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SULPHUR DIOXIDE REACTIONS OF METAL CARBONYLS AND CYCLOPENTADIENYL METAL CARBONYLS CONTAINING METAL–METAL BONDS

D. S. FIELD AND M. J. NEWLANDS
Department of Chemistry, Memorial University of Newfoundland, St. John's, Newfoundland (Canada)

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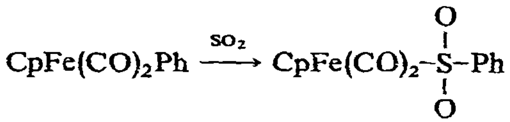
SUMMARY

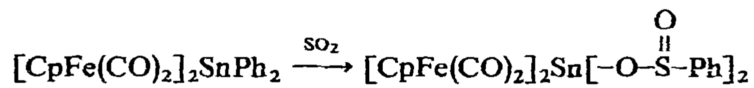
The reactions between sulphur dioxide and several metal carbonyls containing metal–metal bonds {$Fe_2(CO)_9$, $Fe_3(CO)_{12}$, $Co_2(CO)_8$, $(PPh_3)_2Co_2(CO)_6$, $[CpFe(CO)_2]_2$, $Mn_2(CO)_{10}$, $[CpMo(CO)_3]_2$} are reported. Only the compounds containing bridging carbonyl groups were found to react under the prevailing conditions. Diiron nonacarbonyl gives, in addition to the previously reported $Fe_2(CO)_8SO_2$, iron pentacarbonyl in comparable yield. Two crystalline isomeric compounds were obtained from bis(dicarbonyl-π-cyclopentadienyliron) and sulphur dioxide; structures for these isomers are proposed on the basis of IR evidence.

INTRODUCTION

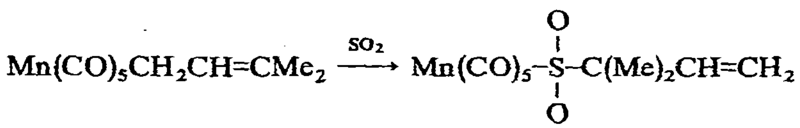
The reaction between sulphur dioxide and many organometallic compounds has been studied recently by several workers (*e.g.* refs. 1–6 and references therein). In the majority of cases a reaction occurs in which a sulphur dioxide molecule inserts in a variety of ways into a metal–carbon bond, *e.g.*[7,8,15]:



$$CpFe(CO)_2Ph \xrightarrow{SO_2} CpFe(CO)_2\text{–}\overset{\displaystyle O}{\underset{\displaystyle O}{S}}\text{–}Ph$$



$$[CpFe(CO)_2]_2SnPh_2 \xrightarrow{SO_2} [CpFe(CO)_2]_2Sn[\text{–}O\text{–}\overset{\displaystyle O}{\overset{\|}{S}}\text{–}Ph]_2$$



$$Mn(CO)_5CH_2CH{=}CMe_2 \xrightarrow{SO_2} Mn(CO)_5\text{–}\overset{\displaystyle O}{\underset{\displaystyle O}{S}}\text{–}C(Me)_2CH{=}CH_2$$

Insertions between Sn–Sn[4a], Fe–Sn[4a], Mn–Sn[4a], Cr–Cr[4b] and W–W[4b] have been claimed on the basis of IR evidence.

Sulphur dioxide also reacts with metal carbonyls in an exchange reaction with carbon monoxide in the presence of UV light. The tungsten and chromium products were not isolated pure but identified by IR spectroscopy and isolated as pyridine derivatives[9]:

$$(\mathrm{MeCp})\mathrm{Mn(CO)_3} \xrightarrow[\mathrm{UV}]{\mathrm{SO_2}} (\mathrm{MeCp})\mathrm{Mn(CO)_2SO_2}$$

