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## REACTION OF SODIUM $\eta^5$ -CYCLOPENTADIENYLDICARBONYLFERRATE(0) WITH SULFUR DIOXIDE. SYNTHESIS OF IRON–SULFUR DIOXIDE COMPLEXES

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### Summary

Sulfur dioxide reacts at  $-78^\circ\text{C}$  with  $\text{Na}^+ [\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]^-$ , prepared by the reduction of  $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$  with sodium amalgam in tetrahydrofuran, to give a red solution containing a species which can be alkylated with  $\text{RX}$  to  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{S}(\text{O})_2\text{R}$ . The alkylation reaction with  $\text{CH}_3\text{I}$  affords both  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{S}(\text{O})_2\text{CH}_3$  and  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{I}$ . The nature of this solution and the possible existence of the anion  $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{SO}_2]^-$  therein are discussed. Upon warming to room temperature and chromatography, the solutions of  $\text{Na}^+ [\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]^-$  and  $\text{SO}_2$  afford the isolable iron–sulfur dioxide complexes,  $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2\text{SO}_2$ ,  $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})]_2(\text{CO})\text{SO}_2$ , and  $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{SO}_2]_2$ . The characterization and properties of the first two compounds are described.

### Introduction

Sulfur dioxide behaves as a Lewis acid toward a number of low-valent transition metals in complexes. Examples of such interactions are found in  $\text{Ir}[\text{P}(\text{C}_6\text{H}_5)_3]_2\text{Cl}(\text{CO})\text{SO}_2$  [1,2],  $\text{Rh}[\text{P}(\text{C}_6\text{H}_5)_3]_2\text{Cl}(\text{CO})\text{SO}_2$  [1,3],  $\text{Pt}[\text{P}(\text{C}_6\text{H}_5)_3]_2(\text{SO}_2)_2 \cdot \text{C}_7\text{H}_8$  [4], and  $\text{Pt}[\text{P}(\text{C}_6\text{H}_5)_3]_3\text{SO}_2 \cdot 0.7 \text{SO}_2$  [5]. These complexes contain nonplanar  $\text{MSO}_2$  moieties with a pyramidal configuration about the sulfur, indicative of the presence of a lone pair of valence electrons thereon.

Transition metal carbonyl anions undergo reactions with a number of electrophilic reagents, including protic acids, alkyl halides, and various other organic as well as organometallic compounds, especially those containing halogens [6]. The anion  $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]^-$ , in particular, has been found to behave as a powerful nucleophile [7]. The observed high degree of nucleophilicity of

$[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]^-$  suggested that it would react readily with  $\text{SO}_2$  to form a 1/1 adduct. This adduct is expected to exhibit "nonplanar"  $\text{Fe}-\text{SO}_2$  bonding, similar in nature to that found for the aforementioned noble metal complexes. The interaction of  $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]^-$  with  $\text{CS}_2$ , a weaker electrophile than  $\text{SO}_2$ , to yield  $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CS}_2]^-$  was reported very recently [8].

In this paper are described our studies on reaction between  $\text{Na}^+ [\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]^-$  and  $\text{SO}_2$ . As the investigation progressed it became apparent that the reaction in question is quite complex and affords several  $\text{Fe}-\text{SO}_2$  products, the nature of which depends on the experimental conditions. Some aspects of this study were communicated earlier [9,10]. Presented herein is a full account.

## Results and discussion

### Reaction of $\text{Na}^+ [\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]^-$ with $\text{SO}_2$

Gaseous  $\text{SO}_2$  was passed slowly into a tetrahydrofuran solution of an approximately equimolar amount of  $\text{Na}^+ [\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]^-$ , prepared by the reduction of  $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$  with sodium amalgam and cooled to ca.  $-78^\circ\text{C}$ . The resulting solution was treated with bis(triphenylphosphine)iminium chloride ( $\text{PPN}^+ \text{Cl}^-$ ) [11] at  $-78^\circ\text{C}$  and above in attempts to obtain  $[\text{PPN}^+ [\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{SO}_2]^-]$ . However, none of the additions of  $\text{PPN}^+ \text{Cl}^-$  resulted in the isolation of a solid with infrared spectroscopic properties expected for  $[\text{PPN}^+ [\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{SO}_2]^-]$ . There was no evidence of such metathesis, and the isolated materials were those likely originating from oxidation and/or decomposition of the iron carbonyl anions (*vide infra*) \*.

