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Reactions of Cyclopentadienylmetal–2-Alkenyl Carbonyl Complexes with Sulfur Dioxide. Isolation and Characterization of Metal–η^2-Alkenesulfinate Intermediates

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The isolation and characterization of the 2-alkene-S-sulfinato products of the reactions of transition metal–2-alkenyl complexes η^5-$C_5H_5M(CO)_xCH_2C(R)$=$CR'R''$ *(M = Fe and x = 2, M = Mo and x = 3, M = W and x = 3; R = R' = R'' = H, R = R' = H and R'' =* CH_3*, R = H and R' = R'' =* CH_3*, R = R' = H and R'' =* C_6H_5*, R =* CH_3 *and R' = R'' = H, and/or R = R' = H and R'' = Cl) with* SO_2 *under a variety of conditions are described. Products containing a 1,3 rearranged,* $MS(O)_2C(R')(R'')C(R)$=CH_2*, and/or an unrearranged,* $MS(O)_2CH_2C(R)$=$CR'R''$*, allylic fragment are obtained from unsymmetrical 2-alkenyl complexes. In addition, some metal 2-alkene-S-sulfinates exhibit cis–*trans *isomerism associated with the allylic C=C bond. The formation of the rearranged S-sulfinato isomers is promoted by the use of M = Fe over M = Mo or W, low temperatures of neat* SO_2*, and nonpolar over polar organic solvents. Moreover, the ratio of the rearranged to the unrearranged isomer decreases with the nature of the substituents R, R', and R'' in the order R = R' = H, R'' =* CH_3 *> R = H, R' = R'' =* CH_3 *⩾ R = R' = H, R'' =* C_6H_5*. The isomers were found not to interconvert under several different experimental conditions. The incidence of the above isomerism is rationalized in terms of a mechanism that entails the formation and subsequent dissociation of a metal–*η^2*-alkenesulfinate zwitterion, a 1,3 rearrangement via "internal return" of the dissociated alkenesulfinate anion, and a recombination of the rearranged and/or unrearranged anion with the cationic cyclopentadienylmetal carbonyl species. The desulfination of* η^5-$C_5H_5Fe(CO)_2S(O)_2$-C_6F_5 *thermally in toluene at reflux and photochemically in toluene is also described.*

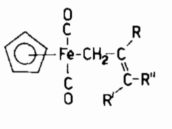
Introduction

In the preceding paper [1] described are the reactions of cyclopentadienyliron- and -molybdenum–2-alkenyl carbonyl complexes with sulfur dioxide to give initially the corresponding metal–η^2-alkenesulfinate zwitterions, and their rearrangement to the final, isolable products. Considered now in detail is the characterization of the *S*-sulfinato products of such SO_2 insertion reactions of various complexes η^5-$C_5H_5Fe(CO)_2CH_2C(R)$=$CR'R''$ (**1**), η^5-$C_5H_5Mo(CO)_3CH_2C(R)$=$CR'R''$ (**2**), and η^5-$C_5H_5W(CO)_3CH_2C(R)$=$CR'R''$ (**3**). The corresponding reactions of SO_2 with several metal 2-alkenyls $Mn(CO)_5CH_2C(R)$=$CR'R''$ [2], $Re(CO)_5CH_2C(R)$=$CR'R''$ [2] and $Co(dmgH)_2(py)CH_2C(R)$=$CR'R''$ [3] (dmgH = dimethylglyoximato, py = pyridine) to yield *S*-sulfinato derivatives have been reported.

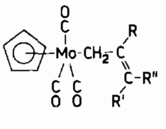
Results and Discussion

Synthesis and Characterization of 2-Alkenyl Complexes

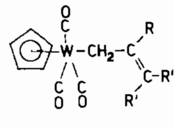
The 2-alkenyl complexes employed in this study are either known compounds or their close analogs. All of the new compounds were prepared by the reaction of the cyclopentadienyliron, -molybdenum or -tungsten carbonyl anion with the appropriate alkenyl chloride, $ClCH_2C(R)$=$CR'R''$. Because of the general thermal instability and sensitivity to air of these products, only few were characterized by elemental analyses. Characterization was accomplished by infrared and ^1H NMR spectroscopy and by conversion to the corresponding *S*-sulfinates, which were analyzed. The spectroscopic data for new metal–2-alkenyl complexes are set out in Table I.



1 a–f



2 a-d , f-g



3 b-c

a R = R′ = R″ = H
b R = R′ = H, R″ = CH_3 (*trans*) and/or R = R″ = H, R′ = CH_3 (*cis*)
c R = H, R′ = R″ = CH_3
d R = R′ = H, R″ = C_6H_5
e R = CH_3, R′ = R″ = H
f R = R′ = H, R″ = Cl (*trans*) and/or R = R″ = H, R′ = Cl (*cis*)
g R = R′ = Cl, R″ = H (*trans*) and/or R = R″ = Cl, R′ = H (*cis*)

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TABLE I. Infrared and ^{1}H NMR Spectra of New Metal–2-Alkenyl Complexes.

Complex	Ir, cm^{-1} [a]			^{1}H NMR, τ[b]
	ν(C≡O)	ν(C=C)	π(CH) of η^5-C_5H_5	
η^5-$C_5H_5Fe(CO)_2CH_2CH{=}C(CH_3)_2$, **1c**	2005vs, 1945vs[d]	1640w[d]	825s[d]	4.55t (J = 9Hz, CH), 5.29s (C_5H_5), 7.64d (J = 9Hz, CH_2), 8.37s ($2CH_3$)
η^5-$C_5H_5Fe(CO)_2CH_2CH{=}CHC_6H_5$, **1d**	2010vs, 1955vs	1620w	829m	2.77m (C_6H_5), 3.16–4.00m (CH=CH), 5.37s (C_5H_5), 7.72d (J = 7.5Hz, CH_2)
η^5-$C_5H_5Fe(CO)_2CH_2CH{=}CHCl$, **1f**	2018vs, 1968vs	[e]	[e]	[e]
η^5-$C_5H_5Mo(CO)_3CH_2CH{=}CHCH_3$, **2b**[c]	2015vs, 1930vs, br	1640w	811s	3.80–5.03m (CH=CH), 4.75s, 4.82s (C_5H_5), 7.67d (J = 7Hz, CH_2), 8.33d (J = 6Hz, CH_3)
η^5-$C_5H_5Mo(CO)_3CH_2CH{=}C(CH_3)_2$, **2c**	2015vs, 1930vs, br[f]	1635w[f]	815s[f]	4.60t (J = 9Hz, CH), 4.80s (C_5H_5), 7.67d (J = 9Hz, CH_2), 8.29s, 8.35s ($2CH_3$)
η^5-$C_5H_5Mo(CO)_3CH_2CH{=}CHC_6H_5$, **2d**	2020vs, 1930vs, br	1620w	814s	2.76m (C_6H_5), 3.17–4.00m (CH=CH), 4.82s (C_5H_5), 7.47d (J = 8Hz, CH_2)
η^5-$C_5H_5Mo(CO)_3CH_2CH{=}CHCl$, **2f**[c]	2025vs, 1940vs, br[g]	1660vw[g]	814s[g]	3.58–4.50m (CH=CH), 4.70s, 4.79s (C_5H_5), 7.71d (J = 8.5Hz), 7.82d (J = 8Hz)(CH_2)
η^5-$C_5H_5Mo(CO)_3CH_2CH(Cl){=}CHCl$, **2g**	2030vs, 1940vs, br[d]	1570w[d]	822s[d]	4.29s (CH), 4.62s (C_5H_5), 7.53s (CH_2)
η^5-$C_5H_5W(CO)_3CH_2CH{=}CHCH_3$, **3b**[c]	2010vs, 1920vs, br	1640vw	822s	4.03–5.26m (CH=CH), 4.72s, 4.77s (C_5H_5), 7.70d (J = 7Hz, CH_2), 8.37d (J = 6Hz, CH_3)
η^5-$C_5H_5W(CO)_3CH_2CH{=}C(CH_3)_2$, **3c**	2010vs, 1920vs, br	1640w	820s	4.63t (J = 9Hz, CH), 4.71s (C_5H_5), 7.67d (J = 9Hz, CH_2), 8.30s, 8.36s ($2CH_3$)

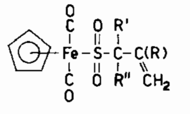
[a] Recorded on a Perkin–Elmer Model 337 spectrophotometer in $CHCl_3$ solution unless otherwise indicated. Abbreviations: vs, very strong; s, strong; m, medium; w, weak; vw, very weak; br, broad. [b] In $CDCl_3$ solution with TMS as an internal standard. Abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet. [c] A mixture of the *cis* and *trans* isomers. [d] Neat oil. [e] Not measured because of instability. [f] CH_2Cl_2 solution. [g] Nujol mull.

