Sulfur Dioxide Insertion. III. The Synthesis and Characterization of π-Cyclopentadienyliron S-Sulfinatodicarbonyl Complexes[1]

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Abstract: Several cyclopentadienyliron sulfinatodicarbonyl complexes have been prepared as stable yellow crystalline solids by one or more of the following reactions: $C_5H_5Fe(CO)_2R$ (R = CH_3, C_2H_5, C_6H_5, $CH_2C_6H_5$, p-$C_6H_4CH_3$) and $[C_5H_5Fe(CO)_2]_2(CH_2)_3$ with sulfur dioxide, $C_5H_5Fe(CO)_2Cl$ with RSO_2Na (R = C_6H_5, p-$C_6H_4CH_3$), $[C_5H_5Fe(CO)_2]_2$ with RSO_2Cl (R = CH_3, C_2H_5, C_6H_5), and $Na[C_5H_5Fe(CO)_2]$ with RSO_2Cl (R = CH_3, C_2H_5, C_6H_5) and with CH_3SO_2F. A brief discussion of these reactions, especially of the novel sulfur dioxide insertion, is presented. The infrared and nmr spectra of the new cyclopentadienyliron sulfinatocarbonyls are tabulated and discussed. It is inferred from the proton magnetic resonance spectra of the ethyl and benzyl complexes that the iron–sulfur–carbon attachments prevail in the $FeSO_2R$ moieties. The relatively high infrared carbonyl stretching frequencies and the unusually low sulfur–oxygen stretching frequencies along with the values of the cyclopentadienyl proton resonances indicate strong iron–sulfur π bonding, which may be compared with that between the iron and cyanide in $C_5H_5Fe(CO)_2CN$. The attempted cleavage of the sulfur–carbon bonds in $C_5H_5Fe(CO)_2(SO_2CH_3)$, $-(SO_2C_6H_5)$, and $-(SO_2CH_2C_6H_5)$ using chlorine and/or bromine resulted in a complete decomposition of the $C_5H_5Fe(CO)_2$ moiety, as did also reduction with $NaBH_4$ and ultraviolet irradiation.

Since the observation of Coffield, Kozikowski, and Closson[3] that methylmanganese pentacarbonyl readily and reversibly absorbs carbon monoxide to form the corresponding acetyl derivative, the so-called carbon monoxide insertion has created a widespread interest in synthesis[4] and in mechanistic studies.[5] At present, numerous transition metal alkyl and aryl complexes are known to undergo this type of reaction.[6]

Other investigations have established that transition metal alkyl complexes are capable of reacting also with unsaturated hydrocarbons and fluorocarbons to produce organometallic compounds which may be regarded as derived from insertion of the organic substrate into metal–carbon bonds.[7] It therefore appeared that insertion reactions of the metal alkyls are quite general in nature and that other unsaturated molecules can take part in them as well.

A recent growth of interest in transition metal complexes containing sulfur-donor ligands[8] prompted us to explore a rather intriguing possibility derived from the following developments and observations. First, the existence of sulfur dioxide complexes has been well documented;[9] infrared spectral evidence indicates that the ligand is capable of considerable π bonding with transition metals in lower oxidation states.[9b-d] Secondly, because of their unsaturation, carbon monoxide and sulfur dioxide exhibit remarkable structural similarities with respect to hypothetical formation of a variety of organic compounds. For example, ketones and sulfones may be regarded as resulting from addition of two hydrocarbon radicals to CO and SO_2, respectively.

This structural analogy coupled with the ability of SO_2 to function as a ligand raised a possibility that some of the chemical relationships found among the carbonyl, alkyl, and acyl complexes may also extend to certain sulfur dioxide, alkyl, and sulfinate systems. The chemical analogy of special interest to us concerned the insertion reactions into metal–alkyl (–aryl) carbon bonds and the reverse of these processes.

In order to test the above supposition we have now commenced a study on sulfinato complexes of several transition metals and on reactions of sulfur dioxide with a variety of metal alkyls and aryls. This paper reports in detail the first successful synthesis and characterization of some sulfinato complexes of the type $C_5H_5Fe(CO)_2(SO_2R)$ (R = alkyl or aryl group).[10,11]

Experimental Section

Materials. Sulfur dioxide (Matheson, anhydrous grade) was dried by passage through concentrated sulfuric acid and a phosphorus(V) oxide–calcium chloride column. Chlorine, also from Matheson (high purity grade), was used without further purification.

The compounds CH_3SO_2Cl, CH_3SO_2F, and $C_2H_5SO_2Cl$ were purchased from Eastman Organic Chemicals; $C_6H_5SO_2Cl$ was

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[1] Presented in part at the 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965. For part II of this series, see: F. A. Hartman and A. Wojcicki, *J. Am. Chem. Soc.*, **88**, 844 (1966).

[2] Based on the Ph.D. thesis submitted by J. P. B. to The Ohio State University, 1965.

[3] T. H. Coffield, J. Kozikowski, and R. D. Closson, *J. Org. Chem.*, 22, 598 (1957).

[4] R. F. Heck, *J. Am. Chem. Soc.*, **85**, 1220 (1963), and references therein.

[5] C. S. Kraihanzel and P. K. Maples, *ibid.*, **87**, 5267 (1965), and references therein.

[6] See, for example, (a) G. Booth and J. Chatt, *Proc. Chem. Soc.*, 67 (1961); (b) R. B. King and M. B. Bisnette, *J. Organometal. Chem.*, 2, 15 (1964); (c) F. Calderazzo and K. Noack, *ibid.*, 4, 250 (1965), and references therein.

[7] (a) R. F. Heck, Advances in Chemistry Series, No. 49, American Chemical Society, Washington, D. C., 1965, p 181; (b) J. B. Wilford and F. G. A. Stone, *Inorg. Chem.*, 4, 93 (1965), and references therein.

[8] H. B. Gray, *Progr. Transition Metal Chem.*, 1, 239 (1965).

[9] (a) L. H. Vogt, Jr., J. L. Katz, and S. E. Wiberley, *Inorg. Chem.*, **4**, 1157 (1965); (b) W. Strohmeier and J. F. Guttenberger, *Chem. Ber.*, **97**, 1871 (1964); (c) L. Vaska and S. S. Bath, *J. Am. Chem. Soc.*, **88**, 1333 (1966); (d) L. Vaska, Abstracts, 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966, Paper No. 79H; (e) S. J. La Placa and J. A. Ibers, *Inorg. Chem.*, **5**, 405 (1966), and references therein.

[10] For a preliminary account of this work, see: J. P. Bibler and A. Wojcicki, *J. Am. Chem. Soc.*, **86**, 5051 (1964).

[11] For other transition metal sulfinato complexes prepared recently and independently see (a) J. P. Collman and W. R. Roper, *J. Am. Chem. Soc.*, **88**, 181 (1966); (b) R. D. Gidden, Ph.D. Thesis, Oxford University, England, 1965.

obtained from Baker Chemical Co., $C_6H_5SO_2Na$ from Matheson Coleman and Bell, and p-$CH_3C_6H_4SO_2Na \cdot 2H_2O$ from Aldrich Chemical Co. They were not purified further. All other chemicals used were of reagent grade or equivalent.

Tetrahydrofuran was distilled from $LiAlH_4$ under a nitrogen atmosphere immediately before use. Technical grade pentane was used without further purification. All other solvents were analytical reagent grade. Woelm alumina (neutral, activity grade III) was employed in all chromatographic separations.

Cyclopentadienyliron alkyl, aryl, and acyl dicarbonyls were prepared using procedures reported in the literature ($C_5H_5Fe(CO)_2CH_3$,[12] $C_5H_5Fe(CO)_2C_2H_5$,[12] $C_5H_5Fe(CO)_2C_6H_5$,[13] $C_5H_5Fe(CO)_2(COCH_3)$,[13] $C_5H_5Fe(CO)_2(COC_6H_5)$[13]). The derivative $[C_5H_5Fe(CO)_2]_2(CH_2)_3$ was synthesized by the method of King[14] with the following modifications. The time of reaction between $Na[C_5H_5Fe(CO)_2]$ and 1,3-dibromopropane was shortened to 3 hr (27°), and pentane, in place of dichloromethane, was used for extractions. Concentration of pentane solutions and cooling (−78°) afforded the product in *ca.* 90% yields. The compound $C_5H_5Fe(CO)_2C_6F_5$ was kindly donated by Dr. R. B. King of the Mellon Institute. Two new derivatives of the type $C_5H_5Fe(CO)_2R$ ($R = CH_2C_6H_5$ and p-$C_6H_4CH_3$) were prepared as follows.