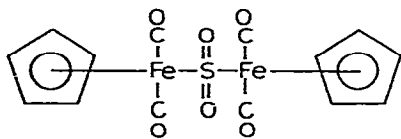
In subsequent experiments, reaction mixtures of  $\text{SO}_2$  and  $\text{Na}^+ [\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]^-$  in tetrahydrofuran at ca.  $-78^\circ\text{C}$  were allowed to warm to approximately room temperature, whereupon they acquired a dark reddish-brown color. Depending on the ratio of  $\text{SO}_2$  to  $\text{Na}^+ [\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]^-$  employed, different products were isolated when solvent was removed and the residue was chromatographed as described in the Experimental section.

When the ratio of  $\text{SO}_2$  to  $\text{Na}^+ [\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]^-$  was 1.5/1, work-up of the reaction mixture afforded  $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$  and two red solids, characterized (*vide infra*) as  $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2\text{SO}_2$ , a major product, and  $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})]_2(\text{CO})\text{SO}_2$ , a minor product. With a much higher, 30/1 ratio of  $\text{SO}_2$  to  $\text{Na}^+ [\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]^-$ , the isolated products were  $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$ ,  $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2\text{SO}_2$ , and the dithionite complex  $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{SO}_2]_2$ . The properties of the sulfur dioxide complexes  $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2\text{SO}_2$  and  $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})]_2(\text{CO})\text{SO}_2$ , both characterized by X-ray crystallography [9,12,13], are described in this paper, whereas the characterization and properties of  $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{SO}_2]_2$  [10] will be treated together with those of other, recently synthesized dithionite complexes in a separate publication [14].

The dinuclear  $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2\text{SO}_2$  (I) is reasonably stable in the solid; however, its solutions in benzene,  $\text{CHCl}_3$  or acetone decompose quite rapidly when exposed to air. An attempted sublimation at  $110^\circ\text{C}$  (0.15 Torr) for 17 h afforded

\* The anion  $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{SO}_2]^-$  was recently isolated as the potassium salt from reaction of  $\text{SO}_2$  with  $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]^-$ , prepared by the reduction of  $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$  with Na/K alloy in tetrahydrofuran (C.R. Jablonski, private communication).

only  $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$  in 66% yield. Likewise, heating  $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2\text{SO}_2$  in tetrahydrofuran at reflux for 2 h resulted in the formation of  $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$  (60% yield). This mode of decomposition and the apparent lack of volatility of  $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2\text{SO}_2$  both accord with its observed mass spectrum, which is essentially that of  $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$  [15].



(I)

The complex was characterized by elemental analysis and an osmometric molecular weight determination (Table 1), and its structure (I) was determined by X-ray crystallography [9,12]. A salient feature of the structure is the presence of sulfur dioxide as an unsupported bridging ligand attached to the iron atoms at short Fe—S bond distances of 2.28 Å. Such short bond lengths suggest considerable Fe—to—S  $\pi$ -bonding in these linkages. The infrared  $\nu(\text{SO}_2)$  absorptions, listed in Table 1, appear to support the above structural feature. The values of 1135 and 993  $\text{cm}^{-1}$  are appreciably lower than those reported for the  $\nu(\text{SO}_2)$  absorptions of metal carbonyl and related complexes containing either terminally bound  $\text{SO}_2$  or bridging  $\text{SO}_2$  in conjunction with a metal—metal bond. However, they are comparable to the  $\nu(\text{SO}_2)$  values of other metal carbonyl complexes that incorporate  $\text{SO}_2$  as an unsupported bridging group. These frequencies are given in Table 2. Other factors being equal, a sulfur dioxide ligand bonded to two metals would be expected to receive more  $\pi$ -electron density than an  $\text{SO}_2$  linked to only one metal, thus accounting for its lower  $\nu(\text{SO}_2)$ .

The second red complex,  $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})]_2(\text{CO})\text{SO}_2$  (II), a decomposition product of  $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2\text{SO}_2$  in solution, was isolated in low and erratic yields from the reaction mixtures of  $\text{SO}_2$  and  $\text{Na}^+ [\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]^-$ . The compound crystallizes as large octahedra which, however, undergo rather rapid decomposition on the surface upon exposure to air. This relatively low stability may account for the poor analytical data shown in Table 1. The mass spectrum of  $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})]_2(\text{CO})\text{SO}_2$ , like that of  $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2\text{SO}_2$ , is almost identical with the spectrum of  $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$  [15], indicating decomposition during the measurement.

The structure II of this complex was elucidated unambiguously by X-ray crystallography [13]. The molecules contain bridging CO and  $\text{SO}_2$  ligands and possess an overall *cis* geometry. The presence of a bridging CO is indicated by infrared absorptions at 1817(sh) and 1807  $\text{cm}^{-1}$  (Table 1). The  $\nu(\text{SO}_2)$  absorptions at 1185, 1175, 1045 and 1037  $\text{cm}^{-1}$  occur at higher frequencies than those for  $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2\text{SO}_2$ , which, as stated earlier, empirically accords with the presence of a metal—metal bond in the tricarbonyl complex.