All of the compounds contain a 2-alkenyl fragment bonded to the metal via a primary, CH_2 carbon atom. This is inferred from the appearance of a proton resonance of the CH_2 group at τ 7.47–7.82 with the expected relative intensity. The observed resonance occurs as a doublet with J = 7–9Hz, consistent with the presence of an $MCH_2CH=$ fragment, except for **2g** where it occurs as a singlet owing to the presence of an $MCH_2C(Cl)=$ moiety.

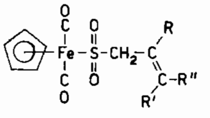
The ^{1}H NMR spectra of **2b**, **2f**, and **3b** each show two η^5-C_5H_5 resonances, and that of **2f** also displays two CH_2 signals as doublets. These features most likely indicate the presence of the *cis* and *trans* isomers associated with the allylic C=C bond. Significantly, in the ^{1}H NMR spectra of **1d**, **2d**, and **2g** there occurs only one η^5-C_5H_5 signal, suggesting that a single isomer is present in each case. Complex **1d** was synthesized independently by Rosenblum, *et al.* [4] and assigned a *trans* structure. From the similarity of the ^{1}H NMR spectra of **1d** and **2d** it is likely that the isolated **2d** also has a *trans* geometry. In contrast, the stereochemistry of the single isomer of **2g** cannot be inferred from the ^{1}H NMR spectrum.

Synthesis and Characterization of S-Sulfinato Complexes

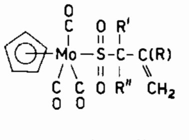
The iron–2-alkenyl complexes **1a–e** and the molybdenum–2-alkenyl complexes **2a–d**, **f** readily react with neat SO_2 at reflux to give, after evaporation of the solvent and chromatography, the corresponding *S*-sulfinates **4a–e** and/or **5c–d** and **6a–b** and/or **7b–d**, **f**, respectively. Complexes **1a** and **2a** additionally afford, as major products, 1:1 cycloaddition compounds which are described fully in the preceding paper [1]. The iron 2-alkenyl **1f** reacted slowly and with considerable decomposition with SO_2 to yield a small amount of what appears to be the corresponding *S*-sulfinate from its infrared spectrum. Likewise, the reaction between **2g** and SO_2 proceeded slowly to give a minute quantity of what seems to be the expected insertion product. Neither of the two products was obtained in a sufficient amount for full characterization. The tungsten–2-alkenyl complexes **3b–c** also underwent very slow insertion reaction with SO_2 at reflux. Low yields of **8b** and/or **9b–c** were isolated and appreciable amounts of the starting materials were recovered. Thus the relative reactivities toward neat SO_2 of the 2-alkenyl complexes of iron, molybdenum, and tungsten qualitatively parallel the reported reactivities of the corresponding metal alkyls [5–9].



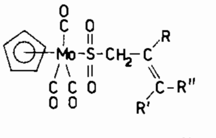
4a R = R′ = R″ = H
4b R = R′ = H, R″ = CH_3
4c R = H, R′ = R″ = CH_3
4d R = R′ = H, R″ = C_6H_5
4e R = CH_3, R′ = R″ = H



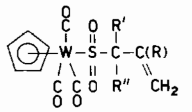
5c R = H, R′ = R″ = CH_3
5d R = R′ = H, R″ = C_6H_5



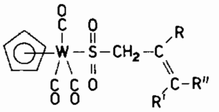
6a R = R′ = R″ = H
6b R = R′ = H, R″ = CH_3



7b R = R′ = H, R″ = CH_3 (*trans*) and/or R = R″ = H, R′ = CH_3 (*cis*)
7c R = H, R′ = R″ = CH_3
7d R = R′ = H, R″ = C_6H_5
7f R = R′ = H, R″ = Cl (*trans*) and/or R = R″ = H, R′ = Cl (*cis*)



8b R = R′ = H, R″ = CH_3



9b R = R′ = H, R″ = CH_3 (*trans*) and/or R = R″ = H, R′ = CH_3 (*cis*)
9c R = H, R′ = R″ = CH_3

The 2-alkene-*S*-sulfinato complexes isolated in this work generally exhibit properties that are very similar to those of the *S*-sulfinates derived from the corresponding metal alkyls [5–7]. Accordingly, the iron complexes **4** and **5** are very stable to air at room temperature; however, the molybdenum compounds **6** and **7** gradually turn from orange (golden) to green upon storage. The stability of the tungsten compounds **8** and **9** is intermediate between those of iron and molybdenum. The iron *S*-sulfinates melt sharply whereas the molybdenum analogs decompose before melting. All of the *S*-sulfinates are readily soluble in polar organic solvents such as CH_2Cl_2, $CHCl_3$, and acetone, but only moderately soluble in benzene.

The gross *S*-sulfinato structural assignment for complexes **4–9** rests on the infrared and ^{1}H NMR spectroscopic data set out in Table II. Specifically, the infrared ν(C≡O) and $\nu(SO_2)$ absorptions and the ^{1}H NMR η^5-C_5H_5 resonances match closely those of the *S*-sulfinato complexes derived from the corresponding metal alkyls [5–8].

Two types of isomerism must be considered for some of the isolated 2-alkene-*S*-sulfinato products. First, if the carbon atoms 1 and 3 of the allyl fragment in the precursor 2-alkenyl complex are not equivalent, then the resultant *S*-sulfinate may contain either a 1,3 rearranged (**4b–d**, **6b**, and **8b**) or an unrearranged (all of **5**, **7**, and **9**) unsaturated hydrocarbon moiety. Second, when R′ ≠ R″ for **5**, **7**, and **9**, *cis–trans* isomerism about the allylic C=C bond is to be expected.

Whether or not an unsymmetrical 2-alkenyl fragment underwent 1,3 rearrangement in the insertion is readily ascertained by ^{1}H NMR spectroscopy. When

TABLE II. Infrared and ^{1}H NMR Spectra of New Metal–*S*-Sulfinato Complexes.

