive in the solid and decompose gradually upon storage in solution. The proposed structures are based on the conductivity measurements which show **6a** to be a 1:1 electrolyte in acetone*, the infrared $\nu(SO_2)$ values typical of the organic sulfones [28], and the relatively high infrared $\nu(C{\equiv}O)$ values as well as the rather deshielded ^1H NMR η^5-C_5H_5 resonance of **6a'**, both of which point to the positive charge at the iron [5, 19–21]. Complex **6a** was also reported recently by Rosenblum, *et al.* [4].



6a R = CH_3, X = BF_4
6a' R = CH_3, X = PF_6
7a R = $(C_6H_5)_3C$, X = PF_6

The trapping of the zwitterion **3a** in liquid SO_2 was also achieved by the use of $(C_6H_5)_3CCl$, with the resulting cation having been isolated as the yellow PF_6^- salt, **7a**. This complex has solubility and stability properties comparable to those of **6a–a'**. Its structural formulation likewise rests on conductivity, infrared $\nu(SO_2)$ and $\nu(C{\equiv}O)$, and ^1H NMR data, which are furnished in the Experimental.

Storage of liquid SO_2 solutions of **3a** leads to a behavior that appears to be considerably influenced by the concentration of the zwitterion. At the lower concentrations ($\sim 7 \times 10^{-3}$ *M*), the infrared spectrum in the $\nu(C{\equiv}O)$ region reveals the appearance and growth of the bands of the *S*-sulfinato complex **4a** (Table I). In addition, however, a shoulder at *ca.* 2005 cm^{-1} and a broad absorption at 1967–1960 cm^{-1} become discernible; they are assigned to another, in this case relatively minor product(s) (**8a** and/or **9a**) that will be discussed fully later in the paper. The spectrum recorded *ca.* 200 min after dissolution of **2a** in liquid SO_2 at –18 °C is shown in Fig. 1.

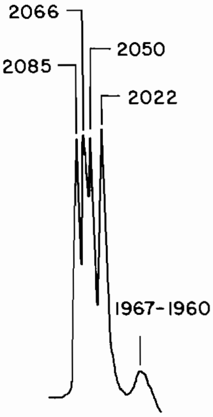


Figure 1. Infrared spectrum in the $\nu(C{\equiv}O)$ region (in cm^{-1}) of a solution of **2a** in liquid SO_2 aged for *ca.* 200 min at –18 °C.

The ^1H NMR spectrum in the region τ 4.0–5.5 of the more concentrated ($\geqslant 0.2 M$) **3a** in liquid SO_2 undergoes the following changes with time at –22 °C. The signal at τ 4.36 of **3a** decreases in intensity and resonances appear at τ 4.78 of **4a** and 5.00. This is followed by a gradual appearance of yet another signal, at τ 5.03, and a diminution of intensity of the

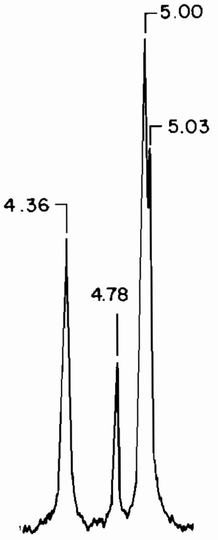


Figure 2. ^1H NMR spectrum in the η^5-C_5H_5 resonance region of a solution of **2a** in liquid SO_2 aged for *ca.* 120 min at –22 °C. The chemical shifts are in τ.

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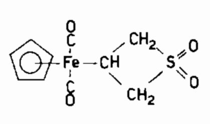
*Molar conductivities for *ca.* 10^{-3} *M* solutions of 1:1 electrolytes in acetone are in the range 100–150 ohm^{-1} cm^2 (ref. 27).

peak at τ 5.00. At 140 min the intensities of the η^5-C_5H_5 resonances reflect the following composition of the solution: unreacted **3a** 25%, **4a** 16%, and the two species (**8a** and **9a**) absorbing at τ 5.00 and 5.03 combined 59%. A representative spectrum of the solution showing the resonances of the four compounds is reproduced in Fig. 2. After the signal at τ 4.36 has virtually disappeared, the combined intensity of the resonances at τ 5.00 and 5.03 remains constant, with the latter increasing and the former decreasing. The limiting spectrum, obtained after approximately 5 days, shows only the peaks at τ 4.78 and 5.03 of the relative intensity 2:7.

To summarize, at the lower concentrations the zwitterion **3a** appears to rearrange preferentially to the *S*-sulfinate **4a**; at the higher concentrations its rearrangement to the products **8a** and **9a** seems to be favored. A discussion of this difference in behavior will be deferred until the structures of **8a** and **9a** are considered in the following subsection of the paper.

Isolation and Characterization of $[\eta^5\text{-}C_5H_5Fe(CO)_2\text{-}(C_3H_5SO_2)]_x$

Rapid removal of the solvent from a freshly prepared solution of **2a** in liquid SO_2 afforded yellow **8a** along with some (~5%) **4a**. Since **8a** undergoes dimerization and/or polymerization upon storage in solution, all measurements performed with a view to characterizing this complex were carried out rapidly on freshly made solutions. The molecular weight of **8a** obtained in this manner by osmometry in $CHCl_3$ was only 1-2% higher than the theoretical value for the monomeric composition. It was not possible to obtain a meaningful mass spectrum of **8a** because of a reaction to form **9a** and decomposition. Elemental analyses were not attempted, since the compound gradually and cleanly converts to its dimer or trimer, **9a**, which was satisfactorily characterized by microanalyses.