The complex  $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})]_2(\text{CO})\text{SO}_2$  joins a growing family of  $\eta^5$ -cyclopentadienyliron carbonyls that adopt one or both of the isomeric structures IIIa (*cis*) and IIIb (*trans*). This group includes members with  $\text{L} = \text{L}' = \text{CO}$  [16,17],  $\text{L} = \text{L}' = \text{CS}$  [18],  $\text{L} = \text{CO}$  and  $\text{L}' = \text{Ge}(\text{CH}_3)_2$  [19],  $\text{L} = \text{L}' = \text{CNR}$  [20,21], and

TABLE 1  
PHYSICAL AND ANALYTICAL DATA FOR IRON-SULFUR DIOXIDE COMPLEXES

Complex	IR (cm <sup>-1</sup> ), <sup>a</sup>		<sup>1</sup> H NMR ( $\tau$ , ppm) <sup>b</sup>	Analysis (Found (calcd.)) (%)			Mol. wt. (Found (calcd.))
	$\nu(\text{CO})$	$\nu(\text{SO}_2)$		C	H	S	
[ $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2$ ] <sub>2</sub> SO <sub>2</sub>	2027s, 2015vs, 1965s, 1953vs <sup>c</sup>	1185, 998	5.06s	40.46 (40.28)	2.61 (2.41)	7.75 (7.67)	416 (418)
[ $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2(\text{CO})\text{SO}_2$	2040vs, 1995m-s, <sup>d</sup> 1817(sh), 1807m-s	1185, 1175, 1045, 1037	5.06s (5.18s)	35.0-36.5 (40.04)	2.16-2.27 (2.58)	6.71-7.90 (8.22)	518, 538 (390)

<sup>a</sup> Nujol mull except as noted. Abbreviations: vs, very strong; s, strong; m, medium; (sh) shoulder. <sup>b</sup> CDCl<sub>3</sub> or (acetone-d<sub>6</sub>) solution and tetramethylsilane as an internal standard. Abbreviation: s, singlet. <sup>c</sup> Simple group theoretical considerations predict 2, 3 or 4 IR-active  $\nu(\text{CO})$  absorptions for complexes of the type  $\eta^5\text{-C}_5\text{H}_5(\text{CO})_2\text{Fe-E}(\text{X})_2\text{-Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)$ , depending on the conformation. <sup>d</sup> CHCl<sub>3</sub> solution.

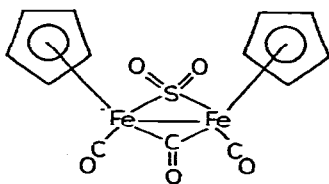
TABLE 2

INFRARED  $\nu(\text{SO}_2)$  ABSORPTIONS OF SOME METAL-SULFUR DIOXIDE COMPLEXES

Complex	Type <sup>a</sup>	$\nu(\text{SO}_2)$ ( $\text{cm}^{-1}$ ) <sup>b</sup>	Reference
$\eta^5\text{-C}_5\text{H}_5(\text{CO})_2\text{Fe-S(O)}_2\text{-Fe(CO)}_2(\eta^5\text{-C}_5\text{H}_5)$	A [9,12]	1135, 993	This work
$\text{K}_6[(\text{CN})_5\text{Co-S(O)}_2\text{-Co(CN)}_5]$	A	1078, 1072, 984	[33]
$[(\text{CH}_3)_4\text{N}]_2[(\text{CO})_5\text{Cr-S(O)}_2\text{-Cr(CO)}_5]$	A	1138, 980	[34]
$[(\text{CH}_3)_4\text{N}]_2[(\text{CO})_5\text{W-S(O)}_2\text{-W(CO)}_5]$	A	1138, 978	[34]
$\eta^5\text{-C}_5\text{H}_5(\text{CO})\text{Fe}(\mu\text{-CO})(\mu\text{-SO}_2)\text{Fe(CO)}(\eta^5\text{-C}_5\text{H}_5)$	B [13]	1185, 1175, 1045, 1037	This work
$(\text{CO})_4\text{Fe}(\mu\text{-SO}_2)\text{Fe(CO)}_4$	B [30]	1210, 1196, 1049 <sup>c</sup>	[28]
$\eta^5\text{-C}_5\text{H}_5\text{Mn(CO)}_2\text{SO}_2$	C [31]	1282 <sup>d</sup>	[35]
$\eta^6\text{-C}_6\text{H}_6\text{Cr(CO)}_2\text{SO}_2$	C	1253 <sup>d</sup>	[36]
$\eta^5\text{-C}_5\text{H}_5\text{Rh(C}_2\text{H}_4)\text{SO}_2$	C [32]	1258, 1105-1093	[37]
$\text{Rh}[\text{P(C}_6\text{H}_5)_3]_2\text{Cl(CO)SO}_2$	C' [3]	1214, 1188, 1057 <sup>c</sup>	[1]
$\text{Ir}[\text{P(C}_6\text{H}_5)_3]_2\text{Cl(CO)SO}_2$	C' [2]	1198, 1185, 1048 <sup>c</sup>	[1]

