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Sulfur Dioxide Insertion. VI. S-Sulfinatopentacarbonyl Complexes of Group VI and VII Transition Metals[1]

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A number of sulfinatopentacarbonyls of manganese(I) and rhenium(I) have been prepared by the reactions of $M(CO)_5R$ (M = Mn, R = CH_3, C_2H_5, and $CH_2C_6H_5$; M = Re, R = CH_3 and $CH_2C_6H_5$) with refluxing sulfur dioxide and of $Mn(CO)_5C_6H_5$ with liquid SO_2 at 35–45° under pressure. Complexes containing the anions $Cr(CO)_5(SO_2C_6H_5)^-$ and $W(CO)_5(SO_2C_6H_5)^-$, the former being isoelectronic with $Mn(CO)_5(SO_2C_6H_5)$, were obtained from $M(CO)_5I^-$ (M = Cr and W) and sodium benzenesulfinate, but the analogous $Mo(CO)_5(SO_2C_6H_5)^-$ could not be prepared. Other attempted syntheses of $M(CO)_5(SO_2R)$ (M = Mn and Re) are described and briefly discussed. All of the sulfinatopentacarbonyl complexes prepared have been assigned structures containing $M-S(O)_2-R$ linkages from the infrared and proton magnetic resonance spectral data. The infrared carbonyl stretching region spectra of the manganese and rhenium S-sulfinatopentacarbonyls are tabulated and the magnitude of the splitting of the E band is discussed in terms of the size of the metal and bulkiness of substituents on the α-carbon atom of R. Thermal and photolytic treatment of $Mn(CO)_5(SO_2CH_2C_6H_5)$ provided no evidence of desulfurylation to give $Mn(CO)_5CH_2C_6H_5$.

Introduction

It was demonstrated by Bibler[2] in these laboratories that cyclopentadienyliron alkyl- and aryldicarbonyls react with liquid sulfur dioxide to give the corresponding S-sulfinato complexes. Later, in a preliminary report,[3] we showed that methyl- and benzylmanganese pentacarbonyls undergo similar reactions to yield $Mn(CO)_5(SO_2R)$ (R = CH_3 and $CH_2C_6H_5$). We now describe in detail sulfur dioxide insertion reactions of manganese pentacarbonyl alkyls (and aryls) and of some analogous rhenium compounds as well as the synthesis of the "isoelectronic" S-phenylsulfinatopentacarbonyl anions of chromium(0) and tungsten(0).

Experimental Section

Materials.—Dimanganese decacarbonyl (Pressure Chemical Co.) and dirhenium decacarbonyl (Alfa Inorganics, Inc.) were converted to alkyl-, aryl-, germanyl-, and acylpentacarbonyls using procedures reported in the literature for $Mn(CO)_5CH_3$,[4] $Mn(CO)_5CH_2C_6H_5$,[4] $Mn(CO)_5C_2H_5$,[5,6] $Mn(CO)_5C_6H_5$,[7] $Mn(CO)_5(COCH_3)$,[7] $Mn(CO)_5(COCF_3)$,[8] $Mn(CO)_5CF_3$,[9] $Mn(CO)_5Ge(C_6H_5)_3$,[10] $Re(CO)_5CH_3$,[6] and $Re(CO)_5CH_2C_6H_5$.[6] The compounds $[(n\text{-}C_4H_9)_4N][M(CO)_5I]$ (M = Cr, Mo, and W) were synthesized by heating (120°) excess metal hexacarbonyl (Pressure Chemical Co. and Climax Molybdenum Co.) with $(n\text{-}C_4H_9)_4NI$ (Eastman) in diethylene glycol dimethyl ether.[11]

Anhydrous grade sulfur dioxide, from Matheson, was passed through concentrated sulfuric acid and a phosphorus(V) oxide–calcium chloride column before condensation in a trap at *ca.* −70°. Chlorine (Matheson, high-purity grade) was used without further purification.

The following were purchased and used as received: $C_6H_5SO_2Na$ (Aldrich Chemical Co.), $C_6F_5SO_2Cl$ (Peninsular Chem-Research), $C_6H_5SO_2Cl$ (Baker Chemical Co.), and CH_3SO_2Cl (Eastman). Technical grade pentane, hexane, and petroleum ether (bp 30–60°) were used without further purification. All other chemicals and solvents were of reagent grade or equivalent.

Synthesis of Sulfinatopentacarbonyl Complexes. $Mn(CO)_5(SO_2CH_3)$.—A 100-ml round-bottom flask equipped with a magnetic stirring bar and containing 2.10 g (10.0 mmol) of $Mn(CO)_5CH_3$ was flushed with dry nitrogen and placed in a Dry Ice–isopropyl alcohol bath at *ca.* −75°. Sulfur dioxide (~50 ml), previously condensed in a separate trap, was poured onto the pentacarbonyl. A low-temperature condenser (7.5 × 30 cm) packed with Dry Ice was attached to the round-bottom flask and the −75° bath was replaced with an ice–water bath. As the temperature rose, the pentacarbonyl dissolved and the solution became orange. Magnetic stirring prevented the solvent from bumping and aided in the dissolution of the carbonyl. After allowing the SO_2 to reflux for 2 hr, the condenser was removed and the reaction mixture was reduced to an orange semisolid mass in a stream of nitrogen. This orange residue was extracted with 25 ml of absolute ethanol. The extract was filtered and then diluted with 10 ml of ether before cooling to −70°. Pale yellow needles that formed were collected and washed three times with 5-ml portions of ether. Concentration of the mother liquor in a stream of nitrogen, followed by cooling, afforded additional product. The batches were combined and dissolved in $CHCl_3$ (15 ml). Insoluble material was filtered off and the solution was treated with 50 ml of pentane. The microcrystalline product was collected, washed with 20 ml of pentane, and air dried. The yield was 2.20 g.