8a

The ^{1}H NMR spectrum of **8a** recorded a few minutes after dissolution in $CHCl_3$ showed two cyclopentadienyl resonances, an intense one at τ 5.03 (τ 5.00 in SO_2) and a weak one at τ 5.08 (τ 5.03 in SO_2). The latter signal is assigned to **9a**; its intensity has been used to measure the monomeric purity of **8a** in solution. Both resonances accord with structures containing an Fe–C σ bond [2, 6, 8, 10]. Additionally, poorly resolved, complex absorption patterns occur at τ 6.5 and 7.8, corresponding to four and one hydrogens, respectively. The position of the first resonance compares satisfactorily with that reported for the α-CH_2 protons of thietene dioxide, $\overline{CH_2S(O)_2CH_2CH_2}$ (τ 5.86) [29], and of the second with those of the secondary alkyl protons of Fe–CH [2, 5, 6, 8, 10].

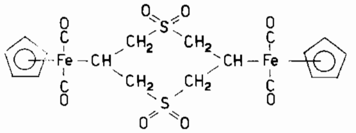
In the infrared spectrum of **8a**, the ν(C≡O) absorptions are typical of those of the secondary alkyl complexes η^5-$C_5H_5Fe(CO)_2R$ [2, 5, 6, 8, 10], and the $\nu(SO_2)$ bands indicate the presence of an organic sulfone group [28]. Hence combined evidence from the osmometric and ^{1}H NMR and infrared spectroscopic measurements points to structure **8a** for this 1:1 adduct of **2a** and SO_2. In further support of the presence of an Fe–C σ bond in **8a** is the formation of η^5-$C_5H_5Fe(CO)_2Cl$ upon cleavage with gaseous HCl. The other product of this cleavage, an organic sulfone, could not be isolated pure for full characterization.

Storage of solutions of **8a** in CH_2Cl_2, $CHCl_3$ or liquid SO_2, *inter alia*, leads to the formation of **9a**, which is less soluble than **8a** and precipitates as a yellow solid from hexane/CH_2Cl_2. The same complex forms upon heating **8a** at 100 °C for 10 hr under nitrogen. It can be also obtained directly from **2a** by reaction with liquid sulfur dioxide for various lenghts of time, evaporation of excess SO_2, and chromatography to remove co-product **4a**. Longer reaction times decrease the ratio of **9a** to **4a**, as the **4a** continually generated from the zwitterion **3a** in liquid SO_2 appears not to rearrange to **8a** or **9a** even upon removal of the solvent. Passage of gaseous SO_2 into a pentane solution of **2a** likewise affords **9a** and **4a** upon work-up. It seems that column chromatography on Florisil or alumina ensures conversion of **8a** to **9a** after these reactions.

The structure of **9a** is not entirely evident from the data on hand. Elemental analyses, including oxygen, agree well with the empirical formula of **8a** (and of the isomeric **4a**). This is not surprising since the compound is derived by a clean aggregation of **8a**. The closely agreeing oxygen analysis is particularly important as it migrates the possibility of a sulfonate formulation, $[\eta^5\text{-}C_5H_5Fe(CO)_2(C_3H_5SO_3)]_x$. The osmometrically determined molecular weight of **9a** in $CHCl_3$ varies somewhat from one preparation to another, but generally falls just above the value calculated for a dimer of **8a**. Since **9a** can be readily converted to insoluble, presumably more highly aggregated units of **8a** (*vide infra*), it is thought to be comprised of more than one species $[\eta^5\text{-}C_5H_5Fe(CO)_2(C_3H_5SO_2)]_x$, with the predominant component apparently being a dimer.

The infrared and ^{1}H NMR spectra of **9a** are very similar to those of **8a**. The values of ν(C≡O) are virtually the same for the two compounds; the $\nu(SO_2)$ spectral region of **9a** is richer than that of **8a** although still diagnostic of an organic sulfone structure. In the ^{1}H NMR spectrum of **9a** complex absorption patterns occur in the same regions and with comparable relative intensities as for **8a**. The mass spectrum exhibits peaks due to $C_5H_5Fe(CO)_2C_3H_5SO^+$ and a few species $C_5H_5Fe(CO)_xC_3H_5^+$ and $C_5H_5Fe(CO)_xCH^+$ (x = 0, 1 or 2), with some of these assignments having been made on the basis of the exact mass values. Complex **9a**, just as **8a**, undergoes cleavage by gaseous HCl to yield η^5-$C_5H_5Fe(CO)_2Cl$ and an organic sulfone that could not be fully characterized.