A. $C_5H_5Fe(CO)_2CH_2C_6H_5$. Benzyl chloride (1.27 g, 0.01 mole) was added to a tetrahydrofuran solution (60 ml) of $Na[C_5H_5Fe(CO)_2]$, prepared from 1.77 g (0.005 mole) of cyclopentadienyliron dicarbonyl dimer and excess 1% sodium amalgam using the procedure and apparatus described by King and Bisnette.[13] The reaction mixture was then stirred at 27° for 3 hr. After removing the solvent at 27° (~20 mm) the residue was extracted with pentane (four 20-ml portions). Addition of 10 g of alumina (to facilitate filtration) was followed by filtration and concentration of the filtrate (in a stream of nitrogen) to *ca.* 10 ml. This solution was then chromatographed on an alumina column (5 × 30 cm) using a pentane eluent. A yellow band of $C_5H_5Fe(CO)_2CH_2C_6H_5$ was eluted while cyclopentadienyliron dicarbonyl dimer remained on the column. Concentration of the eluate to about 5 ml in a stream of nitrogen, followed by cooling in Dry Ice (*ca.* 15 min), afforded yellow-brown crystals, which were collected on a filter and washed with cold pentane. The yield was 1.5 g (56%). *Anal.* Calcd for $C_{14}H_{12}FeO_2$: C, 62.74; H, 4.51; Fe, 20.84; mol wt, 268. Found: C, 62.73; H, 4.68; Fe, 21.09; mol wt (osmometry in $CHCl_3$), 242.

The compound melts at 55–57° and sublimes at 50° (~0.1 mm). It is stable in air for several weeks, slowly decomposing to a brown material. Pentane and benzene dissolve the benzyl derivative quite readily; however, these solutions decompose in a few hours when exposed to air.

Nmr Spectrum. Resonances at τ 7.23 (singlet, $-CH_2$), 5.31 (singlet, $-C_5H_5$), and 2.80 (broad peak, $-C_6H_5$).

Infrared Spectrum. Carbonyl stretching frequencies at 2009 (vs) and 1951 (vs) cm^{-1} ($CHCl_3$ solution); other bands at 3113 (vw), 3098 (vw), 3013 (w), 2996 (vw), 2953 (w), 2920 (w), 1594 (s), 1575 (w), 1489 (s), 1450 (m), 1433 (m), 1421 (m), 1387 (w), 1362 (w), 1334 (w), 1268 (w), 1214 (m), 1179 (m), 1118 (w), 1066 (m), 1032 (w), 1021 (m), 1000 (m), 972 (w), 937 (w), 927 (vw), 905 (w), 858 (m), 845 (s), 832 (s), 808 (w), 763 (s), 702 (s), 634 (vs), 602 (s), 590 (vs), 567 (s), 560 (s), 507 (m), 464 (w), 430 (w) cm^{-1} (KBr pellet).

B. $C_5H_5Fe(CO)_2(p\text{-}C_6H_4CH_3)$. A mixture of $Na[C_5H_5Fe(CO)_2]$ (from 7.08 g, 0.02 mole of cyclopentadienyliron dicarbonyl dimer and excess 1% sodium amalgam) and p-iodotoluene (8.72 g, 0.04 mole) in 60 ml of tetrahydrofuran was refluxed under nitrogen for 12 hr. Removal of the solvent at 27° (~20 mm), extraction of the residue with pentane (four 20-ml portions), filtration through alumina (20 g), and reduction of the volume to *ca.* 5 ml were followed by chromatography on an alumina column (5 × 40 cm). Elution with pentane afforded a yellow band of the product, from which solvent was removed with a stream of nitrogen. The resultant yellow oil was sublimed at 50° (~0.1 mm) into a probe cooled with Dry Ice and isopropyl alcohol. The collected solid reverts back to an oil upon application of pressure (with a spatula or glass rod). The low yield (0.04 g, <0.5%) prevented elemental analyses. The compound was characterized by conversion to its sulfinate derivative (*vide infra*).

Solubility properties and stability to air of solutions of this carbonyl are similar to those of the benzyl analog. However, the pure oil is stable to air for only a few hours.

Infrared Spectrum. Carbonyl stretching frequencies were noted at 2112 (vs) and 1963 (vs) cm^{-1}; other bands at 2970 (sh), 2932 (m), 2860 (m), 2375 (w), 1460 (s), 1380 (w), 1188 (w), 1065 (vw), 1021 (w), 1003 (w), 965 (vw), 895 (w), 847 (sh), 834 (w), 746 (m), 662 (m), 582 (m), 558 (m) cm^{-1} (oil, between KBr plates).

Synthesis of Cyclopentadienyliron Sulfinatodicarbonyl Complexes. $C_5H_5Fe(CO)_2(SO_2CH_3)$. (a) From $C_5H_5Fe(CO)_2CH_3$ and Liquid Sulfur Dioxide. One gram (0.005 mole) of $C_5H_5Fe(CO)_2CH_3$ was placed in a 3 × 20 cm cold trap immersed in a Dry Ice–isopropyl alcohol bath at *ca.* −40°. Dry sulfur dioxide (*ca.* 20 l. of gas) was then passed into the trap, where it condensed and dissolved the alkyl to produce a deep red solution. As soon as all of the solid had dissolved (*ca.* 30 min) the addition of SO_2 was discontinued and the liquid was removed by allowing the cold trap to warm up to room temperature. The red residue was then dissolved in 10 ml of chloroform and chromatographed on an alumina column (5 × 20 cm) using $CHCl_3$ eluent. The yellow eluate was collected (some brown decomposition product remained at the top of the column) and concentrated to about 10 ml at 27° (~20 mm). Pentane (200 ml) was then added slowly with stirring. Yellow crystals formed at once and were collected on a filter under nitrogen. After washing the compound with 20 ml of pentane no further purification was necessary. The yield was 1.27 g (95%).

The sulfinato complexes $C_5H_5Fe(CO)_2(SO_2R)$ ($R = C_2H_5$, C_6H_5, $CH_2C_6H_5$), $[C_5H_5Fe(CO)_2]_2SO_2(CH_2)_3$, and $[C_5H_5Fe(CO)_2SO_2]_2(CH_2)_3$ were prepared by analogous procedures, the pertinent synthetic data being given in Table I. The amount of liquid SO_2 employed ranged from 30 to 90 ml/g of the alkyl (aryl), depending on the latter's solubility. In those cases where the SO_2 insertion had not gone to completion, the unreacted alkyl (aryl) was cleanly eluted with $CHCl_3$ before the sulfinate.

The complex $C_5H_5Fe(CO)_2(p\text{-}SO_2C_6H_4CH_3)$ was prepared by a slightly different method owing to a very small quantity of the oily $C_5H_5Fe(CO)_2(p\text{-}C_6H_4CH_3)$ available. The freshly chromatographed aryl (0.02 g, 7.5 × 10^{-5} mole) was dissolved in 5 ml of pentane to facilitate transfer into the cold trap. Sulfur dioxide (10 ml) was then condensed in the trap to form a two-phase system. The lower layer of SO_2 gradually acquired the orange color of the pentane solution. After the latter had become colorless, the mixture was allowed to remain for 24 hr at *ca.* −40°. Both SO_2 and pentane were then removed, and the residue was treated as described earlier. The yield of the sulfinate was *ca.* 5 mg (20%), about 10 mg of the parent aryl having been recovered.

(b) From $C_5H_5Fe(CO)_2CH_3$ and Sulfur Dioxide in Pentane. One gram (0.005 mole) of $C_5H_5Fe(CO)_2CH_3$ was dissolved in 50 ml of pentane and SO_2 was bubbled slowly through the solution at 27°. The formation of a yellow precipitate was accompanied by a gradual discoloration of the solution. After *ca.* 12 hr, the addition of SO_2 was discontinued, the colorless liquid decanted, and the residue was dissolved in about 10 ml of $CHCl_3$. The product was purified as described in part a. The yield was 1.27 g (95%).

The complex $C_5H_5Fe(CO)_2(SO_2C_6H_5)$ was prepared in an analogous manner (Table I).

(c) From $Na[C_5H_5Fe(CO)_2]$ and CH_3SO_2Cl. A tetrahydrofuran solution (60 ml) of $Na[C_5H_5Fe(CO)_2]$ was prepared from 1.77 g (0.005 mole) of cyclopentadienyliron dicarbonyl dimer and excess 1% sodium amalgam. After removing excess amalgam the solution was filtered and added with stirring and under nitrogen to 1.15 g (0.01 mole) of methanesulfonyl chloride. Subsequent removal of the tetrahydrofuran at 27° (~20 mm) left a red residue which was extracted with chloroform (20 ml). The extracts were then treated with about 10 g of alumina (to facilitate filtration) and filtered. The volume of the solution was reduced to *ca.* 5 ml at 27° (~20 mm), and this was followed by chromatography on alumina (5 × 20-cm column) using chloroform eluent. Three bands were collected in the order indicated: (1) purple, containing 0.19 g of $[C_5H_5Fe(CO)_2]_2$; (2) red, containing 0.56 g of $C_5H_5Fe(CO)_2Cl$; (3) yellow, due to 0.05 g (2% yield) of $C_5H_5Fe(CO)_2(SO_2CH_3)$, which was isolated upon removal of chloroform in a stream of nitrogen. The analytical data on this and other sulfinates prepared by similar procedures are given in Table I.

