Contribution from the McPherson and Evans Chemical Laboratories, The Ohio State University, Columbus, Ohio 43210, U.S.A.

Sulfur Dioxide Insertion. VII. Rearrangement Reactions of 2-Alkenylmanganese and -rhenium Pentacarbonyls[1]

F. A. Hartman and A. Wojcicki

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The reaction of $M(CO)_5R$ ($M = Mn$, $R = CH_2CH=CH_2$, $CH_2CH=CHCH_3$, $CH_2CH=C(CH_3)_2$, $CH_2CH=CHC_6H_5$, *and* $CH_2C(Cl)=CH_2$; $M = Re$, $R = CH_2CH=C(CH_3)_2$) *with refluxing sulfur dioxide affords S-sulfinatopentacarbonyl complexes whose structures have been elucidated by infrared and proton magnetic resonance spectroscopy. When* $M = Mn$ *and* $R = CH_2CH=CHCH_3$ *or* $CH_2CH=C(CH_3)_2$ *and when* $M = Re$ *and* $R = CH_2CH=C(CH_3)_2$, *allylic rearrangement accompanies the insertion. However, no rearrangement is observed with* $Mn(CO)_5CH_2CH=CHC_6H_5$, *both at –10° and at* ca. *–70°. The reaction of* $Mn(CO)_5CH_2CH=CHCl$ *with liquid sulfur dioxide or with* SO_2 *in pentane yields* $Mn(CO)_5Cl$ *as the only carbonyl-containing product. Possible mechanisms of all of these reactions are discussed; it is suggested that the most likely path involves a cyclic activated complex in which sulfur interacts both with the metal and with carbon(3) of the allylic chain.*

Introduction

Insertion reactions of transition metal σ-allyl complexes have not been systematically investigated. The only report[2] known to the authors mentions briefly the reversible carbonylation of 2-propenylmanganese pentacarbonyl, $Mn(CO)_5CH_2CH=CH_2$.

In order to fill this void and to augment our present studies of reactions between SO_2 and various transition metal alkyls,[1,3] we have commenced a comprehensive investigation of insertion reactions of metal σ-allyl complexes with sulfur dioxide. One of the goals of this study is to ascertain whether, and if so, under what experimental conditions, rearrangement of the allylic moiety accompanies the insertion. Some preliminary results on 2-propenyl-, 2-butenyl-, and 3-methyl-2-butenylmanganese pentacarbonyls have been already reported.[4] Communicated here in more detail are the foregoing and further extensions of these studies.

Experimental Section

Materials. Decacarbonyldimanganese and decacarbonyldirhenium were purchased from Pressure Chemical Co. and Alfa Inorganics, Inc., respectively. Anhydrous grade SO_2, from Matheson, was passed through concentrated H_2SO_4 and a P_4O_{10}–$CaCl_2$ column before condensation in a trap at *ca.* –70°. Tetrahydrofuran was distilled from $LiAlH_4$ under a nitrogen atmosphere immediately before use. Technical grade pentane and hexane were used without further purification. All other chemicals and solvents were of reagent grade or equivalent.

The allylpentacarbonyl complexes $Mn(CO)_5CH_2CH=CH_2$, $Mn(CO)_5CH_2CH=CHCH_3$, $Mn(CO)_5CH_2CH=C(CH_3)_2$, and $Mn(CO)_5CH_2CH=CHCl$ were prepared by the method of McClellan, *et al.*[5] using $NaMn(CO)_5$, obtained by reduction of $Mn_2(CO)_{10}$ with excess 1% sodium amalgam. The other 2-alkenylcarbonyls, all new compounds, were synthesized as follows.

(a) $Mn(CO)_5CH_2CH=CHC_6H_5$. A solution of cinnamyl bromide (4.2 g., 21.3 mmoles) in 10 ml. of tetrahydrofuran was added dropwise with stirring to $NaMn(CO)_5$ (prepared from 4.0 g. of $Mn_2(CO)_{10}$ and excess 1% sodium amalgam) in 80 ml. of tetrahydrofuran at 27° and under nitrogen. A white precipitate began to form immediately. The mixture was stirred for 2 hr., insoluble material was filtered off, and solvent was removed at 30° (~20 mm.). The residual semi-solid was washed with three 15-ml. portions of pentane; the washings were combined, filtered, and concentrated in a stream of nitrogen. Cooling the solution at *ca.* –70° for several hours afforded colorless crystals which were collected by filtration. The yield was 4.3 g. (69%). Sublimation at 27° (0.1 mm.) of this material yielded a small amount of an oil, with a white solid remaining in the sublimer. The infrared spectra in the metal carbonyl stretching region (cm^{-1}): (a) oil: 2109 w-m, 2073 w, 2050 m, 2019 vs, 1995 s, 1986 m, 1978 w-m, 1969 w-m; (b) white solid: 2109 m, 2072 vw, 2047 w, 2019 vs, 1995 s, 1980 vw (hexane solutions). These data indicate presence of a mixture, the more volatile component probably being $Mn(CO)_4(\pi\text{–}C_9H_9)$. ^{1}H nmr spectrum of white solid: τ2.79 (rel. int. 5), broad absorption (–C_6H_5);

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(1) For part VI of this series, see F. A. Hartman and A. Wojcicki, *Inorg. Chem.*, 7, 1504 (1968).