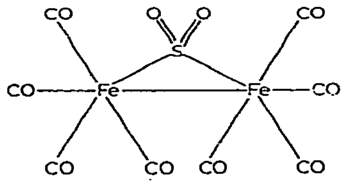
$$\mathrm{Cr(CO)_6} \xrightarrow[\mathrm{UV}]{\mathrm{SO_2}} [\mathrm{Cr(CO)_5SO_2}] \rightarrow \mathrm{Cr(CO)_5Py}$$

$$\mathrm{W(CO)_6} \xrightarrow[\mathrm{UV}]{\mathrm{SO_2}} [\mathrm{W(CO)_5SO_2}] \rightarrow \mathrm{W(CO)_5Py}$$

As part of our studies on sulphur dioxide reactions we have re-examined[10] the reaction between diiron nonacarbonyl and sulphur dioxide. Reactions involving metal carbonyls containing metal–metal bonds have also been studied to discover whether insertion between the metal–metal bond or substitution of carbon monoxide occurs.

DISCUSSION

Although Strohmeier[9] obtained no substitution product when iron pentacarbonyl was treated with sulphur dioxide under UV light, Braye and Hübel[10] found that diiron nonacarbonyl reacts in the absence of UV light to give μ-*S*-sulphinato-octacarbonyldiiron (18%) whose structure has been confirmed by X-ray analysis[11]:



In our hands diiron nonacarbonyl and sulphur dioxide after 2 h at −10° gave the yellow crystalline $\mathrm{Fe_2(CO)_8SO_2}$ (64%) and also a byproduct, iron pentacarbonyl (67%), which was not previously reported. No $\mathrm{Fe_3S_2(CO)_9}$ was detected[10]. The formation of $\mathrm{Fe(CO)_5}$ in reasonable yield suggests that $\mathrm{Fe_2(CO)_9}$ in the presence of sulphur dioxide eliminates $\mathrm{Fe(CO)_5}$ and undergoes reaction by the following process:

$$\mathrm{Fe_2(CO)_9 + SO_2 \rightarrow Fe(CO)_4SO_2 + Fe(CO)_5}$$

$$\mathrm{Fe(CO)_4SO_2 + Fe_2(CO)_9 \rightarrow Fe_2(CO)_8SO_2 + Fe(CO)_5}$$

The alternative mechanism involving reaction between carbon monoxide and $\mathrm{Fe_2(CO)_9}$ seems highly unlikely under the prevailing reaction conditions

$$\mathrm{Fe_2(CO)_9 + SO_2 \rightarrow Fe_2(CO)_8SO_2 + CO}$$

$$\mathrm{CO + Fe_2(CO)_9 \rightarrow 2Fe(CO)_5}$$

$Fe_2(CO)_8SO_2$ and $Fe(CO)_5$ were also obtained from the reaction between triiron dodecacarbonyl and sulphur dioxide although the mechanism of formation is undoubtedly more complex:

$$\begin{array}{lll} Fe_3(CO)_{12} \xrightarrow[50^\circ,\ 18\ h]{SO_2} & Fe_2(CO)_8SO_2 + & Fe(CO)_5 + \text{residue} \\ (6.0\ \text{mmole}) & (0.8\ \text{mmole}) & (6.6\ \text{mmole}) \end{array}$$

The IR spectrum of $Fe_2(CO)_8SO_2$ is tabulated in Table 1. The ν_s and ν_{as} of the SO_2 group are characteristic of *S*-sulfinates (Table 2). The mass spectrum was also

TABLE 1

IR SPECTRA OF $Fe_2(CO)_8SO_2$, (B), AND (A) (cm^{-1})

Assignment	$Fe_2(CO)_8SO_2$ (KBr)	(B) (KBr)	(A) (KBr)	(A) or (B) (CH_2Cl_2)
ν(CH)		3138 vw	3140 vw	
		3093 w	3094 w	
			3082 w	
ν(CO)	2133 vs			
	2088 vs	2055 (sh)	2055 vs	2057 vs
	2068 vs	2037 vs	2033 vs	2044 vs
	2049 vs	1994 vs	1993 (sh)	2010 vs
	2038 vs	1983 vs	1984 vs	1995 (sh)
	2017 vs			
		1426 vw	1427 w	
		1419 vw		
		1360 vw	1360 vw	
ν_{as}(SO)	1210 s	1233 m	1231 s	1232 s
	1196 (sh)	1223 s		
		1070 vw	1116 vw	
		1062 vw	1071 vw	
ν_s(SO)	1049 s	1016 s	1021 s	1022 vs
		1000 vw	969 vw	
δ(CH)		889 vw	888 w	
		864 w		
		855 w	855 w	
		838 vw		
ν(M–C) δ(M–C–O) $\nu(SO_2)$bend	615 s	612 m	608 m	
		592 m		
	554 w	569 m	571 m	
	532 m	543 m		
	502 w	534 m	537 m	
		528 m	531 m	
		511 vw	513 vw	
			493 vw	
	442 m	438 vw	441 vw	
			429 vw	
	394 w	390 vw		
	382 w		362 vw	
	302 vw			
	277 vw			
	267 vw			