The ethyl- and the benzylsulfinato derivatives were prepared in a similar manner. In general, solutions of the alkylpentacarbonyl were allowed to reflux 4–6 hr before isolation of the product.

$Mn(CO)_5(SO_2C_6H_5)$.—A 100-ml glass pressure bottle equipped with a threaded Teflon stopper and a side-arm takeoff was charged with 2.7 g (10 mmol) of $Mn(CO)_5C_6H_5$ and *ca.* 5 ml of liquid SO_2. The vessel was cooled to −126°, evacuated, and then slowly warmed to 45°. Under these conditions enough SO_2 remained in the liquid phase to keep the carbonyl in solution. The reaction mixture slowly changed from pale yellow to orange. After 20 hr at 35–45° the system was cooled and the solvent was removed. The residue was dissolved in absolute ethanol (20 ml) and the resultant solution was maintained at *ca.* −70° over-

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TABLE I

PHYSICAL PROPERTIES, PER CENT YIELDS, ANALYSES, AND OTHER DATA FOR SULFINATOPENTACARBONYL COMPLEXES

Complex	Color	Mp,[a] °C	Molar conductivity, ohm^{-1} cm^2	Yield, %	Mol wt		Analyses, %					
							Calcd			Found		
					Calcd	Found	C	H	S	C	H	S
$Mn(CO)_5(SO_2CH_3)$	Pale yellow[b]	115	<0[c]	84	274	274	26.29	1.10	11.70	26.51	1.33	11.53
$Mn(CO)_5(SO_2CH_2CH_3)$	Pale yellow[b]	69	*d*	62	288	311, 313	29.18	1.75	11.13	28.93	1.73	11.02
$Mn(CO)_5(SO_2CH_2C_6H_5)$	Pale yellow[b]	135	<0[c]	86	350	358, 340	41.16	1.99	9.15	41.03	1.99	9.08
$Mn(CO)_5(SO_2C_6H_5)$	Pale yellow	150 dec	*d*	24		*d*	39.30	1.50	9.54	40.01	1.84	9.77
$Re(CO)_5(SO_2CH_3)$	White	126–127	*d*	92	405	408	17.78	0.75	7.91	17.68	0.75	7.98
$Re(CO)_5(SO_2CH_2C_6H_5)$	White	114	*d*	89	481	480	29.94	1.47	6.66	29.68	1.49	6.77
$Na[Cr(CO)_5(SO_2C_6H_5)] \cdot 1.5CH_3OH$	Yellow	~145 dec	95[e]	80		*d*	37.13	2.74	7.93	36.71	2.36	8.10[f]
$Na[W(CO)_5(SO_2C_6H_5)] \cdot 2CH_3OH$	Yellow	~160 dec	80[e]	76		*d*	28.46	2.37	5.81	28.16	2.31	5.81[g]

[a] Determined with a Fisher-Johns melting-point block and uncorrected. [b] Sublimed samples appear colorless. [c] *Ca.* 10^{-3} *M* in acetonitrile. [d] Not measured. [e] *Ca.* 10^{-3} *M* in acetone. [f] Also found: N, 0.31. [g] Also found: N, 0.00.

night. Pale yellow crystals (2.0 g) were collected on a filter and washed with 10 ml of ether. Fractional crystallization from 20 ml of CH_2Cl_2 and 40 ml of ether–petroleum ether (4:1 by volume) yielded 0.9 g of crude sulfinate and 0.6 g of $Mn(CO)_5(COC_6H_5)$ (identified by its infrared spectrum and melting point[7]). The sulfinate was recrystallized from CH_2Cl_2 (10 ml) and ether–petroleum ether (40 ml). The light yellow material sublimed at 90° (0.1 mm).

$Re(CO)_5(SO_2CH_3)$.—About 50 ml of dry liquid SO_2 was added to 1.00 g (2.93 mmol) of $Re(CO)_5CH_3$ in a 100-ml flask equipped with a magnetic stirring bar and cooled in an ice–water bath. A Dry Ice condenser was attached and the reaction mixture was refluxed with stirring for 6 hr. After this time excess SO_2 was allowed to boil off. The white residue was dissolved in 10 ml of $CHCl_3$ and the solution was filtered. Slow addition of pentane (30 ml) to the filtrate, followed by cooling (−70°), caused white crystals to separate. The product was collected on a filter stick and dried by suction. The yield was 1.10 g. The benzyl derivative was prepared in an analogous fashion.

$Na[Cr(CO)_5(SO_2C_6H_5)] \cdot 1.5CH_3OH$.—Sodium benzenesulfinate (2.00 g, 12.4 mmol) was added in one portion to a golden solution of $[(n\text{-}C_4H_9)_4N][Cr(CO)_5I]$ (3.40 g, 6.06 mmol) in 50 ml of degassed, anhydrous methanol contained in a 100-ml round-bottom flask. A Liebig condenser was attached to the flask and the reaction system was flushed with nitrogen before warming to 65°. After 10 min, the solution became light yellow. Heating was continued for an additional 10 min before removal of the solvent at 40° (~20 mm). The residue was washed with CH_2Cl_2 (three 25-ml portions), and the washings were filtered and set aside for further treatment. The residue was then extracted with dry acetone (five 5-ml portions) leaving approximately 1.0 g of unreacted $C_6H_5SO_2Na$. The extracts were combined, filtered, and then treated with petroleum ether (*ca.* 40 ml). Cooling (to −20°) afforded yellow crystals of the product (1.60 g). An additional 0.40 g of the product and 2.10 g of $(n\text{-}C_4H_9)_4NI$, identified by its infrared spectrum and melting point, were recovered from the residue of the dichloromethane washings by fractional crystallization using CH_2Cl_2–ether mixtures. The combined fractions of the sulfinato complex were dried *in vacuo* for 3 hr at 30°.