(d) From $Na[C_5H_5Fe(CO)_2]$ and CH_3SO_2F. The procedure employed was similar to that described in part c, 0.98 g (0.01 mole) of methanesulfonyl fluoride having been used. Development of the chromatogram and elution with chloroform yielded 0.8 g of $[C_5H_5Fe(CO)_2]_2$ and 0.05 g (2% yield) of the sulfinato complex.

(e) From $[C_5H_5Fe(CO)_2]_2$ and CH_3SO_2Cl. To a solution of 0.5 g (0.0014 mole) of $[C_5H_5Fe(CO)_2]_2$ in 10 ml of freshly distilled

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[12] T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, 3, 104 (1956).

[13] R. B. King and M. B. Bisnette, *J. Organometal. Chem.*, 2, 15 (1964).

[14] R. B. King, *Inorg. Chem.*, 2, 531 (1963).

Table I. Synthetic Procedures, Reaction Temperatures and Times, Per Cent Yields, Analyses, and Other Data on Cyclopentadienyliron Sulfinatodicarbonyl Complexes

Compound	Synthetic procedures[a]	Reaction		Mp, °C[b]	Yield, %	Mol wt		Analyses, %									
		Temp, °C	Time, hr			Calcd	Found[c]	Calcd					Found				
								C	H	S	Fe	O	C	H	S	Fe	O
$C_5H_5Fe(CO)_2$-(SO_2CH_3)	A	−40	<0.5	135	95	256	262	37.52	3.15	12.52	21.81	25.00	37.80	2.99	12.76	21.80	23.94
	B	27	12		95												
	C	27	<0.5		2												
	D	27	<0.5		2												
	E	27	12		90[d]												
$C_5H_5Fe(CO)_2$-$(SO_2C_2H_5)$	A	−40	<0.5	165	91	270	306	40.02	3.73	11.87	20.68	23.69	40.16	3.83	11.68	21.12	23.62
	C	27	<0.5		1.9												
	E	27	12		88[d]												
$C_5H_5Fe(CO)_2$-$(SO_2C_6H_5)$	A	−40	2	137	46[e]	318	348	49.08	3.17	10.08	17.56		49.15	3.25	9.86	17.29	
	B	27	48		89												
	C	27	<0.5		2.3												
	E	27	12		89[d]												
	F	27	12		73												
$C_5H_5Fe(CO)_2$-$(SO_2CH_2C_6H_5)$	A	−40	2	117	40[e]	332	337	50.62	3.64	9.65	16.81		50.47	3.85	9.35	16.90	
$C_5H_5Fe(CO)_2(p$-$SO_2C_6H_4CH_3)$	A[f]	−40	24	212	20	332	352	50.62	3.64	9.65			50.40	3.48	9.80		
	F	27	12		90												
$[C_5H_5Fe(CO)_2]_2SO_2$-$(CH_2)_3$	A	−40	12	86	18.6[g]	460	473	44.38	3.51	6.97	24.28		44.25	3.34	6.74	24.69	
$[C_5H_5Fe(CO)_2SO_2]_2$-$(CH_2)_3$	A	−40	12	185	61.5[e]	524	503	38.95	3.08	12.24	21.31		38.72	3.12	13.05	21.64	

[a] Procedures: A = $C_5H_5Fe(CO)_2R$ + liquid SO_2; B = $C_5H_5Fe(CO)_2R$ + SO_2 in pentane; C = $Na[C_5H_5Fe(CO)_2]$ + RSO_2Cl; D = $Na[C_5H_5Fe(CO)_2]$ + RSO_2F; E = $[C_5H_5Fe(CO)_2]_2$ + RSO_2Cl; F = $C_5H_5Fe(CO)_2Cl$ + RSO_2Na. [b] Determined with a melting-point block and uncorrected. [c] Osmometry (1×10^{-2} to 2×10^{-2} *M* solutions in $CHCl_3$) with a Mechrolab Model 301-A instrument. [d] Calculated from the equation $[C_5H_5Fe(CO)_2]_2 + RSO_2Cl = C_5H_5Fe(CO)_2(SO_2R) + C_5H_5Fe(CO)_2Cl$. [e] Longer reaction times increase yield. [f] A modified procedure; see the Experimental Section. [g] Longer reaction times decrease yield.

tetrahydrofuran was added 0.16 g (0.0014 mole) of methanesulfonyl chloride. The mixture was stirred under nitrogen at 27° for 12 hr, after which time the solvent was removed at 30° (~20 mm), and the red-orange residue was dissolved in 5 ml of chloroform. Chromatography on an alumina column (5 × 20 cm) using chloroform eluent separated the mixture into two bands. The first band contained 0.2 g of $C_5H_5Fe(CO)_2Cl$, and the second band, upon removal of the solvent at 27° (~20 mm), yielded 0.32 g (90% based on the equation $[C_5H_5Fe(CO)_2]_2 + CH_3SO_2Cl = C_5H_5Fe(CO)_2Cl + C_5H_5Fe(CO)_2(SO_2CH_3)$) of $C_5H_5Fe(CO)_2(SO_2CH_3)$. Table I summarizes the synthesis of other sulfinates by this method.

$C_5H_5Fe(CO)_2(SO_2C_6H_5)$. From $C_5H_5Fe(CO)_2Cl$ and $C_6H_5SO_2Na$. Cyclopentadienyliron dicarbonyl chloride[12] (0.5 g, 0.0023 mole) and sodium benzenesulfinate (0.38 g, 0.0023 mole) were dissolved in 50 ml of methanol, and the solution was stirred under nitrogen for 12 hr at 27°. The mixture was then filtered to remove some brown decomposition product (not characterized). Methanol was evaporated from the orange solution at 60° (~20 mm) and the residue was dissolved in 20 ml of chloroform. Chromatography on alumina with chloroform gave two bands. The first contained unreacted $C_5H_5Fe(CO)_2Cl$ (0.05 g), and the second yielded 0.5 g (73%) of the sulfinate upon removal of the solvent in a stream of nitrogen.

The *p*-tolylsufinate derivative was prepared by a similar procedure (Table I).

Attempted Reactions of Liquid Sulfur Dioxide with Other Cyclopentadienyliron Dicarbonyl Complexes. (a) $C_5H_5Fe(CO)_2C_6F_5$. The complex $C_5H_5Fe(CO)_2C_6F_5$ (0.5 g, 0.0015 mole) was dissolved in *ca.* 50 ml of liquid sulfur dioxide at about −40° and allowed to react for 168 hr. After evaporation of the SO_2, the residue was treated with 10 ml of chloroform and the mixture was filtered. Addition of pentane (150 ml) with stirring afforded a yellow precipitate (0.45 g) which was shown by infrared spectroscopy to be the unreacted perfluoroaryl compound.

(b) $C_5H_5Fe(CO)_2(COCH_3)$. One gram (0.0045 mole) of $C_5H_5Fe(CO)_2(COCH_3)$ was dissolved in 20 ml of liquid sulfur dioxide at *ca.* −40° and allowed to react for 12 hr. After the solvent was removed the residue was purified by alumina chromatography using pentane eluent. Only one band appeared on the column. Evaporation of the solvent from the eluate yielded 0.95 g of the unreacted dicarbonyl.

The benzoyl compound, $C_5H_5Fe(CO)_2(COC_6H_5)$, gave similar results.

Reactions of Cyclopentadienyliron Sulfinatodicarbonyl Complexes. A. $C_5H_5Fe(CO)_2(SO_2CH_3)$ and the Halogens. (a) Chlorine. Chlorine was bubbled slowly through a solution containing 1 g (0.004 mole) of $C_5H_5Fe(CO)_2(SO_2CH_3)$ in 100 ml of benzene at 0°. Gas evolution commenced almost immediately from the carbonyl solution; as it became more rapid, the addition of chlorine was discontinued and the liberated gas was passed into an aqueous barium chloride solution. No detectable change was evident at first; eventually, however, a white precipitate, later shown to be $BaSO_3$, began to form. Accompanying the evolution of gas by the sulfinatocarbonyl was the formation of a viscous oil which was immiscible with benzene. When the bubbling had ceased, benzene was distilled off at 80° leaving a dark, viscous residue, which showed no carbonyl stretching frequencies in the infrared spectrum. Distillation of this residue under reduced pressure (~10 mm) at 26° yielded a clear liquid (~0.25 ml), identified by the elemental analyses (*Anal.* Calcd for C_5H_5Cl: C, 59.72; H, 5.01; Cl, 35.26. Found: C, 61.82; H, 5.09; Cl, 32.42) and its boiling point[15] as 5-chloro-1,3-cyclopentadiene. A black tar that remained was not characterized.

