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Reactions of Ring- and Metal-Substituted Cyclopentadienylmetal-2-Alkenyl Carbonyl Complexes with Sulfur Dioxide, Preparation and Characterization of 2-Alkene-*S*-Sulfinato Products

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The preparation of the ring-substituted iron-2-alkenyl complexes $(\eta^5\text{-}CH_3C_5H_4)Fe(CO)_2CH_2CH{=}CRR'$, $[\eta^5\text{-}1,3\text{-}(C_6H_5)_2C_5H_3]Fe(CO)_2CH_2CH{=}CRR'$, *and* $[\eta^5\text{-}(CH_3)_5C_5]Fe(CO)_2CH_2CH{=}CRR'$ *and of the metal-substituted molybdenum-2-alkenyl complexes* $\eta^5\text{-}C_5H_5Mo(CO)_2[P(OC_6H_5)_3]CH_2CH{=}CRR'$ $(R = H, R' = CH_3; R = R' = CH_3; R = H, R' = C_6H_5)$ *is reported. These metal-2-alkenyl compounds react with neat* SO_2 *or with saturated solutions of* SO_2 *in organic solvents to yield the corresponding 2-alkene-S-sulfinates containing a 1,3 rearranged and/or an unrearranged allylic fragment. The reaction products were isolated and characterized; in several cases, various isomeric structures were differentiated on the basis of infrared and* ^1H *NMR spectroscopic data. The formation of the rearranged metal S-sulfinates is promoted by the use of neat* SO_2 *at low temperatures and of organic solutions. The results of this study are compared with those of the earlier investigation by Downs and Wojcicki. It is concluded that methyl substitution at the ring or P-donor ligand substitution at the metal favors the formation of the unrearranged over the rearranged 2-alkene-S-sulfinato products. A mechanism is proposed which satisfactorily explains these results.*

Introduction

Recent papers from this laboratory have reported on the mechanism of reaction between some cyclopentadienylmetal-2-alkenyl carbonyl complexes $\eta^5\text{-}C_5H_5M(CO)_xCH_2C(R){=}CR'R''$ (M = Fe, x = 2; M = Mo, x = 3; M = W, x = 3) and SO_2 [1], and on the isolation and characterization of various isomeric 2-alkene-*S*-sulfinato products, $\eta^5\text{-}C_5H_5M(CO)_xS(O)_2\text{-}C_3H_2RR'R''$, of such insertion reactions [2]. In extending these studies, reactions of additional cyclopentadienylmetal-2-alkenyl carbonyl complexes, $(\eta^5\text{-}CH_3C_5H_4)Fe(CO)_2CH_2CH{=}CRR'$, $[\eta^5\text{-}1,3\text{-}(C_6H_5)_2C_5H_3]Fe(CO)_2CH_2CH{=}CRR'$, $[\eta^5\text{-}(CH_3)_5C_5]Fe(CO)_2CH_2CH{=}CRR'$, and $\eta^5\text{-}C_5H_5Mo(CO)_2[P(OC_6H_5)_3]CH_2CH{=}CRR'$, with SO_2 were examined. It was of particular interest to ascertain what effect, if any, substitution on the cyclopentadienyl ring and on the metal would exert on the relative amounts of the isomeric 2-alkene-*S*-sulfinato products containing a 1,3 rearranged and an unrearranged allylic fragment. Reported herein are the results of this investigation.

Experimental

General procedures and instrumentation were the same as those described previously [2].

Materials

Anhydrous grade SO_2 was purified by standard procedures [1]. Tetrahydrofuran (THF) was freshly distilled from CaH_2 under nitrogen. With the exception of technical grade pentane, all other solvents used in synthesis and purification were reagent grade quality.

The dinuclear cyclopentadienylmetal carbonyl complexes $[(\eta^5\text{-}CH_3C_5H_4)Fe(CO)_2]_2$ [3], $\{[\eta^5\text{-}1,3\text{-}(C_6H_5)_2C_5H_3]Fe(CO)_2\}_2$ [4], $\{[\eta^5\text{-}(CH_3)_5C_5]Fe(CO)_2\}_2$ [5], and $\{\eta^5\text{-}C_5H_5Mo(CO)_2[P(OC_6H_5)_3]\}_2$ [6] were prepared by established procedures. Commercial methylcyclopentadiene dimer was purified by distillation before use in the first of the above syntheses. Other chemicals were obtained commercially in reagent grade or equivalent quality and were used as received.

Preparation of Transition Metal-2-Alkenyl Complexes

The metal-2-alkenyls employed in this study, all new compounds, were synthesized by the appropriate adaptations of the reported procedures for $\eta^5\text{-}C_5H_5M(CO)_xCH_2CH{=}CH_2$ (M = Fe, x = 2 [7]; M = Mo, x = 3 [8]). A representative preparation is described in detail.