The corresponding tungsten compound, $Na[W(CO)_5(SO_2C_6H_5)] \cdot 2CH_3OH$, was prepared by an analogous procedure except that the reaction time was extended to 45 min. In this case the solution changed from yellow to light brown. Analyses and pertinent physical data for the new sulfinato complexes are listed in Table I.

Attempted Synthesis of Sulfinatopentacarbonyl Complexes. (a) **From $Mn(CO)_5R$ and SO_2.**—One to three gram samples each of $Mn(CO)_5C_6H_5$ (10 hr), $Mn(CO)_5CF_3$ (15 hr), $Mn(CO)_5Ge(C_6H_5)_3$ (14 hr), $Mn(CO)_5(COCH_3)$ (6 hr), and $Mn(CO)_5(COCF_3)$ (10 hr) were allowed to interact with refluxing sulfur dioxide (*ca.* 50–60 ml) for the periods noted in parentheses. Removal of SO_2 in a stream of nitrogen afforded solid residues which were shown by infrared spectroscopy to be the unreacted pentacarbonyls.

After sulfur dioxide had been bubbled through a pentane or a benzene solution of $Mn(CO)_5CH_3$ for 4–6 hr at 27°, only the unreacted alkyl was detected by infrared spectroscopy.

(b) **From $NaMn(CO)_5$ and RSO_2Cl.**—A solution of $NaMn(CO)_5$, prepared from 4.60 g (11.8 mmol) of $Mn_2(CO)_{10}$ and excess 1% sodium amalgam in 75 ml of tetrahydrofuran was added slowly with stirring and under nitrogen to $C_6F_5SO_2Cl$ (6.30 g, 23.7 mmol) in 15 ml of tetrahydrofuran at *ca.* −70°. After an additional 125 ml of tetrahydrofuran had been introduced to maintain solution, the mixture was stirred for 1 hr at −70° and then 1 hr at 0° before allowing the temperature to rise to 25°. A white, water-soluble precipitate (3.60 g), later shown to contain sulfinate but no carbon monoxide (infrared spectroscopy), was collected on a suction filter and washed with petroleum ether. The washings and the filtrate were combined, concentrated, and cooled. A pale yellow solid (3.50 g) was collected and characterized (infrared spectroscopy) as $Mn(CO)_5Cl$. A trace amount of $Mn_2(CO)_{10}$ was isolated from the mother liquor and identified as the only other metal carbonyl complex present.

The reaction of $NaMn(CO)_5$ (20.5 mmol) with $C_6H_5SO_2Cl$ (3.60 g, 20.5 mmol) was carried out in a similar manner except that the temperature was maintained at −60 to −40° for 16 hr. The solvent was then removed and the residue was washed with petroleum ether until the extracts were colorless. Removal of the petroleum ether gave 3.30 g of $Mn_2(CO)_{10}$. The residue from the washings was found to be partially soluble in acetone (*ca.* 25 ml). This mixture was filtered and the filtrate was diluted with 25 ml of petroleum ether. A pale yellow solid (0.75 g) separated immediately. On standing for 2–3 hr, the material would not completely redissolve in acetone. Infrared absorption bands of the freshly precipitated solid occur at 3450 (s, br), 3071 (w), 2056 (vs), 1990 (s, br), 1650 (m, br), 1585 (m), 1480 (m–s), 1445 (s), 1387 (w), 1370 (vw), 1345 (w), 1310 (w), 1237 (w), 1180 (sh), 1144 (vs), 1098 (s), 1042 (vs), 1032 (s), 1013 (m–s), 1000 (s), 950 (w), 762 (m), 705 (vs), 695 (s), 660 (s), 620 (vs), 585 (vs), 540 (s), and 450 (m) cm^{-1} (KBr pellet). *Anal.* Found: C, 36.16, 36.41; H, 3.38, 3.28; S, 8.28; Mn, 8.32. This corresponds to a partial empirical formula $MnS_{1.7}C_{20}H_{22}$.

In other, separate experiments $NaMn(CO)_5$ was allowed to react with $C_6H_5SO_2Cl$ and CH_3SO_2Cl at 27°. In both cases, the isolated products had infrared spectra (metal carbonyl and SO stretching regions) and physical properties similar to those described above. Neither $Mn(CO)_5Cl$ nor $Mn(CO)_5(SO_2R)$ could be isolated from these reactions.

(c) **From Halogenopentacarbonyls and $C_6H_5SO_2Na$.**—A mixture of $Mn(CO)_5Br$ (1.20 g, 4.37 mmol) and $C_6H_5SO_2Na$ (1.00 g, 6.09 mmol) in acetone (125 ml) was refluxed with stirring under nitrogen for 15 min. The solvent was then removed and the residue was extracted twice with 20-ml portions of $CHCl_3$.

The extracts were filtered and the filtrate was treated with 40 ml of petroleum ether to give a pale yellow precipitate. After unreacted $Mn(CO)_5Br$ was removed from this solid by sublimation at *ca.* 50° (0.1 mm), the infrared spectrum showed metal carbonyl stretching absorptions at 2103 (s), 2050 (vs), 2035 (sh), 1968 (s), and 1936 (s), cm^{-1} ($CHCl_3$ solution); other bands were observed at 3070 (w), 3025 (w), 1482 (w), 1447 (m), 1228 (w–m), 1131 (s), 1095 (s), 1072 (w), 1034 (s), 1019 (s), 998 (m), 789 (m, br), 709 (s), 695 (m), 675 (w), 660 (sh), 625 (m), 595 (s), 537 (m), and 443 (w) cm^{-1} (KBr pellet). The compound gradually lost its solubility in polar organic solvents upon exposure to air and light.