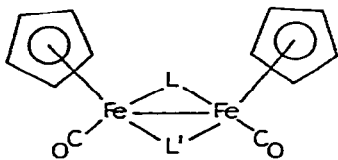
<sup>a</sup> A = unsupported  $\text{SO}_2$  bridge; B =  $\text{SO}_2$  bridge and M-M bond; C = terminal  $\text{SO}_2$ , planar  $\text{MSO}_2$ ; C' = terminal  $\text{SO}_2$ , nonplanar  $\text{MSO}_2$ . Structures determined by X-ray techniques are referenced. <sup>b</sup> In Nujol mull except as noted. <sup>c</sup> KBr pellet. <sup>d</sup> Benzene solution.

L = CO and L' = CNR [21], inter alia. The infrared spectra of the L = L' = CO complexes, in particular, have been thoroughly investigated in several solvents,

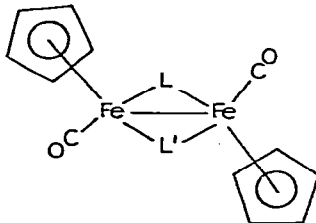


(II)

and an assignment of the  $\nu(\text{CO})$  bands was made to the two isomeric species [22]. By analogy with this assignment, the  $\nu(\text{CO})$  absorptions at 2040, 1995, and  $1807\text{ cm}^{-1}$  in  $\text{CHCl}_3$  solution (Table 1) may be attributed to the *cis* isomer of  $[\eta^5\text{-C}_5\text{H}_5\text{Fe(CO)}]_2(\text{CO})\text{SO}_2$ , which appears to be the sole species in the isolated solid. The origin of the shoulder at  $1817\text{ cm}^{-1}$  is uncertain. It may well be that some *trans*- $[\eta^5\text{-C}_5\text{H}_5\text{Fe(CO)}]_2(\text{CO})\text{SO}_2$  exists in solution, for its infrared terminal  $\nu(\text{CO})$  absorption would probably overlap with the band at  $1995\text{ cm}^{-1}$  [22].



(III a)



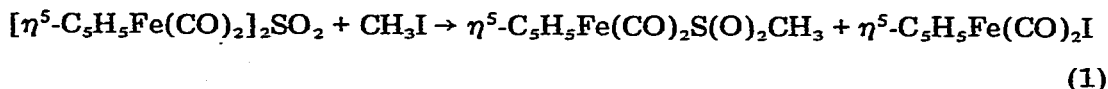
(III b)

However, if this isomer does exist, it must be present in low concentrations as inferred from the relative intensities of the  $\nu(\text{CO})$  bands at 2040 and 1995  $\text{cm}^{-1}$ . It is worthy of note that only one  $\eta^5\text{-C}_5\text{H}_5$  signal occurs in the  $^1\text{H}$  NMR spectra of the complex in  $\text{CDCl}_3$  or acetone- $d_6$ . Detailed studies on *cis-trans* isomerism in  $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})]_2(\text{CO})\text{SO}_2$  were not undertaken because of a rather low stability of the complex in solution.