A THF solution (50 ml) of $[(\eta^5\text{-}CH_3C_5H_4)Fe(CO)_2]_2$ (1.00 g, 2.61 mmol) was allowed to react with excess 1% sodium amalgam for 2 hours. The resulting solution of $Na^+[(\eta^5\text{-}CH_3C_5H_4)Fe(CO)_2]^-$,

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

Complex	Ir ν(C≡O), cm^{-1} [a]	^{1}H NMR, τ [b]
$(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Fe(CO)}_2\text{CH}_2\text{CH=CHCH}_3$, **1a**	2011vs, 1961vs	3.89–5.13m (CH=CH), 5.58s (C_5H_4), 7.93d (J = 7Hz, CH_2), 8.13s (C_5CH_3), 8.42d (J = 6Hz, =CCH_3)
$(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Fe(CO)}_2\text{CH}_2\text{CH=C(CH}_3)_2$, **1b**	2011vs, 1960vs	4.52t (J = 10Hz, CH), 5.46s (C_5H_4), 7.84d (J = 10Hz, CH_2), 8.12s (C_5CH_3), 8.38s (=$C(CH_3)_2$)
$(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Fe(CO)}_2\text{CH}_2\text{CH=CHC}_6\text{H}_5$, 1c	2010vs, 1955vs	2.83m (C_6H_5), 3.14–4.00m (CH=CH), 5.58s (C_5H_4), 7.78d (J = 8Hz, CH_2), 8.18s (C_5CH_3)
$[\eta^5\text{-1,3-(C}_6\text{H}_5)_2\text{C}_5\text{H}_3]\,\text{Fe(CO)}_2\text{CH}_2\text{CH=C(CH}_3)_2$, **2b**	2010vs, 1961vs	2.65–3.15m ($2C_6H_5$), 4.78t (J = 2Hz, 1H of C_5H_3), 4.83s, br (CH), 5.05d (J = 2Hz, 2H of C_5H_3), 7.90d (J = 9Hz, CH_2), 8.57s, br (=$C(CH_3)_2$)
$[\eta^5\text{-(CH}_3)_5\text{C}_5]\,\text{Fe(CO)}_2\text{CH}_2\text{CH=CHCH}_3$, **3a**	1988vs, 1938vs	4.05–5.22m (CH=CH), 8.25s ($C_5(CH_3)_5$), 8.45d (J = 6Hz, =CCH_3)[e]
$[\eta^5\text{-(CH}_3)_5\text{C}_5]\,\text{Fe(CO)}_2\text{CH}_2\text{CH=C(CH}_3)_2$, **3b**	1995vs, 1944vs	4.50t (J = 10Hz, CH), 8.28s ($C_5(CH_3)_5$), 8.43s (=$C(CH_3)_2$), 8.55d (J = 10Hz, CH_2)
$[\eta^5\text{-(CH}_3)_5\text{C}_5]\,\text{Fe(CO)}_2\text{CH}_2\text{CH=CHC}_6\text{H}_5$, **3c**	2000vs, 1950vs	2.84m (C_6H_5), 3.25–4.00m (CH=CH), 8.13d (J = 8Hz, CH_2), 8.26s ($C_5(CH_3)_5$)
$\eta^5\text{-C}_5\text{H}_5\text{Mo(CO)}_2[\text{P(OC}_6\text{H}_5)_3]\,\text{CH}_2\text{CH=CHCH}_3$, **4a/5a** [c]	1950vs, 1880vs[d]	2.45m ($3C_6H_5$), 4.38–5.03m (CH=CH), 5.22s, 5.32s, 5.38d (J = 1.5Hz[f]), 5.45d (J = 1.5Hz[f]) (C_5H_5), 7.78d (J = 7Hz, CH_2), 8.35d (J = 6Hz, CH_3)
$\eta^5\text{-C}_5\text{H}_5\text{Mo(CO)}_2[\text{P(OC}_6\text{H}_5)_3]\,\text{CH}_2\text{CH=C(CH}_3)_2$, **4b/5b**	1955vs, 1877vs[d]	2.45m ($3C_6H_5$), 4.34t (J = 9Hz, CH), 5.20s, 5.37d (J = 1.2 Hz[f]) (C_5H_5), 7.73d, d (J = 1.5[f], 9Hz, CH_2), 8.27s, 8.34s, 8.40s, 8.47s (=$C(CH_3)_2$)
$\eta^5\text{-C}_5\text{H}_5\text{Mo(CO)}_2[\text{P(OC}_6\text{H}_5)_3]\,\text{CH}_2\text{CH=CHC}_6\text{H}_5$, **4c/5c**	1955vs, 1878vs[d]	2.45m ($4C_6H_5$), 2.70–3.28m (CH=CH), 5.23s, 5.37d (J = 1.5Hz[f]) (C_5H_5), 7.57d, d (J = 1.5[f], 9Hz, CH_2)

[a] Recorded on a Perkin–Elmer Model 337 spectrophotometer in pentane solution unless otherwise indicated. Abbreviation: vs, very strong. [b] In $CDCl_3$ solution with TMS as an internal standard. Abbreviations: s, singlet; t, triplet; m, multiplet; br, broad. [c] Each of **4a** and **5a** is a mixture of the *cis* and *trans* isomers. [d] CH_2Cl_2 solution. [e] Resonance of the CH_2 protons masked by those of $C_5(CH_3)_5$ and =CCH_3. [f] P–H coupling.

freed from excess sodium amalgam and mercury, was added slowly with stirring to 0.55 g (5.2 mmol) of $ClCH_2CH{=}C(CH_3)_2$ in 10 ml of THF. The mixture was stirred for 3 hours at room temperature under nitrogen. The solvent was removed from the reaction mixture (25 °C, 0.1 Torr) and the residue was extracted with 100 ml of pentane. The extract was filtered through 5 g of Zeolite and concentrated before chromatography on a 2 X 20-cm column of neutral alumina (10% H_2O) made up with pentane. Elution with pentane separated a yellow band of $(\eta^5\text{-}CH_3C_5H_4)Fe(CO)_2CH_2CH{=}C(CH_3)_2$ (**1b**) from a purple one containing an approximately equal amount of $[(\eta^5\text{-}CH_3C_5H_4)Fe(CO)_2]_2$. The yellow band was eluted off first and the solvent was removed in a stream of nitrogen to leave an orange oil, which was used without further transfer in the subsequent reaction with SO_2 (*vide infra*).