The remarkable resemblances in the infrared and ^1H NMR spectroscopic data of **8a** and **9a**, the appearance of certain mass spectral peaks for **9a**, and the observed course of cleavage of both compounds by HCl all suggest similar structural features for **8a** and **9a**. The proposed structure of dimeric **9a**, although admittedly somewhat speculative, accords with these data and observations. Attempts were made to grow crystals of **8a** and **9a** for X-ray crystallography; however, they proved unsuccessful.



9a

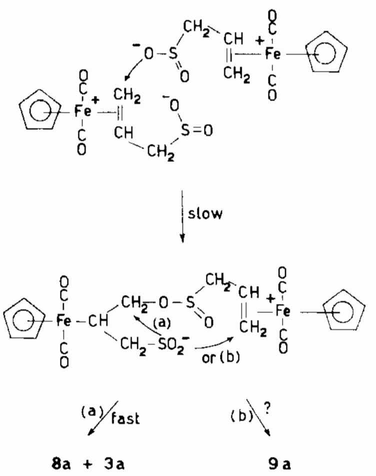
Prolonged storage of **8a** or **9a** in solution leads to the formation of insoluble, presumably more highly aggregated species $[\eta^5\text{-}C_5H_5Fe(CO)_2(C_3H_5SO_2)]_x$. However, no attempts were made at their characterization.

It is of interest that η^5-$C_5H_5Fe(CO)_2\overline{CHCH_2CH_2S(O)_2C}H_2$, the higher homolog of **8a**, is stable with respect to aggregation. Instead it rearranges to η^5-$C_5H_5Fe(CO)_2S(O)_2CH_2CH_2CH{=}CH_2$ in high yield upon heating [7]. In contrast, **9a** afforded only a trace of **4a** when heated at 110–125 °C for 48 hr. The instability of **8a** may be ascribed to steric strain in its four-membered sulfone ring, but continued reactivity of **9a** in solution cannot be given a simple rationalization.

The question of mechanism of rearrangement of the zwitterion **3a** to **4a** and **8a** (possibly along with **9a**) will be addressed next. A reasonable explanation of the preferential formation of **4a** at the lower concentrations of **3a**, and of **8a** at the higher concentrations of **3a** follows.

At the lower concentrations of **3a**, employed in the infrared measurements, unimolecular rearrangements are expected to be more important relative to bimolecular rearrangements. Under these conditions the primary process appears to be dissociation of the η^2-alkenesulfinate anion from **3a** and subsequent recombination of the ions to yield **4a**. It is noteworthy that this reaction, whether completely unimolecular or in part bimolecular (eq 3), proceeds more slowly than the corresponding rearrangement of the zwitterions **3b–d** (Table II). The difference probably arises from the stronger iron–η^2-alkenesulfinate bonding in **3a** than in **3b–d**, since transition metal–η^2-alkene bonds tend to be destabilized by alkyl substitution in or adjacent to the C=C fragment [5, 23]. The competing ring closure reaction of **3a** to afford **8a** is a relatively slow process under these conditions, suggesting that it does not occur readily in a unimolecular fashion. The reason for this behavior is not obvious, but it may be a combination of such factors as considerable flexibility of the *dihapto*coordinated alkene sulfinate anion, low nucleophilicity of the sulfinate terminus, and insufficient activation of the η^2-alkene moiety by the metal toward nucleophilic attack. In this context it is of interest to note that the zwitterions **3b–d** do not react by such ring closure. There the iron binds the η^2-alkene moiety more weakly than in **3a** and apparently activates it less effectively toward attack by the sulfinate anion.

At the higher concentrations of **3a**, used in the ^1H NMR measurements, the rate of the formation of **8a** (possibly along with **9a**) increases markedly compared to the rate of the generation of **4a**. This would seem to indicate a bimolecular (or a higher molecularity) nature of the former process under these conditions. A reasonable pathway for this conversion is depicted in eq (5). It seems that a better activation of the *dihapto*coordinated alkenesulfinate by the iron toward nucleophilic attack and a stronger metal–η^2-alkenesulfinate bond in **3a** compared to **3b–d** both favor ring closure (eq 5) over apparent insertion via dissociation (eq 3) for the zwitterion in point.

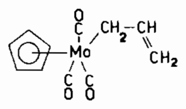


(5)

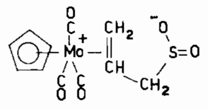
Finally it should be noted that the formation of **8a** upon removal of the solvent from a solution of **3a** in liquid SO_2 accords well with the above behavior. Evaporation of the SO_2 leads to high concentrations of **3a** and therefore promotes cycloaddition at the expense of the insertion through dissociation.

Reaction of η^5-$C_5H_5Mo(CO)_3CH_2CH{=}CH_2$ with Sulfur Dioxide

The reaction of the molybdenum–2-alkenyl complex **10** with neat SO_2 shows many similarities to that of its iron counterpart **2a**. However it was not investigated in as much detail as the latter.