#### Attempts at trapping $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{SO}_2]^-$

Unsuccessful attempts at isolation of  $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{SO}_2]^-$  from tetrahydrofuran solution by the addition of  $\text{PPN}^+\text{Cl}^-$  (vide supra) led to experiments aimed at trapping the above anion with various alkylating reagents, particularly with  $\text{CH}_3\text{I}$ . These reactions were conducted by adding the alkyl halide (or another alkylating reagent) to a tetrahydrofuran solution of  $\text{Na}^+[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]^-$  and  $\text{SO}_2$  prepared at low temperatures (generally  $-78^\circ\text{C}$ ). The reaction conditions and the results of these experiments are summarized in Table 3. Focussing on the data from the reactions that utilized  $\text{CH}_3\text{I}$ , it is of interest that both  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{I}$  and  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{S}(\text{O})_2\text{CH}_3$  were isolated as products. In those experiments where the quantities of the two iron dicarbonyl products were determined, the yield of the *S*-sulfinato complex (46%) substantially exceeded that of the iodo complex ( $\leq 15\%$ ). The formation of  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{I}$  may appear surprising and suggestive that the iron carbonyl-sulfur dioxide precursor of the isolated products is not  $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{SO}_2]^-$ . This is because metal carbonyl anions generally react with alkyl halides to afford the alkyl-metal carbonyls, but not the corresponding metal carbonyl halides [6]. Since the presumed  $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{SO}_2]^-$  appears to undergo conversion to the isolable  $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2\text{SO}_2$  under the experimental conditions that parallel those of the alkylation, reactions of this dinuclear complex with  $\text{CH}_3\text{I}$  were examined to shed more light on the origin of the products.

The reaction (eq. 1), conducted neat and in tetrahydrofuran solution, pro-



ceeded at a reasonable rate upon heating to afford good yields of  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{I}$  (54–56%) and much lower yields of  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{S}(\text{O})_2\text{CH}_3$  (21–26%). Thus it appears that  $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2\text{SO}_2$  is not the primary source of the *S*-sulfinato product formed by the alkylation of the solutions of  $\text{Na}^+[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]^-$  and  $\text{SO}_2$  at low temperatures. Whether the anion  $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{SO}_2]^-$  is the principal precursor of the *S*-sulfinato cannot be stated with certainty. However, this may well be so for the following reasons.

Reactions of  $\text{CH}_3\text{I}$  with tetrahydrofuran solutions of  $\text{Na}^+[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]^-$  and equimolar  $\text{SO}_2$  yield very little, if any,  $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2\text{SO}_2$  when the solutions are allowed to warm to approximately room temperature. This indicates that  $\text{CH}_3\text{I}$  quite effectively traps either  $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2\text{SO}_2$  or a precursor thereof. The low temperatures employed in these reactions, along with considerations of reactivity of  $\text{CH}_3\text{I}$  toward various iron carbonyl-sulfur dioxide complexes, both suggest that the trapped species is either  $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{SO}_2]^-$  or one with similar expected chemical properties. The reaction of  $\text{Na}^+$

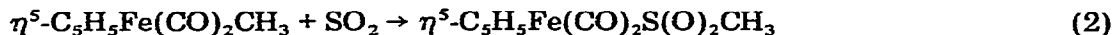
TABLE 3

REACTIONS OF Na<sup>+</sup> [ $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2$ ]<sup>-a</sup> WITH SO<sub>2</sub>-RX IN TETRAHYDROFURAN

Experiment	Addition of SO <sub>2</sub>	Addition of RX <sup>b</sup>	Products <sup>c, d, e</sup>
I	21.4 mmol over 80 min at -78°C, stir 100 min at -78°C, warm <sup>f</sup> for 25 min	48 mmol of CH <sub>3</sub> I, stir 21 h	46% $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{S}(\text{O})_2\text{CH}_3$ , 4% $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{I}$
II	28.4 mmol over 4 h at -78°C, warm <sup>f</sup> for 1 h	30 mmol of CH <sub>3</sub> I, stir 12 h	18.4% $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{S}(\text{O})_2\text{CH}_3$ <sup>g</sup>
III	41.6 mmol over 3 h at -78°C, warm <sup>f</sup> for 6 h	32.1 mmol of CH <sub>3</sub> I, stir 15 h	26.1% $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{S}(\text{O})_2\text{CH}_3$ <sup>g</sup> , [ $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2$ ] <sub>2</sub> SO <sub>2</sub>
IV	20 mmol over 4 h at -78°C, stir 1 h at -78°C	40.1 mmol of CH <sub>3</sub> I at -78°C, stir 10.5 h, warm for 3.5 h	22.4% $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{S}(\text{O})_2\text{CH}_3$ <sup>g</sup>
V	20 mmol at -70°C	20 mmol of CH <sub>3</sub> I at -70°C, stir 11 h at -70 to -30°C	46% $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{S}(\text{O})_2\text{CH}_3$ , 15% $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{I}$
VI	21.4 mmol over 80 min at -78°C, stir 100 min at -78°C, warm <sup>f</sup> for 25 min	48 mmol of <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SO <sub>3</sub> CH <sub>3</sub> , stir 21 h	2% $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{S}(\text{O})_2\text{CH}_3$ , [ $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2$ ] <sub>2</sub> SO <sub>2</sub> , [ $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})$ ] <sub>2</sub> (CO)SO <sub>2</sub>
VII	41.6 mmol over 5.5 h at -78°C, warm <sup>f</sup> for 2.5 h	21.1 mmol of (CH <sub>3</sub> O) <sub>2</sub> SO <sub>2</sub> , stir 22 h	No IR evidence of $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{S}(\text{O})_2\text{CH}_3$ ; [ $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2$ ] <sub>2</sub> SO <sub>2</sub> , [ $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})$ ] <sub>2</sub> (CO)SO <sub>2</sub>
VIII	20 mmol at -70 to -60°C	100 mmol of CH <sub>3</sub> Br at -70 to -60°C, stir 22 h at -70 to -60°C, stir 6 h at -20 to -13°C	69% $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{S}(\text{O})_2\text{CH}_3$ ; no IR evidence of $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{Br}$
IX	20 mmol at -70°C	20 mmol of C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl at -70°C, stir 60 h at -70 to -43°C	15% $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{S}(\text{O})_2\text{CH}_2\text{C}_6\text{H}_5$ ; no IR evidence of $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{Cl}$