(2) T. H. Coffield, J. Kozikowski, and R. D. Closson, «Lecture to International Conference on Coordination Chemistry», London, England, April (1959); quoted by G. E. Coates, «Organometallic Compounds», John Wiley and Sons, Inc., New York, N. Y., p. 280 (1960).

(3) J. P. Bibler and A. Wojcicki, *J. Am. Chem. Soc.*, *88*, 4862 (1966).

(4) F. A. Hartman, P. J. Pollick, R. L. Downs, and A. Wojcicki, *J. Am. Chem. Soc.*, *89*, 2493 (1967).

(5) W. R. McClellan, H. H. Hoehn, H. N. Cripps, E. L. Muetterties, and B. W. Howk, *J. Am. Chem. Soc.*, *83*, 1601 (1961).

3.28-3.95 (rel. int. 2), complex multiplets ($=CH-$ and $-CHC_6H_5$); 8.03 (rel. int. 2), doublet, $J \sim 7$ cps ($-CH_2-$) ($CDCl_3$ solution).

Anal. (white solid): Calcd. for $C_{14}H_9O_5Mn$: C, 53.86; H, 2.90. Found: C, 53.88; H, 2.94.

(b) $Mn(CO)_5CH_2C(Cl)=CH_2$. Sodium pentacarbonylmanganate(–I) (prepared from 4.0 g. of $Mn_2(CO)_{10}$ and excess 1% sodium amalgam) in 60 ml. of tetrahydrofuran was added to 2.4 g. (21.8 mmoles) of 1,2-dichloro-2-propene in 10 ml. of tetrahydrofuran at 27° and under nitrogen. The mixture was stirred for 1.5 hr., filtered, and solvent was removed. The residual oil was distilled at 30° (0.1 mm.) to give *ca.* 0.8 ml. of a light yellow liquid. The product was characterized only through its conversion to the corresponding sulfinate and analysis of the latter.

(c) $Re(CO)_5CH_2CH=C(CH_3)_2$. This compound was prepared by the addition of $NaRe(CO)_5$ (from $Re_2(CO)_{10}$ and excess 1% sodium amalgam) in tetrahydrofuran to a slight excess of 1-chloro-3-methyl-2-butene, also in tetrahydrofuran, at 27° and under nitrogen. The mixture was stirred for 1 hr., then filtered and evaporated to a light orange oil. The oil could not be distilled up to 55° ($\sim$0.1 mm.). It was characterized indirectly by conversion to the corresponding sulfinate, which was analyzed.

Synthesis of Sulfinatopentacarbonyl Complexes. The reactions of the allyl complexes with liquid SO_2 were carried out in a manner strictly analogous to that employed previously for manganese alkylpentacarbonyls.[1] In general, SO_2 solutions of the parent allylcarbonyls were allowed to reflux for 2 hr. (except $Mn(CO)_5CH_2CH=CHC_6H_5$ (7 hr.) and $Re(CO)_5CH_2CH=C(CH_3)_2$ (0.5 hr.)) before isolation of the products, which were recrystallized from chloroform-pentane. Per cent yields, melting points, molecular weights, and chemical analyses for the sulfinato complexes are given in Table I.

Low Temperature Reaction between $Mn(CO)_5CH_2CH=CHC_6H_5$ *and* SO_2. Approximately 40 ml. of dry SO_2 was condensed onto $Mn(CO)_5CH_2CH=CHC_6H_5$ in a U-trap at *ca.* –70°. The resulting solution was stirred at this temperature for 48 hr. Excess SO_2 was then removed at *ca.* –40° and the product was purified in the usual manner. Its proton nmr spectrum was identical with that of the sulfinate from the reaction between $Mn(CO)_5CH_2CH=CHC_6H_5$ and SO_2 at –10°.

Reaction of $Mn(CO)_5CH_2CH=CHCl$ *with* SO_2. Sulfur dioxide was condensed onto 2.0 g. (7.4 mmoles) of $Mn(CO)_5CH_2CH=CHCl$ in a flask containing a magnetic stirring bar at *ca.* –40°. The solution gradually turned orange as the reaction was allowed to proceed for 1 hr. before removing the bath. After excess SO_2 had boiled off, the residual oil was vacuum treated at 27° ($\sim$20 mm.) to ensure complete removal of SO_2. Addition of cold absolute ethanol to the oil resulted in the formation of a light yellow powder, identified by infrared spectroscopy as $Mn(CO)_5Cl$[6] (1.40 g., 82% yield).