Complex	Ir, cm^{-1}				^{1}H NMR, τ[d]
	$\nu(C\equiv O)$[a]	$\nu(C{=}C)$[b]	$\nu(SO_2)$[c]	$\pi(CH)$ of η^5-C_5H_5[b]	
η^5-$C_5H_5Fe(CO)_2S(O)_2CH_2CH{=}CH_2$, **4a**	2064vs, 2008vs	1650w-m, 1640m	1174s, 1164sh, 1037s, 1021sh	864m	3.58–4.83m ($CH{=}CH_2$), 4.78s (C_5H_5), 6.24d (J = 7Hz, CH_2)
η^5-$C_5H_5Fe(CO)_2S(O)_2CH(CH_3)CH{=}CH_2$, **4b**	2062vs, 2005vs	1630w	1178s, 1045s	855m	3.42–5.15m ($CH{=}CH_2$), 4.75s (C_5H_5), 5.84–6.67m (CH), 8.58d (J = 7Hz, CH_3)
η^5-$C_5H_5Fe(CO)_2S(O)_2C(CH_3)_2CH{=}CH_2$, **4c**	2061vs, 2017vs	1620w	1178s, 1164sh, 1037s, 1028sh	857m	3.44–4.68m ($CH{=}CH_2$), 4.76s (C_5H_5), 8.65s ($2CH_3$)[m]
η^5-$C_5H_5Fe(CO)_2S(O)_2CH_2CH{=}C(CH_3)_2$, 5c	2069vs, 2003vs	1670w-m	1179s, 1041s, 1026sh	846s	4.56t (J = 8Hz, CH), 4.78s (C_5H_5), 6.27d (J = 8Hz, CH_2), 8.17s, 8.22s ($2CH_3$)
η^5-$C_5H_5Fe(CO)_2S(O)_2CH(C_6H_5)CH{=}CH_2$, 4d	h	h	h	h	2.62m (C_6H_5), 4.33–5.00 ($CH{=}CH_2$), 5.11s (C_5H_5), 5.45d (J = 8.5Hz, CH_2)[n]
η^5-$C_5H_5Fe(CO)_2S(O)_2CH_2CH{=}CHC_6H_5$, **5d**	2062vs, 2011vs	1635w	1186s, 1177sh, 1042sh, 1036s	847m	2.60m (C_6H_5), 3.00–3.93m (CH=CH), 4.85s (C_5H_5), 6.08d (J = 6.5Hz, CH_2)
η^5-$C_5H_5Fe(CO)_2S(O)_2CH_2C(CH_3){=}CH_2$, 4e[e]	2045vs, 2000vs[i]	h	1178s, 1044s[i]	h	4.81s (C_5H_5), 4.90s ($=CH_2$), 6.27s (CH_2), 8.00s (CH_3)
η^5-$C_5H_5Mo(CO)_3S(O)_2CH_2CH{=}CH_2$, **6a**	2058vs, 1984vs, 1972vs	1630w-m	1177s, 1169sh, 1046s	852m	3.85–4.89m ($CH{=}CH_2$), 4.19s (C_5H_5), 6.23d (J = 7Hz, CH_2)
η^5-$C_5H_5Mo(CO)_3S(O)_2CH(CH_3)CH{=}CH_2$, 6b	2057vs, 1985vs, 1969sh	1625vw	1175s, 1166sh, 1052sh, 1042s	848m	3.78–4.95m ($CH{=}CH_2$), 4.26s (C_5H_5), 6.03–6.70m (CH, CH_2 of minor isomer), 8.25d (J = 5Hz, CH_3 of minor isomer), 8.65d (J = 7Hz, CH_3)[o]
η^5-$C_5H_5Mo(CO)_3S(O)_2CH_2CH{=}C(CH_3)_2$, 7c	2055vs, 1980vs, 1970vs	1660vw	1187s, 1176sh, 1050sh, 1044s	841m	4.22s (C_5H_5), 4.63t (J = 8Hz, CH), 6.24d (J = 8Hz, CH_2), 8.18s, 8.26s ($2CH_3$)
η^5-$C_5H_5Mo(CO)_3S(O)_2CH_2CH{=}CHC_6H_5$, 7d	2056vs, 1983vs, 1969vs	k	1192s, 1176sh, 1046sh, 1043s	849w	2.65m (C_6H_5), 3.24–3.91m (CH=CH), 4.26s (C_5H_5), 6.08d (J = 6Hz, CH_2)
η^5-$C_5H_5Mo(CO)_3S(O)_2CH_2CH{=}CHCl$, 7f[f]	2059vs, 1978vs, br	1620w	1204sh, 1190s, 1054s[l]	850m	3.29–4.47m (CH=CH), 4.23, 4.27s (C_5H_5, *cis* and *trans* isomers), 6.00d (J = 7.5Hz), 6.29d (J = 7Hz) (CH_2, *cis* and *trans* isomers)
η^5-$C_5H_5W(CO)_3S(O)_2CH(CH_3)CH{=}CH_2$, 8b[g]	2050vs, 1995vs, 1969vs, 1955vs	1635vw	1175s, 1043s	852w	4.13s (C_5H_5), 4.18–4.90m ($CH{=}CH_2$, impurity), 5.88–6.55m (CH, impurity), 8.30m (impurity) 8.70d (J = 7Hz, CH_3)

η^5-$C_5H_5W(CO)_3S(O)_2CH_2CH{=}C(CH_3)_2$, 9c	2052vs, 1966vs, 1958vs	1660vw	1189s, 1178sh 1048s	845m	4 11s (C_5H_5), 4 66t (J = 8Hz, CH), 6 12d (J = 8Hz, CH_2), 8 22s, 8 27s ($2CH_3$)
η^5-$C_5H_5Fe(CO)_2S(O)_2C_6H_4F$-*p*	2057vs, 2011vs^j	—	1205m, 1047s^j	h	2 62m (C_6H_4), 4 94s (C_5H_5)
η^5-$C_5H_5Fe(CO)_2S(O)_2C_6F_5$	2068vs, 2025vs^j	—	1230s, 1078s, 1064sh	h	h
η^5-$C_5H_5Fe(CO)_2S(O)_2CCl_3$	2065vs, 2025vs^j	—	1235s, 1081s, 1068sh^j	h	h

[a] Recorded on a Beckman Model IR-9 spectrophotometer in $CHCl_3$ solution unless otherwise indicated Abbreviations vs, very strong, s, strong, m, medium, w, weak, vw, very weak, br, broad, sh, shoulder [b] Recorded on a Perkin–Elmer Model 337 spectrophotometer in Nujol mull [c] Recorded on a Beckman Model IR-9 spectrophotometer in Nujol mull unless otherwise indicated [d] In $CDCl_3$ solution with TMS as an internal standard Abbreviations s, singlet, d, doublet, t, triplet, m, multiplet [e] Prepared and characterized by D W Lichtenberg (mp 153 °C (dec), calcd mol wt 295, found by mass spectrometry P^+ m/e 295) [f] A mixture of the *cis* and *trans* isomers [g] Impure complex [h] Not measured [i] KBr pellet [j] Recorded on a Perkin–Elmer Model 337 spectrophotometer in CH_2Cl_2 solution [k] Not observed [l] In CH_2Cl_2 solution [m] Values from the spectrum of a mixture containing 94% **4c** and 6% **5c** [n] Values from the spectrum of a mixture containing 70% **4d** and 30% **5d**. [o] The minor isomer appears to be **7b**

only one isomer is present, the determination of its structure follows a straightforward analysis of the spectrum [2] Accordingly, all of the unrearranged 2-alkene-*S*-sulfinato isomers display a resonance of the $S(O)_2CH_2C(R){=}$ methylene protons at τ 6 00–6 29, split into a doublet (J = 6 5–8Hz) when R = H, with a relative intensity of 2 compared to that of the signal of the η^5-C_5H_5 being 5 For the rearranged isomers a signal in the τ 5 3–7 0 region either is missing ($S(O)_2C(CH_3)_2CH{=}CH_2$) or occurs with a lower relative intensity of 1 and/or different multiplicity ($S(O)_2CH(CH_3)CH{=}CH_2$ and $S(O)_2CH(C_6H_5)$-$CH{=}CH_2$) Another distinguishing feature in the spectra of the complexes containing the $S(O)_2C$-$(CH_3)_2CH{=}CH_2$ fragment is the appearance of a single CH_3 proton resonance with a relative intensity of 6, the isomeric $S(O)_2CH_2CH{=}C(CH_3)_2$ gives two CH_3 resonances, each with a relative intensity of 3 The remaining parts of the ^1H NMR spectra also serve to distinguish between such isomeric structures

Mixtures of the rearranged and unrearranged 2-alkene-*S*-sulfinato isomers were similarly analyzed by ^1H NMR spectroscopy For **4c**/**5c** the ratios of the two species were determined by the integration of the respective CH_3 proton resonances, which do not overlap To establish the identity of **4c** and **5c** in such mixtures, each isomer was prepared essentially pure from contamination by the other Complex **4c** was isolated in *ca* 94% purity from reaction of **1c** with SO_2 (*vide infra*) whereas isomerically pure **5c** was obtained by reaction of $Na^+[\eta^5$-$C_5H_5Fe(CO)_2]^-$ with SO_2 followed by addition of $ClCH_2CH{=}C(CH_3)_2$* The ^1H NMR spectra of these isomers are shown in Fig 1

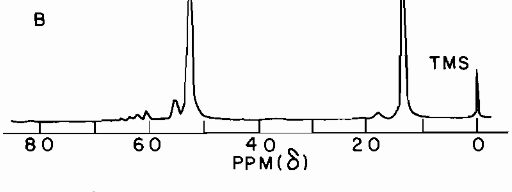


Figure 1 ^1H NMR spectra of (A) **5c** and (B) 94 6 **4c**/**5c**, both in $CDCl_3$

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*This general synthetic procedure for the *S*-sulfinates η^5-$C_5H_5Fe(CO)_2S(O)_2R$ where R = alkyl, 2-alkenyl or 2-alkynyl will be described in a later publication, P Reich-Rohrwig, A C. Clark, R L Downs and A. Wojcicki, *J Organomet Chem*, in press

Partial separation of the above isomers was achieved by using a 2.2 X 35-cm column of alumina (10% H_2O) made up with $CHCl_3$. A 0.5-g sample of 70:30 **5c/4c** in 10ml of $CHCl_3$ was eluted with this solvent and the effluent was collected in two fractions, the first one containing *ca.* 40% of the sample. On the basis of the ^1H NMR spectra the first cut contained a 50:50 mixture of **5c/4c**, and the second cut 86:14 **5c/4c**.