The other metal-2-alkenyl complexes were synthesized analogously. The cyclopentadienylmetal carbonyl anions, prepared by reduction of the dinuclear cyclopentadienylmetal carbonyls with sodium amalgam in THF for *ca.* 2 hours, were allowed to react with equimolar (Fe complexes) or 5-fold excess (Mo complexes) alkenyl chloride, $ClCH_2CH{=}CRR'$, for 1–4 hours (Fe complexes) or 8–12 hours (Mo complexes). Chromatography of the reaction mixtures on alumina (10% H_2O) eluting with pentane (Fe complexes) or 2:1 pentane/CH_2Cl_2 (Mo complexes) separated the metal-2-alkenyl complex from any dinuclear cyclopentadienylmetal carbonyl. The former were isolated as orange or yellow oils. No attempt was made to induce crystallization of these complexes. They were characterized entirely by infrared (ir) and ^1H NMR spectroscopy, and the pertinent data are set out in Table I. Reaction yields were not determined (however, *cf.* yields of the *S*-sulfinato products, *vide infra*).

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

In Neat SO_2 at Reflux

In a typical preparation, *ca.* 25 ml of liquid SO_2 was condensed onto the above-synthesized $(\eta^5\text{-}CH_3C_5H_4)Fe(CO)_2CH_2CH{=}C(CH_3)_2$ (**1b**) and the resulting solution was maintained at reflux by using a Dry Ice-cooled condenser directly attached to the reaction flask. After 6 hours, the SO_2 was allowed to boil off and the residue was purified by chromatography on a 2 X 20-cm column of neutral alumina (10% H_2O) made up with $CHCl_3$. Elution with $CHCl_3$ removed a broad yellow band, the effluent was concentrated to *ca.* 10 ml on a rotary evaporator (30 °C, 20 Torr), and slow addition of pentane (100 ml) with stirring yielded 0.48 g (30% based on $[(\eta^5\text{-}CH_3C_5H_4)Fe(CO)_2]_2$) of yellow–orange crystals of $(\eta^5\text{-}CH_3C_5H_4)Fe(CO)_2S(O)_2C_5H_9$ (**6b/7b**).

TABLE II. Yields, Analytical and Molecular Weight Data, and Physical Properties of New Metal-*S*-Sulfinato Complexes.

Complex	Yield, %[a]	Mp, °C[b]	Color	Analysis, %					
				C		H		Mol. wt.	
				Calcd	Found	Calcd	Found	Calcd	Found[c]
$(\eta^5\text{-}CH_3C_5H_4)Fe(CO)_2S(O)_2CH(CH_3)CH{=}CH_2$, **6a**	30	64–66	yellow–orange	46.49	46.47	4.52	4.32	310	305
$(\eta^5\text{-}CH_3C_5H_4)Fe(CO)_2S(O)_2C_5H_9$, **6b/7b**	40	70–71	yellow–orange	48.19	47.86	4.94	4.94	324	332
$(\eta^5\text{-}CH_3C_5H_4)Fe(CO)_2S(O)_2C_9H_9$, **6c/7c**	30	125–127	yellow–orange	54.88	54.03	4.30	4.33	372	377
$[\eta^5\text{-}1,3\text{-}(C_6H_5)_2C_5H_3]Fe(CO)_2S(O)_2C_5H_9$, **8b/9b**	70	d	yellow	62.37	61.90	4.76	4.82	462	476
$[\eta^5\text{-}(CH_3)_5C_5]Fe(CO)_2S(O)_2CH_2CH{=}CHCH_3$, **10a**	27	117–119	yellow	52.49	52.29	6.01	5.81	366	354
$[\eta^5\text{-}(CH_3)_5C_5]Fe(CO)_2S(O)_2CH_2CH{=}C(CH_3)_2$, **10b**	30	135	yellow	53.72	54.09	6.32	6.48	380	388
$[\eta^5\text{-}(CH_3)_5C_5]Fe(CO)_2S(O)_2CH_2CH{=}CHC_6H_5$, **10c**	25	163–165	yellow	58.92	59.26	5.61	6.11	428	433
$\eta^5\text{-}C_5H_5Mo(CO)_2[P(OC_6H_5)_3]S(O)_2C_4H_7$, **12a/13a**	54	118–120[e]	yellow	53.90	53.07	4.18	4.35	646	638
$\eta^5\text{-}C_5H_5Mo(CO)_2[P(OC_6H_5)_3]S(O)_2CH_2CH{=}C(CH_3)_2$, **13b**	60	116–117[e]	yellow	54.50	54.46	4.40	4.55	660	657
$\eta^5\text{-}C_5H_5Mo(CO)_2[P(OC_6H_5)_3]S(O)_2CH_2CH{=}CHC_6H_5$, **13c**	42	130[e]	yellow	57.50	57.41	4.10	4.17	708	713

[a] For the reaction in neat SO_2 at reflux. Based on the dinuclear cyclopentadienylmetal carbonyl. [b] Uncorrected. [c] By osmometry using 0.01–0.02 *M* solution in $CHCl_3$. [d] Not determined. [e] With decomposition.