<sup>a</sup> From 10 mmol of [ $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2$ ]<sub>2</sub>. <sup>b</sup> Following "addition of SO<sub>2</sub>". <sup>c</sup> [ $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2$ ]<sub>2</sub> was obtained in all experiments. <sup>d</sup> The formation of  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{I}$  was not examined in experiments II, III, and IV. <sup>e</sup> Other, minor products were also detected upon chromatography but were not fully characterized. <sup>f</sup> After the cooling bath had been removed, the reaction flask was maintained at room temperature. <sup>g</sup> Possible losses sustained through coprecipitation with NaI.

$[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]^-$  with  $\text{CH}_3\text{I}$  to give  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CH}_3$ , followed by  $\text{SO}_2$  insertion (eq. 2), a reasonable alternative to the above proposal, may be readily



dismissed from the reported kinetic data [23] and from the following additional experiments. First, there is no observable reaction between  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{-CH}_2\text{C}_6\text{H}_5$  and  $\text{SO}_2$  under the conditions that mirror those of Experiment IX in Table 3. Second, as reported previously [24], reaction of  $\text{Na}^+ [\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]^-$  with  $\text{SO}_2$  followed by  $\text{BrCH}_2\text{C}\equiv\text{CCH}_3$  yields  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{S}(\text{O})_2\text{CH}_2\text{C}\equiv\text{CCH}_3$ , whereas  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CH}_2\text{C}\equiv\text{CCH}_3$  and  $\text{SO}_2$  afford  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{C}=\text{C}(\text{CH}_3)\text{-S}(\text{O})\text{OCH}_2$ . Third, the interaction of  $\text{ClCH}_2\text{CH}=\text{C}(\text{CH}_3)_2$  with a mixture of  $\text{Na}^+ [\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]^-$  and  $\text{SO}_2$  affords  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{S}(\text{O})_2\text{CH}_2\text{CH}=\text{C}(\text{CH}_3)_2$  exclusively, but  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CH}_2\text{CH}=\text{C}(\text{CH}_3)_2$  and  $\text{SO}_2$  yield the two isomers  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{S}(\text{O})_2\text{CH}_2\text{CH}=\text{C}(\text{CH}_3)_2$  and  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{S}(\text{O})_2\text{C}(\text{CH}_3)_2\text{CH}=\text{CH}_2$  [25].

The formation of both  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{S}(\text{O})_2\text{CH}_3$  and  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{I}$  in the reactions under discussion may indicate that these products are derived in part from  $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2\text{SO}_2$  and  $\text{CH}_3\text{I}$ . Alternatively however, the interaction between  $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{SO}_2]^-$  (or a species with similar expected reactivity) and  $\text{CH}_3\text{I}$  may be a free radical one, affording both the iodo and *S*-sulfinato complexes. An earlier study [26] of the reaction of a tetrahydrofuran solution of  $\text{Na}^+ [\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]^-$  and  $\text{SO}_2$  with optically active  $\text{BrCH}(\text{CH}_3)\text{C}_6\text{H}_5$ \* revealed complete loss of stereochemistry upon the formation of  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{S}(\text{O})_2\text{CH}(\text{CH}_3)\text{C}_6\text{H}_5$ . This would seem to indicate a free radical pathway, a mechanism consistent with the nature of the products obtained in the alkylation reactions described herein.

Notwithstanding uncertainties in the identity of the reactive iron carbonyl-sulfur dioxide species, the solutions of  $\text{Na}^+ [\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]^-$  and  $\text{SO}_2$  serve as a useful reagent for the preparation of iron *S*-sulfinates that are inaccessible via the  $\text{SO}_2$  insertion reaction [24,25]. Very likely they possess a wider synthetic utility, which, however, still remains to be explored.