The reaction of $[(n\text{-}C_4H_9)_4N][Mo(CO)_5I]$ with $C_6H_5SO_2Na$, carried out as described for the analogous chromium compound (*vide supra*), resulted in an extensive decomposition of the carbonyl, both at 45 and at 65°. Infrared spectra of these solutions taken at various time intervals showed only the presence of the iodopentacarbonyl.

(d) **From $Mn_2(CO)_{10}$ and Methanesulfonyl Halides.**—A tetrahydrofuran solution of $Mn_2(CO)_{10}$ (1 g) and methanesulfonyl chloride (0.3 g) was stirred under nitrogen at 40° for 48 hr. Removal of the solvent gave only unreacted $Mn_2(CO)_{10}$. A similar result was obtained with $Mn_2(CO)_{10}$ and CH_3SO_2F in pentane after 96 hr of reaction time.

(e) **From $Mn(CO)_5H$ and $C_6H_5SO_2H$.**—A solution of $C_6H_5SO_2H$ (0.71 g, 5.1 mmol) in ether (10 ml) was treated with $Mn(CO)_5H$ (1.0 g, 5.1 mmol) at room temperature under nitrogen. After the mixture had been allowed to react for 24 hr, the solvent was removed and the infrared spectrum of the residue revealed the presence of $Mn_2(CO)_{10}$ as the only carbonyl-containing material.

Reactions of Sulfinatopentacarbonyl Complexes. (a) **With the Halogens.**—Chlorine was bubbled slowly through a magnetically stirred dispersion of $Mn(CO)_5(SO_2CH_3)$ (0.3 g, 1.10 mmol) in benzene (50 ml) at 25° and into an aqueous barium chloride solution. After approximately 1 hr, a white precipitate, later shown to be $BaSO_3$, began to form as the dispersed material dissolved completely in benzene. The reaction was continued for 1.5 hr, the benzene solution was filtered, and the filtrate was evaporated to dryness leaving 0.20 g of $Mn(CO)_5Cl$.

Solutions of $Mn(CO)_5(SO_2CH_3)$ in CH_2Cl_2 also reacted with chlorine to give SO_2 and $Mn(CO)_5Cl$ in 30 min. Treatment of $Mn(CO)_5(SO_2CH_2C_6H_5)$ in CH_2Cl_2 with chlorine or bromine afforded the corresponding halogenopentacarbonyl in a nearly quantitative yield. No reaction occurred when $Mn(CO)_5(SO_2CH_3)$ and iodine in CH_2Cl_2 were stirred for 16 hr at 30°.

(b) **Thermal Treatment.**—Solid $Na[Cr(CO)_5(SO_2C_6H_5)] \cdot 1.5CH_3OH$ ($\sim$0.4 g) was heated to 150° and maintained at this temperature under nitrogen until its initial yellow color had changed to green (*ca.* 2 hr). No formation of sulfur dioxide was indicated when the evolved gases were passed through aqueous $BaCl_2$; some $Cr(CO)_6$ was detected upon completion of pyrolysis.

A similar treatment of $Mn(CO)_5(SO_2CH_2C_6H_5)$ at 120–130° also resulted in gas evolution but no SO_2 was detected. The infrared spectrum of the solid residue showed absorptions in the CO stretching region at 2100 (m), 2030 (s), 2010 (s), and 1960 (s) cm^{-1} and very intense, broad bands in the SO stretching region at 1130 and 950 cm^{-1} (KBr pellet).

(c) **Ultraviolet Irradiation.**—Irradiation of a benzene solution (375 ml) of $Mn(CO)_5(SO_2CH_2C_6H_5)$ (0.5 g) at 30° for 10 min, using photochemical equipment described previously,[2] afforded a white precipitate. This powder was shown by infrared spectroscopy to contain both CO and SO_2 groups but was not characterized further. No $Mn(CO)_5CH_2C_6H_5$ could be detected in the benzene solution upon termination of the reaction.

Infrared Spectra.—Spectra were recorded on a Beckman Model IR-9 spectrophotometer. When carbon tetrachloride 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. A matched set of Irtran-2 cells was used to record the spectra of acetone solutions. Spectra of solid samples were taken either as Nujol and hexachlorobutadiene mulls or as KBr pellets.

Proton Magnetic Resonance Spectra.—Nmr spectra were recorded on a Varian Associates A-60 spectrometer. Tetramethylsilane was used as an external reference.

Electrical Conductivity.—An Industrial Instruments Co. Model RC 16B2 conductivity bridge and a cell with platinum electrodes were employed.

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

Analyses.—Elemental analyses were done by Dr. F. Pascher, Mikroanalytisches Laboratorium, Bonn, Germany, and by Galbraith Laboratories, Inc., Knoxville, Tenn.

Results and Discussion

Synthesis of Complexes.—The reactions of $NaMn(CO)_5$ with the organic sulfonyl chlorides (RSO_2Cl) afford a number of products the nature of which depends, among other factors, on the group R. Thus, using the fluorinated $C_6F_5SO_2Cl$, one obtains (a) $Mn(CO)_5Cl$, (b) a noncarbonyl compound containing $C_6F_5SO_2$, and (c) a trace of $Mn_2(CO)_{10}$. The behavior of this sulfonyl chloride contrasts that of CF_3SO_2Cl, which yields $Mn(CO)_5(SO_2CF_3)$ and $Re(CO)_5(SO_2CF_3)$ when allowed to react with $NaMn(CO)_5$ and $NaRe(CO)_5$, respectively, at −60 to −80°. However, even there, the main products are the pentacarbonyl chlorides.[12,13]

The interaction of the aryl- and alkylsulfonyl chlorides with $NaMn(CO)_5$ results in the formation of yellow solids which contain both the sulfinate and carbon monoxide. When $C_6H_5SO_2Cl$ is used at low temperatures, dimanganese decacarbonyl becomes the major product. The yellow solids, which probably represent mixtures of two or more species as evidenced by elemental analyses and some variations in their infrared spectra, exhibit a tendency to polymerize on storage or repeated crystallization. It is likely that polymerization occurs *via* formation of RSO_2 bridges, with either the two oxygens or one oxygen and the sulfur bonding to manganese. Similar products were obtained by Beck[14] using $NaMn(CO)_5$ in conjunction with each $C_6H_5SO_2Cl$, $p\text{-}H_3CC_6H_4SO_2Cl$, and $p\text{-}O_2NC_6H_4SO_2Cl$. The interaction of $Mn(CO)_5Br$ with $C_6H_5SO_2Na$ also affords analogous, ill-defined carbonyl sulfinates. No reaction was observed between $Mn_2(CO)_{10}$ and CH_3SO_2X (X = Cl and F).