The other 2-alkene-*S*-sulfinato complexes were prepared by using strictly analogous procedures. The crude iron products were chromatographed on neutral alumina (10% H_2O) eluting with $CHCl_3$ whereas the molybdenum products were chromatographed on Florisil eluting with 1:1 $CHCl_3$/acetone. Yields, analytical and molecular weight data, and physical properties of all new 2-alkene-*S*-sulfinato complexes are given in Table II.

In Neat SO_2 at ca. *−45 °C*

These reactions were carried out as described previously [2]. The temperature was maintained at *ca.* −45 °C (generally ±5°) by means of a chlorobenzene slush bath [9]. Unreacted metal-2-alkenyl complex was eluted off the chromatographic column before the *S*-sulfinato product. Yields ranged from 16 to 30% based on the dinuclear cyclopentadienylmetal carbonyl.

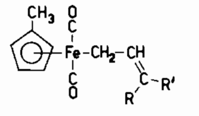
In Organic Solvents

Gaseous SO_2 was bubbled through a solution of the 2-alkenyl complex (*ca.* 1 g) in 20–50 ml of hexane, benzene or CH_2Cl_2 at room temperature. Progress of the reaction was followed by ir spectroscopy. After 1–48 hours solvent was removed on a rotary evaporator and the residue was chromatographed as described above. Yields of the *S*-sulfinato complexes ranged from 13–15% (Fe) to 37–46% (Mo) based on the dinuclear cyclopentadienylmetal carbonyl.

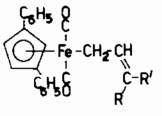
Results and Discussion

The 2-alkenyl complexes prepared in this work are all new compounds. They were obtained by the reaction between the appropriate cyclopentadienylmetal carbonyl anion and the alkenyl chloride, $ClCH_2CH{=}CRR'$. Characterization of these products was accomplished entirely by infrared and ^1H NMR spectroscopy (Table I) and by conversion to the corresponding *S*-sulfinates, which were microanalyzed. Commercial microanalyses were not attempted on the 2-alkenyl complexes because of their general thermal instability and sensitivity to air. The molybdenum compounds appeared to be more stable than the iron compounds.

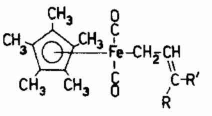
The bonding of the allylic fragment to the metal through the CH_2 carbon atom in these complexes is indicated by the ^1H NMR spectra. Thus the CH_2 proton resonance appears at τ 7.57–8.55, generally as a doublet (J = 7–10Hz) of the expected relative intensity 2, consistent with the presence of an MCH_2-$CH{=}$ moiety. For complexes **4b**/**5b** and **4c**/**5c**, isolated as mixtures, an additional splitting owing to the coupling (J = 1.5Hz) with the phosphorus nucleus of the $P(OC_6H_5)_3$ ligand is discernible.



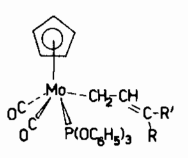
1a–c



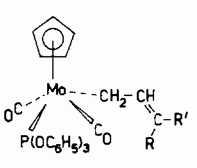
2b



3a–c



4a–c



5a–c

a R = H, R′ = CH_3 (trans) and/or R = CH_3, R′ = H (cis)

b R = R′ = CH_3

c R = H, R′ = C_6H_5

The molybdenum-2-alkenyl complexes can exist in two isomeric forms, **4** and **5**, which differ with respect to the relative positions of the four basal ligands. This type of geometric isomerism has received considerable attention, especially for η^5-$C_5H_5Mo(CO)_2(L)X$ [10–12], and spectroscopic criteria have been developed which allow differentiation between lateral (or *cis*) and diagonal (or *trans*) structures.* For example, lateral isomers show the η^5-C_5H_5 proton resonance as a singlet whereas diagonal isomers display this resonance as a doublet (J = 0.9–2.3Hz [11]) when L is a P-donor ligand. Since the three molybdenum-2-alkenyl complexes synthesized in this study show singlet and doublet resonances of η^5-C_5H_5, it is inferred that they exist as mixtures of the lateral and diagonal isomers, the latter being the major species. Interestingly, the ^1H NMR spectrum of **4b**/**5b** shows two pairs of CH_3 resonances of different intensities, further supporting the presence of the lateral and diagonal isomers.

A third type of isomerism is possible for the crotyl and cinnamyl complexes **1**,**3**–**5a** and **1**,**3**–**5c**, respectively. This isomerism arises from *cis* and *trans* orientations of the substituents at the allylic C=C bond. The ^1H NMR spectrum of **4a**/**5a** shows two η^5-C_5H_5 singlet resonances, consistent with the presence of the *cis* and *trans* isomers of **4a**, and two η^5-C_5H_5 doublet (J = 1.5Hz) resonances, in agreement with the presence of the *cis* and *trans* isomers of **5a**. By contrast, the ^1H NMR spectrum of **4c**/**5c** exhibits only two η^5-C_5H_5 signals, a singlet and a doublet (J = 1.5Hz), suggesting that each of **4c** and **5c** exists in a single

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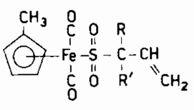
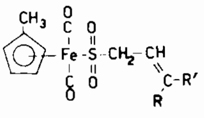
*The terms *lateral* and *diagonal* (ref. 13) are preferred to the more commonly used terms *cis* and *trans*, since the latter nomenclature will be used here to designate the geometry about the allylic C=C bond (*vide infra*).

isomeric form. The spectra of **1a**, **1c**, **3a**, and **3c** likewise seem to accord with the presence of only one isomer in each case. For the cinnamyl complexes **1,3–5c**, the single isomers almost certainly have a *trans* configuration because of similarities between their ^{1}H NMR spectra and those of η^5-$C_5H_5Fe(CO)_2$-$CH_2CH{=}CHC_6H_5$ and [η^5-$(CH_3)_5C_5$]$Fe(CO)_2S(O)_2$-$CH_2CH{=}CHC_6H_5$ (**11c**) (*vide infra*), both containing *trans*-$CH_2CH{=}CHC_6H_5$ [14, 15]. For the crotyl complexes **1a** and **3a**, the stereochemistry of the allylic C=C bond is not readily apparent. Furthermore, the possibility that these substances are mixtures of the *cis* and *trans* isomers cannot be dismissed from the ^{1}H NMR data, especially since metal–crotyl complexes, including **4a** and **5a**, are often isolated in both isomeric forms [2].