TABLE 2

THE ν_s AND ν_{as}(S–O) STRETCHING FREQUENCIES (cm^{-1}) FOR SOME KNOWN *S*-SULPHINATES

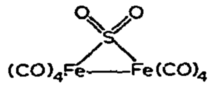
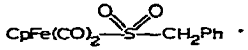
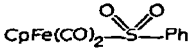
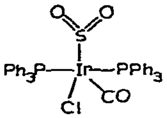
Compound	ν_{as}(S=O)	ν_s(S=O)	Ref.
	1210 1196	1049	This work
	1205	1050, 1045, 1038	7
	1195	1039	7
	1198 1185	1048	24
SO_2	1330 1308	1147	24

TABLE 3

MASS SPECTRUM OF $Fe_2(CO)_8SO_2$

Direct insertion probe at 100°, ionising electron beam of 70 eV. Abundance measured relative to *m/e* 64 (100%).

m/e	Abundance	Assignment (X^+)
456	0.05	$P+(CO)_2$
428	0.05	$P+CO$
400	0.05	P
372	0.05	$P-CO$
344	0.05	$P-(CO)_2$
316	0.15	$P-(CO)_3$
288	0.15	$P-(CO)_4$
260	0.15	$P-(CO)_5$
232	0.75	$Fe(CO)_4SO_2$
224	0.10	$Fe_2(CO)_4$
204	0.60	$Fe(CO)_3SO_2$
196	6.5	$Fe(CO)_5$
176	1.0	$Fe(CO)_2SO_2$
168	11	$Fe(CO)_4$
140	5.6	$Fe(CO)_3$
112	12	$Fe(CO)_2$
84	74	Fe(CO)
76	4.2	CSO_2?
64	100	SO_2
56	82	Fe
28	∞	CO

obtained although the parent ion was very weak compared with m/e 28 (CO^+) which formed the base peak (∞ abundance) and m/e 64 (SO_2^+) (100% abundance). The mass spectrum is shown in Table 3. The peaks at $m/e > 400$ are undoubtedly due to catalytic effects in the ion source[16,17].

Dicobalt octacarbonyl reacts with sulphur dioxide in an ampoule at 45° for 42 h. The black, air-sensitive product was not characterised, although it was shown to contain sulphur and carbonyl groups. The more stable cobalt carbonyl derivative, $Co_2(CO)_6(PPh_3)_2$, did not react with liquid sulphur dioxide, probably owing to its insolubility.

Bis(dicarbonyl-π-cyclopentadienyliron) has been shown to undergo insertion reactions with a variety of reagents, *e.g.*[12]:

$$[CpFe(CO)_2]_2 + SnCl_2 \cdot 2H_2O \rightarrow CpFe(CO)_2\text{–}SnCl_2\text{–}CpFe(CO)_2$$

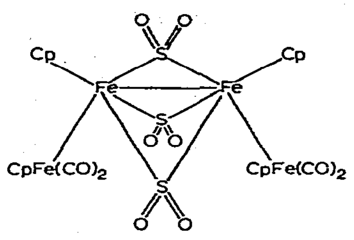
Thus, we were interested to see whether sulphur dioxide would insert in a similar manner to give $CpFe(CO)_2\text{–}SO_2\text{–}CpFe(CO)_2$ or whether substitution of carbon monoxide would occur, *cf.*[13].