The sulfinates $C_5H_5Fe(CO)_2(SO_2C_6H_5)$ and $-(SO_2CH_2C_6H_5)$ reacted analogously. After the gas evolution had ceased and solvent had been removed (80°), the viscous residue was fractionally distilled at 22 and 26° (~10 mm) to yield, in both cases, C_6H_5Cl and C_5H_5Cl, respectively, identified by infrared spectroscopy. No benzyl chloride was detected in reaction products from $C_5H_5Fe(CO)_2(SO_2CH_2C_6H_5)$.

(b) Bromine. To 1 g (0.004 mole) of $C_5H_5Fe(CO)_2(SO_2CH_3)$ in 100 ml of benzene at 0° bromine (0.8 g, 0.005 mole) was added with stirring. The evolution of gas and the precipitation of $BaSO_3$ from aqueous $BaCl_2$ took place, as in the reaction with chlorine. The residual liquid was not examined in detail after its infrared spectrum revealed that all carbonyl groups had been lost.

The phenylsulfinato complex reacted similarly.

(c) Iodine. One gram (0.004 mole) of $C_5H_5Fe(CO)_2(SO_2CH_3)$ and 1.27 g (0.005 mole) of iodine were dissolved in 100 ml of benzene and the solution was kept at 80° for 1 hr. No gas evolution occurred. Solvent was then removed at 50° (~20 mm) to give unreacted iodine and the sulfinato complex.

B. $C_5H_5Fe(CO)_2(SO_2C_6H_5)$ and $NaBH_4$. Two grams (0.006 mole) of $C_5H_5Fe(CO)_2(SO_2C_6H_5)$ was dissolved in 10 ml of freshly distilled tetrahydrofuran, and the mixture was cooled to 0°. To this solution was added with stirring 0.2 g (0.006 mole) of sodium borohydride. There was considerable effervescence accompanied by the formation of an insoluble brown solid. When the bubbling had ceased the solvent was removed at 27° (~20 mm); the infrared spectrum of the residue showed no carbonyl stretching frequencies.

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(15) M. Kleinman and J. C. Tapas, U. S. Patent 2,904,599 (Sept 15, 1959).

C. Thermal Treatment of $C_5H_5Fe(CO)_2(SO_2CH_2C_6H_5)$. A solution of $C_5H_5Fe(CO)_2(SO_2CH_2C_6H_5)$ (1 g, 0.003 mole) in 20 ml of dioxane was refluxed at 101° for 2 hr under nitrogen. Removal of the solvent at 50° (~20 mm) yielded the unreacted sulfinate, characterized by infrared spectroscopy.

D. Ultraviolet Irradiation of $C_5H_5Fe(CO)_2(SO_2CH_3)$. The essential parts of the photochemical equipment used were purchased from the Hanovia Lamp Division of Engelhard Hanovia, Inc. The source of radiant energy was a 450-w, high-pressure quartz mercury-vapor lamp, Model 679 A-36. Of the total energy radiated, approximately 30% is in the ultraviolet portion of the spectrum, 18% in the visible, and the balance in the infrared. The lamp is operated by a reactive-type transformer, Model 34245-1, which supplies the extra voltage and current required to initiate the arc and the reduced power for operation. A double-walled (3.4 and 4.4 cm i.d.), water-cooled quartz immersion well, Model 19434, holds the lamp in the center of the reaction vessel (23 cm high; 6.4 cm i.d.), which was thermostated using a constant-temperature water bath. An outlet on the reaction vessel was connected to a gas buret.

A solution of $C_5H_5Fe(CO)_2(SO_2CH_3)$ (2 g, 0.008 mole) in 100 ml of benzene was irradiated for 72 hr at *ca.* 30°; 94.2 ml (*ca.* 0.0038 mole) of carbon monoxide was collected in the buret. The reaction mixture was then filtered to remove an insoluble brown solid (no carbonyl stretching frequencies in the infrared spectrum), and the volume of the filtrate was reduced to about 5 ml at 27° (~20 mm). Chromatography on alumina using chloroform eluent gave two bands: orange and yellow, respectively. The first was shown to contain a trace (<5 mg) of ferrocene (identified by its infrared spectrum[16]), and the second over 0.5 g of the unreacted sulfinate. Irradiation of the phenyl- and benzylsulfinato complexes yielded similar results.

Infrared Spectra. Spectra were recorded on a Beckman Model IR-9 spectrophotometer. Solutions were placed in a 0.05-mm KBr cell, a matched reference cell being used at all times. Spectra of solid samples were taken either as Nujol and hexachlorobutadiene mulls or as KBr pellets.

Proton Magnetic Resonance Spectra. Nmr spectra were obtained using a Varian Associates A-60 spectrometer. Tetramethylsilane was employed as an internal standard. The solvents used were $CDCl_3$ and liquid SO_2.

Analyses. Most of the elemental analyses were by Galbraith Laboratories, Inc., Knoxville, Tenn. Oxygen analyses were done by A. Bernhardt Analytical Laboratories of the Max Planck Institute, Mülheim, Germany.

Results and Discussion

Synthesis of the Compounds. Seven cyclopentadienyliron sulfinatodicarbonyls have been prepared using one or more of the procedures illustrated by eq 1–5. Of the five methods tried, the least successful

$$Na[C_5H_5Fe(CO)_2] + RSO_2Cl \longrightarrow C_5H_5Fe(CO)_2Cl + [C_5H_5Fe(CO)_2]_2 + C_5H_5Fe(CO)_2(SO_2R) + \cdots \quad (1)$$

$$Na[C_5H_5Fe(CO)_2] + RSO_2F \longrightarrow [C_5H_5Fe(CO)_2]_2 + C_5H_5Fe(CO)_2(SO_2R) + \cdots \quad (2)$$

$$[C_5H_5Fe(CO)_2]_2 + RSO_2Cl \longrightarrow C_5H_5Fe(CO)_2(SO_2R) + C_5H_5Fe(CO)_2Cl \quad (3)$$

$$C_5H_5Fe(CO)_2Cl + RSO_2Na \longrightarrow C_5H_5Fe(CO)_2(SO_2R) + NaCl \quad (4)$$

$$C_5H_5Fe(CO)_2R + SO_2 \longrightarrow C_5H_5Fe(CO)_2(SO_2R) \quad (5)$$

were the reactions of $Na[C_5H_5Fe(CO)_2]$ with the alkyl (aryl) sulfonyl chlorides and with methanesulfonyl fluoride. Here only about 2% yields of the iron sulfinates were obtained, the principal products being $C_5H_5Fe(CO)_2Cl$ and $[C_5H_5Fe(CO)_2]_2$ with the sulfonyl chlorides, and cyclopentadienyliron dicarbonyl dimer with methanesulfonyl fluoride. The results are somewhat unexpected since cyclopentadienyliron dicarbonyl anion reacts readily with the alkyl and the acyl halides to afford σ-bonded organoiron complexes rather than the dicarbonyl halides, $C_5H_5Fe(CO)_2X$.[17] The formation of $C_5H_5Fe(CO)_2Cl$ in this study may be attributed to the chlorine atom in the alkyl and aryl sulfonyl chlorides being slightly positive and the sulfonyl group being negative owing to the presence of the electronegative oxygens. A similar situation presents itself in the reaction of the metal carbonyl anions with perfluoroalkyl iodides; there the iodocarbonyls are obtained.[18] It is possible that the small amounts of the cyclopentadienyliron sulfinato complexes isolated here may result from the initial reaction of the dicarbonyl anion with the sulfonyl chloride to form $C_5H_5Fe(CO)_2Cl$ and the sodium salt of the sulfinic acid, followed by the interaction of the two products according to eq 4. Alternatively, cyclopentadienyliron dicarbonyl dimer, also formed, may react with the sulfonyl chloride or fluoride to produce the sulfinatocarbonyl complex directly (eq 3). Because of the impracticality of these synthetic methods, they were not investigated further.

Cyclopentadienyliron dicarbonyl sulfinates may be prepared conveniently and in good yields (*ca.* 90% based on eq 3) from $[C_5H_5Fe(CO)_2]_2$ and an alkyl (aryl) sulfonyl chloride. The sulfinato- and chlorodicarbonyl complexes, both formed in the reaction, can be readily separated by alumina chromatography. This behavior of the sulfonyl chlorides toward the carbonyl dimer resembles that of some perfluoroalkyl iodides toward $[C_5H_5Ni(CO)]_2$.[19] The success of the method in the synthesis of other organometallic sulfinates may depend on the relative strength of the metal–metal bond in the parent dinuclear carbonyl. Although such information is not yet available, it is of interest that the compound $[C_5H_5Mo(CO)_3]_2$ does not react with CH_3SO_2Cl under the experimental conditions similar to those for the iron carbonyl dimer.[20]

The reaction of $C_5H_5Fe(CO)_2Cl$ and sodium salts of sulfinic acids also affords the sulfinatocarbonyls in good yields.[21] This synthesis is analogous to that of $C_5H_5Fe(CO)_2CN$ from the dicarbonyl chloride and cyanide ion.[22] Since both the alkyl (aryl) sulfinates and cyanide are π-bonding ligands (*vide infra*), it is reasonable to postulate that the above metathesis represents a general synthetic procedure for cyclopentadienylmetal complexes of the type $C_5H_5Fe(CO)_2Y$ where Y is a strong π bonder.