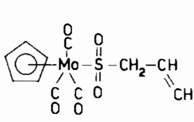


10

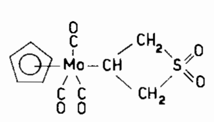


11

The infrared spectrum of a freshly prepared solution of **10** in liquid SO_2 at *ca.* −60 °C shows ν(C≡O) absorptions at 2115 m, 2063 vs, 2018 s, 1988 sh, and 1968 m cm^{-1}. Those at 2115, 2063, and 2018 cm^{-1} are assigned to the zwitterion **11** on the basis of a structurally similar η^2-alkene complex, $[\eta^5\text{-}C_5H_5Mo(CO)_3(\eta^2\text{-}CH_2{=}CHCH_3)]^+PF_6^-$, absorbing at 2110 vs, 2062 vs, and 2008 vs cm^{-1} [30]. The absorptions at 2063, 1988, and 1968 cm^{-1} belong to the *S*-sulfinato product **12** as verified by an independent measurement on isolated **12**. There was no evidence of any ν(C≡O) bands of unreacted **10**. Supporting these assignments is the behavior of the five bands upon storage of the solution. Those at 2115 and 2018 cm^{-1} decrease in intensity while the two at 1988 and 1968 cm^{-1} become more intense. The absorption at 2063 cm^{-1}, which is very strong as a result of the overlap of the bands of **11** and **12**, gains intensity slightly. No other bands were discernible which could be assigned to **13** or its dimer (or polymer). After several hours only the absorptions of **12** were evident. Although the relative intensities of the ν(C≡O) bands were not monitored as closely as those of the iron complexes, it was apparent that the rearrangement of **11** to **12** is faster than that of **3a** to **4a**. The faster reaction of the molybdenum complex may be a result of steric acceleration of dissociation of the metal-η^2-alkenesulfinate bond in the more bulky **11** relative to **3a**.



12



13

In the ^1H NMR spectrum of **10** in the τ 3.7–5.5 region, recorded at −30 to −10 °C, singlet resonances of η^5-C_5H_5 are initially noted at τ 4.01, 4.18, 4.38, and 4.44. The resonance at τ 4.01 decreases in intensity with time and is assigned to **11***; the other signals become more intense and correspond τ 4.18 to **12** and τ 4.38 and 4.44 most probably to **13** and its aggregate. Again there was no evidence of unreacted **10**. A representative spectrum, obtained after *ca.* 40 min, is provided in Fig. 3. It is noteworthy that the observed rearrangement of **11** is faster than that of **3a** and affords a higher ratio of the *S*-sulfinate to the cycloadduct than does **3a**.

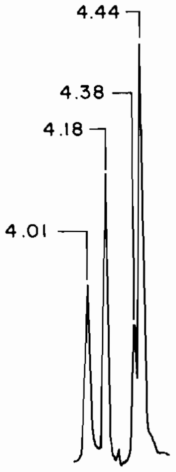


Figure 3. ^1H NMR spectrum in the η^5-C_5H_5 resonance region of a solution of **10** in liquid SO_2 aged for *ca.* 40 min at −30 to −10 °C. The chemical shifts are in τ.

Rapid removal of the solvent from a freshly prepared solution of **10** in liquid SO_2 affords a yellow–brown solid after crystallization of the residue from $CHCl_3$/pentane. This solid, apparently a mixture of **13** and its dimer or trimer (or of two differently aggregated species) from the ^1H NMR spectrum (two η^5-C_5H_5 resonances), displays a lower stability than its iron counterpart(s), **8a** and/or **9a**, and could not be satisfactorily analyzed. However its infrared ν(C≡O) absorptions fall in the range expected for a structure containing a Mo–C σ bond [6, 10], and its infrared $\nu(SO_2)$ absorptions and ^1H NMR resonances, given in the Experimental section, match closely the corresponding data for **8a** and **9a**. Instability precluded chemical studies on the constitution of the isolated solid, including the extent of and propensity toward aggregation.

Reaction of η^5-$C_5H_5Fe(CO)_2CH_2C{\equiv}CCH_3$ with Sulfur Dioxide

The reaction of transition metal–2-alkynyl complexes with SO_2 is thought also to proceed via a zwitterionic intermediate [1, 3]. In an attempt possibly to detect such a species freshly prepared solutions of η^5-$C_5H_5Fe(CO)_2CH_2C{\equiv}CCH_3$ in liquid SO_2 at *ca.* −60 °C were examined by infrared and ^1H NMR spectroscopy. However, spectra recorded a few minutes after preparation of these solutions showed the ν(C≡O) absorptions and the η^5-C_5H_5 resonance

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*By analogy with the corresponding resonance of $[\eta^5\text{-}C_5H_5Mo(CO)_3(\eta^2\text{-}CH_2{=}CHCH_3)]^+PF_6^-$ (ref. 30).

only of the cycloaddition product, η^5-$C_5H_5Fe(CO)_2$-$\overline{C{=}C(CH_3)S(O)OCH_2}$.*

The apparently rapid rearrangement of the zwitterion derived from this iron–2-alkenyl complex may be ascribed to its favorable, more rigid geometry for ring closure and to a strong activation by the positively charged iron of the *dihapto*coordinated allenesulfinate toward nucleophilic attack. In this context it is of interest to note that η^2-allene complexes of the type $[\eta^5\text{-}C_5H_5Fe(CO)_2(\eta^2\text{-allene})]^+BF_4^-$ exhibit much higher stability than the corresponding η^2-alkene complexes [21]. Presumably this will be reflected in a stronger activation of the *dihapto*coordinated allene than alkene.