$$[CpFe(CO)_2]_2 + PPh_3 \rightarrow Cp_2Fe_2(CO)_3(PPh_3) + CO$$

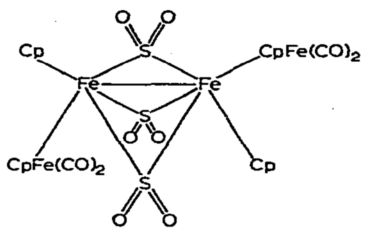
Bis(dicarbonyl-π-cyclopentadienyliron) and sulphur dioxide reacted during 48 h at 40° in an ampoule although no reaction occurred at room temperature. Extraction with acetone yielded a red-brown crystalline compound (B) on addition of a little petroleum ether and cooling.

On recrystallising from methylene chloride/petroleum ether, (B) gave a reddish crystalline material (A) with a slightly different IR spectrum from that of (B) (see Table 1). In solution both (A) and (B) are identical (NMR, IR) and can be interconverted since their formation depends on which solvent is last used for the recrystallisation. A similar situation has recently been reported with the parent compound. Bis(dicarbonyl-π-cyclopentadienyliron) can exist as two isomers in the solid phase which dissolve to give identical (IR, NMR) solutions[14].

The IR spectra of (A) and (B) are shown in Table 1. The strong absorptions at 1232 and 1022 cm^{-1} are assigned to ν_{as} and ν_s of an *S*-sulphinate group by comparison with other *S*-sulphinates (Table 2). The $\nu(CO)$ and $\tau(C_5H_5)$ of (A) or (B) in solution are very similar to those for $CpFe(CO)_2SO_2R$ and related compounds (Table 4). A $[CpFe(CO)(SO_2)]$ complex would be expected to show $\nu(CO)$ at a lower frequency and $\tau(C_5H_5)$ at a higher τ value than those observed for (A) and (B) based on a comparison with the analogous thiophenyl and other derivatives (Table 4). Furthermore, the 2 major bands at ca. 2050 and 2000 cm^{-1} observed for (A) and (B) in the solid phase can be assigned to a $[CpFe(CO)_2]$ group (plus a solid phase effect) whereas a $[CpFe(CO)]$ group should yield only one major absorption. The $\delta(CH)$ region for cyclopentadienyl groups in (A) and (B) indicates that all these groups are not equivalent. There are two absorptions at ca. 888 and 855 cm^{-1} suggesting that there are two types of C_5H_5 grouping in both (A) and (B). The lower absorption is assigned to $[CpFe(CO)_2]$ attached to an electron withdrawing group such as $-SO_2Ph$. The absorption at ca. 888 cm^{-1} indicates a cyclopentadienyl group attached to an iron atom having stronger electron withdrawing groups attached. The structures which are consistent with these observations and with an osmometric molecular weight determination (found: 781, calcd.: 788) are shown below:



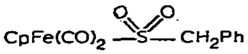
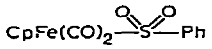
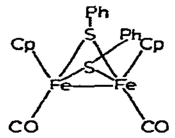
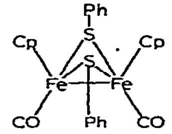
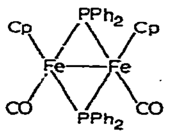
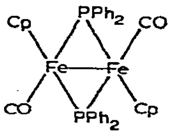
(B)*



(A)

TABLE 4

THE $\tau(C_5H_5)$ AND $\nu(CO)$ VALUES FOR SOME $CpFe(CO)_2X$ AND $CpFe(CO)LX$ COMPOUNDS[a]