The outcome of the above reaction is independent of the isomeric nature (*cis* or *trans*) of the allylpentacarbonyl employed. Using pure *cis*- or pure *trans*-1,3-dichloro-1-propene in conjunction with $NaMn(CO)_5$, one obtains *cis*- and *trans*-$Mn(CO)_5CH_2CH=CHCl$, respectively, characterized by proton nmr spectroscopy Sulfur dioxide reacts with either pure isomer or with a mixture thereof to yield $Mn(CO)_5Cl$ as the only carbonyl-containing product.

Several unsuccessful attempts were made to identify a possible intermediate in this chlorination and to determine the nature of the organic product containing the hydrocarbon moiety. Accordingly, a solution of *ca.* 0.2 ml. of $Mn(CO)_5CH_2CH=CHCl$ in 0.5 ml. of SO_2 was prepared in an nmr tube at approximately –60°. The spectrum at –35° showed the methylene proton signal (τ 8.65) not to change during the first hour. However, after *ca.* 1.5 hr. its intensity started to decrease. Following a storage period of 24 hr. at –30° to –60° the recorded $-CH_2-$ proton signal was only half as intense as that of the fresh sample and less intense than the signals due to olefinic hydrogens (τ 5.2-3.2). However, no conclusion could be reached about the reaction taking place because of the complexity of the spectrum and poor resolution.

Table I. Per Cent Yields, Melting Points, and Analytical Data for Sulfinato Complexes Derived from Manganese and Rhenium Allylpentacarbonyls

	Yield, %	M.p., °C[a]		Mol. wt.	Analyses, %			
					C	H	S	Cl
$Mn(CO)_5SO_2CH_2CH=CH_2$	79	100	Calcd.	300	32.01	1.68	10.68	
			Found	294	32.27	1.82	10.68	
$Mn(CO)_5SO_2CH(CH_3)CH=CH_2$	70-80	99	Calcd.	316	34.41	2.25		
			Found	314	34.38	2.28		
$Mn(CO)_5SO_2C(CH_3)_2CH=CH_2$	70-80	110	Calcd.	328	36.59	2.76	9.77	
			Found	326	36.74	3.00	9.49	
$Mn(CO)_5SO_2CH_2CH=CHC_6H_5$	88	132	Calcd.	376	44.69	2.41	8.52	
			Found	372	44.51	2.32	8.29	
$Mn(CO)_5SO_2CH_2C(Cl)=CH_2$	<10	77	Calcd.		28.72	1.20	9.58	10.60
			Found		28.55	1.22	9.20	11.07
$Re(CO)_5SO_2C(CH_3)_2CH=CH_2$	53	113	Calcd.	460	26.14	1.97	6.98	
			Found	523	26.20	2.12	6.77	

[a] Determined with a Fisher-Johns melting-point block and uncorrected.

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[6] J. C. Hileman, D. K. Huggins, and H. D. Kaesz, *Inorg. Chem.*, *1*, 933 (1962).

In order to ascertain the fate of the hydrocarbon moiety the reaction of $Mn(CO)_5CH_2CH{=}CHCl$ with SO_2 was carried out on a vacuum line at 26°, and volatile matter was collected in a trap cooled with liquid nitrogen. Infrared spectral examination of the condensate revealed that only sulfur dioxide was present. The residual oil exhibited two strong infrared bands at 1135 and 1000 cm^{-1} but was not characterized further because of contamination with $Mn(CO)_5Cl$, which could not be completely separated by successive extractions of the former into ether. The nmr spectrum of the oil-carbonyl mixture in deuteroacetone was insufficiently resolved to be useful.

When SO_2 was passed through a pentane solution (25 ml.) of $Mn(CO)_5CH_2CH{=}CHCl$ (0.27 g.) at 0-5°, approximately 20 mg. of $Mn(CO)_5Cl$ precipitated in 10 hr.

Reaction of $Mn(CO)_5SO_2CH_2CH{=}CH_2$ with the Halogens. After chloride had been bubbled through a solution of $Mn(CO)_5SO_2CH_2CH{=}CH_2$ in dichloromethane for about 30 min., removal of the solvent yielded only $Mn(CO)_5Cl$. Evolution of SO_2 was confirmed by the precipitation of $BaSO_3$ from aqueous $BaCl_2$. Treatment of the allylpentacarbonyl in CH_2Cl_2 with an equimolar amount of bromine for *ca.* 2 hr. at each 27° and 0° resulted in the formation of $Mn(CO)_5Br$.