Conclusion

This study has shown conclusively that iron–2-alkenyl complexes of the type η^5-$C_5H_5Fe(CO)_2CH_2$-$C(R){=}CR'R''$ react with SO_2 via the intermediacy of an iron–η^2-alkenesulfinate zwitterion. The observation that η^5-$C_5H_5Mo(CO)_3CH_2CH{=}CH_2$ reacts strictly analogously to η^5-$C_5H_5Fe(CO)_2CH_2CH{=}CH_2$ points to the generality of this mechanism for the reaction of transition metal–2-alkenyl carbonyl complexes with SO_2. Since protonation [19, 30] and alkylation [4] of the same complexes proceed also by attack at the C=C bond, this mode of interaction with transition metal 2-alkenyls appears to be general of electrophilic reagents.

It has been also demonstrated that the dual behavior of the generated zwitterion, cycloaddition *vs.* insertion, can be rationalized for the SO_2 electrophile in terms of the predicted lability of the metal–η^2-alkenesulfinate bond. Those zwitterions that are thought to be more labile react by insertion via dissociation, whereas those expected to be more inert react by cycloaddition. However, other factors, including concentration of the rearranging zwitterion, also exert an important influence on the mechanism of these reactions.

Experimental

General Procedures

All reactions except those involving sulfur dioxide were carried out in an atmosphere of nitrogen, which was also used routinely in handling organometallic compounds. Florisil (60–100 mesh), from Fisher, and Ventron alumina, deactivated with distilled H_2O (6–10%), were employed in chromatographic separations and purifications. Melting points were measured *in vacuo* on a Thomas–Hoover capillary melting point apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn., and by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.

Materials

Anhydrous grade SO_2, from Matheson, was passed through concentrated H_2SO_4 and a column packed with $CaCl_2$ and P_4O_{10} before condensation. All other solvents and chemicals were reagent grade or equivalent quality and were used as received.

The complexes η^5-$C_5H_5Fe(CO)_2CH_2C(R){=}CR'R''$ (**2a**: R = R' = R'' = H [19]; **2b**: R = R' = H, R'' = CH_3 [19]; **2c**: R = H, R' = R'' = CH_3 [18]; **2d**: R = CH_3, R' = R'' = H [6]), η^5-$C_5H_5Mo(CO)_3CH_2CH{=}CH_2$ (**10**) [30], and η^5-$C_5H_5Fe(CO)_2CH_2C{\equiv}CCH_3$ [16] were synthesized according to published methods. The corresponding *S*-sulfinates η^5-C_5H_5Fe-$(CO)_2S(O)_2C_3H_2RR'R''$ [18] (**4a**: R = R' = R'' = H; **4b**: R = R' = H; R'' = CH_3; **4c**: R = H, R' = R'' = CH_3; **4d**: R = CH_3, R' = R'' = H) and η^5-C_5H_5Fe-$(CO)_2\overline{C{=}C(CH_3)S(O)OCH_2}$ [16] were prepared and isolated as described in the appropriate references.

Measurements on Solutions of Metal–2-Alkenyl Complexes in Liquid SO_2

Infrared

Freshly chromatographed metal–2-alkenyl or related complexes (~30 mg) were dissolved in approximately 15 ml of liquid SO_2 and the resulting solutions were examined by infrared (ir) spectroscopy in the $\nu(C{\equiv}O)$ region on a Beckman Model IR-9 spectrophotometer. Aliquots (~3 ml) of these solutions were injected by means of a syringe cooled with Dry Ice into a VLT-2 variable low-temperature cell unit manufactured by Research and Industrial Instruments Co., London, England (available in the U.S. from Beckman Instruments Co., Fullerton, Calif.). This unit incorporated a 0.5-mm AgCl sample cell. Suitable adaptations in the cell unit were made for work with liquid SO_2; these adaptations and details of the procedure have been already published [31]. Temperature of the cell was maintained constant to within ±1°.

^1H NMR

Using standard vacuum-line techniques sulfur dioxide was condensed (~1 ml) into an NMR tube containing freshly chromatographed metal–2-alkenyl or related complex (~50–60 mg) and tetramethylsilane (TMS) at –78 °C. The tube was then sealed under vacuum at –196 °C. Measurements were made on a Varian Associates A-60A spectrometer equipped with low-temperature accessories. Temperature was controlled to within ±7°.

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*The observed values match closely those reported in ref. 16.

Reactions of Freshly Prepared Solutions of η^5-C_5H_5-$Fe(CO)_2CH_2CH{=}CH_2$ (2a) in Liquid SO_2

With KI

Sulfur dioxide was condensed (25 ml) into a 100-ml round-bottom flask containing freshly chromatographed **2a** (0.45 g, 2.1 mmol) at −78 °C. The flask was then charged with KI (21.0 g, 126 mmol) and after 15 min allowed to warm to −10 °C. The contents were stirred for 2 hr, the SO_2 was allowed to evaporate, and the residue was extracted with $CHCl_3$ (250 ml). The extracts were filtered, and the filtrate was evaporated to a brown oil on a rotary evaporator. Chromatography of the oil on alumina (10% H_2O) eluting with $CHCl_3$ afforded two bands which contained, respectively, η^5-$C_5H_5Fe(CO)_2I$ [32] (0.40 g, 70%) and η^5-$C_5H_5Fe(CO)_2S(O)_2CH_2$-$CH{=}CH_2$ (**4a**) (0.06 g, 10%) characterized by ir spectroscopy.