In the case of **4d/5d** the isomeric ratios in mixtures were elucidated by the integration of the nonoverlapping respective η^5-C_5H_5 proton resonances. For these measurements pure **5d** was obtained via reaction of **1d** with SO_2 (*vide infra*), followed by chromatography and crystallization of the *S*-sulfinato product mixture substantially enriched in this isomer. Complex **4d** was prepared as an 80:20 mixture of **4d/5d**, also by SO_2 insertion (*vide infra*). The ^1H NMR spectra of pure **5d** and 70:30 **4d/5d** are shown in Fig. 2.

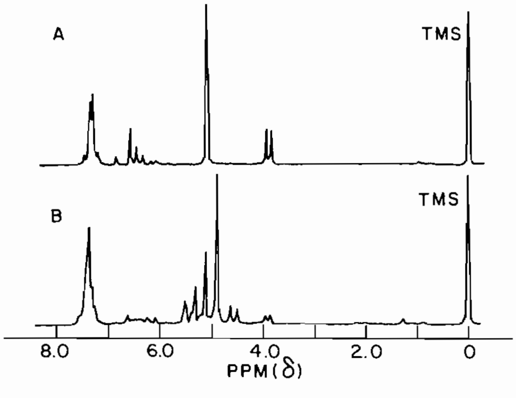


Figure 2. ^1H NMR spectra of (A) **5d** and (B) 70:30 **4d/5d**, both in $CDCl_3$.

The ^1H NMR spectrum of the *S*-sulfinato product derived from **2b** and SO_2 indicates that the predominant (85–90%) isomer is **6b**. However, the appearance of a low intensity doublet in the CH_3 proton region (τ 8.25) points to the presence of another species, which may be the isomeric **7b**. Likewise, on the basis of the ^1H NMR spectrum one cannot dismiss the possibility that some **9b** is present along with **8b** in the impure *S*-sulfinato product isolated from the reaction of **3b** with SO_2.

Turning now to *cis–trans* isomerism of the 2-alkene-*S*-sulfinato products, complexes **5d** and **7d**, like their precursors **1d** and **2d**, respectively, appear to be present exclusively in the *trans* form. This assignment is made on the basis of their ^1H NMR spectra which show only one η^5-C_5H_5 signal each and which resemble the spectra of **1d** and **2d**. Furthermore, an analogous *S*-sulfinato complex, $[\eta^5\text{-}(CH_3)_5\text{-}C_5]Fe(CO)_2S(O)_2CH_2CH{=}CHC_6H_5$ [10], was shown by X-ray crystallography to adopt a *trans* configuration [11].

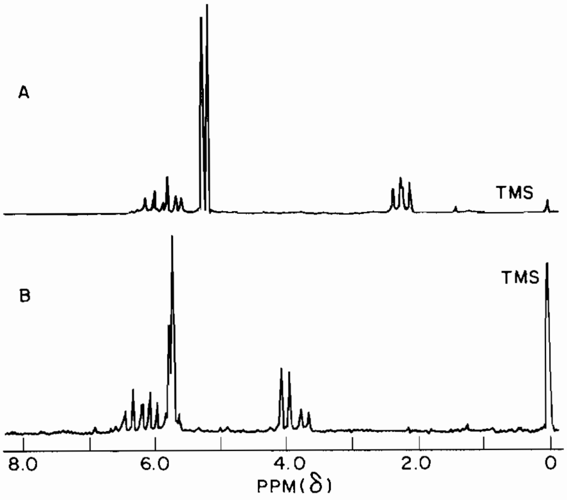


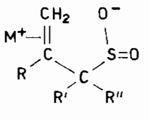
Figure 3. ^1H NMR spectra of (A) *ca.* 50:50 *cis/trans* **2f** and (B) 77:23 *cis/trans* (or *trans/cis*) **7f**, both in $CDCl_3$.

The ^1H NMR spectra of the *S*-sulfinate **7f** and its precursor **2f** are shown in Fig. 3. The starting material is approximately a 50:50 mixture of the *cis* and *trans* isomers as evidenced by the appearance of two resonances of comparable intensities for both the η^5-C_5H_5 and the CH_2 protons. The resulting *S*-sulfinate also shows two η^5-C_5H_5 signals of unequal intensity, and two doublets of the relative intensity 77:23 at τ 6.00 and 6.29. Both doublets are assigned to the methylene protons of the $S(O)_2CH_2CH{=}CHCl$ ligand of **7f**. The alternative formulation, $S(O)_2CH(Cl)CH{=}CH_2$, appears unlikely. Organic compounds containing a $CH_2S(O)_2CH(Cl)$ fragment show CH_2 proton signals at τ 6.73–6.91 and CH proton signals at much lower fields, τ 5.0–5.4 [12]. These values, when compared with the CH_2 proton resonance of **6a–b** at *ca.* τ 6.2, suggest that the $S(O)_2CH(Cl)$ proton of $MoS(O)_2CH(Cl)CH{=}CH_2$ would absorb below τ 5. Thus it appears that **7f** is a mixturc of the *cis* and *trans* isomers; however, the identity of the major constituent is not unequivocal. For $ClCH_2CH{=}CHCl$, employed in the synthesis of **2f**, the low boiling, *cis* isomer exhibits a lower field CH_2 proton resonance than the high boiling, *trans* isomer [13]. If this trend extends to the *cis–trans* isomers of the 2-alkenyl complexes and their SO_2 insertion products, then the isolated **7f** is 77:23 *cis/trans*. It is noteworthy that the **2f** recovered in the insertion reaction consisted of unequal, *ca.* 72:28 amounts of the *cis* and *trans* isomers, in favor of the *cis* isomer if the above empirical assumption for ^1H NMR peak assignment holds true.

The principal isolated product of the above insertion reaction is the carbonyl chloride η^5-$C_5H_5Mo(CO)_3Cl$. The mode of the formation of η^5-$C_5H_5Mo(CO)_3Cl$ is uncertain; however, it cannot be ruled out that this compound originates from decomposition of the *S*-sulfinate containing a rearranged 2-alkenyl moiety, η^5-$C_5H_5Mo(CO)_3S(O)_2CH(Cl)CH{=}CH_2$. The isolated isomeric **7f** decomposes only very slowly upon storage at room temperature, yielding trace η^5-$C_5H_5Mo(CO)_3Cl$ after 3 months, and alone cannot account for all of the η^5-$C_5H_5Mo(CO)_3Cl$ produced in the SO_2 insertion. In a similar reaction, the formation of $Mn(CO)_5Cl$ from $Mn(CO)_5CH_2CH{=}CHCl$ and SO_2 was noted earlier [2].

Mechanism of Allylic Rearrangement Accompanying Sulfur Dioxide Insertion

It remains to consider a reasonable mechanism for the formation of the *S*-sulfinato products that contain either a rearranged or an unrearranged 2-alkenyl fragment. In doing so it will be assumed that the precursor of every metal 2-alkene-*S*-sulfinate prepared via SO_2 insertion in this work is the corresponding zwitterion **10**. Such a zwitterion was detected and/or trapped for several of these complexes, as described fully in the preceding paper [1]. Moreover, **10** was shown to rearrange to the *S*-sulfinato product without the intermediacy of any other species in spectroscopically detectable concentrations.