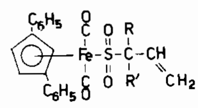
The 2-alkenyl complexes **1–5** react with neat SO_2 at reflux to give, after evaporation of the solvent and chromatography, the corresponding *S*-sulfinates **6–13**. Several of these insertion reactions were also carried out in neat SO_2 at *ca.* –45 °C and in organic solvents saturated with SO_2. The insertion at *ca.* –45 °C failed to go to completion in the allowed time and afforded considerable amounts of decomposition materials, thus accounting for *ca.* 50% lower yields of the *S*-sulfinates than the insertion in neat SO_2 at reflux. Likewise, lower yields of the *S*-sulfinates and considerable decomposition were observed in the reactions conducted in organic solvents.



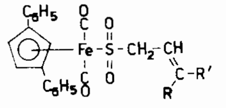
6a R=H , R′=CH_3
6b R= R′= CH_3
6c R= H, R′=C_6H_5



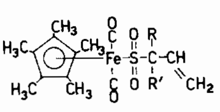
7b R= R′=CH_3
7c R=H, R′=C_6H_5



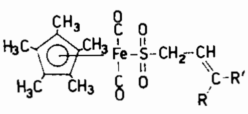
8b R=R′= CH_3



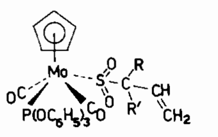
9b R=R′= CH_3



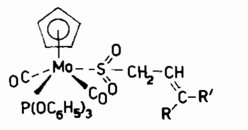
10a R=H, R′=CH_3
10b R=R′=CH_3



11b R=R′=CH_3
11c R=H, R′=C_6H_5



12a R=H , R′=CH_3



13a R=H , R′=CH_3 (trans) and/or R=CH_3 , R′= H (cis)
13b R=R′=CH_3
13c R=H, R′=C_6H_5

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 [16, 17]. Accordingly, they show considerable stability to air at room temperature, with the complexes **8–11** being the most stable, and **6–7** being the least stable. In general, the iron *S*-sulfinates melt sharply whereas the molybdenum *S*-sulfinates melt with decomposition. All of these compounds are readily soluble in polar organic solvents, but insoluble in saturated hydrocarbons.

The *S*-sulfinato mode of bonding in complexes **6–13** rests on the infrared ν(C≡O) and $\nu(SO_2)$ spectroscopic data set out in Table III. The frequencies of these modes match closely those of the *S*-sulfinato complexes derived from the corresponding alkyls [16, 17]. The molecular structure of one complex, **11c**, was confirmed by X-ray crystallographic techniques [15].

Again, as for the precursor 2-alkenyl complexes, three types of isomerism must be considered for these 2-alkene-*S*-sulfinato products. They are: (1) allylic isomerism, (2) lateral–diagonal isomerism for the molybdenum complexes, and (3) *cis–trans* isomerism associated with the allylic C=C bond. The three will be considered in the above order.

Whether or not a given 2-alkenyl ligand underwent 1,3 rearrangement in the insertion is readily ascertained by ^{1}H NMR spectroscopy (*cf.* Table III). Since the basis for such an assignment was described in some detail in a previous paper [2], it will only be summarized at this point. All of the unrearranged 2-alkene-*S*-sulfinato isomers (**7, 9, 11**, and **13**) display a resonance of the $S(O)_2CH_2$ protons with the relative intensity 2, split into a doublet by the adjacent CH proton. If the unrearranged isomer is present along with the corresponding rearranged isomer, then the relative intensity of the above doublet reflects the percentage of the former species in the mixture. The rearranged 2-alkene-*S*-sulfinato isomers (**6, 8, 10**, and **12**) can be identified in several ways, depending on the nature of the 2-alkenyl fragment. Of the complexes derived from metal-crotyl precursors, **6a** and **10a** exhibit the resonance of the $S(O)_2CH$ methine proton as a multiplet at τ 6.03–6.75. Furthermore, all three **6a**, **10a**, and **12a** (in **12a/13a** mixtures) show the signal of the $S(O)_2C(CH_3)$ protons as a doublet at τ 8.62–8.77 with a characteristic coupling constant of 7 Hz. The complexes containing the $S(O)_2C(CH_3)_2$-$CH{=}CH_2$ ligand display a single CH_3 proton resonance in the narrow range τ 8.67–8.69; this may be contrasted with the appearance of two CH_3 resonances, at lower fields (τ 8.19–8.37), for the isomeric unrearranged $S(O)_2CH_2CH{=}C(CH_3)_2$. And finally, the rearranged **6c**, derived from the cinnamyl precursor **1c**, was detected in **6c/7c** mixtures by the appearance of an additional signal of the ring-bonded CH_3 group; the relative amounts of **6c** and **7c** were