### Summary of reactions

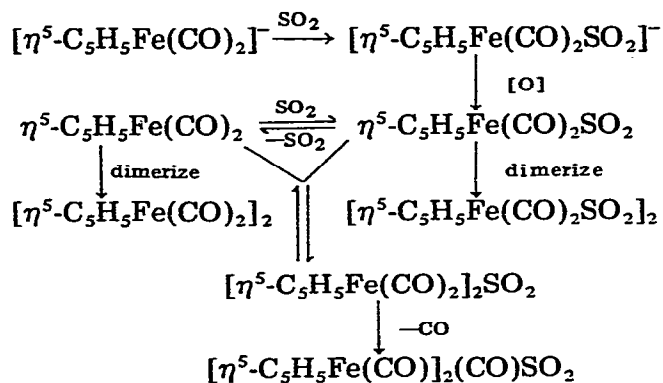
In conclusion, we wish to present a summary of reasonable pathways leading to the formation of various iron-sulfur dioxide products investigated in this work. These pathways are depicted in Scheme 1.

Because of the complexity of the reaction system  $\text{Na}^+ [\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]^-$  and  $\text{SO}_2$ , parts of the scheme are admittedly speculative. Moreover, no attempt was made to present all possible reactions; only those thought to be essential in the formation of various observed products are included. The identity of the oxidizing agent [O] is unknown; it may be  $\text{SO}_2$ , as air was excluded from these solutions. The species  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{SO}_2$  may undergo loss of  $\text{SO}_2$  by analogy

\* The experimental conditions for this reaction were similar to those employed for the reaction of  $\text{Na}^+ [\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]^- + \text{SO}_2$  with  $\text{ClCH}_2\text{CH}=\text{C}(\text{CH}_3)_2$  [25].



## SCHEME 1



with the reported [27] lability of metal carbonyl radicals. Coupling between the radicals  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2$  and  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{SO}_2$  would then account for the formation of  $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$ ,  $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2\text{SO}_2$ , and  $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{SO}_2]_2$ . The complex  $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2\text{SO}_2$  does not arise directly from  $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$  and  $\text{SO}_2$ , since we have shown that such an insertion reaction does not proceed at temperatures up to  $25^\circ\text{C}$ . However, it is worthy of note that reaction between  $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$  and  $\text{SO}_2$  at  $40^\circ\text{C}$  led to the isolation of a polynuclear  $(\eta^5\text{-C}_5\text{H}_5)_4\text{Fe}_4(\text{CO})_4(\text{SO}_2)_3$  upon work-up [28] \*.

### Experimental

Reactions were conducted in an atmosphere of nitrogen, which was also used routinely in the handling of organometallic compounds. Florisil (60–100 mesh) and Ventron or Woelm alumina, deactivated with  $\text{H}_2\text{O}$  (generally 6%), were employed in chromatographic separations and purifications. Anhydrous grade  $\text{SO}_2$  was purified as described previously [24]. Tetrahydrofuran (THF) was freshly distilled from  $\text{CaH}_2$  or  $\text{LiAlH}_4$  under nitrogen. All other chemicals and solvents procured commercially were reagent grade or equivalent quality and were used without further purification.

Melting points were obtained on a Thomas–Hoover capillary melting point apparatus and are uncorrected. Proton NMR spectra were taken on a Varian Associates A-60 or A-60A spectrometer. Infrared (IR) spectra were recorded on a Perkin–Elmer 337 or Beckman IR-9 spectrophotometer using polystyrene film for calibration. Mass spectra were recorded by Mr. C.R. Weisenberger on an A.E.I. Model MS-9 spectrometer at 70 eV. Molecular weights were measured on a Mechrolab Model 301-A vapor pressure osmometer in  $\text{CHCl}_3$  solution. Elemental analyses and some molecular weights were obtained by Galbraith Laboratories, Inc., Knoxville, Tenn., and Pascher Mikroanalytisches Laboratorium, Bonn, Germany.

\* The possibility that  $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2\text{SO}_2$  was formed in this reaction but decomposed to the "recovered"  $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$  cannot be ruled out because of the rather high temperatures employed in the work-up.