HCl followed by NH_4PF_6

Gaseous HCl was passed for 30–60 sec into a freshly prepared solution of chromatographically pure **2a** (1.0 g, 4.6 mmol) in liquid SO_2 (30 ml) at −78 °C. The solution changed color from yellow to greenish brown. It was then treated with 0.57 g (3.5 mmol) of NH_4PF_6 with shaking and the SO_2 was allowed to evaporate by removal of the cold bath. The yellow residue was washed first with CH_2Cl_2 and then with 10:1 $CHCl_3$/acetone. The washings were evaporated to dryness to yield a trace amount of red solid characterized by its ir ν(C≡O) absorptions at 2052 vs and 2001 vs cm^{-1} (CH_2Cl_2 solution) as η^5-$C_5H_5Fe(CO)_2Cl$ [32].

The yellow solid was treated with liquid SO_2 at −78 °C and the insoluble material was removed by filtration. The solvent was allowed to evaporate from the filtrate by removal of the cold bath. The yellow crystalline solid (0.5 g, 40%) obtained in this manner showed ir ν(C≡O) bands (Nujol mull) at 2080 vs and 2045 vs cm^{-1} (lit. [19] for $[\eta^5$-$C_5H_5Fe(CO)_2$-$(\eta^2$-$CH_2{=}CHCH_3)]^+PF_6^-$ 2082 vs, 2053 vs cm^{-1}, Nujol mull). Λ_M (1.2×10^{-3} *M* solution in nitrobenzene) 29.0 ohm^{-1} cm^2. ^{1}H NMR (acetone-d_6) τ 4.21 s (5H, C_5H_5), 4.79 c (1H, =CH–), 5.98 d (J = 17 Hz) and 6.36 d (J = 8 Hz) (2H, =CH_2), 8.10 d (J = 6 Hz, 3H, CH_3).

Anal. Calcd for $C_{10}H_{11}F_6FeO_2P$: C, 33.0; H, 3.02. Found: C, 32.68; H, 3.44%.

With CH_3SO_3F followed by NH_4PF_6

Sulfur dioxide was condensed (~5 ml) into a 100-ml round-bottom flask containing freshly chromatographed **2a** (0.83 g, 3.8 mmol) at −78 °C. The resulting solution was treated first with CH_3SO_3F (0.57 g, 5.1 mmol) and then with NH_4PF_6 (6.52 g, 40 mmol) in 20 ml of anhydrous methanol. The precipitated yellow solid was filtered off and recrystallized from 1:1 acetone/pentane (1.1 g, 79% yield). Its ir and ^{1}H NMR spectra were identical with those of the $[\eta^5$-$C_5H_5Fe(CO)_2(\eta^2$-$CH_2{=}CHCH_3)]^+PF_6^-$ prepared by the preceding reaction.

With $(CH_3)_3OBF_4$. Preparation of $[\eta^5$-C_5H_5Fe-$(CO)_2(\eta^2$-$CH_2{=}CHCH_2S(O)_2CH_3)]^+X^-$ where X = BF_4 (6a) and PF_6 (6a′)

Sulfur dioxide was condensed (~5 ml) into a flask containing freshly chromatographed **2a** (1.0 g, 4.6 mmol) at −78 °C, and to the resulting solution was added with stirring $(CH_3)_3OBF_4$ (0.85 g, 6.0 mmol). Stirring was continued for 10 min as the flask was removed from the cold bath, the SO_2 was evaporated in a stream of nitrogen, and CH_2Cl_2 (10 ml) was added to the residue. The insoluble yellow solid, **6a**, was filtered off and washed first with three 10-ml portions of methanol and then with two 10-ml portions of CH_2Cl_2, mp 137–139 °C (dec). The yield was 1.2 g (70%). Ir (Nujol mull) ν(C≡O) 2072 vs, 2041 vs cm^{-1}, $\nu(SO_2)$ 1302 s, 1139 s cm^{-1}. Λ_M (~5×10^{-4} *M* solution in acetone) 111 ohm^{-1} cm^2.

Anal. Calcd for $C_{11}H_{13}BF_4FeO_4S$: C, 34.42; H, 3.41; S, 8.34. Found: C, 34.17; H, 3.31; S, 8.22%.

The salt **6a** was added to a methanol solution of a large excess (~10 fold) of NH_4PF_6. The resulting suspension was stirred for 5 hr, filtered, and the collected yellow solid, **6a′**, was washed with H_2O, methanol, and ether, mp 140–145 °C (dec). Ir (Nujol mull) $\nu(SO_2)$ 1307 s, 1138 s cm^{-1}, $\nu(PF_6^-)$ 870 m, 830 vs, br cm^{-1}. ^{1}H NMR (acetone-d_6) τ 4.00 s (5H, C_5H_5), 6.95 s (3H, CH_3), other signals poorly resolved because of decomposition.