Infrared Spectra. Spectra were recorded on a Beckman Model IR-9 spectrophotometer. When CCl_4 was employed as a solvent, saturated solutions were placed in a 0.05-mm. KBr cell used in conjunction with a matched reference cell. The vertical scale expansion mechanism was then employed to obtain an approximate fourfold enlargement.

Proton Magnetic Resonance Spectra. Nmr spectra were recorded on Varian Associates A-60 and A-60A spectrometers. Tetramethylsilane (TMS) was used as a standard.

Molecular Weights. Measurements were made on *ca.* 10^{-2} *M* $CHCl_3$ solutions using a Mechrolab Model 301-A osmometer.

Analyses. Elemental analyses were done by Dr. F Pascher, Mikroanalytisches Laboratorium, Bonn, Germany.

Results

The reactions of manganese and rhenium allylpentacarbonyls with liquid sulfur dioxide afford products which analyze chemically as 1:1 compounds of the parent carbonyl and SO_2. Physical properties such as color, volatility, and solubility of these derivatives are very similar to those of the alkyl- and arylsulfinatopentacarbonyls reported earlier.[1] This general similarity extends also to chemical properties; for example, the complexes are converted to the halogenopentacarbonyls when allowed to react with chlorine or bromine. Interestingly, the reaction of the SO_2-insertion product of $Mn(CO)_5CH_2CH{=}CH_2$ with one mole of bromine results in the formation of $Mn(CO)_5Br$ rather than in addition to the C=C double bond.

The structures of the SO_2-containing products can be elucidated with the aid of the infrared and proton nmr spectra, listed in Tables II and III, respectively. The number, positions, and relative intensities of the CO and SO stretching absorptions are virtually identical with those of the previously synthesized $M(CO)_5SO_2R$ (M = Mn and Re)[1] and indicate a common $MS(O)_2C$ bonding sequence in all sulfinato complexes. The question concerning the position of attachment of the unsymmetrical allylic moieties to sulfur in the sulfinates derived from $Mn(CO)_5CH_2CH{=}CHCH_3$, $Mn(CO)_5CH_2CH{=}C(CH_3)_2$, $Mn(CO)_5CH_2CH{=}CHC_6H_5$, and $Re(CO)_5CH_2CH{=}C(CH_3)_2$ is resolved upon examination of the proton nmr spectra of these compounds. The spectra of $Mn(CO)_5CH_2CH{=}CHCH_3$ and its SO_2-insertion product and of $Mn(CO)_5CH_2CH{=}C(CH_3)_2$ and its sulfinate are reproduced in Figures 1 and 2, respectively.

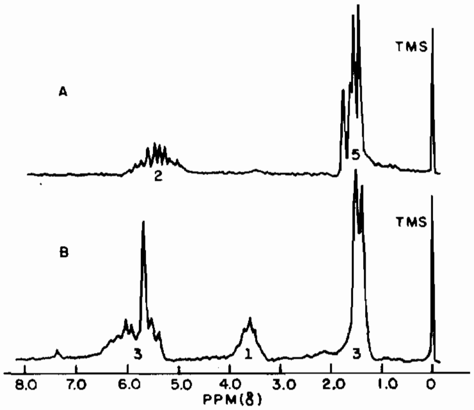

Figure 1. Proton magnetic resonance spectra of (A) $Mn(CO)_5CH_2CH{=}CHCH_3$ and (B) $Mn(CO)_5SO_2CH(CH_3)CH{=}CH_2$, both recorded in $CDCl_3$.

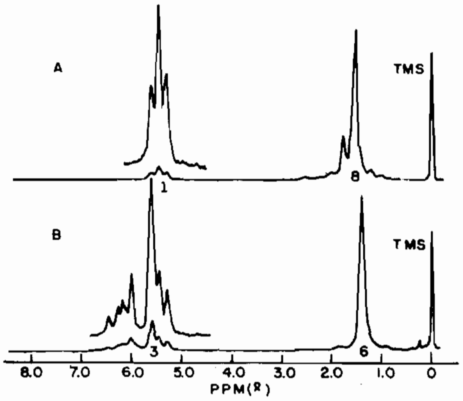

Figure 2. Proton magnetic resonance spectra of (A) $Mn(CO)_5CH_2CH{=}C(CH_3)_2$ and (B) $MnCO)_5SO_2C(CH_3)_2CH{=}CH_2$, both recorded in $CDCl_3$.