From the standpoint of novelty, particular attention attaches to the reaction of cyclopentadienyliron alkyls and aryls with liquid sulfur dioxide to yield the corresponding sulfinates. This reaction proceeds very readily at temperatures between −60 and −40° and affords no isolable side products. Thus the method is generally applicable to the synthesis of those cyclopentadienyliron dicarbonyl sulfinates whose parent alkyls or aryls are available.

The formation of the sulfinatodicarbonyls rather

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(16) G. Wilkinson, P. L. Pauson, and F. A. Cotton, *J. Am. Chem. Soc.*, **76**, 1970 (1954).

(17) R. B. King, *Advan. Organometal. Chem.*, **2**, 229 (1964), and references therein.

(18) (a) W. R. McClellan, *J. Am. Chem. Soc.*, **83**, 1598 (1961); (b) W. Beck, W. Hieber, and H. Tengler, *Chem. Ber.*, **94**, 862 (1961).

(19) D. W. McBride, E. Dudek, and F. G. A. Stone, *J. Chem. Soc.*, 1752 (1964).

(20) J. P. Bibler, unpublished observations.

(21) These reactions were also studied independently by J. P. Collman, *et al.*, paper presented at The Second International Symposium on Organometallic Chemistry, Madison, Wis., Aug 30–Sept 3, 1965.

(22) T. S. Piper, F. A. Cotton, and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **1**, 165 (1955).

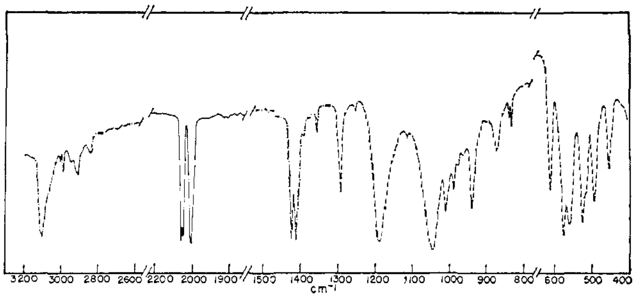


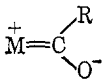
Figure 1. The infrared spectrum of $C_5H_5Fe(CO)_2(SO_2CH_3)$: ———, chloroform solution; — — —, Nujol mull; — · —, hexachlorobutadiene mull.

than the sulfur dioxide acylmonocarbonyl complexes, $C_5H_5Fe(CO)(COR)SO_2$, merits comment, since the latter are the expected products from mechanistic considerations of the carbon monoxide insertion and decarbonylation reactions of some manganese carbonyl systems.[23] In this respect the SO_2 insertion is analogous to the reaction of $Mn(CO)_5CH_3$ with tetrafluoroethylene, which yields the compound $Mn(CO)_5CF_2CF_2CH_3$.[24] In both cases, the incoming substrate rather than one of the carbonyl groups present in the complex becomes inserted into the metal–carbon bond. It seems reasonable to suggest that products of this nature will result when the entering ligand is an unsaturated species, capable of readily expanding its coordination number (*e.g.*, an alkene, SO_2, etc.).

Two simple mechanisms can account for the formation of the sulfinatodicarbonyl products. The first one involves a direct attack of SO_2 on iron, accompanied or immediately followed by a migration of R onto the dioxide. The second path consists of an initial migration of R onto a carbonyl group (possibly a solvent-assisted process) followed by a rapid transfer of R onto the SO_2 ligand. Although the latter, two-step mechanism cannot be ruled out for $C_5H_5Fe(CO)_2R$, it is known not to be operative for several dialkyl- and diarylmercury compounds, which yield $RHg(SO_2R)$ with SO_2.[25]

In an attempt possibly to resolve between the two suggested mechanisms, experiments were conducted with the objective of trapping the intermediates $C_5H_5Fe(CO)(COR)SO_2$. Accordingly, the reactions of $C_5H_5Fe(CO)_2CH_3$ and of $C_5H_5Fe(CO)_2C_6H_5$ with SO_2 were run in pentane, where the solubility of the acyl sulfur dioxide compounds is expected to be low. However, examination of the products revealed that only the $C_5H_5Fe(CO)_2(SO_2R)$ derivatives were obtained. Hence nothing concrete can be said about the mechanism of the sulfur dioxide insertion at present. Worthy of notice, however, is the observation that whereas the complex $C_5H_5Fe(CO)_2CH_3$ reacts rapidly with liquid SO_2 at −40°, it does so very slowly with saturated pentane solutions of the dioxide at 27°. Therefore, concentration of SO_2 appears to influence tremendously the rate of the insertion.

Observations on the synthesis of the sulfinato complexes in liquid SO_2 give the following order of reactivity of the parent alkyls and aryls toward the dioxide: $C_5H_5Fe(CO)_2CH_3 \sim C_5H_5Fe(CO)_2C_2H_5 \gg [C_5H_5Fe(CO)_2]_2(CH_2)_3 > C_5H_5Fe(CO)_2C_6H_5 \sim C_5H_5Fe(CO)_2CH_2C_6H_5$. No reactions were detected with $C_5H_5Fe(CO)_2C_6F_5$, $C_5H_5Fe(CO)_2(COCH_3)$, and $C_5H_5Fe(CO)_2(COC_6H_5)$. The results are in accord with the qualitative order of stability reported for these complexes.[12] The unreactive nature of the acyl and the perfluoroaryl derivatives may be attributed to the relatively strong metal–carbon bonding therein, resulting from significant contributions of resonance structures I and II, respectively.[26,27] Supporting this argument is the fact that no neutral transition metal perfluoroalkyl or aryl compound has yet been successfully carbonylated.[28]



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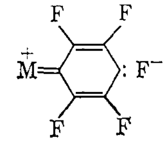

II

It is of interest that the relative reactivities of the $C_5H_5Fe(CO)_2R$ compounds toward SO_2 do not completely parallel the rates of the carbonylation of the analogous $Mn(CO)_5R$ complexes. Among the latter, the rate constant was found to decrease in the series $R = C_2H_5 > C_6H_5 > CH_3 \gg CH_2C_6H_5$.[29] Thus, for example, $Mn(CO)_5C_6H_5$ appears to be relatively more reactive, and $Mn(CO)_5CH_3$ less reactive than the $C_5H_5Fe(CO)_2R$ counterparts.

These variations are probably due to mechanistic differences between the carbon monoxide and the sulfur dioxide insertions. Whereas the former has been shown in certain cases[30] to proceed *via* alkyl group migration onto a carbonyl ligand already present in the compound, the latter very likely does not directly involve the carbonyl groups (*vide supra*). Studies on the mechanism of the sulfur dioxide reaction with several $C_5H_5Fe(CO)_2R$ complexes, now in progress, may resolve some of these problems.

Properties and Characterization of the Compounds. The sulfinato derivatives of cyclopentadienyliron dicarbonyl are yellow, crystalline compounds with sharp melting points. The solids appear to be stable to air for at least several months; however, chloroform solutions show signs of decomposition after about 24 hr of exposure to air. The $C_5H_5Fe(CO)_2(SO_2R)$ complexes are soluble in benzene, chloroform, methyl and ethyl alcohols, acetone, water, and 6 *M* hydrochloric acid (from which they can be recovered unchanged), but insoluble in hexane and carbon disulfide. The dinuclear sulfinates dissolve less readily, especially in benzene and chloroform. Furthermore, they tend to become gummy in moist air.

All of the compounds have been characterized through elemental analyses and molecular weight deter-

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(23) R. J. Mawby, F. Basolo, and R. G. Pearson, *J. Am. Chem. Soc.*, **86**, 3994 (1964), and references therein.

(24) J. B. Wilford, P. M. Treichel, and F. G. A. Stone, *J. Organometal. Chem.*, 2, 119 (1964).

(25) J. P. Bibler and A. Wojcicki, to be published.

(26) R. B. King, *J. Am. Chem. Soc.*, **85**, 1918 (1963).

(27) F. A. Cotton and J. A. McCleverty, *J. Organometal. Chem.*, **4**, 490 (1965).

(28) The only perfluoroalkyl compound known to undergo CO insertion is the ionic $C_5H_5Co(CO)_2C_3F_7{}^+ClO_4{}^-$; see P. M. Treichel and G. Werber, Abstracts, 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965, p 23-O.