It is interesting, and unexpected, that CF_3SO_2Cl, in which the charge distribution $RSO_2^-Cl^+$ should be more important than the corresponding distribution in an alkyl- or arylsulfonyl chloride, represents the only sulfonyl chloride affording $Mn(CO)_5(SO_2R)$ on reaction with $NaMn(CO)_5$. The incidence of polymeric sulfinatocarbonyls may result from the initial formation of $Mn(CO)_5Cl$, its reaction with RSO_2^- to yield $Mn(CO)_4(SO_2R)Cl^-$, and a subsequent association *via* loss of chloride and/or CO. That $Mn(CO)_5Cl$

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[12] E. Lindner and H. Weber, *Angew. Chem.*, **78**, 752 (1966).

[13] E. Lindner, private communication, 1967.

[14] W. Beck, private communication, 1965. Professor Beck has kindly informed us that the compounds obtained in his study behaved analogously, were polymeric and paramagnetic (1.26–4.18 BM), exhibited infrared spectral features similar to those reported here, and, where analyzed for, contained chlorine.

reacts readily with anionic ligands (X^-) to give $Mn(CO)_4XCl^-$ has been already demonstrated.[15,16]

The only general synthetic procedure for sulfinatopentacarbonylmanganese(I) and -rhenium(I) complexes involves insertion of sulfur dioxide into metal–alkyl (or –aryl) carbon bonds. No attempt has been made in this study to elucidate the relative rates of reaction with SO_2 of various alkylpentacarbonyl compounds; however, after 6 hr of refluxing $Mn(CO)_5R$ ($R = CH_3$, C_2H_5, and $CH_2C_6H_5$) and $Re(CO)_5R$ ($R = CH_3$ and $CH_2C_6H_5$) in sulfur dioxide, no unreacted material was recovered. The complex $Mn(CO)_5C_6H_5$ did not insert sulfur dioxide under these conditions but afforded some (24%) $Mn(CO)_5(SO_2C_6H_5)$ and $Mn(CO)_5(COC_6H_5)$ in liquid SO_2 at 35–45° under pressure. The other pentacarbonyls examined—$Mn(CO)_5CF_3$, $Mn(CO)_5(COCF_3)$, $Mn(CO)_5(COCH_3)$, and $Mn(CO)_5Ge(C_6H_5)_3$—did not undergo insertion with refluxing SO_2. Further, and in contrast to the behavior of $C_5H_5Fe(CO)_2CH_3$,[2] there was no apparent reaction between $Mn(CO)_5CH_3$ and SO_2 in hydrocarbon solutions at room temperature.

The markedly low reactivity of $Mn(CO)_5C_6H_5$ toward sulfur dioxide compared to the corresponding methyl, ethyl, and benzyl analogs contrasts the general behavior of these pentacarbonyl complexes toward carbon monoxide. Calderazzo and Cotton[17] report that the rate of insertion of CO with $Mn(CO)_5R$ decreases in the order $R = C_2H_5 > C_6H_5 > CH_3 \gg CH_2C_6H_5$. Hence, $Mn(CO)_5C_6H_5$ undergoes a relatively facile insertion of CO but not of SO_2. This may reflect mechanistic differences between the two kinds of reaction; however, in the absence of kinetic data we shall not elaborate this point at present. In the context of the above comparison, it is worth mentioning that the analogous iron complex, $C_5H_5Fe(CO)_2C_6H_5$, does insert sulfur dioxide even at *ca.* −40°.[2]

Iodopentacarbonylchromate(0) and -tungstate(0) react with $C_6H_5SO_2Na$ in methanol to yield the corresponding phenylsulfinatopentacarbonyl anions, $M(CO)_5(SO_2C_6H_5)^-$ (M = Cr and W), isolated as the solvated sodium salts. The extent of solvation was determined by elemental analyses and examination of the relative intensities of the hydroxy, methyl, and phenyl proton peaks in the nmr spectra (Table II). Under similar experimental conditions, $Mo(CO)_5I^-$ afforded only unidentified decomposition products. The replacement of iodide in $M(CO)_5I^-$ (M = Cr and W) with benzenesulfinate bears resemblance to the reaction of $M(CO)_5I^-$ (M = Cr, Mo, and W) with the isonitriles (RNC), which yields, among other products, $M(CO)_5(CNR)$.[18] The lower stability of anionic molybdenum pentacarbonyls compared to the corresponding chromium and tungsten complexes has been already reported.[19]

TABLE II

PROTON MAGNETIC RESONANCE SPECTRA OF SULFINATOPENTACARBONYL COMPLEXES (τ)