*Reaction of  $\text{Na}^+ [\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]^-$  with  $\text{SO}_2$*

A THF solution (120 ml) of  $\text{Na}^+ [\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]^-$ , prepared from 1.77 g (5.0 mmol) of  $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$  and freed from excess sodium amalgam and mercury, was cooled to ca.  $-78^\circ\text{C}$  and treated with 0.96 g (15 mmol) of  $\text{SO}_2$  dissolved in 20 ml of THF over a period of 10 min. The cooling bath was removed and the reaction mixture was allowed to warm to room temperature in 45–60 min. The solvent was evaporated in vacuo at room temperature, the residue was dissolved in  $\text{CHCl}_3$ , and the resulting solution was filtered through Florisil. The Florisil was washed with acetone and the combined wash and filtrate were evaporated to dryness. The residue was dissolved in minimum  $\text{CHCl}_3$  and chromatographed on a  $2.7 \times 25$  cm column of Florisil. Chloroform eluted off a purple band containing  $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$ , 10/1  $\text{CHCl}_3$ /acetone removed a narrow red band of  $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2(\text{CO})\text{SO}_2]$ , and then acetone removed another red band of  $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})]_2(\text{CO})\text{SO}_2$ , and then acetone removed another red dryness, the residue was dissolved in minimum  $\text{CHCl}_3$ , filtered, and the product was precipitated by the addition of pentane at  $0^\circ\text{C}$ . The yields of  $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})]_2(\text{CO})\text{SO}_2$  and  $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2\text{SO}_2$ , dec.  $142^\circ\text{C}$ , were 0.04 (2%) and 0.4–0.6 g (20–30%), respectively. Physical and analytical data for these complexes are furnished in Table 1.

Reaction between  $\text{Na}^+ [\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]^-$  and  $\text{SO}_2$  in THF was also carried out exactly as described above, but with a much larger, 7.0 g (110 mmol) amount of  $\text{SO}_2$ . Chromatography on Florisil afforded a purple band containing  $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$  (0.36 g), which was eluted off with  $\text{CHCl}_3$ , an orange band ( $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{SO}_2]_2$ ) removed with 5/1  $\text{CHCl}_3$ /acetone, and a red band ( $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2\text{SO}_2$ ) removed with acetone. The yields of  $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{SO}_2]_2$  and  $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2\text{SO}_2$  were 0.40 (17%) and 0.14 g (7%), respectively.

*Reaction of  $\text{Na}^+ [\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]^-$  with  $\text{SO}_2$  followed by  $\text{CH}_3\text{I}$*

A representative alkylation reaction of a mixture of  $\text{Na}^+ [\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]^-$  and  $\text{SO}_2$  is described below.

A THF solution (150 ml) of  $\text{Na}^+ [\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]^-$ , prepared from 3.54 g (10.0 mmol) of  $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$ , was cooled to  $-78^\circ\text{C}$ . Sulfur dioxide (0.94 ml of liquid, 21 mmol) was then passed into this solution in a stream of nitrogen over a period of 80 min. The resulting red reaction mixture was stirred at  $-78^\circ\text{C}$  for 100 min, allowed to warm for 25 min, treated with  $\text{CH}_3\text{I}$  (6.8 g, 48 mmol) and stirred at room temperature under a Dry Ice-cooled condenser for 21 h. Filtration, solvent removal from the filtrate, and chromatography of the residue on alumina (6%  $\text{H}_2\text{O}$ ) eluting with  $\text{CHCl}_3$ /acetone led to the isolation of a mixture of  $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$  and  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{I}$  (0.80 g, 15 and 4%, respectively, by IR spectroscopy) and of  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{S}(\text{O})_2\text{CH}_3$  (2.36 g, 46%). The insoluble solid from the reaction mixture was shown to be  $\text{NaI}$  (1.25 g).

Several other alkylation reactions were carried out under analogous and somewhat modified experimental conditions. These conditions and the results are summarized in Table 3. The *S*-sulfates  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{S}(\text{O})_2\text{R}$ , all known compounds [29], were characterized by IR spectroscopy.

### Reaction of $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2\text{SO}_2$ with $\text{CH}_3\text{I}$

A solution of 0.300 g (0.718 mmol) of  $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2\text{SO}_2$  in 20 ml of  $\text{CH}_3\text{I}$  in a sealed glass tube was maintained at 80–85°C for 3 h. The tube was cooled to room temperature and opened, the solvent was removed, and the residue was chromatographed on alumina to afford 0.245 g (56% yield) of  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{I}$  and 0.096 g (26% yield) of  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{S}(\text{O})_2\text{CH}_3$ .

When the same reaction between 0.230 g (0.550 mmol) of  $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2\text{SO}_2$  and 3.0 ml (48 mmol) of  $\text{CH}_3\text{I}$  was carried out in THF (20 ml) at reflux, 0.179 g (54% yield) of  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{I}$  and 0.059 g (21% yield) of  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{S}(\text{O})_2\text{CH}_3$  were isolated upon chromatography. There was no evidence of  $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$ .

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