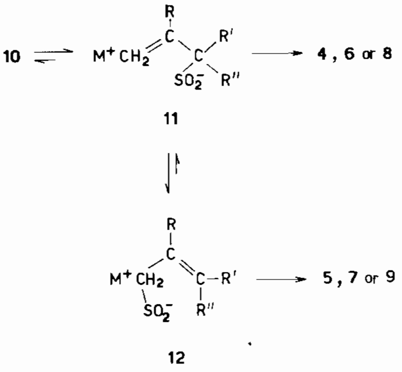


10

M = η^5-$C_5H_5Fe(CO)_2$, η^5-$C_5H_5Mo(CO)_3$ or η^5-$C_5H_5W(CO)_3$

A point of utmost importance in these mechanistic considerations concerns possible interconversion of such 2-alkene-*S*-sulfinato isomers under reaction conditions. Control experiments revealed that neither **4c** nor **5c** shows any tendency to undergo isomerization in neat SO_2 at reflux in 4–8 hr*, in acetonitrile in the presence or absence of SO_2 in 10 hr or in *ca.* 75:25 methanol/SO_2 at 25 °C in 10 hr. However, **5c** is somewhat more stable than **4c** as indicated by an experiment in which a 94:6 mixture of **4c**/**5c** was stored in benzene at reflux. After 13 hr the ^1H NMR spectrum showed a composition of 84:16 **4c**/**5c**. Under milder conditions, *e.g.*, stirring in THF at 25 °C for 12 hr, the two isomers exhibited the same apparent degree of stability. It will be assumed that the other isomers obtained here also are stable with respect to interconversion. This stability contrasts with the observation that the kinetically favored tin *O*-sulfinates $[R_3SnOS(O)CH(C_6H_5)CH{=}CH_2]_x$ ($R = CH_3$ or C_6H_5) isomerize to $[R_3SnOS(O)CH_2CH{=}CHC_6H_5]_x$ by an unknown pathway in solution [15].

Taking into account the above information, the following general mechanism appears to be in accord with the ratios of the isomeric 2-alkene-*S*-sulfinato products isolated from the insertion reactions under a variety of conditions and summarized in Table III.



M = η^5-$C_5H_5Fe(CO)_2$, η^5-$C_5H_5Mo(CO)_3$ or η^5-$C_5H_5W(CO)_3$

The salient feature of this mechanism is the equilibrium between the two ionic species (or ion pairs) **11** and **12**. The two are thought to interconvert by the so-called "internal return" [16], with the initially generated **11** being kinetically favored and the sterically less crowded **12** being thermodynamically preferred. Neither species appears to be present in a sufficiently high concentration for spectroscopic detection.

For a given metal system, *e.g.*, η^5-$C_5H_5Fe(CO)_2$-$CH_2C(R){=}CR'R''$, the ratio of the isomeric 2-alkene-*S*-sulfinato products is expected to depend on the relative amounts of **11** and **12** which, in turn, vary with the nature of the substituents R, R′, and R″. Accordingly, in neat SO_2 at reflux the sterically less encumbered **1b** affords exclusively the rearranged **4b** whereas the more crowded **1c** and **1d** yield the mixtures **4c**/**5c** and **4d**/**5d**, respectively, each rich in the unrearranged product. Similarly, **2b** affords principally the rearranged isomer **6b** whereas **2c** and **2d** give the unrearranged *S*-sulfinato isomers, **7c** and **7d**, respectively. The generally larger ratio of the unrearranged to the rearranged *S*-sulfinato product observed for molybdenum as compared to iron possibly results from a slower rate of the conversion of **11** or **12** to **6** or **7** than to **4** or **5**. This difference in rate, expected on steric grounds, would allow a closer approach to equilibrium between **11** and **12** when the metal is molybdenum (or tungsten) than when it is iron.

Inspection of the data in Table III also reveals that the formation of the rearranged 2-alkene-*S*-sulfinate **4c** over its isomer **5c** is promoted by the use of nonpolar over polar organic solvents and of very low temperatures of neat SO_2. The observed preference may be a consequence of the slower rate of attainment of equilibrium between **11** and **12** under stated conditions.

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*The previous report (ref. 14) that **4c** undergoes isomerization to **5c** in neat SO_2 at reflux has been later shown to be incorrect.

TABLE III. Relative Percentages of Isomeric 2-Alkene-*S*-Sulfinato Products in Reactions of Unsymmetrical 2-Alkenyl Complexes of Iron, Molybdenum, and Tungsten with Sulfur Dioxide.

2-Alkenyl Complex	Reaction Conditions	Relative % of *S*-Sulfinate[a]	
		Rearranged 2-Alkenyl Group	Unrearranged 2-Alkenyl Group
η^5-$C_5H_5Fe(CO)_2CH_2CH{=}CHCH_3$, **1b**	SO_2 at reflux	100 **4b**	0
η^5-$C_5H_5Fe(CO)_2CH_2CH{=}C(CH_3)_2$, **1c**	SO_2 at reflux	25 **4c**	75[b] **5c**
	SO_2 at −45 to −35 °C, 1.25hr	60 **4c**	40 **5c**
	SO_2 at −65 to −55 °C, 4–7hr	85 **4c**	15[b] **5c**
	SO_2 in hexane, 27 °C, 36 hr	93 **4c**	7[c] **5c**
	SO_2 in 1:1 hexane/benzene, 27 °C, 24hr	80 **4c**	20 **5c**
	SO_2 in benzene, 27 °C, 24hr	73 **4c**	27[d] **5c**
	SO_2 in acetonitrile, 27 °C, 18–24hr	53 **4c**	47[e] **5c**
	SO_2 in nitromethane, 27 °C, 24hr	49 **4c**	51 **5c**
η^5-$C_5H_5Fe(CO)_2CH_2CH{=}CHC_6H_5$, **1d**	SO_2 at reflux	20 **4d**	80[f] **5d**
	SO_2 in hexane, 27 °C, 14hr	80 **4d**	20 **5d**
η^5-$C_5H_5Mo(CO)_3CH_2CH{=}CHCH_3$, **2b**	SO_2 at reflux	85–90 **6b**	10–15 **7b**[g]
η^5-$C_5H_5Mo(CO)_3CH_2CH{=}C(CH_3)_2$, **2c**	SO_2 at reflux	0	100 **7c**
η^5-$C_5H_5Mo(CO)_3CH_2CH{=}CHC_6H_5$, **2d**	SO_2 at reflux	0	100 **7d**
η^5-$C_5H_5Mo(CO)_3CH_2CH{=}CHCl$, **2f**	SO_2 at reflux	0[h]	100 **7f**
η^5-$C_5H_5W(CO)_3CH_2CH{=}CHCH_3$, **3b**	SO_2 at reflux	100[i] **8b**	0
η^5-$C_5H_5W(CO)_3CH_2CH{=}C(CH_3)_2$, **3c**	SO_2 at reflux	0	100 **9c**

[a] Estimated accuracy ±3%. [b] Average of two runs, ±2%. [c] Average of two runs, ±1%. [d] Average of two runs, ±3%. [e] Average of two runs, ±4%. [f] Average of three runs, ±3%. [g] The presence of **7b** has not been conclusively demonstrated; see the text. [h] The *S*-sulfinate with a rearranged 2-alkenyl group was not isolated although its formation in the insertion cannot be ruled out; see the text. [i] This percentage is based on the assumption that **9b** is not present among the contaminants; see the text.

Photolysis and Thermolysis of η^5-$C_5H_5Fe(CO)_2S(O)_2R$ where R = C_6H_4F-p, C_6F_5, and CCl_3

This study, although not directly related to the main theme of the paper, is nevertheless described here because of its relevance to the subject of SO_2 insertion reactions. The starting complexes η^5-$C_5H_5Fe(CO)_2S(O)_2R$ were prepared by the appropriate adaptations of the literature procedure [5] and characterized routinely by elemental analyses and ^1H NMR and infrared spectroscopy (Table II).