Complex	Chem shift, ppm	Rel intens	Assignment
$Mn(CO)_5(SO_2CH_3)$[a]	6.85 (singlet)	...	CH_3
$Mn(CO)_5(SO_2CH_2CH_3)$[a]	8.55 (triplet, $J \sim$ 8cps)	3.0	CH_3
	6.82 (quartet, $J \sim$ 8cps)	2.0	CH_2
$Mn(CO)_5(SO_2CH_2C_6H_5)$[a]	5.61 (singlet)	2.0	CH_2
	2.40 (multiplet)	5.0	C_6H_5
$Mn(CO)_5(SO_2C_6H_5)$[a]	2.58–1.92 (multiplet)	...	C_6H_5
$Re(CO)_5(SO_2CH_3)$[a]	6.65 (singlet)	...	CH_3
$Re(CO)_5(SO_2CH_2C_6H_5)$[a]	5.63 (singlet)	2.0	CH_2
	2.38 (multiplet)	5.0	C_6H_5
$Na[Cr(CO)_5(SO_2C_6H_5)]\cdot 1.5CH_3OH$[b]	7.90 (singlet)	1.6	OH
	6.70 (singlet)	4.6	CH_3
	2.67–2.15 (multiplet)	5.0	C_6H_5
$Na[W(CO)_5(SO_2C_6H_5)]\cdot 2CH_3OH$[b]	8.13 (singlet)	2.0	OH
	6.92 (singlet)	6.0	CH_3
	2.93–2.33 (multiplet)	5.0	C_6H_5

[a] $CDCl_3$ solution. [b] $CD_3C(O)CD_3$ solution.

Properties and Characterization of Complexes.—The sulfinatopentacarbonyl complexes of manganese(I) and rhenium(I) prepared in this study are pale yellow to white solids, readily soluble in polar organic solvents and stable to air. They can be sublimed under reduced pressure at 60–90° and behave as nonelectrolytes in acetonitrile. The corresponding complexes of chromium(0) and tungsten(0), also stable to air, are, as expected, 1:1 electrolytes in acetone.[20,21]

The bonding in $Mn(CO)_5(SO_2R)$ and $Re(CO)_5(SO_2R)$ may be elucidated with the aid of infrared and proton magnetic resonance spectroscopy. The nmr spectra of the benzylsulfinato derivatives (Table II) show the signals due to the methylene protons as sharp singlets at τ 5.61 (Mn) and 5.63 (Re), indicating that the attachments therein are $M–S(O)_2–CH_2–$.[22] The infrared spectra of all $M(CO)_5(SO_2R)$ (M = Mn and Re) complexes in the metal carbonyl stretching frequency region (Table III) exhibit alsmost identical features, reflecting a common mode of bonding of SO_2 to the metal and the hydrocarbon moiety. This is further supported by the virtual identity of both the asymmetric and the symmetric SO stretching frequencies for all of the manganese and rhenium complexes and their close similarity to the frequencies found for $C_5H_5Fe(CO)_2(SO_2R)$.[2]

The nature of metal–sulfinate attachment in $Cr(CO)_5(SO_2C_6H_5)^-$ and $W(CO)_5(SO_2C_6H_5)^-$—whether through the sulfur or an oxygen—is of some interest, since it was previously demonstrated with the analogous thiocyanato complexes that in going from $Mn(CO)_5(SCN)$ to $Cr(CO)_5(NCS)^-$ the bonding of the metal to the harder nitrogen becomes preferred.[19,23] Comparison of the carbonyl stretching frequencies of $M(CO)_5(SO_2C_6H_5)^-$ with those of $M(CO)_5X^-$ (M = Cr and W; X = Cl, Br, and I)[11] reveals that the former are 12–69 cm^{-1} higher than the latter, the difference being most pronounced for the $A_1{}^1$ bands (39–69 cm^{-1}).

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[18] H. D. Murdoch and R. Henzi, *J. Organometal. Chem.* (Amsterdam), **5**, 166 (1966).

[19] A. Wojcicki and M. F. Farona, *J. Inorg. Nucl. Chem.*, **26**, 2289 (1964).

[20] Reynolds and Kraus[21] reported that molar conductivities for *ca.* 10^{-3} *M* solutions of 1:1 electrolytes in acetone are in the range 100–150 ohm^{-1} cm.^{2}

[21] M. B. Reynolds and C. A. Kraus, *J. Am. Chem. Soc.*, **70**, 1709 (1948).

[22] Details of the argument invoked in making this assignment are to be found in ref 2.

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TABLE III

INFRARED SPECTRA OF SULFINATOPENTACARBONYL COMPLEXES (cm^{-1})

	Metal–carbonyl stretches[a,b]				
Complex	$A_1^{(2)}$	B_1	E	$A_1^{(1)}$	SO stretches[c,d]
$Mn(CO)_5(SO_2CH_3)$[a,c,e]	2139 w–m	2090 w	2059 s, 2044 s	2027 m	1201 s, 1183 sh, 1053 s, 1044 sh
$Mn(CO)_5(SO_2CH_2CH_3)$[a,c,f]	2137 w–m	2088 w	2053 s, 2038 s	2021 m	1189 s, 1175 sh, 1053 s, 1023 sh
$Mn(CO)_5(SO_2CH_2C_6H_5)$[a,c,g]	2137 w–m	2089 w	2059 s, 2041 s	2024 m	1209 s, 1205 sh, 1197 sh, 1054 s, 1043 sh
$Mn(CO)_5(SO_2C_6H_5)$[a,c,h]	2137 w–m	2089 w	2054 s, 2050 s	2027 m	1192 s, 1033 s
$Re(CO)_5(SO_2CH_3)$[a,c,i]	2159 w	2097 w	2053 s, 2050 s	2018 m	1192 s, 1054 s
$Re(CO)_5(SO_2CH_2C_6H_5)$[a,d,j]	2158 w	2095 w	2059 s, 2044 s	2022 m	1199 s, 1185 s, 1045 s
$Na[Cr(CO)_5(SO_2C_6H_5)] \cdot 1.5CH_3OH$[b,d,k]	2070 w–m	1989 w	1944 s[m]	1914 m	1110 sh, 1102 s, 1015 s, 1001 s
$Na[W(CO)_5(SO_2C_6H_5)] \cdot 2CH_3OH$[b,d,l]	2077 w–m	1984 w	1940 s[m]	1909 m	1112 sh, 1100 s, 1050 sh, 1030 s, 1018 s, 1000 s