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

Complex	Ir, cm^{-1}		^{1}H NMR, τ^c
	$\nu(C{\equiv}O)^a$	$\nu(SO_2)^b$	
$(\eta^5\text{-}CH_3C_5H_4)Fe(CO)_2S(O)_2CH(CH_3)CH{=}CH_2$, **6a**	2060vs, 2000vs	1175s, 1160sh, 1045s, 1025sh	3.70–5.25m ($CH{=}CH_2$), 4.83m, 5.17m (C_5H_4), 6.16–6.66m (CH), 7.92s (C_5CH_3), 8.66d (J = 7Hz, CCH_3)
$(\eta^5\text{-}CH_3C_5H_4)Fe(CO)_2S(O)_2C_5H_9$, **6b/7b**[d]	2059vs, 1998vs	1180s, 1170sh, 1040s	4.36–5.14m ($=CH$, $CH{=}CH_2$), 5.05m, 5.23m (C_5H_4), 6.32d (J = 9Hz, CH_2), 7.92s (C_5CH_3), 8.19s, 8.23s ($=C(CH_3)_2$), 8.69s ($C(CH_3)_2$)
$(\eta^5\text{-}CH_3C_5H_4)Fe(CO)_2S(O)_2C_9H_9$, **6c/7c**[e]	2060vs, 1998vs	1180s, 1035s	2.70m (C_6H_5), 3.15–3.85m ($CH{=}CH$, $CH{=}CH_2$), 4.98m, 5.02m (C_5H_4), 6.15d (J = 6Hz, CH_2), 8.07s, 8.08s (C_5CH_3)
$[\eta^5\text{-}1,3\text{-}(C_6H_5)_2C_5H_3]Fe(CO)_2S(O)_2C_5H_9$, **8b/9b**[f]	2059vs, 1998vs	1175s, 1040s	1.90–2.57s ($2C_6H_5$), 3.72–4.88m ($=CH$, $CH{=}CH_2$, C_5H_3), 6.46d (J = 8Hz, CH_2), 8.28s, 8.34s ($=C(CH_3)_2$), 8.67s ($C(CH_3)_2$)
$[\eta^5\text{-}(CH_3)_5C_5]Fe(CO)_2S(O)_2CH(CH_3)CH{=}CH_2$, **10a**	2031vs, 1976vs	1175s, 1160sh, 1045s	3.28–4.66m ($CH{=}CH_2$), 6.03–6.75m (CH), 8.05s ($C_5(CH_3)_5$), 8.62d (J = 7Hz, CCH_3)
$[\eta^5\text{-}(CH_3)_5C_5]Fe(CO)_2S(O)_2C_5H_9$, **10b/11b**[g]	i	i	4.35–4.98m ($=CH$, $CH{=}CH_2$), 6.42d (J = 9Hz, CH_2), 8.08s, 8.09s ($C_5(CH_3)_5$), 8.21s, 8.25s ($=C(CH_3)_2$), 8.68s ($C(CH_3)_2$)
$[\eta^5\text{-}(CH_3)_5C_5]Fe(CO)_2S(O)_2CH_2CH{=}C(CH_3)_2$, **11b**	2030vs, 1975vs	1180s, 1170sh, 1040s, 1020sh	4.56t (J = 9Hz, $=CH$), 6.42d (J = 9Hz, CH_2), 8.08s ($C_5(CH_3)_5$), 8.21s, 8.25s ($=C(CH_3)_2$)
$[\eta^5\text{-}(CH_3)_5C_5]Fe(CO)_2S(O)_2CH_2CH{=}CHC_6H_5$, **11c**	2031vs, 1976vs	1180s, 1040s, 1030sh	2.50m (C_6H_5), 2.90–3.72m ($CH{=}CH$), 6.05d (J = 7Hz, CH_2), 8.07s ($C_5(CH_3)_5$)
$\eta^5\text{-}C_5H_5Mo(CO)_2[P(OC_6H_5)_3]S(O)_2C_4H_7$, **12a/13a**[h]	1995m–s, 1918vs	1182s, 1045s	2.65m ($3C_6H_5$), 4.20–4.78m ($CH{=}CH$, $CH{=}CH_2$), 4.75d (J = 1Hz[j]), 4.83d (J = 1Hz[j]) (C_5H_5), 5.99–6.49m (CH, CH_2), 8.33d (J = 5Hz, $=CCH_3$), 8.77d (J = 7Hz, CCH_3)
$\eta^5\text{-}C_5H_5Mo(CO)_2[P(OC_6H_5)_3]S(O)_2CH_2CH{=}C(CH_3)_2$, **13b**	1993m–s, 1917vs	1177s, 1047s	2.66m ($3C_6H_5$), 4.48–4.82m ($=CH$), 4.84d (J = 1Hz[j], C_5H_5), 6.50d, br (J = 8Hz, CH_2), 8.28s, 8.37s ($=C(CH_3)_2$)
$\eta^5\text{-}C_5H_5Mo(CO)_2[P(OC_6H_5)_3]S(O)_2CH_2CH{=}CHC_6H_5$, **13c**	1994m–s, 1918vs	1180s, 1040s	2.72m ($4C_6H_5$), 3.27–3.78m ($CH{=}CH$), 4.85d (J = 1.2Hz[j], C_5H_5), 6.26d, br (J = 6Hz, CH_2)

[a] Recorded on a Beckman Model IR-9 spectrophotometer in $CHCl_3$ solution. [b] Recorded on a Perkin–Elmer Model 337 spectrophotometer in a KBr pellet. Abbreviations: vs, very strong; s, strong; m, medium; sh, shoulder. [c] In $CDCl_3$ solution with TMS as an internal standard. Some weak signals of the minor isomers are not included. Abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet; br, broad. [d] 75:25 **7b/6b**. [e] 85:15 **7c/6c**. [f] 75:25 **9b/8b**. [g] 60:40 **11b/10b**. [h] 80:20 **13a/12a**. [i] Not measured. [j] P–H coupling.