Previous attempts at photochemical and thermal desulfination of various complexes η^5-$C_5H_5Fe(CO)_2S(O)_2R$ had been unsuccessful [5]. It was felt, however, that the presence of electronegative fluorine or chlorine in the group R would render the resultant η^5-$C_5H_5Fe(CO)_2R$ sufficiently stable to these reaction conditions to permit isolation.

No products of desulfination could be isolated from photolysis and/or thermolysis of the η^5-$C_5H_5Fe(CO)_2S(O)_2R$ where R = C_6H_4F-*p* and CCl_3. However, thermal treatment in toluene at reflux or photolysis in toluene of η^5-$C_5H_5Fe(CO)_2S(O)_2C_6F_5$ afforded the desired iron–aryl complex, η^5-$C_5H_5Fe(CO)_2C_6F_5$. It is worthy of note that the thermolysis of η^5-$C_5H_5Fe(CO)_2S(O)_2C_6F_5$ depends markedly on the reaction conditions, and the use of benzene or dioxane at reflux afforded no detectable η^5-$C_5H_5Fe(CO)_2C_6F_5$. This unusual selectivity is described fully in the Experimental. A failure to effect thermal desulfination of η^5-$C_5H_5Fe(CO)_2S(O)_2C_6F_5$ was mentioned earlier by other workers [17] but their experimental conditions were not disclosed.

Experimental

General Procedures

All reactions except some of 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 or Woelm neutral alumina, deactivated with distilled H_2O (usually 6–10%), were employed in chromatographic separations and purifications. Melting points were determined on a Fisher–Johns melting point block and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn., Pascher Mikroanalytisches Laboratorium, Bonn, Germany, and Bernhardt Analytical Laboratories of the Max Planck Institute, Mülheim, Germany.

Materials

Anhydrous grade SO_2 was purified as described previously [1]. Tetrahydrofuran (THF) was freshly distilled from CaH_2 under nitrogen. Hexane, cyclohexane, and petroleum ether were technical grade. All other solvents and chemicals obtained commercially were reagent grade or equivalent quality and were used as received.

Preparation of Transition Metal–2-Alkenyl Complexes

The complexes η^5-$C_5H_5Fe(CO)_2CH_2C(R){=}CR'R''$ (**1a**: R = R′ = R″ = H [18]; **1b**: R = R′ = H, R″ = CH_3 [18]; **1e**: R = CH_3, R′ = R″ = H [19]) and η^5-$C_5H_5Mo(CO)_3CH_2CH{=}CH_2$ (**2a**) [20] were prepared as described in the literature. The other metal 2-alkenyls employed in this study, all new compounds, were synthesized by appropriate adaptations of the reported procedures for η^5-$C_5H_5M(CO)_xCH_2CH{=}CH_2$ (M = Fe, x = 2 [18]; M = Mo, x = 3 [20]; M = W, x = 3 [21]). These procedures entailed reaction of $Na^+[\eta^5$-$C_5H_5M(CO)_x]^-$ with excess $ClCH_2C(R){=}CR'R''$ in THF for 2–8 hr at 25 °C when M = Fe and Mo (or 40 °C when M = Mo) and 9–10 hr at 30–45 °C when M = W, concentration of the resulting mixture under reduced pressure, addition of 5–10g of alumina, filtration, and removal of the solvent from the filtrate. The residue was then dissolved in minimum benzene and chromatographed on alumina (generally 10% H_2O) eluting with pentane or hexane (or pentane/benzene for M = Mo) to remove $[\eta^5$-$C_5H_5Fe(CO)_2]_2$, $[\eta^5$-$C_5H_5Mo(CO)_3]_2$, $[\eta^5$-$C_5H_5Fe(CO)_2]_2Hg$, $[\eta^5$-$C_5H_5Mo(CO)_3]_2Hg$, and/or any other contaminants. Evaporation of the solvent from the collected leading band afforded the 2-alkenyl complex, which was often employed without further transfer in a subsequent reaction. Thus yields were generally not determined but are estimated to range from 40 to 80% when M = Fe and from 60 to 80% when M = Mo. All complexes were characterized by infrared (ir) and/or ^1H NMR spectroscopy, and the pertinent data are set out in Table I. Only the more stable complexes were microanalyzed. Specific details concerning the synthesis of various metal 2-alkenyls are given below.

η^5-$C_5H_5Fe(CO)_2CH_2CH{=}C(CH_3)_2$ (**1c**): obtained as an amber oil, 88% yield based on $[\eta^5$-$C_5H_5Fe(CO)_2]_2$.

η^5-$C_5H_5Fe(CO)_2CH_2CH{=}CHC_6H_5$ (**1d**): a yellow solid, 72% yield based on $[\eta^5$-$C_5H_5Fe(CO)_2]_2$. *Anal.* Calcd for $C_{16}H_{14}FeO_2$: C, 65.33; H, 4.80. Found: C, 65.59; H, 4.97%.

η^5-$C_5H_5Fe(CO)_2CH_2CH{=}CHCl$ (**1f**): obtained as a yellow, very unstable oil; extensive decomposition prevented a meaningful ^1H NMR spectrum from being recorded.

η^5-$C_5H_5Mo(CO)_3CH_2CH{=}CHCH_3$ (**2b**): isolated as a yellow oil that can be induced to crystallize.

η^5-$C_5H_5Mo(CO)_3CH_2CH{=}C(CH_3)_2$ (**2c**): a yellow–orange soft crystalline material.

η^5-$C_5H_5Mo(CO)_3CH_2CH{=}CHC_6H_5$ (**2d**): obtained as an orange solid; contaminated with $[\eta^5$-$C_5H_5Mo(CO)_3]_2Hg$, which could not be completely removed by chromatography.

η^5-$C_5H_5Mo(CO)_3CH_2CH{=}CHCl$ (**2f**): obtained as a yellow oil.

η^5-$C_5H_5Mo(CO)_3CH_2C(Cl){=}CHCl$ (**2g**): isolated as a yellow oil.

η^5-$C_5H_5W(CO)_3CH_2CH{=}CHCH_3$ (**3b**): a yellow solid, 65% yield based on $W(CO)_6$.

Anal. Calcd for $C_{12}H_{12}O_3W$: C, 37.14; H, 3.12. Found: C, 37.82; H, 3.21%.

η^5-$C_5H_5W(CO)_3CH_2CH{=}C(CH_3)_2$ (**3c**): a yellow solid, 70% yield based on $W(CO)_6$.

Anal. Calcd for $C_{13}H_{14}O_3W$: C, 38.85; H, 3.51. Found: C, 41.19; H, 3.85% (^{1}H NMR spectrum suggests solvent contamination).

Reactions of Transition Metal–2-Alkenyl Complexes with SO_2. Preparation of 2-Alkene-S-Sulfinato Complexes

In Neat SO_2 at Reflux. General Procedure

The reactions of transition metal–2-alkenyl complexes with liquid SO_2 were carried out in a manner analogous to that employed previously for manganese 2-alkenyls [2] and for various metal alkyls [5, 6]. In general, SO_2 solutions of a freshly prepared 2-alkenyl complex were maintained at reflux by using a Dry Ice-cooled condenser directly attached to the reaction flask. Upon completion of the reaction the excess SO_2 was allowed to boil off and the residue was purified by chromatography.

Reaction times varied from *ca.* 0.5 hr for the iron-2-alkenyls and 1–2 hr for the molybdenum 2-alkenyls (with the exception of the cinnamyl complexes, **1d** and **2d**, which required *ca.* 3 hr) to 32–48 hr for the tungsten analogs. The *S*-sulfinato complexes of iron were generally best purified by chromatography on alumina (10% H_2O) eluting with $CHCl_3$ after elution with benzene removed starting material and impurities, or on Florisil eluting with 1:1 $CHCl_3$/acetone. Those of molybdenum and tungsten could most consistently be purified using Florisil columns and 1:1 $CHCl_3$/acetone. Any unreacted 2-alkenyl complex was first removed from these Florisil columns with benzene and then other impurities were eluted off with $CHCl_3$ before the *S*-sulfinate. The yields based on $[\eta^5\text{-}C_5H_5M(CO)_x]_2$ (M = Fe, x = 2; M = Mo, x = 3) and $W(CO)_6$ usually ranged from 60 to 70% for the iron *S*-sulfinates, from 10 to 50% (generally closer to 10%) for the molybdenum *S*-sulfinates, and from 5 to 20% for the tungsten *S*-sulfinates. Analytical and molecular weight data and physical properties of these products are given in Table IV.