[a] Saturated CCl_4 solution (fourfold scale expansion). [b] Acetone solution. [c] Nujol mull (2800–1500 and 1300–400 cm^{-1}) and hexachlorobutadiene mull (4000–2800 and 1500–1300 cm^{-1}). [d] KBr pellet. [e–l] Other bands for these compounds: (e) 3012 vw, 2932 w, 2924 sh, 1431 w, 1415 m, 1308 m–s, 950 m–s, 723 m–s, 638 vs, 549 vw, 520 s, 467 w–m, 440 w–m; (f) 3000 m, 2950 m, 2910 w, 2882 w–m, 1464 m, 1450 m, 1417 m–s, 1369 w, 1245 m, 984 m, 971 m, 922 vw, 911 vw, 893 vw, 781 w–m, 678 s, 635 vs, 585 s, 544 m, 535 m, 480 m–s, 422 m–s; (g) 3094 vw, 3050 vw, 3035 vw, 3016 vw, 2939 w, 1601 w, 1582 vw, 1497 w–m, 1460 m, 1421 sh, 1412 sh, 1235 w, 1197 sh, 1186 m, 1165 w–m, 1138 m, 1133 sh, 1078 w–m, 1030 m, 1007 sh, 999 w, 979 w, 876 w, 831 m, 818 w, 773 m–s, 700 m–s, 678 s, 650 sh, 639 s, 624 s, 513 s, 500 s, 447 m–s, 439 sh; (h) 3071 vw, 2964 w, 2927 w, 2856 vw, 1474 w, 1444 w–m, 1170 w, 1122 w, 1094 m–s, 1069 w, 1044 m–s, 1017 m, 995 w, 756 m, 708 m, 690 m, 669 vw, 635 s, 620 sh, 583 s, 537 w, 519 w, 459 vw, 444 vw, 418 vw; (i) 3012 w, 2932 w, 1419 m, 1411 w–m, 1300 vw, 1264 w, 1170 s, 938 sh, 934 w, 912 m, 810 w, 721 m, 670 vw, 668 w, 642 m, 592 s, 580 s, 559 sh, 525 m–s, 495 w–m, 460 w–m; (j) 3094 vw, 3055 vw, 3038 w, 2975 vw, 2920 w, 1605 w, 1582 w, 1500 m, 1490 sh, 1455 m–s, 1408 m, 1338 vw, 1322 vw, 1235 w–m, 1159 m, 1125 m, 1071 m, 1005 sh, 992 w, 970 w, 944 w, 922 m–s, 874 s, 827 w, 815 w, 773 s, 700 s, 632 w, 622 w, 599 s, 513 s, 505 s, 455 w, 442 w; (k) 3671 m, 3642 m, 3595 m, 3450 w, br, 3074 w, 3060 w, 3010 vw, 2975 w, 2850 vw, 1613 m–s, 1584 m, 1479 m, 1447 s, 1350 w, 1302 w, 1180 w, 1165 vw, 1075 m–s, 950 sh, 925 w, 907 w, 853 w, 756 s, 706 s, 694 s, 670 w, 580 s, br, 524 m, 458 w; (l) 3670 m, 3640 m, 3595 m, 3450 w, br, 3075 w, 3060 w, 3010 vw, 2975 vw, 2850 vw, 1612 m–s, 1584 m, 1480 w–m, 1447 s, 1350 w, 1302 w, 1180 w, 1165 w, 1074 m, 948 w, 927 w, 907 w, 853 w, 757 s, 707 s, 695 s, 670 w, 582 s, br, 524 m, 505 w, 495 w, 460 w. [m] No splitting of this band was observed also in tetrahydrofuran solution.

This is indicative that the carbonyl groups are competing for π-electron density of the metal with the sulfinate and suggests a metal–sulfur linkage in these complexes.

Additional support for an $M–S(O)_2–R$ attachment is provided by the values of the asymmetric and the symmetric SO stretching frequencies. These occur in the ranges 1112–1100 and 1050–1000 cm^{-1}, respectively, considerably lower than for the neutral $M(CO)_5(SO_2R)$ (M = Mn and Re) compounds. Nevertheless, sulfinato complexes containing metal–oxygen linkages give rise to even lower SO stretching frequencies: 998 and 938 cm^{-1} for $Cu(H_2O)_4(p\text{-}OS(O)C_6H_4CH_3)_2$,[24] known to contain Cu–O–S(O)–bonds,[25] and 979–954 and 933 cm^{-1} for $(C_6H_5)_3Sn–O–S(O)–C_6H_5$,[26] which has been assigned an Sn–O–S(O)– linkage on the basis of chemical evidence.[27] Therefore, the infrared spectral data point to a common mode of $M–S(O)_2–R$ attachment in all of the pentacarbonyls prepared in this study. The relatively low SO stretching frequencies in $Cr(CO)_5(SO_2C_6H_5)^-$ and $W(CO)_5(SO_2C_6H_5)^-$ are undoubtedly due to an increased amount of M=S π bonding brought about by a lower oxidation state of the metals. A similar effect has been observed for the complexes $Mn(CO)_3L_2(SO_2CH_3)$ (L = $p\text{-}H_2NC_6H_4F$ and $p\text{-}H_2NC_6H_4CH_3$), where presence of non-π-bonding *para*-substituted anilines enhances the degree of M=S double bonding.[28]