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

2-Alkenyl Complex	Reaction Conditions	Relative % of *S*-Sulfinate[a]	
		Rearranged 2-alkenyl group	Unrearranged 2-alkenyl group
$(\eta^5\text{-}CH_3C_5H_4)Fe(CO)_2CH_2CH{=}CHCH_3$, **1a**	SO_2 at reflux	100 **6a**	0
$(\eta^5\text{-}CH_3C_5H_4)Fe(CO)_2CH_2CH{=}C(CH_3)_2$, **1b**	SO_2 at reflux	25 **6b**	75 **7b**
$(\eta^5\text{-}CH_3C_5H_4)Fe(CO)_2CH_2CH{=}CHC_6H_5$, **1c**	SO_2 at reflux	15 **6c**	85 **7c**
	SO_2 in hexane, 27 °C, 48 hr	75 **6c**	25 **7c**
$[\eta^5\text{-}1,3\text{-}(C_6H_5)_2C_5H_3]Fe(CO)_2CH_2CH{=}C(CH_3)_2$, **2b**	SO_2 at reflux	25 **8b**	75 **9b**
$[\eta^5\text{-}(CH_3)_5C_5]Fe(CO)_2CH_2CH{=}CHCH_3$, **3a**	SO_2 at reflux	100 **10a**	0
$[\eta^5\text{-}(CH_3)_5C_5]Fe(CO)_2CH_2CH{=}C(CH_3)_2$, **3b**	SO_2 at reflux	0	100 **11b**
	SO_2 at *ca.* −45 °C, 6 hr	10^b **10b**	90 **11b**
	SO_2 in hexane, 27 °C, 48 hr	40^b **10b**	60 **11b**
$[\eta^5\text{-}(CH_3)_5C_5]Fe(CO)_2CH_2CH{=}CHC_6H_5$, **3c**	SO_2 at reflux	0	100 **11c**
$\eta^5\text{-}C_5H_5Mo(CO)_2[P(OC_6H_5)_3]CH_2CH{=}CHCH_3$, **4a/5a**	SO_2 at reflux	20 **12a**	80 **13a**
	SO_2 at *ca.* −45 °C, 8 hr	40 **12a**	60 **13a**
	SO_2 in benzene, 27 °C, 10 hr	20 **12a**	80 **13a**
	SO_2 in CH_2Cl_2, 27 °C, 1 hr	20 **12a**	80 **13a**
$\eta^5\text{-}C_5H_5Mo(CO)_2[P(OC_6H_5)_3]CH_2CH{=}C(CH_3)_2$, **4b/5b**	SO_2 at reflux	0	100 **13b**
	SO_2 at *ca.* −45 °C, 6 hr	0	100 **13b**
$\eta^5\text{-}C_5H_5Mo(CO)_2[P(OC_6H_5)_3]CH_2CH{=}CHC_6H_5$, **4c/5c**	SO_2 at reflux	0	100 **13c**

[a] Estimated accuracy ±3%. [b] An error exists in the percentages of **10b** and **11b** reported in A. Wojcicki, *Adv. Organomet. Chem.*, *12*, 31 (1974), Table VI, and *Accounts Chem. Res.*, *4*, 344 (1971), Table IV.

determined by intensity considerations. The relative percentages of the rearranged and unrearranged 2-alkene-*S*-sulfinato products isolated in reactions of the 2-alkenyl complexes **1**–**5** with SO_2 under different conditions are furnished in Table IV. The ^1H NMR spectra of the *S*-sulfinate **11b**, a mixture of **11b** and the isomeric **10b**, and their precursor **3b** are shown in Fig. 1.

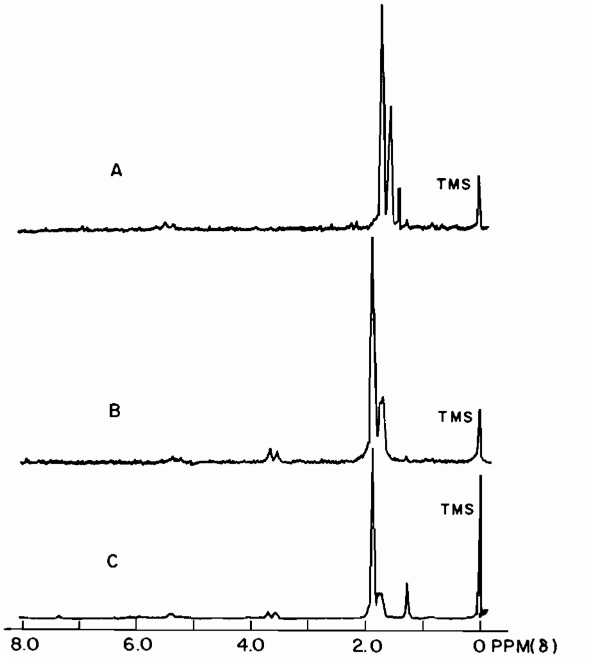
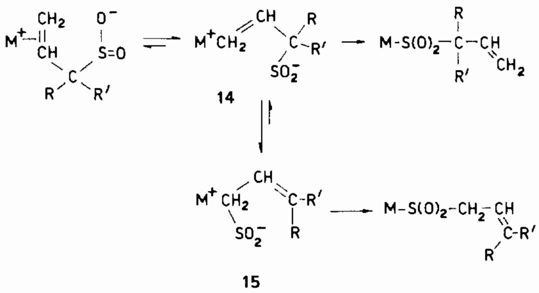


Figure 1. ^1H NMR spectra of (A) **3b**, (B) **11b**, and (C) 60:40 **11b**/**10b**, all in $CDCl_3$.