(29) F. Calderazzo and F. A. Cotton, Proceedings of the 7th International Conference on Coordination Chemistry, Stockholm, Sweden, 1962, p 296.

(30) R. J. Mawby, F. Basolo, and R. G. Pearson, *J. Am. Chem. Soc.*, **86**, 5043 (1964).

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

Compound	CO stretches[a]	SO stretches[b]	Other bands[c]
$C_5H_5Fe(CO)_2(SO_2CH_3)$	2063 vs, 2053 vs, 2015 vs, 2009 vs	1194 s, 1181 sh, 1061 sh, 1052 s	3120 sh, 3111 m, 3017 vw, 3000 w, 2965 vw, 2931 sh, 2922 w, 2859 vw, 1429 m, 1417 m, 1409 sh, 1395 vw, 1359 w, 1297 m, 1256 vw, 1115 vw, 1016 m, 993 w, 963 vw, 943 m, 877 w, 838 vw, 835 vw, 722 w, 615 m, 580 s, 564 s, 530 s, 498 m, 455 m, 446 sh
$C_5H_5Fe(CO)_2(SO_2C_2H_5)$	2061 vs, 2055 vs, 2016 vs, 2011 vs	1185 s, 1173 sh, 1055 sh, 1051 s	3111 m, 3102 sh, 3080 sh, 3000 w, 2986 w, 2972 vw, 2941 w, 2929 w, 2874 vw, 1445 w, 1428 m, 1414 m, 1378 w, 1357 w, 1246 m, 1116 vw, 1029 m, 1013 m, 991 m, 912 w, 876 w, 841 w, 834 w, 780 w, 724 w, 678 s, 614 m, 584 s, 565 s, 496 m, 480 m, 452 w
$C_5H_5Fe(CO)_2(SO_2C_6H_5)$	2060 vs,[d] 2013 vs	1195 s, 1182 sh, 1164 sh, 1039 s	3111 w, 3100 m, 3090 m, 3080 m, 1476 w, 1443 m, 1436 m, 1422 m, 1400 vw, 1360 w, 1302 w, 1115 vw, 1089 s, 1071 w, 1024 m, 1015 sh, 999 w, 970 vw, 890 w, 855 m, 849 sh, 842 w, 839 vw, 835 vw, 754 s, 725 vw, 703 s, 694 s, 620 sh, 615 m, 609 sh, 590 s, 579 s, 561 s, 529 w, 503 w, 489 w, 478 vw
$C_5H_5Fe(CO)_2(SO_2CH_2C_6H_5)$	2060 vs,[d] 2010 vs	1205 s, 1050 s, 1045 s, 1038 s	3113 sh, 3096 m, 3070 w, 3036 vw, 2985 w, 2929 w, 2913 vw, 1494 m, 1456 m, 1433 m, 1427 sh, 1415 w, 1361 vw, 1235 vw, 1179 m, 1163 vw, 1158 vw, 1134 sh, 1127 w, 1118 sh, 1072 w, 1024 w, 1004 w, 975 vw, 934 vw, 921 vw, 880 w, 857 m, 836 vw, 827 vw, 769 m, 709 sh, 702 m, 675 w, 628 m, 613 m, 603 sh, 587 w, 578 sh, 573 s, 563 m, 557 sh, 518 s, 506 m, 489 m, 486 sh
$C_5H_5Fe(CO)_2(p\text{-}SO_2C_6H_4CH_3)$	2060 vs,[d] 2012 vs	1194 s, 1178 sh, 1040 s	3114 w, 3096 sh, 3079 m, 2960 vw, 2930 vw, 1492 w, 1457 w, 1437 m, 1422 m, 1397 vw, 1384 w, 1361 w, 1300 vw, 1090 m, 1072 vw, 1015 m, 1010 sh, 883 w, 857 m, 840 vw, 838 vw, 812 m, 710 w, 647 m, 636 w, 618 w, 605 vw, 581 s, 570 s, 560 s, 519 vw, 501 w, 486 w
$[C_5H_5Fe(CO)_2]_2SO_2(CH_2)_3$[e]	2060 s, 2010 vs, 1948 s	1200 s, 1052 s	1067 w, 1036 m, 1022 vw, 867 m, 845 vw, 742 vw, 727 vw
$[C_5H_5Fe(CO)_2SO_2]_2(CH_2)_3$[e]	2060 vs, 2016 vs	1185 s, 1169 sh, 1049 s	1128 vw, 855 m, 733 w

[a] Chloroform solution. Abbreviations: vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder. [b] Nujol mull. [c] 400–1300 and 1500–2800 cm^{-1}, Nujol mull; 1330–1500 and 2800–3200 cm^{-1}, hexachlorobutadiene mull. [d] The absorption band is not Gaussian. [e] Measured only in the 700–1220- and 1900–2100-cm^{-1} spectral regions; the carbonyl stretching absorptions were not examined under highest possible resolution.

minations in conjunction with the infrared and proton magnetic resonance spectra. The infrared absorption bands and the proton magnetic resonances are listed in Tables II and III, respectively, and the infrared spectrum of $C_5H_5Fe(CO)_2(SO_2CH_3)$ is shown in Figure 1.

A notable absence of absorption bands in the acyl carbonyl region (1590–1700 cm^{-1})[31] of the infrared spectra of the derivatives clearly demonstrates that the alkyl (aryl) groups are not attached to a carbonyl ligand and rules out acyl sulfur dioxide structural formulations. The absence of iron–carbon bonding for R is best attested by the nmr spectra. The methylsulfinate complex, for example, exhibits sharp proton signals at τ 4.75 and 6.85 (relative intensities 5:3). These are assigned to the cyclopentadienyl and methyl hydrogens, respectively. The proton resonance absorption in CH_3SO_2Cl occurs at τ 6.36 and that in CH_3SO_2F at τ 6.73,[32] whereas methyl groups bonded to transition metals give rise to signals at much higher fields (*ca.* τ 10).[33] As further evidence for the absence of Fe–R linkages in the complexes, the hydrogens attached to carbon atoms which were bonded to the metal in the parent alkyls absorb at considerably lower fields after the reaction with SO_2.[34] It is therefore concluded from these data that the alkyl or aryl group is attached to sulfur dioxide which is bonded to the metal.

The question of the bonding in the $FeSO_2R$ moiety of

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(31) J. P. Bibler and A. Wojcicki, *Inorg. Chem.*, **5**, 889 (1966), and references therein.

(32) Communication from Dr. G. V. D. Tiers to the Department of Chemistry, The Ohio State University.

(33) A. Davison, J. A. McCleverty, and G. Wilkinson, *J. Chem. Soc.*, 1133 (1963).

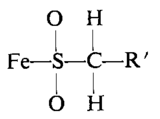
(34) For example, the CH_2 group protons absorb at τ 8.45 (ref 33) and 7.23 in $C_5H_5Fe(CO)_2C_2H_5$ and $C_5H_5Fe(CO)_2CH_2C_6H_5$, respectively, but at τ 6.70 and 5.61 in the corresponding sulfinates.

Table III. Proton Magnetic Resonance Spectra of Cyclopentadienyliron Sulfinatodicarbonyl Complexes (τ)

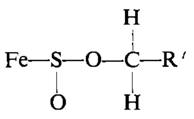
Compound	Chemical shift[a]	Rel intensity	Assignment
$C_5H_5Fe(CO)_2(SO_2CH_3)$	4.75 (singlet)	5	C_5H_5
	6.85 (singlet)	3	CH_3
$C_5H_5Fe(CO)_2(SO_2C_2H_5)$	4.58 (singlet)	5	C_5H_5
	6.70 (quartet, $J \sim 8$ cps)	2	CH_2
	8.49 (triplet, $J \sim 8$ cps)	3	CH_3
$C_5H_5Fe(CO)_2(SO_2C_6H_5)$	2.0–2.5 (complex multiplets)	5	C_6H_5
	4.70 (singlet)	5	C_5H_5
$C_5H_5Fe(CO)_2(SO_2CH_2C_6H_5)$	2.4 (singlet, broad)	5	C_6H_5
	4.90 (singlet)	5	C_5H_5
	5.61 (singlet)	2	CH_2
$C_5H_5Fe(CO)_2(SO_2CH_2C_6H_5)$[b]	2.46 (singlet)	5	C_6H_5
	4.82 (singlet)	5	C_5H_5
	5.77 (singlet)	2	CH_2
$C_5H_5Fe(CO)_2(p\text{-}SO_2C_6H_4CH_3)$	2.11–2.44 (multiplet)	2	C_6H_4
	2.50–2.82 (multiplet)	2	
	4.91 (singlet)	5	C_5H_5
	7.58 (singlet)	3	CH_3
$[C_5H_5Fe(CO)_2]_2SO_2(CH_2)_3$	4.60 (singlet)	10	C_5H_5
	6.28 (triplet, $J \sim 6$ cps)	2	SO_2CH_2
	6.62 (triplet, $J \sim 6$ cps)	2	CH_2Fe
	7.23–7.67 (multiplet)	2	$C\text{-}CH_2\text{-}C$
$[C_5H_5Fe(CO)_2SO_2]_2(CH_2)_3$	4.60 (singlet)	10	C_5H_5
	6.48 (triplet, $J \sim 6$ cps)	4	SO_2CH_2
	7.31–7.51 (multiplet)	2	$C\text{-}CH_2\text{-}C$