With $(C_6H_5)_3CCl$ followed by NH_4PF_6. Preparation of $[\eta^5$-$C_5H_5Fe(CO)_2(\eta^2$-$CH_2{=}CHCH_2S(O)_2$-$C(C_6H_5)_3]^+PF_6^-$ (7a)

Sulfur dioxide was condensed (~5 ml) into a flask containing freshly chromatographed **2a** (1.0 g, 4.6 mmol) at −78 °C, and to the resulting solution was added with stirring $(C_6H_5)_3CCl$ (1.4 g, 5.0 mmol) dissolved in 20 ml of CH_2Cl_2. The flask was removed from the cold bath and stirring was continued for a few minutes as a pale yellow precipitate appeared. The volume of the mixture was reduced in a stream of nitrogen and the precipitate was filtered off and washed with three 5-ml portions of CH_2Cl_2. The yield of $[\eta^5$-$C_5H_5Fe(CO)_2(\eta^2$-$CH_2{=}CHCH_2S(O)_2C(C_6$-$H_5)_3]^+Cl^-$, mp 53–55 °C (dec), was 1.8 g (73%).

The above salt (0.5 g, 0.9 mmol) was added with stirring to a methanol solution (15 ml) of NH_4PF_6 (1.5 g, 9.2 mmol). After 2 min the yellow solid was filtered off and washed first with three 10-ml portions of methanol and then with three 10-ml portions of CH_2Cl_2. The yield of **7a**, mp 153–155 °C (dec), was 0.37 g (62%). Ir (Nujol mull) ν(C≡O) 2081 vs, 2039 vs cm^{-1}, $\nu(SO_2)$ 1296 s, 1127 s cm^{-1}, $\nu(PF_6^-)$ 870 m, 830 vs, br cm^{-1}. ^{1}H NMR (acetone-d_6) τ 4.10 s (5H, C_5H_5), other signals, besides that of

C_6H_5, not readily assigned because of a high noise level. Λ_M (~5 × 10^{-4} *M* solution in acetone) 134 ohm^{-1} cm^2.

Anal. Calcd for $C_{29}H_{25}F_6FeO_4PS$: C, 51.96; H, 3.76; S, 4.77. Found: C, 51.80; H, 3.76; S, 4.57%.

Preparation of $[\eta^5\text{-}C_5H_5Fe(CO)_2(C_3H_5SO_2)]_x$ *(***8a** *and* **9a***)*

The following procedure was found to yield the title compound as a monomer (x = 1, **8a**) of relatively high purity.

Onto *ca.* 2 g of freshly chromatographed **2a** at −20 to −10 °C sulfur dioxide was condensed (~2 ml) and then immediately removed from the resulting solution by pumping at −10 to 0 °C for *ca.* 10 min. The yellow residue melted at 62–65 °C. Ir (KBr pellet) $\nu(C{\equiv}O)$ 2064 w, 2012 vs, 2008 w, 1957 vs cm^{-1}, $\nu(SO_2)$ 1302 s, 1174 w, 1109 s, 1037 w cm^{-1} (the weak absorptions are those of the contaminant **4a**, ~5%). ^{1}H NMR ($CDCl_3$) τ 4.78 s (~0.1 H, C_5H_5 of **4a**), 5.03 s (5H, C_5H_5), 5.08 s (variable but low intensity, C_5H_5 of x = 2 and/or 3 title complex, **9a**), 6.5 c (4H, 2CH_2), 7.8 c (~1H, CH). Calcd mol. wt. for $C_{10}H_{10}FeO_4S$: 282. Found ($CHCl_3$, osmometric): 285–288 (the compound was carefully degassed by pumping *in vacuo* and weighed in a dry box for these measurements). Mass spectrum (60 °C), no ions above m/e 220.

When **8a** was dissolved in minimum 2:1 CH_2Cl_2/hexane and the resulting solution was stored at 25 °C, yellow needles of **9a** (x = 2 and/or 3) separated gradually and were filtered off, mp 150–160 °C (dec). Ir ($CHCl_3$) $\nu(C{\equiv}O)$ 2020 vs, 1961 vs cm^{-1}, (KBr pellet) $\nu(C{\equiv}O)$ 2010 vs, 1957 vs cm^{-1}, $\nu(SO_2)$ 1324 s, 1298 s, 1126 s, 1109 s cm^{-1}. ^{1}H NMR ($CDCl_3$) τ 5.08 (5H, C_5H_5), 6.5 c (4H), 7.8 c (~1H). Calcd mol. wt. for $(C_{10}H_{10}FeO_4S)_2$: 564; for $(C_{10}H_{10}FeO_4S)_3$: 846. Found ($CHCl_3$, osmometric): 571–577, 604–660 (two different preparations). Mass spectrum (100 °C, intensity of peak at m/e 121 ($C_5H_5Fe^+$) = 100) includes peaks at m/e 266 ($C_5H_5Fe(CO)_2C_3H_5SO^+$, intensity 4.9), 190.018464 (exact mass) ($C_5H_5Fe(CO)C_3H_5^+$ 190.0080601, but $C_5H_5Fe(CO)_2CH^+$ 189.9716758, intensity 11.7), 162 ($C_5H_5Fe(CO)CH^+$ and/or $C_5H_5FeC_3H_5^+$, intensity 30.2), 133.98386 (exact mass) ($C_5H_5FeCH^+$ 133.9818476, intensity 10.8), 64 (SO_2^+, intensity 56); no peaks at m/e 282, 564 corresponding to $[C_5H_5Fe(CO)_2(C_3H_5SO_2)]^+_{1,2}$.