Infrared Spectra of Complexes.—The salient features in the carbonyl stretching region of the infrared spectra of the sulfinatopentacarbonyl complexes of manganese(I) and rhenium(I) are the appearance of the B_1 band and the removal of the degeneracy of the E band (Table III). Both effects may be attributed to a lowering of the molecular symmetry from C_{4v} to not higher than C_s, owing to the presence of the RSO_2 moiety. The magnitude of the splitting of the E band varies strikingly with the nature of the group R.[29] For $Mn(CO)_5(SO_2R)$ it increases in the order R = C_6H_5 (4 cm^{-1}) < CH_3 (15 cm^{-1}) ~ C_2H_5 (15 cm^{-1}) < $CH_2C_6H_5$ (18 cm^{-1}), and for $Re(CO)_5(SO_2R)$, in the order R = CH_3 (3 cm^{-1}) < $CH_2C_6H_5$ (15 cm^{-1}). Thus it appears that the extent of the splitting depends mainly on (a) the size of the metal and (b) bulkiness of substituents on the α-carbon atom of R. Accordingly, the manganese compounds show greater splitting than their rhenium analogs, and the benzylsulfinate is somewhat more effective than the ethylsulfinate and considerably more so than the phenylsulfinate. The

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(29) All of the spectral measurements of the carbonyl E bands were carried out on saturated solutions of the complexes. Because of the limited solubility of the pentacarbonyls, it was not possible to ascertain the constancy of the splitting using solutions of different concentrations.

behavior of $Mn(CO)_5(SO_2CH_3)$, which gives the splitting comparable to that for $Mn(CO)_5(SO_2C_2H_5)$ and much greater than for $Mn(CO)_5(SO_2C_6H_5)$, is rather unexpected. The infrared carbonyl stretching spectra of the anions $M(CO)_5(SO_2C_6H_5)^-$ (M = Cr and W) show the B_1 band; however, the E band is not split, probably owing to the polar nature of acetone and tetrahydrofuran employed as solvents.

Wilford and Stone[30] as well as Calderazzo, *et al.*,[31,32] have examined the infrared spectra of a number of manganese and rhenium pentacarbonyl alkyl and acyl complexes. Our observations are in a qualitative agreement with those of the above authors; however, the splitting of the E mode for the sulfinates is in many cases considerably greater than that for the analogous acyls. Accordingly, the following values have been reported for $Mn(CO)_5(COR)$: R = CH_3, 0 (heptane solution);[32] C_2H_5, 0 (heptane solution);[32] C_6H_5, 11 cm^{-1} (cyclohexane solution);[30] and $CH_2C_6H_5$, 14 cm^{-1} (heptane solution).[32] The differences in the magnitude of the splitting between the sulfinates and the corresponding acyls may be ascribed to a nearly tetrahedral M–S–C bond angle in the former as compared to a *ca.* 120° M–C–C bond angle in the latter. This would place a substituent on the α-carbon atom of the sulfinate in a better position than the corresponding substituent on the β-carbon atom of the acyl to interact with one E vibration of the four equatorial CO groups, thus causing a larger splitting in the spectrum of the former. It is conceivable that this effect may give rise to an unusually large difference in the degree of separation of the two components of the E mode between the sulfinate and the analogous acyl when both the metal and the substituent are relatively small, as has been observed for $Mn(CO)_5(SO_2CH_3)$ and $Mn(CO)_5(COCH_3)$. The unexpectedly large splitting reported for $Mn(CO)_5(COC_6H_5)$ compared to that for $Mn(CO)_5(SO_2C_6H_5)$ does not conform to the above rationale and is not understood at present.[33]

Another interesting feature in the carbonyl stretching spectra of $Mn(CO)_5(SO_2R)$ is the essential invariance of the frequencies to the nature of the group R. Even when R = CF_3, the positions of the carbonyl bands [2158, 2100, 2045, 2041, and 2028 cm^{-1} (CH_2Cl_2 solution)][12] are almost identical with those for the complexes containing R = CH_3, C_2H_5, $CH_2C_6H_5$, and C_6H_5. It therefore appears that the presence of two electronegative oxygens on the sulfur determines virtually exclusively the π-bonding capacity of RSO_2. Addition of another electron-withdrawing moiety, CF_3, provides very little further strength to such interaction.

Reactions of Complexes.—The reactions of manganese sulfinatopentacarbonyl complexes with the halogens (X_2) were investigated with a view to elucidating the feasibility of synthesis of the derivatives $Mn(CO)_5(SO_2X)$. However, all attempts at preparation of such compounds using chlorine or bromine yielded $Mn(CO)_5X$ as the only metal carbonyl. Iodine did not react with $Mn(CO)_5(SO_2CH_3)$ at 30°.

In order to ascertain whether insertion reactions of $Mn(CO)_5R$ with sulfur dioxide are reversible, solutions of $Mn(CO)_5(SO_2CH_2C_6H_5)$ were subjected to (a) photolysis and (b) thermal treatment at 150°. The products of these reactions contained both $C_6H_5CH_2SO_2$ and CO; however, their exact nature was not determined. No $Mn(CO)_5CH_2C_6H_5$ was detected upon completion of these processes. This observation is in concert with recent mass spectral studies of the pentacarbonyl sulfinates,[34,35] which demonstrate that the primary fragmentation step is loss of R to yield $Mn(CO)_5SO_2^+$. The ions $Mn(CO)_5R^+$ are present only in very low abundance, indicating that desulfurylation represents a minor decomposition path.

The pentacarbonyls $Mn(CO)_5(SO_2R)$ react with a number of neutral ligands (L) to yield the complexes $Mn(CO)_4L(SO_2R)$ and $Mn(CO)_3L_2(SO_2R)$. The results of this study will be reported at a later date.[28]

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[33] It is of interest that both $Mn(CO)_5(p\text{-}COC_6H_4F)$ and $Mn(CO)_5(p\text{-}COC_6H_4OCH_3)$, structurally very similar to $Mn(CO)_5(COC_6H_5)$, have been reported not to give any splitting of the carbonyl E band in *n*-heptane solution.[31]

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