Compound		$\tau(C_5H_5)$ (ppm)	$\nu(CO)$ (cm^{-1})	Ref.
 $CpFe(CO)_2{-}S(O)_2{-}CH_2Ph$		4.90 ($CDCl_3$)	2060, 2010 ($CHCl_3$)	7
 $CpFe(CO)_2{-}S(O)_2{-}Ph$		4.70 ($CDCl_3$)	2060, 2013 ($CHCl_3$)	7
$CpFe(CO)_2{-}S{-}Ph$		5.17 (CS_2)	2030, 1987 (CCl_4)	21
$CpFe(CO)_2{-}As(CF_3)_2$		5.08 (CCl_3F)	2038, 1995 (CS_2)	22
		5.51 (CS_2)	1978 (CCl_4)	21
		5.97 (CS_2)	1938 (CCl_4)	21
$[CpFe(CO)As(CF_3)_2]_2$		5.43 (CCl_3F)	1998, 1985, 1973 (CS_2)	22
	*cis*	6.01 (CS_2)	1961 (CS_2)	23
	*trans*	6.13 (CS_2)	1917 (CS_2)	23

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* There are in fact two *cis* isomers for an approximately octahedrally coordinated iron compound. In one the two cyclopentadienyl groups are *cis* to a SO_2 group, while in the other the two $CpFe(CO)_2$ groups are *cis* to SO_2.

As has been shown for the *cis* and *trans* isomers of bis(dicarbonyl-π-cyclopentadienyliron)[14], the *cis* isomer has the greater number of bands [ν(M–C) and δ(M–C–O)] around 600 cm^{-1} and also has the greater splitting of the δ(CH) around 850 cm^{-1}. Consequently we suggest that (B) is the *cis* isomer and (A) is the *trans* isomer.

In solution there are still 4 ν(CO) bands which indicates that there is a mixture of isomers in solution. The ν(CH) region (800–900 cm^{-1}) now shows only one absorption indicating that the cyclopentadienyl groups are in very similar environments and this is confirmed by the NMR spectrum which likewise shows only one absorption at room temperature. Hence the two isomers probably exist in equilibrium in solution, as has been found with $[CpFe(CO)_2]_2$[18,19].

A second major product was obtained from this reaction and recrystallised as a yellow powder from ethanol/petroleum ether. The IR spectrum and element analysis suggest that the compound is $CpFe(CO)_2$–$FeSO_3H \cdot H_2O$, possibly a decomposition product of (A) or (B) in ethanol solution.

The mass spectra of these products yielded very little information. This is probably due to the relative involatility of the samples and their thermal instability.

Dimanganese decacarbonyl and bis(tricarbonyl-π-cyclopentadienylmolybdenum) were completely recovered after treatment with sulphur dioxide in an ampoule (50°, 45 h; 50°, 48 h, respectively). The former readily dissolved in the sulphur dioxide whereas the latter was only slightly soluble. However, this lack of reactivity may be due to the absence of bridging carbonyl groups since these are present in the other compounds reported here which do react with sulphur dioxide*.

The results of this work show that metal carbonyl compounds with bridging carbonyl groups react with sulphur dioxide in the absence of UV light, whereas most compounds without carbonyl bridges appear to need UV irradiation for reaction to occur*. The formation of $Fe_2(CO)_8SO_2$ is not a simple carbon monoxide substitution reaction as might be inferred from a previous report. The product from bis(dicarbonyl-π-cyclopentadienyliron) and sulphur dioxide requires that a substitution process occurs, although the formation of this compound appears to be somewhat complex.

EXPERIMENTAL

The starting materials are commercially available and were purified where necessary by recrystallisation. Anhydrous grade sulphur dioxide (ex. Matheson) was dried by passing through conc. sulphuric acid and over phosphorus pentoxide/calcium chloride. The experiments were carried out under an atmosphere of nitrogen. IR spectra were obtained as KBr discs or in methylene chloride solution using a Perkin–Elmer Model 457 spectrometer. NMR spectra were recorded on a Varian HA-100 instrument operating at 100 MHz and for mass spectrometry a Perkin–Elmer–Hitachi RMU-6E spectrometer was employed. Element analyses were carried out by the A. Bernhardt Microanalytical Laboratory, West Germany.