The allylpentacarbonyls $Mn(CO)_5CH_2CH{=}CH_2$, $Mn(CO)_5CH_2CH{=}CHCH_3$, $Mn(CO)_5CH_2CH{=}C(CH_3)_2$, and $Mn(CO)_5CH_2CH{=}CHCl$, prepared earlier,[5] were all assigned structures with Mn—CH_2—

Table II. Infrared Spectra of Sulfinatopentacarbonyl Complexes (cm^{-1})

Compound	Metal carbonyl stretches [a] $A_1^{(2)}$	B_1	E	$A_1^{(1)}$	SO stretches	Other bands
$Mn(CO)_5SO_2CH_2CH=CH_2$	2137 w-m	2088 w	2057 s, 2042 s	2025 m	1190 s, 1043 s [b]	3100 vw, 3016 vw, 2970 vw, 2940 vw, 2901 vw, 1637 vw, 1429 w, 1400 vw, 1223 w, 1078 m-s, 1010 m-s, 948 s, 874 m-s, 750 w-m, 722 w-m, 635 s, 604 m-s, 551 w-m, 521 m-s, 485 m, 446 m [b]
$Mn(CO)_5SO_2CH(CH_3)CH=CH_2$	2136 w-m	2089 w	2057 s, 2040 s	2024 m	1189 s, 1163 sh, 1048 s [b]	3089 vw, 3012 vw, 2989 vw, 2942 vw, 1639 w, 1451 m, 1426 m, 1364 w, 1219 m, 1026 m-s, 1005 m, 974 w, 955 m, 945 sh, 872 w, 640 s, 594 s, 536 w, 517 m, 502 w, 443 m-s [b]
$Mn(CO)_5SO_2C(CH_3)_2CH=CH_2$	2135 w-m	2088 w	2058 s, 2039 s	2020 m	1190 s, 1176 sh, 1041 s [b]	3092 w-m, 3014 sh, 3006 w-m, 2983 w-m, 2942 sh, 2930 m, 2914 sh, 2861 w, 1638 w, 1464 w, 1412 m, 1379 w, 1356 w, 1134 w, 1015 m, 929 m, 645 sh, 641 s, 596 m, 577 m-s, 546 w, 540 w, 513 w, 503 vw, 444 w-m [b]
$Mn(CO)_5SO_2CH_2CH=CHC_6H_5$	2140 w-m	2092 w	2061 s, 2044 s	2027 m	1218 sh, 1205 s, 1198 sh, 1054 s, 1046 sh [b]	3092 w, 3061 w, 3037 w, 2960 w, 1602 w-m, 1580 w, 1500 w, 1454 w-m, 1413 w-m, 1309 w, 1287 w, 1255 w, 1245 w, 1166 w, 1143 m-s, 987 w, 965 s, 897 m-s, 855 w, 845 w, 819 w, 760 vs, 740 sh, 695 s, 678 s, 640 vs, 682 s, 645 w, 509 m-s, 476 m, 445 m [b]
$Mn(CO)_5SO_2CH_2C(Cl)=CH_2$	2142 w-m	2095 w	2063 s, 2053 s	2032 m	1199 s, 1057 s [c]	3116 w, 2985 w, 1624 m, 1415 w, 1229 m, 1112 m, 952 w, 920 m, 887 m, 755 w, 693 m, 640 vs, 549 m, 519 m-s, 454 m, 445 sh [c]
$Re(CO)_5SO_2C(CH_3)_2CH=CH_2$	2157 w	2097 w	2058 s, 2043 s	2019 m	1187 s, 1173 sh, 1045 s [c]	3090 vw, 3015 w, 3005 w, 2988 w, 2940 w-m, 1638 w-m, 1475 w, 1416 w-m, 1370 w, 1358 w, 1140 w-m, 1018 m-s, 931 s, 907 w, 620 s, 602 s, 589 s, 579 s, 536 w-m, 515 w-m, 497 w-m, 455 w-m [c]

[a] Saturated CCl_4 solution (fourfold scale expansion). [b] Nujol mull (2800-1500 and 1300-400 cm^{-1}) and hexachlorobutadiene mull (4000-2800 and 1500-1300 cm^{-1}). [c]-KBr pellet. Abbreviations: vs, very strong; s, strong, m, medium; w, weak; vw, very weak; sh, shoulder.

linkages. This has been confirmed by proton nmr spectroscopy in our study. The nmr spectrum of $Mn(CO)_5CH_2CH=CHC_6H_5$ is consistent with the presence of a cinnamyl group; the rhenium compound undoubtedly contains an $Re{-}CH_2{-}$ attachment by analogy with the corresponding derivative of manganese and because of a much greater stability associated with transition metal-primary carbon bonds than with transition metal-tertiary carbon bonds. Hence, all of the pentacarbonyls with unsymmetrical allylic moieties exhibit a common $M{-}CH_2{-}$ structural feature, a point of utmost importance in ascertaining occurrence of rearrangement upon insertion.