Anal. Calcd for $C_{10}H_{10}FeO_4S$: C, 42.58; H, 3.57; O, 22.69. Calcd for $C_{10}H_{10}FeO_5S$: O, 26.85. Found: C, 42.33, 42.41; H, 3.63, 3.76; O, 22.65%.

Complex **9a** was obtained also by condensing sulfur dioxide onto **2a** at temperatures ranging from −78 to −10 °C or by passing gaseous SO_2 through a solution of **2a** in pentane at *ca.* −75 °C. Removal of the SO_2 (and pentane) after varying reaction times and chromatography of the residue on Florisil first eluted **9a** with CH_2Cl_2 or $CHCl_3$ and then **4a** with 5:1 $CHCl_3$/acetone.

Reaction of $[\eta^5\text{-}C_5H_5Fe(CO)_2(C_3H_5SO_2)]_x$ *(***8a** *and* **9a***) with HCl*

Gaseous HCl was passed slowly through a freshly prepared solution of **8a** (~0.2 g) in pentane (25 ml) at 25 °C. Immediately the solution changed color from yellow–brown to red. After 2 hr solvent was removed on a rotary evaporator to leave a red–brown oil. The ir spectrum of this oil (neat) showed absorptions at 2052 vs and 2001 vs cm^{-1} ($\nu(C{\equiv}O)$, η^5-C_5H_5-$Fe(CO)_2Cl$) and at 1318 m and 1114 m cm^{-1} ($\nu(SO_2)$, organic sulfone). Chromatography on Florisil eluting with benzene afforded pure η^5-C_5H_5-$Fe(CO)_2Cl$, but the unknown organic sulfone could not be completely separated from a small amount of η^5-$C_5H_5Fe(CO)_2Cl$.

A similar result was obtained when solid **8a** was treated with gaseous HCl for 30 min.

Gaseous HCl was passed slowly into a solution of **9a** (0.25 g) in THF, CH_3CN, $CHCl_3$ or CH_2Cl_2 (30 ml) for 15–60 min. The yellow solution gradually turned red. Solvent was then removed on a rotary evaporator to leave a red–brown oil that showed (neat) ir $\nu(C{\equiv}O)$ bands at 2057 vs, 2001 vs cm^{-1} (η^5-$C_5H_5Fe(CO)_2Cl$), 2023 m, and 1962 m cm^{-1} (**9a**), and $\nu(SO_2)$ bands at 1316 m, 1120 m (organic sulfone), 1298 w, and 1110 w cm^{-1} (**9a**). Chromatography of this oil on alumina (10% H_2O) afforded η^5-$C_5H_5Fe(CO)_2Cl$ as the only pure product.

Preparation of $[\eta^5\text{-}C_5H_5Mo(CO)_3(C_3H_5SO_2)]_x$ (**13** *and/or its aggregate)*

Onto *ca.* 1 g of freshly chromatographed η^5-$C_5H_5Mo(CO)_3CH_2CH{=}CH_2$ (**10**) at −10 °C sulfur dioxide was condensed (2–3 ml) and then rapidly removed from the resulting solution in a stream of nitrogen. The residue was degassed by pumping *in vacuo* at 25 °C and dissolved in 4 ml of $CHCl_3$. Addition of pentane yielded a yellow–brown precipitate (0.2 g), dec *ca.* 105 °C. Ir (KBr pellet) $\nu(C{\equiv}O)$ 2057 w, 2021 vs, 1959 vs, sh, 1918 vs, br cm^{-1}, $\nu(SO_2)$ 1298 s, 1107 s cm^{-1} (the weak absorption is that of η^5-$C_5H_5Mo(CO)_3S(O)_2CH_2CH{=}CH_2$, **12**). ^{1}H NMR ($SO_2$) τ 4.38 s, 4.44 s (variable intensity, both signals 5 H), 6.56 c (4 H), 7.65 c (1 H).

Physical Measurements

Ir spectra were recorded on a Beckman Model IR-9 spectrophotometer whenever high precision and/or resolution was required. Other ir spectra were taken on a Perkin–Elmer Model 337 spectrophotometer. Room-temperature ^{1}H NMR spectra were recorded on Varian Associates A-60 and A-60A spectrometers using TMS as a reference. Mass spectral measurements were made at 70 eV on an A.E.I. Model MS-9 spectrometer by Mr. C. R. Weisenberger. Molar conductivities (Λ_M) were determined in various solvents using an Industrial Instruments, Inc., Model RC 16B2 conductivity bridge in conjunction with a cell with platinum electrodes. Molecular weights were obtained on a Mechrolab Model 301-A vapor pressure osmometer using *ca.* 10^{-2} *M* solutions.

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