[a] $CDCl_3$ solution, 25°. [b] Liquid SO_2, −15°.

the derivatives was also resolved with the aid of nmr spectroscopy. The methylene proton signals for the benzyl- and ethylsulfinate complexes appear as a simple singlet and a 1:3:3:1 quartet, respectively, at ambient temperatures, indicating that the CH_2 hydrogens are magnetically equivalent in each compound. This evidence supports structure III,[35] but is in discord with


$\mathrm{Fe{-}\overset{O}{\underset{O}{S}}{-}\overset{H}{\underset{H}{C}}{-}R'}$

III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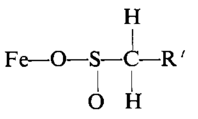
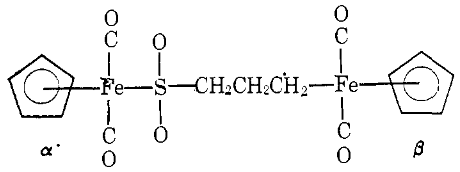
IV


$\mathrm{Fe{-}O{-}\underset{O}{S}{-}\overset{H}{\underset{H}{C}}{-}R'}$

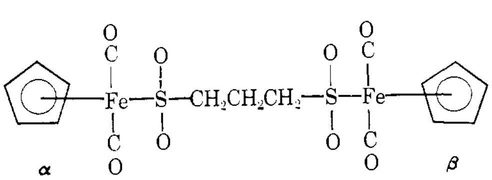
V

structures IV and V, which are expected to give rise to AB and ABX_3 type spectra for the methylene and ethyl group protons when $R' = C_6H_5$ and CH_3, respectively.[36] Furthermore, attachment IV presupposes rearrangements in the RSO_2 group during the reactions of $C_5H_5Fe(CO)_2Cl$ with RSO_2Na, of $Na[C_5H_5Fe(CO)_2]$ with RSO_2X (X = Cl, F), and of $[C_5H_5Fe(CO)_2]_2$ with RSO_2Cl, all of which are rather unlikely in view of the mild reaction conditions employed. Structure V contains an iron–oxygen linkage and therefore cannot account for the excellent π-bonding properties of the sulfinate ligands (*vide infra*). On the basis of similarities among the infrared spectra and physical properties of the compounds, the bonding depicted for structure III is assigned to all of the derivatives reported herein.

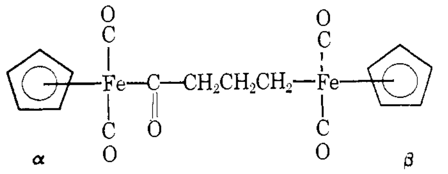
The proton magnetic resonance spectra of the sulfinates are entirely consistent with the assigned structures. It is rather unexpected, however, that the dinuclear $[C_5H_5Fe(CO)_2]_2SO_2(CH_2)_3$ (VI) gives only one signal for the two kinds of cyclopentadienyl hydrogens (α and β). Furthermore, the signal occurs at the same field as that for the C_5H_5 protons in $[C_5H_5Fe(CO)_2SO_2]_2(CH_2)_3$ (VII). This observation is to be contrasted with the one made on the complex $[C_5H_5Fe(CO)_2]_2CO(CH_2)_3$ (VIII), the nmr spectrum of which shows two cyclo-



VI



VII



VIII

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(35) The presence of only one line in the methylene proton spectra of the benzyl derivative in $CDCl_3$ at 25° and in liquid SO_2 at −15° indicates that rotation about the $C_6H_5CH_2\text{–}SO_2Fe$ bond is sufficiently rapid to average the environments experienced by the CH_2 hydrogens; see L. M. Jackman, "Application of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," The Macmillan Co., New York, N. Y., 1959, pp 99–103.

(36) The methylene protons in some sulfinic esters $RCH_2\text{–}O\text{–}SO\text{–}C_6H_4CH_3$ have been recently found[37] to give AB-type nmr spectra with internal chemical shifts of τ 0.54–0.7. On the basis of the close structural similarity between these compounds and iron sulfinate complexes of structure IV, analogous spectra are expected for the latter. Structure V, which contains a methylene group attached to the asymmetric sulfur, should give nmr spectra similar to those predicted for structure IV. Nevertheless, it is possible, in principle, that either structure IV or V could give rise to the splitting of the methylene proton resonance which would be too small to detect under the conditions of resolution achieved in this study. However, such a situation is extremely unlikely and, to our knowledge, has never been encountered in investigations concerned with similar compounds. Therefore, we shall dismiss this possibility.

(37) J. W. Wilt and W. J. Wagner, *Chem. Ind.* (London), 1389 (1964).

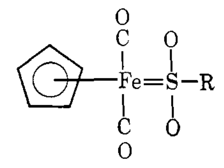
pentadienyl, proton resonances, at τ 5.17 (α) and 5.27 (β).[26] Hence, in complex VI, the effect responsible for the deshielding of the five hydrogens of the cyclopentadienyl group bonded to the iron which is attached to the sulfinate moiety (α) must be somehow transmitted to the protons belonging to the other cyclopentadienyl ring (β). Noteworthy in this connection is the fact that the hydrogens of the methylene groups bonded to the iron and sulfur atoms in VI absorb at very similar fields (Table III).

The chemical shifts of the cyclopentadienyl ring protons in the sulfinato complexes occur at τ values which are 0.41–0.82 unit lower than the corresponding signals for the parent alkyls or aryls. King[26] reports that electronegative groups (Y) attached to iron in $C_5H_5Fe(CO)_2Y$ cause shifts of the proton resonance to lower fields, most likely owing to the inductive effects of Y. Similarly, it is suggested here that the observed position of the C_5H_5 proton resonance signal in the sulfinates results from a strong electron-withdrawing effect of the RSO_2 group.

Examination of the infrared carbonyl stretching frequency region of the sulfinato complexes (Table II) reveals that the CO absorptions occur at wavenumbers about 40–60 cm^{-1} higher than in the parent alkyl or aryl.[12,33] Furthermore, the stretching frequencies of the former are almost identical with those reported for $C_5H_5Fe(CO)_2CN$,[22] indicating considerable π-bonding capacity of the RSO_2^- ligands. It is also interesting that the frequencies of both the asymmetric and the symmetric modes are rather insensitive to the nature of the alkyl or aryl group, suggesting that the presence of the electronegative oxygens determines almost exclusively the degree of π bonding of the sulfur atom.

A very surprising feature in the spectra of several derivatives is the splitting of the carbonyl absorption bands into two components of equal intensity. The magnitude of the separation appears to depend on the size of R bonded to the sulfur; for example, when R = CH_3 the splitting of the asymmetric mode is 10 cm^{-1}, and of the symmetric mode 6 cm^{-1}; when R = C_2H_5, these are 6 and 5 cm^{-1}, respectively. For bulkier R groups no splitting is discernible; however, some absorption bands are definitely not Gaussian. This unusual phenomenon is now being studied further.

The infrared spectra also reveal two intense absorptions in the 1035–1205 cm^{-1} range. These bands, absent in the spectrum of $C_5H_5Fe(CO)_2(SCH_3)$,[38] are assigned to the asymmetric and symmetric SO-stretching frequencies. In a number of cases there are shoulders on each absorption band; the symmetric mode in the spectrum of the benzylsufinato complex appears to be split most. A similar splitting of one or both fundamentals was also encountered by Collman and Roper[11a] and is commonly found in organic sulfones.[39] The SO-stretching frequencies show little dependence on the nature of R; moreover, they are displaced by 100–120 cm^{-1} to lower wavenumbers from the values reported for the sulfones.[40] The latter effect is undoubtedly due to strong π interaction between the iron and sulfur (resonance structure IX).


IX

Reactions of the Compounds. In view of the evidence for considerable iron–sulfur π bonding and because of the structural analogy between the sulfinato and the acyl metal complexes, mentioned earlier, it was of interest to study some aspects of chemical behavior of the iron sulfinates. The attempted reactions may be classified as (1) oxidative cleavage of the sulfur–carbon bond, (2) reduction of the SO_2 moiety, and (3) desulfurylation.