Methylene group protons of $MS(O)_2CH_2{-}$ ($M=Mn$ and Re) give rise to nmr signals in the region τ 6.82-5.81.[1,4] Moreover, these occur as doublets ($J\sim 8$ cps) if the structure is $MS(O)_2CH_2{-}CH=$. Keeping the above as points of reference, it may be seen (Table III and Figures 1 and 2) that allylic rearrangement did occur in the formation of $Mn(CO)_5SO_2CH(CH_3)CH=CH_2$, $Mn(CO)_5SO_2C(CH_3)_2CH=CH_2$, and $Re(CO)_5SO_2C(CH_3)_2CH=CH_2$ (equation (1)).

$$M(CO)_5CH_2CH=CRR'+SO_2 \rightarrow M(CO)_5SO_2C(R)(R')CH=CH_2$$
$$(M=Mn,\ R=H \text{ and } CH_3,\ R'=CH_3;\ M=Re,\ R=R'=CH_3) \qquad (1)$$

Had there been no rearrangement, the nmr spectra would have displayed doublets at τ 6.82-5.81 (rel. intensity=2); further, vinylic and methyl proton ab-

Table III. Proton Magnetic Resonance Spectra of Sulfinatopentacarbonyl Complexes (τ)[a]

Compound	Chemical shift	Rel. intensity	Assignment
$Mn(CO)_5SO_2CH_2CH=CH_2$	6.25 (doublet, J ~ 8 cps) 4.55-3.50 (complex pattern)	2 3	$—CH_2—$ $—CH=CH_2$
$Mn(CO)_5SO_2CH(CH_3)CH=CH_2$	8.55 (doublet, J ~ 8 cps) 6.38-6.10 (multiplet) 4.66-3.59 (complex pattern)	3 1 3	$—CH_3$ SO_2CH $—CH=CH_2$
$Mn(CO)_5SO_2C(CH_3)_2CH=CH_2$	8.59 (singlet) 4.83-3.50 (complex pattern)	2 1	$—CH_3$ $—CH=CH_2$
$Mn(CO)_5SO_2CH_2CH=CHC_6H_5$[b]	6.13 (doublet, J ~ 7 cps) 3.80-3.00 (complex pattern) 2.83-2.33 (broad absorption)	2 2 5	$—CH_2—$ $—CH=CH—$ $—C_6H_5$
$Mn(CO)_5SO_2CH_2C(Cl)=CH_2$	6.05 (apparent singlet)[c] 4.39 (apparent singlet)[c] 4.33 (apparent singlet)[c]	1 1	$—CH_2—$ $=CH_2$
$Re(CO)_5SO_2C(CH_3)_2CH=CH_2$	8.48 (singlet) 4.58-3.33 (complex pattern)	2 1	$—CH_3$ $—CH=CH_2$

[a] Recorded in $CDCl_3$ solution unless noted otherwise. [b] Recorded in CD_3CN solution. [c] Insufficient resolution to discern any splitting.

sorptions would have occurred at their usual fields (*ca.* τ 4-5 and 8-9, respectively) as a multiplet (rel. intensity = 2) and a doublet (rel. intensity = 3), respectively, for the former and as a 1:2:1 triplet (rel. intensity = 1) and an approximate singlet (rel. intensity = 6), respectively, for the latter two compounds. However, no rearrangement accompanied SO_2 insertion reaction of $Mn(CO)_5CH_2CH=CHC_6H_5$ (equation (2)), as evidenced by the nmr spectrum.

$$Mn(CO)_5CH_2CH=CHC_6H_5 + SO_2 \rightarrow Mn(CO)_5SO_2CH_2CH=CHC_6H_5 \qquad (2)$$

The infrared spectra of the sulfinates lend additional support to the foregoing conclusions. They exhibit a weak- to medium-intensity band at 1639-1624 cm^{-1}, which is assigned to the C=C stretching mode; this band is shifted to 1602 cm^{-1} for $Mn(CO)_5SO_2CH_2CH=CHC_6H_5$, in agreement with the presence of a phenyl-conjugated C=C double bond.[7] Further, the cinnamyl complex displays an absorption at 965 cm^{-1}, which is provisionally assigned to a CH out-of-plane deformation mode for a *trans* –CH=CH– moiety.[7] A *trans* arrangement is favored here on steric grounds.

Since it has been shown in this laboratory that low temperatures favor the formation of $C_5H_5Fe(CO)_2SO_2C(CH_3)_2CH=CH_2$ over $C_5H_5Fe(CO)_2SO_2CH_2CH=C(CH_3)_2$ from $C_5H_5Fe(CO)_2CH_2CH=C(CH_3)_2$ and liquid SO_2,[8] the insertion with $Mn(CO)_5CH_2CH=CHC_6H_5$ was carried out at *ca.* –70°. However, the only product detected by nmr spectroscopy was again $Mn(CO)_5SO_2CH_2CH=CHC_6H_5$.