Turning now to the lateral–diagonal isomerism for the molybdenum complexes **12** and **13**, the infrared spectra of these *S*-sulfinato products exhibit a medium-to-strong intensity symmetric $\nu(C{\equiv}O)$ absorption at 1995–1993 cm^{-1} and the corresponding antisymmetric $\nu(C{\equiv}O)$ absorption of very strong intensity at 1918–1917 cm^{-1}. This intensity pattern is indicative of the presence of the diagonal isomer [11–13], either exclusively or as the predominant component of a lateral–diagonal mixture. The ^1H NMR spectra of **12** and **13** each show the η^5-C_5H_5 resonance as a doublet with J = 1–1.2 Hz, thus indicating that the lateral isomer is the only species present in a spectroscopically detectable concentration. It is noteworthy that the precursor 2-alkenyl complexes were all mixtures of lateral and diagonal isomers (*vide supra*). This stereochemical result may be compared with that obtained for the SO_2 insertion reaction of η^5-$C_5H_5Mo(CO)_2[P(C_6H_5)_3]CH_3$, where the starting alkyl complex and the product η^5-C_5H_5-$Mo(CO)_2[P(C_6H_5)_3]S(O)_2CH_3$ both adopt diagonal geometry [17]. Since a delicate balance of steric and electronic effects is at work in controlling lateral/diagonal ratios in η^5-$C_5H_5Mo(CO)_2(L)X$, an explanation of the results of this work is not warranted.

Each of the *S*-sulfinates containing the cinnamyl moiety, **7c**, **11c**, and **13c**, is assigned a structure with *trans* geometry about the allylic C=C bond. For **11c** this structure was determined crystallographically [15], and for **7c** and **13c** it is inferred on the basis of a close similarity of the CH=CH regions of the ^1H NMR spectra of the three complexes. The stereochemistry about the allylic C=C bond of **13a** cannot be deduced from the ^1H NMR spectrum of a **12a**/**13a** mixture.

The final point to be addressed in this paper concerns the mechanism of the formation of the 2-alkene-*S*-sulfinato products containing either a rearranged or an unrearranged 2-alkenyl fragment. It was shown previously [1] that the reactions of η^5-$C_5H_5M(CO)_xCH_2C(R){=}CR'R''$ (M = Fe, x = 2, M = Mo, x = 3) with SO_2 proceed via the intermediacy of metal–η^2-alkenesulfinate zwitterions. These intermediates then collapse to the final 2-alkene-S-sulfinato products. Such a mechanism also accommodates satisfactorily the results of this work and is depicted below for the systems described herein.



M = $(\eta^5$-$CH_3C_5H_4)Fe(CO)_2$, $[\eta^5$-$1,3$-$(C_6H_5)_2C_5H_3]Fe(CO)_2$, $[\eta^5$-$(CH_3)_5C_5]Fe(CO)_2$ or η^5-$C_5H_5Mo(CO)_2[P(OC_6H_5)_3]$

As shown in Table IV, the formation of the rearranged 2-alkene-*S*-sulfinates **6c**, **10b**, and **12a** over the unrearranged isomers **7c**, **11b**, and **13a**, respectively, is promoted by the use of 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 **14** and **15** (which would favor **15** for steric reasons) under stated conditions, thus promoting the formation of the rearranged species. It is of further interest that methyl substitution on the cyclopentadienyl ring decreases the ratio of the rearranged to the unrearranged 2-alkene-*S*-sulfinate. To illustrate, the said ratios for the insertion reaction in SO_2 at reflux are 25:75 for η^5-$C_5H_5Fe(CO)_2CH_2CH{=}C(CH_3)_2$ [2] and **1b**, but 0:100 for **3b**; also 20:80 for η^5-C_5H_5Fe-$(CO)_2CH_2CH{=}CHC_6H_5$ [2], 15:85 for **1c**, and 0:100 for **3c**. Similarly, replacement of a carbonyl group by $P(OC_6H_5)_3$ decreases the ratio of the rearranged to the unrearranged 2-alkene-*S*-sulfinate. Illustrating this point are the ratios for the reaction in SO_2 at reflux: 85–90: 10–15 for η^5-$C_5H_5Mo(CO)_3CH_2CH{=}CHCH_3$ [2], but 20:80 for **4a/5a**. The observed differences may arise from a slower rate of the conversion of **14** (and **15**) to the products for the unsubstituted compounds than for the substituted ones because of steric and/or electronic effects. The latter effects would be caused by the better electron-releasing properties of $P(OC_6H_5)_3$ compared to CO and of η^5-$(CH_3)_xC_5H_{5-x}$ (especially when x = 5) compared to η^5-C_5H_5, thus leading to the slower recombination of the ions. As a result, a closer approach to equilibrium between **14** and **15** can be expected with increased substitution, favoring the formation of the unrearranged 2-alkene-*S*-sulfinato products.

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