*Procedure for η^5-$C_5H_5Fe(CO)_2S(O)_2CH_2CH{=}CH_2$ (**4a**) and η^5-$C_5H_5Mo(CO)_3S(O)_2CH_2CH{=}CH_2$ (**6a**).* The reactions of η^5-$C_5H_5Fe(CO)_2CH_2CH{=}CH_2$ (**1a**) and η^5-$C_5H_5Mo(CO)_3CH_2CH{=}CH_2$ (**2a**) with liquid SO_2 produced the corresponding *S*-sulfinates as well as the metal–carbon σ-bonded $[\eta^5\text{-}C_5H_5Fe(CO)_2(C_3H_5SO_2)]_x$ and $[\eta^5\text{-}C_5H_5Mo(CO)_3(C_3H_5SO_2)]_x$, respectively. These reactions and the separation of the products are described in the preceding paper [1].

*Procedure for η^5-$C_5H_5Mo(CO)_3S(O)_2CH_2CH{=}CHCl$ (**7f**).* Onto 3.3g of freshly chromatographed η^5-$C_5H_5Mo(CO)_3CH_2CH{=}CHCl$ (**2f**) (a 50:50 mixture of the *cis* and *trans* isomers) sulfur dioxide was condensed (~50ml) and the resulting solution was maintained at reflux for 8 hr. The SO_2 was allowed to boil off and the residue was chromatographed on a Florisil column made up with benzene. Elution with benzene removed a yellow band from which 0.46g (14%) of **2f** was recovered upon evaporation of the solvent. Then elution with 4:1 benzene/acetone yielded after evaporation of the solvent 1.28g (46%) of the red η^5-$C_5H_5Mo(CO)_3Cl$. Finally elution with 1:1 benzene/acetone and acetone removed a yellow–orange band which afforded 0.37g (~10% yield) of **7f** after evaporation to dryness.

In Neat SO_2 at Low Temperatures

In reactions carried out at temperatures below −10 °C, SO_2 was condensed into a flask containing the metal–2-alkenyl complex in a sealed thin-walled glass ampoule. The flask was immersed in an appropriate bath and the ampoule was broken with a glass rod after the desired temperature had been attained. The resulting solution was maintained at constant temperature (generally ±5°) for various lengths of time, the excess SO_2 was removed by pumping at *ca.* 0.1 Torr, and then the residue was allowed to warm to room temperature. The product was purified as described above.

In Organic Solvents

Gaseous SO_2 was passed slowly with stirring through a solution containing 1–2g of the 2-alkenyl complex dissolved in *ca.* 150ml of an organic solvent, generally at room temperature. After 14–36 hr solvent was removed on a rotary evaporator and the residue was chromatographed as described above.

With benzene, nitromethane or acetonitrile as the solvent the reactions were exothermic and required a cooling bath. The reactions in benzene and hexane did not go to completion in the allowed time. Yields usually ranged from 20–30% in hexane and benzene to 50–70% in acetonitrile and nitromethane.

Attempted Reactions of Transition Metal–2-Alkenyl Complexes with SO_2

*Of η^5-$C_5H_5Fe(CO)_2CH_2CH{=}CHCl$ (**1f**)*

Freshly chromatographed **1f** was allowed to react with neat SO_2 at reflux and with an SO_2-saturated 1:1 hexane/ether solution at 25–30 °C for 11 hr. Considerable decomposition was observed in both reactions. Chromatography on alumina (6% H_2O) or Florisil of the solid residue yielded η^5-$C_5H_5Fe(CO)_2$-

TABLE IV. Analytical and Molecular Weight Data and Physical Properties of New Metal–*S*-Sulfinato Complexes.

Complex	Mp, °C	Color	Analysis, %							
			C		H		S		Mol. wt.	
			Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found[a]
η^5-$C_5H_5Fe(CO)_2S(O)_2CH_2CH{=}CH_2$, 4a	77[d]	yellow–golden	42.58	41.90	3.57	3.85	11.37	11.00	282	270
η^5-$C_5H_5Fe(CO)_2S(O)_2CH(CH_3)CH{=}CH_2$, 4b	110–111[e]	yellow	44.43	44.81	4.10	4.12	10.86	10.95	295	306(295)
η^5-$C_5H_5Fe(CO)_2S(O)_2C_5H_9$, 4c/5c	[f]	yellow	46.47	46.28	4.55	4.19	10.34	9.90	310	(310)
η^5-$C_5H_5Fe(CO)_2S(O)_2CH_2CH{=}C(CH_3)_2$, 5c	125–126	yellow	46.47	46.53	4.55	4.45	10.34	9.96	310	319
η^5-$C_5H_5Fe(CO)_2S(O)_2C_9H_9$, 4d/5d	132–133[g]	yellow	53.65	53.37	3.94	3.97	8.95	8.83	358	379
η^5-$C_5H_5Mo(CO)_3S(O)_2CH_2CH{=}CH_2$, 6a	dec 119–120	golden	37.73	37.84	2.88	2.80	9.16	8.96	350	365
η^5-$C_5H_5Mo(CO)_3S(O)_2CH(CH_3)CH{=}CH_2$, 6b	dec ~115	golden	39.46	39.85	3.31	3.31	8.78	8.98	365	373
η^5-$C_5H_5Mo(CO)_3S(O)_2CH_2CH{=}C(CH_3)_2$, 7c	dec 136.5–137.5	golden	41.17	41.32	3.72	3.63	8.45	8.32	379	374
η^5-$C_5H_5Mo(CO)_3S(O)_2CH_2CH{=}CHC_6H_5$, 7d	[f]	orange	47.78	47.81	3.30	3.64	7.50	7.54	427	439
η^5-$C_5H_5Mo(CO)_3S(O)_2CH_2CH{=}CHCl$, 7f	[f]	orange	34.26	35.64	2.35	2.38	8.31	9.09[h]	386	386
η^5-$C_5H_5W(CO)_3S(O)_2CH(CH_3)CH{=}CH_2$[b], 8b	[f]	yellow	31.88	33.12	2.68	2.82	7.10	6.09	452	465
η^5-$C_5H_5W(CO)_3S(O)_2CH_2CH{=}C(CH_3)_2$, 9c	[f]	yellow–orange	33.49	34.30	3.03	3.28	6.88	6.70	466	482
η^5-$C_5H_5Fe(CO)_2S(O)_2C_6H_4F$-*p*	174–175	yellow	46.45	47.11	2.70	2.76		[f]	336	348
η^5-$C_5H_5Fe(CO)_2S(O)_2C_6F_5$[c]	dec 165	golden	38.26	38.28	1.24	1.29	7.86	7.77	408	405
η^5-$C_5H_5Fe(CO)_2S(O)_2CCl_3$	141.5–142	golden	26.76	27.26	1.40	1.47	8.92	8.76	359	371

[a] By osmometry using 0.01–0.02 *M* solution in $CHCl_3$ and (in parentheses) parent ion in the mass spectrum. [b] Impure complex. [c] Structure determined by X-ray crystallography; see A. D. Redhouse, *J. Chem. Soc. Dalton Trans.*, 1106 (1974). [d] Sublimes at 95–105 °C (~0.1 Torr). [e] Sublimes with decomposition at 100–105 °C (~0.1 Torr). [f] Not determined. [g] Isomerically pure 5d. [h] Also Cl analysis. Calcd: 9.91. Found: 9.09%.

Cl and a yellow material, eluted off with 1:1 CH_2Cl_2/acetone, which showed ir bands at 1183 and 1053 cm^{-1}. This material was not investigated further because of instability.

Of η^5-$C_5H_5Mo(CO)_3CH_2C(Cl)=CHCl$ (2g)

Chromatographically pure **2g** (~4g) was allowed to react with neat SO_2 at reflux for 50 hr. Solvent was then evaporated and the residue was chromatographed on Florisil. Benzene removed unreacted **2g**, 4:1 benzene/acetone eluted off η^5-$C_5H_5Mo(CO)_3Cl$, and acetone removed an orange band. Evaporation of the solvent from the last effluent yielded *ca.* 20mg of an orange solid with ir bands at 2065, 2050, 2000sh, 1950, 1207, and 1050 cm^{-1} (Nujol mull). Not enough of this material was present for complete characterization.