A unique reaction encountered in this study is that of SO_2 (both liquid and pentane solution) with $Mn(CO)_5CH_2CH=CHCl$, the only carbonyl-containing product being $Mn(CO)_5Cl$ (equation (3)).

$$Mn(CO)_5CH_2CH=CHCl + xSO_2 \rightarrow Mn(CO)_5Cl + C_3H_4 \cdot (SO_2)_x \qquad (3)$$

Attempts to ascertain by nmr spectroscopy whether $Mn(CO)_5Cl$ arises directly from the interaction of the parent allyl with SO_2 or whether $Mn(CO)_5SO_2CH(Cl)CH=CH_2$ is the precursor of the chloropentacarbonyl have been unsuccessful. It has been shown, however, that the hydrocarbon moiety is not eliminated as the volatile $CH_3C\equiv CH$ or $CH_2=C=CH_2$ but instead remains combined with SO_2 as an oily substance of unknown composition.

Discussion

Infrared Spectra. The salient features in the infrared spectra of the sulfinato complexes in the metal carbonyl stretching region are presence of a weak-intensity B_1 absorption and removal of the degeneracy of the E band. Both of these phenomena have been observed and discussed previously.[1,9,10,11] Nevertheless, the magnitude of the splitting of the E band ($\Delta\nu(E)$) is the largest yet reported and as such merits a brief comment.[12]

It has been suggested earlier[1] that both the size of the metal and bulkiness of substituents on the α-carbon atom of R in $Mn(CO)_5SO_2R$ play a major role in determining the degree of separation of the two components of the E band. The first point is illustrated by comparison of the values of $\Delta\nu(E)$ for $Mn(CO)_5SO_2C(CH_3)_2CH=CH_2$ and $Re(CO)_5SO_2C(CH_3)_2CH=CH_2$, which are 19 and 15 cm^{-1}, respectively. The large magnitude of $\Delta\nu(E)$ for all of the allylsulfinates may be rationalized in terms of the relatively long, 3-carbon atom chain bonded to sulfur in each complex.

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Replacement of hydrogen in the allylic moiety with an alkyl or aryl group tends to increase further the splitting as illustrated by the relative values of $\Delta\nu(E)$ for $Mn(CO)_5SO_2CH_2CH{=}CH_2$ (15 cm^{-1}), $Mn(CO)_5SO_2CH_2CH{=}CHC_6H_5$ (17 cm^{-1}), $Mn(CO)_5SO_2CH(CH_3)CH{=}CH_2$ (17 cm^{-1}), and $Mn(CO)_5SO_2C(CH_3)_2CH{=}CH_2$ (19 cm^{-1}). The relatively small $\Delta\nu(E)$ for $Mn(CO)_5SO_2CH_2CH(Cl){=}CH_2$ (10 cm^{-1}) is rather unexpected.

Possible Mechanisms. Although detailed mechanistic studies on sulfur dioxide insertion have begun only recently in this laboratory, it is fitting to comment briefly on the reactions reported herein. A plausible mechanism must rationalize the following experimental findings: (a) allylic rearrangement with $Mn(CO)_5CH_2CH{=}CHCH_3$ and $M(CO)_5CH_2CH{=}C(CH_3)_2$ (M = Mn and Re), (b) no rearrangement with $Mn(CO)_5CH_2CH{=}CHC_6H_5$, and (c) formation of $Mn(CO)_5Cl$ from $Mn(CO)_5CH_2CH{=}CHCl$. It should be stated at the outset that the isolated complexes represent the thermodynamically stable and, to our knowledge, the only sulfinates formed in these reactions; there is no evidence to suggest that other isomeric species may be the initial products of the insertion.

As liquid sulfur dioxide is a good polar solvent, one must consider the possibility of ionization into $M(CO)_5^-$allyl$^+$ or $M(CO)_5^+$allyl$^-$ followed by reaction of $M(CO)_5^-$ and $M(CO)_5^+$ (or allyl$^-$), respectively, with SO_2 and recombination of the ions. The former mode of ionization, however, cannot account for the unrearranged product from manganese cinnamylpentacarbonyl, since the secondary carbonium ion, $CH_2{=}CH{-}CHC_6H_5^+$, should be more stable than the corresponding primary ion, $^+CH_2{-}CH{=}CHC_6H_5$. The influence of steric factors cannot readily be invoked here as the corresponding 3-methyl-2-butenyl complex does undergo rearrangement.