Attempts were made to cleave the $O_2S–R$ bonds using chlorine, bromine, and iodine (X), the objective being to synthesize organoiron analogs of the alkyl sulfonyl halides of the type $C_5H_5Fe(CO)_2(SO_2X)$. Such compounds are expected to exhibit strong iron–sulfur π bonding owing to the presence of three electronegative atoms on the sulfur.[41]

The reactions of chlorine with the methyl-, phenyl-, and benzylsulfinato derivatives resulted in a complete loss of both carbon monoxide and sulfur dioxide and the formation of 5-chloro-1,3-cyclopentadiene, chlorobenzene (when R = C_6H_5 and $CH_2C_6H_5$), and other unidentified products. Bromine reacted analogously with the methyl and phenyl complexes, whereas iodine did not affect the methylsulfinate at 80°. Since the compounds $C_5H_5Fe(CO)_2Cl$[42] and $C_5H_5Fe(CO)_2Sn(C_6H_5)_3$[43] are also decomposed by chlorine at 0–10°, the above results may be due to the inherent instability of the $C_5H_5Fe(CO)_2$ moiety toward the reactive halogens.

The iron sulfinato complexes may be regarded as organometallic analogs of the sulfones; it was therefore of interest to determine whether the $FeSO_2R$ fragment can be reduced either to FeSOR or to FeSR.[44] Accordingly, the reaction of $NaBH_4$ with $C_5H_5Fe(CO)_2(SO_2CH_3)$ was carried out at 0°. However, the brown, insoluble solid formed was shown not to contain any carbonyl groups.

Since a characteristic reaction of transition metal acyl complexes is loss of carbon monoxide to form the corresponding alkyls or aryls,[45] it was of interest to ascertain whether the analogous process, desulfurylation, occurs with $C_5H_5Fe(CO)_2(SO_2R)$.

Refluxing a dioxane solution of $C_5H_5Fe(CO)_2(SO_2CH_2C_6H_5)$ at 101° for 2 hr under nitrogen subsequently led to a complete recovery of the sulfinate. However, ultraviolet irradiation of the methyl-, phenyl-, and benzylsulfinates resulted in considerable decomposition and afforded trace amounts of ferrocene as the only tractable product. Although these attempts at the desulfurylation have not been successful, Collman and Roper[11a] have recently converted quantitatively

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[38] R. B. King and M. B. Bisnette, *Inorg. Chem.*, 4, 482 (1965).

[39] P. M. G. Bavin, G. W. Gray, and A. Stephenson, *Spectrochim. Acta*, 16, 1312 (1960).

[40] K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, Inc., San Francisco, Calif., 1962, p 54.

[41] Although organic sulfones are extremely resistant to carbon–sulfur bond cleavage under oxidizing conditions it was felt that an increase in iron–sulfur π bonding in going from $Fe–SO_2R$ to $Fe–SO_2X$ might provide the driving force for the reaction.

[42] J. P. Bibler, unpublished data.

[43] R. D. Gorsich, *J. Am. Chem. Soc.*, 84, 2486 (1962).

[44] Open-chain aliphatic and phenyl sulfones exhibit considerable resistance to reduction with $LiAlH_4$; see F. G. Bordwell and W. H. McKellin, *J. Am. Chem. Soc.*, 73, 2251 (1951).

[45] Reference 17, p 209.

the complex $Ir(CO)Cl_2[P(C_6H_5)_3]_2(p\text{-}SO_2C_6H_4CH_3)$ to the corresponding aryl by heating it in boiling toluene. Thus both the SO_2 insertion and the desulfurylation can be effected but so far not on the same system, as is the case with the analogous carbon monoxide reactions.[45] It becomes evident that additional studies are necessary before factors influencing reactions of this general nature are reasonably well understood.

Acknowledgment. This investigation was supported by the Petroleum Research Fund, administered by the American Chemical Society, and in part by the National Science Foundation. Acknowledgment is also made to the National Science Foundation for a grant for purchase of the infrared spectrophotometer. Finally, we wish to thank F. A. Hartman for recording many of the infrared spectra.

Characterization and Electronic Structures of Metal Complexes Containing Benzene-1,2-dithiolate and Related Ligands

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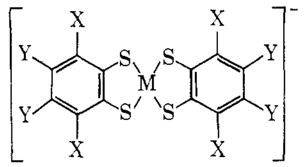
Received May 12, 1966

Abstract: The syntheses and properties of a series of square-planar complexes with the general formula $[(n\text{-}C_4H_9)_4N][M(S_2C_6X_2Y_2)_2]$, where M = Co, Ni, and Cu (X = Y = H, CH_3, Cl; X = H, Y = CH_3), are reported. Spectral and magnetic properties, as well as polarographic half-wave potentials, are strongly dependent on the electronic nature of the substituent. This is shown to be consistent with an electronic structural model in which the highest filled molecular orbitals are largely ligand in composition. Possible interpretations of the unusual magnetic properties of the $[(n\text{-}C_4H_9)_4N][Co(tcdt)_2]$ complex are discussed.

The ligand toluene-3,4-dithiolate (tdt) forms a series of square-planar complexes with interesting magnetic properties.[3] For example, with Ni as central metal, the complexes $Ni(tdt)_2$, $Ni(tdt)_2^-$, and $Ni(tdt)_2^{2-}$ have been characterized.[3,4] It is of interest that the unusual, paramagnetic ($S = {}^1/_2$) $Ni(tdt)_2^-$ complex is unquestionably the most air stable of the three entries.

In view of the recent interest in metal complexes containing sulfur-donor ligands,[5] we have undertaken studies aimed at the preparation, characterization, and electronic structural study of the monoanionic planar systems of the general formula I. In system I, the effect of different substituents on the electronic structure of the MS_4 group can be systematically investigated. In this paper, we report our studies on the I complexes with M = Co, Ni, Cu (X = Y = H, CH_3, Cl; X = H, Y = CH_3).



I

Experimental Section

Preparation of Ligands. Benzene-1,2-dithiol (bdt), *o*-xylene-4,5-dithiol (xdt), and 3,4,5,6-tetramethylbenzene-1,2-dithiol, or prehnitene-5,6-dithiol (pdt), were prepared according to the method of Adams and Ferretti.[6] Substituted *o*-dibromobenzenes were treated with cuprous butyl mercaptan to form thioethers which were subsequently cleaved by sodium in liquid ammonia, yielding the substituted benzene-1,2-dithiols.

3,4,5,6-Tetrachlorobenzene-1,2-dithiol (tcdt) was prepared by treating hexachlorobenzene, sodium sulfhydrate, and iron powder in N,N-dimethylformamide at 145°. After reaction was complete, base was added to precipitate the iron complex. The precipitate was collected and boiled with excess zinc oxide in methanol. The mixture was filtered and the filtrate acidified to precipitate the free dithiol. The *o*-dithiol configuration was verified by a Raney nickel degradation which produced 1,2,3,4-tetrachlorobenzene. Recrystallization from benzene gave a pale yellow compound, mp 265–266°.

Anal. Calcd for $C_6Cl_4S_2H_2$: C, 25.75; Cl, 50.64; S, 22.90; H, 0.72. Found: C, 25.81; Cl, 49.37; S, 24.60; H, 0.75.

Preparation of Complexes. $[(n\text{-}C_4H_9)_4N][Co(bdt)_2]$. Benzene-1,2-dithiol (1.6 g, 0.011 mole) was added to potassium metal (0.85 g, 0.022 g-atom) dissolved in 25 ml of absolute ethanol. Addition of a solution of $CoCl_2 \cdot 6H_2O$ (1.19 g, 0.005 mole) in 10 ml of absolute ethanol resulted in an intense dark blue color. A solution of $(n\text{-}C_4H_9)_4NBr$ (1.71 g, 0.005 mole) in 15 ml of ethanol was added, and the mixture was cooled in ice and filtered. The precipitate was washed with absolute ethanol and ether and dried. The solid was then dissolved in 200 ml of methylene chloride and filtered, leaving a residue of halide salts. The filtrate was concentrated to 20 ml under reduced pressure and then cooled. A 2.55-g sample of dark blue crystals was collected, washed, and dried as before. This crude material was recrystallized twice from methylene chloride to give 2.05 g of blue-black needles.

The complexes $[n\text{-}(C_4H_9)_4N][Co(xdt)_2]$ and $[(n\text{-}C_4H_9)_4N][Co(pdt)_2]$ were prepared by the same procedure.

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(3) R. Williams, E. Billig, J. H. Waters, and H. B. Gray, *J. Am. Chem. Soc.*, 88, 43 (1966).

(4) E. I. Stiefel, J. H. Waters, E. Billig, and H. B. Gray, *ibid.*, 87, 3016 (1965).

(5) (a) S. E. Livingstone, *Quart. Rev.* (London), 19, 386 (1965); (b) H. B. Gray, *Transition Metal Chem.*, 1, 239 (1965).

(6) (a) R. Adams and A. Ferretti, *J. Am. Chem. Soc.*, 81, 4927 (1959); (b) *Org. Syn.*, 42, 22, 54 (1962).