Reaction of $Na^+[\eta^5$-$C_5H_5Fe(CO)_2]^-$ with SO_2 Followed by $ClCH_2CH=C(CH_3)_2$. Preparation of η^5-$C_5H_5Fe(CO)_2S(O)_2CH_2CH=C(CH_3)_2$ (5c)

Sulfur dioxide (0.9ml of liquid, ~20mmol) was allowed to bubble slowly into a solution of $Na^+[\eta^5$-$C_5H_5Fe(CO)_2]^-$ (prepared from 3.5g (10mmol) of $[\eta^5$-$C_5H_5Fe(CO)_2]_2$ in 145ml of THF and freed from excess sodium amalgam and mercury) contained in a three-neck round-bottom flask at *ca.* –70 °C. After the addition of SO_2 was complete, $ClCH_2CH=C(CH_3)_2$ (10.5g, 100mmol) was introduced dropwise with stirring in 4 hr to the resulting solution at the above temperature. The contents of the flask were first warmed to –23 °C in 11 hr and then stirred for an additional 3 hr at 25 °C. Upon warming the solution changed color from brown to red–brown. Solvent was removed on a rotary evaporator and the residue was extracted with *ca.* 200ml of benzene. The extract was filtered, concentrated, and chromatographed on Florisil. Benzene eluted off a red band of $[\eta^5$-$C_5H_5Fe(CO)_2]_2$ and a narrow orange band, and then CH_2Cl_2 and 1:1 CH_2Cl_2/acetone removed yellow and red bands. Continued elution led to the removal of another yellow band with acetone. After evaporation of the solvent from the last effluent, the residue was rechromatographed on Florisil eluting with 1:1 CH_2Cl_2/acetone. Narrow orange and red bands were removed before the major yellow band, which was eluted off with acetone. Removal of the solvent and drying at 25 °C (0.1 Torr) for 20 min afforded 0.82g (13% yield) of the pure *S*-sulfinate 5c. Analytical data are given in Table IV.

Reaction of $[\eta^5$-$C_5H_5Fe(CO)_2]_2$ with RSO_2Cl where $R = C_6H_4F$-p and C_6F_5. Preparation of η^5-$C_5H_5Fe(CO)_2S(O)_2R$

These iron *S*-sulfinates were prepared by a suitably adapted procedure of Bibler and Wojcicki [5]. Equimolar amounts of $[\eta^5$-$C_5H_5Fe(CO)_2]_2$ and RSO_2Cl in THF were stirred for 19 hr at 25–30 °C. Solvent was removed and the residue was chromatographed on alumina (6% H_2O) or Florisil to separate η^5-$C_5H_5Fe(CO)_2Cl$ and η^5-$C_5H_5Fe(CO)_2S(O)_2R$. The yields of the *S*-sulfinato products were 70% for $R = C_6H_4F$-*p* and 40% for $R = C_6F_5$.

Reaction of $[\eta^5$-$C_5H_5Fe(CO)_2]_2$ with CCl_3SO_2Cl

A THF solution (50ml) of $[\eta^5$-$C_5H_5Fe(CO)_2]_2$ (1.72g, 4.86mmol) and CCl_3SO_2Cl (2.06g, 9.45mmol) was stirred for 12 hr at room temperature resulting in the formation of a yellow–orange precipitate. Solvent was removed, the residue was extracted with 1:1 CH_2Cl_2/benzene, and the resulting slurry was filtered.

The pale yellow solid $[\eta^5$-$C_5H_5Fe(CO)_3]^+FeCl_4^-$ was washed with petroleum ether, yield 1.06g. Ir (acetone) $\nu(C\equiv O)$ 2130vs, 2075vs cm^{-1}. Λ_M (1.5×10^{-4} *M* solution in nitromethane) 78 ohm^{-1} cm^2. $\mu_{eff} = 6.1$ B.M.

Anal. Calcd for $C_8H_5Cl_4Fe_2O_3$: C, 23.86; H, 1.25; Cl, 35.22. Found: C, 24.76; H, 1.20; Cl, 35.57%.

The filtrate was chromatographed on Florisil to give 0.66g (64% yield) of η^5-$C_5H_5Fe(CO)_2Cl$ and 0.54g (31% yield) of η^5-$C_5H_5Fe(CO)_2S(O)_2CCl_3$. Analytical data for the latter compound are given in Table IV.

Desulfination of η^5-$C_5H_5Fe(CO)_2S(O)_2C_6F_5$

A solution of η^5-$C_5H_5Fe(CO)_2S(O)_2C_6F_5$ (0.22g, 0.54mmol) in 15ml of toluene was heated at reflux for 1 hr. Solvent was removed, the residue was extracted with CH_2Cl_2, and the extract was chromatographed on Florisil. A yellow band was eluted off with 1:1 CH_2Cl_2/benzene, solvent was removed, and the residue was sublimed at 80 °C (~0.1 Torr) to afford 0.068g (34% yield) of η^5-$C_5H_5Fe(CO)_2C_6F_5$, mp 141–142 °C (lit. [22] mp 142–143 °C).

Subsequent elution of a yellow–orange band with 1:1 CH_2Cl_2/acetone led to the recovery of 0.077g (35%) of η^5-$C_5H_5Fe(CO)_2S(O)_2C_6F_5$.

By varying the solvent, time, and temperature the following additional results were obtained. (1) Heating η^5-$C_5H_5Fe(CO)_2S(O)_2C_6F_5$ in toluene at 100 °C for 3 hr reduced the yield of η^5-$C_5H_5Fe(CO)_2C_6F_5$ to 12%. (2) There was no observable desulfination in benzene at reflux for 5 hr, in dioxane at reflux for 3 hr, and in heptane slurry at reflux.

A toluene solution (40ml) of η^5-$C_5H_5Fe(CO)_2S(O)_2C_6F_5$ (0.08g, 0.2mmol) in a quartz tube fitted with a stopcock adapter leading to a mineral oil bubbler was placed 24 cm from a 450-watt high-pressure mercury-vapor lamp contained in a water-cooled immersion well [5]. The solution was irradiated with stirring for 1 hr. The mixture was then worked-up as described above to give 6–7mg (~8%

yield) of η^5-$C_5H_5Fe(CO)_2C_6F_5$, characterized by ir spectroscopy [22], and a trace amount of the unreacted *S*-sulfinate. There was extensive decomposition.

Attempted Desulfination of η^5-$C_5H_5Fe(CO)_2S(O)_2R$ where R = C_6H_4F-p and CCl_3

A solution of 0.1g of η^5-$C_5H_5Fe(CO)_2S(O)_2C_6H_4$-F-*p* in 30ml of toluene was heated at reflux for 2.5 hr. Usual work-up that followed gave no evidence of η^5-$C_5H_5Fe(CO)_2C_6H_4F$-*p*.

The *S*-sulfinate η^5-$C_5H_5Fe(CO)_2S(O)_2CCl_3$ was heated in THF at 65 °C for 5.5 hr, in benzene at 80 °C for 1 hr, and in toluene at 110 °C for 0.3, 0.5, and 1 hr. The reaction residue contained only recovered starting material and/or decomposition products in each case. Photolysis in toluene, using the same conditions as for η^5-$C_5H_5Fe(CO)_2S(O)_2C_6F_5$, likewise gave no evidence of desulfination. Only non-carbonyl decomposition products and some unreacted *S*-sulfinate were observed.

Physical Measurements

Ir spectra were recorded on a Beckman Model IR-9 spectrophotometer or a Perkin–Elmer Model 337 spectrophotometer. ^1H NMR spectra were taken on a Varian Associates A-60 spectrometer using tetramethylsilane (TMS) as an internal standard. Mass spectral measurements were made at 70eV on an A.E.I. Model MS-9 spectrometer by Mr. C. R. Weisenberger. Molar conductivities (Λ_M) were determined 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. Magnetic moments were measured using the Faraday method by Mr. T. D. Dubois.

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