The second mode of ionization, into $M(CO)_5^+$allyl$^-$, does not explain any of the rearrangements. Moreover, neither of these ionization schemes offers a simple rationale for the formation of $Mn(CO)_5Cl$ from $Mn(CO)_5CH_2CH{=}CHCl$. A homolytic cleavage of the M–C bond in $M(CO)_5$ allyl, followed by reaction of either species with SO_2 and recombination of the radicals is rather unlikely, since no $Mn_2(CO)_{10}$ has been detected in any of the reactions studied.

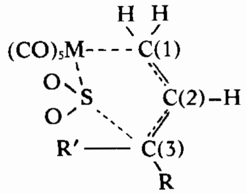
A mechanism which merits some consideration involves initial insertion of SO_2 without rearrangement of the allylic moiety to give an allyl(oxy)sulfinyl complex. This then undergoes allylic rearrangement to form the sulfinate. The sequence is illustrated in equations (4) and (5) for $Mn(CO)_5CH_2CH{=}C(CH_3)_2$.

$$Mn(CO)_5CH_2CH{=}C(CH_3)_2 + SO_2 \rightarrow Mn(CO)_5S(O)OCH_2CH{=}C(CH_3)_2 \qquad (4)$$

$$Mn(CO)_5S(O)OCH_2CH{=}C(CH_3)_2 \rightarrow Mn(CO)_5SO_2C(CH_3)_2CH{=}CH_2 \qquad (5)$$

Such a scheme receives support from the known rearrangements of unsymetrically substituted allylic esters of sulfinic acids to the corresponding sulfones.[13] Also in this context it is of interest to note that the sulfenate $CCl_3SOCH_2CH{=}CHC_6H_5$ undergoes conversion to the sulfoxide $CCl_3S(O)CH_2CH{=}CHC_6H_5$ without rearrangement of the cinnamyl group,[14] in contrast to the behavior of several allylic toluene-*p*-sulfenates.[15]

The above mechanism for SO_2 insertion requires that the intermediate allyl(oxy)sulfinyl complexes rearrange very rapidly to the sulfinates, as the former have never been detected in this study. The recent isolation of $Mn(CO)_5S(O)OC(R){=}C{=}CH_2$ (R = H and CH_3) and demonstration of their thermodynamic stability with respect to isomerization to $Mn(CO)_5SO_2C_3H_3R$[16] do, however, cast some doubt on the foregoing mechanistic scheme.


(I)

The mechanism which is most consistent with the results presented herein involves a simultaneous interaction of the incoming SO_2 with the metal and carbon(3) of the allylic chain (I). Whether the attack of SO_2 on the metal is electrophilic or nucleophilic cannot be ascertained at present. When R = H and R′ = C_6H_5, conjugation of the allylic C=C double bond with the phenyl ring may prevent interaction of SO_2 with carbon(3) and lead instead to a direct insertion into M–C(1) bond. Further, with R = H and R′ = Cl there exists a possibility of a transfer of chlorine onto the sulfur to yield $Mn(CO)_5SO_2Cl$. From the evidence on hand—reaction of $NaMn(CO)_5$ with FSO_2Cl to give $Mn(CO)_5Cl$, SO_2, and NaF[17]—such a compound is expected to eliminate SO_2 giving $Mn(CO)_5Cl$. Alternatively, $Mn(CO)_5SO_2CH(Cl)CH{=}CH_2$ could be formed initially from the insertion and then decompose rapidly to $Mn(CO)_5Cl$ and an unknown organic SO_2-containing compound. At present we cannot differentiate between these two possibilities. The fact that $Mn(CO)_5Cl$ is formed using either liquid SO_2 or solutions of SO_2 in pentane may reflect a common mechanism for the two reactions and is entirely in keeping with the above-proposed scheme. Moreover, since $Mn(CO)_5CH_2CH{=}CHCl$ undergoes conversion to $Mn(CO)_4(\pi{-}C_3H_4Cl)$ on heating[5] and since the latter does not react with SO_2,[18] the possibility of decomposition of the allylpentacarbonyl to $Mn(CO)_5Cl$ without intervention of sulfur dioxide must be ruled out. In this context it is also pertinent to note that the allylpentacarbonyl $Mn(CO)_5CH_2C(Cl){=}CH_2$, which

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contains a carbon(2)-chlorine bond, undergoes insertion of SO_2 rather than conversion to $Mn(CO)_5Cl$.

Finally, it is in order to mention that similar concerted mechanisms have been suggested for reactions of related organic sulfur compounds. Braverman[13] proposed that rearrangements of unsymmetrically substituted allylic benzenesulfinates to the corresponding sulfones proceed *via* a cyclic intramolecular mechanism. Mislow, *et al.*[15] studied the reaction of *p*-toluenesulfenyl chloride with several unsymetrically substituted allyl alcoholates and obtained the sulfoxides containing rearranged allylic moieties, presumably formed by a concerted process from the precursor sulfenates.

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