Reaction between sulphur dioxide and metal carbonyls

(1). *Diiron nonacarbonyl*

Diiron nonacarbonyl (4.43 g, 12.2 mmole) and sulphur dioxide (ca. 25 ml) were

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* It should be noted, however, that Ruff achieved SO_2 insertion into the nonbridged carbonyl anions $[M_2(CO)_{10}]^{2-}$ (M = Cr, W) (ref. 4b). The rationale for the reactivity of metal carbonyls with respect to sulfur dioxide is by no means clear at present.

stirred under N_2 at $-10°$ during 2 h. The volatile material at room temperature was removed under reduced pressure and was collected in a trap at $-78°$. The contents of the trap were allowed to come to room temperature; the sulphur dioxide evaporated leaving a yellow liquid which was identified (IR, mass spec.) as iron pentacarbonyl (1.60 g, 8.17 mmole, 67%). The non volatile residue was a reddish-brown solid which recrystallised from methylene chloride to yield yellow crystals of μ-S-sulphinato-octacarbonyldiiron (1.55 g, 3.88 mmole, 64%) m.p. 100° decompn. (Found: C, 24.20; H, 0.00; S, 7.83; Residue, 38.66. $C_8Fe_2O_{10}$ calcd.: C, 24.03; H, 0.00; S, 8.02; Fe_2O_3, 39.95%.)

(2). *Triiron dodecacarbonyl*

Sulphur dioxide (ca. 25 ml) and triiron dodecacarbonyl (3.04 g, 6.04 mmole) were sealed *in vacuo* in a 100 ml thick-walled pyrex ampoule and placed in an oven at 50° for 18 h during which the initial dark green suspension/solution became a light brown precipitate in a yellowish solution. The volatile material was removed under reduced pressure and collected in a trap at $-78°$. The contents of the trap were allowed to come to room temperature; the sulphur dioxide evaporated leaving an orange liquid which was identified (IR) as iron pentacarbonyl (1.29 g, 6.56 mmole). The non-volatile residue was treated with acetone; recrystallisation from acetone/petroleum ether (b.p. 100–120°) yielded yellow crystals of μ-S-sulphinato-octacarbonyldiiron (0.164 g, 0.787 mmole). An insoluble brown material was obtained but not identified (0.94 g).

(3). *Dicobalt octacarbonyl*

Dicobalt octacarbonyl (4.26 g, 12.8 mmole) and sulphur dioxide (ca. 30 ml) were stirred under reflux ($-10°$) for 2 h. The brownish crystalline material appeared to dissolve in the sulphur dioxide to form a dark solution. The sulphur dioxide was removed under a stream of nitrogen leaving a brown residue which was shown by IR spectroscopy to be dicobalt octacarbonyl (4.07 g, 12.2 mmole, 96% recovery).

Reaction between dicobalt octacarbonyl and sulphur dioxide in an ampoule at 45° for 42 h and also by passing the gas through a benzene solution at 23° for 6 h led to the recovery (IR) of a small proportion of starting material. The remainder of the reaction product was found to contain sulphur but was not obtained in a pure state or characterised.

(4). *Bis[tricarbonyl(triphenylphosphine)cobalt]*

Sulphur dioxide (ca. 25 ml) and bis[tricarbonyl(triphenylphosphine)cobalt] (1.93 g, 2.38 mmole) were sealed *in vacuo* in a 100 ml pyrex ampoule and left at 22° for 24 h. No visible change occurred after 24 h; the cobalt compound appeared to be insoluble in the sulphur dioxide. The volatile material was removed under reduced pressure leaving a brownish solid identified by IR spectroscopy as bis[tricarbonyl-(triphenylphosphine)cobalt] (1.84 g, 2.27 mmole, 96% recovery).

(5). *Bis[dicarbonyl-π-cyclopentadienyliron]*

Bis(dicarbonyl-π-cyclopentadienyliron) (8.05 g, 22.7 mmole) and sulphur dioxide (ca. 25 ml) were sealed *in vacuo* in a 100 ml pyrex ampoule and placed in an oven at 40° for 48 h. The sulphur dioxide was removed under reduced pressure and the residue transferred to a Soxhlet apparatus. Extraction with benzene (150 ml) gave a black solid which was shown (IR) to be bis(dicarbonyl-π-cyclopentadienyliron) (1.92 g, 5.42 mmole, 24% recovery). The residue was treated with hot acetone (4 × 40 ml); addition of petroleum ether (b.p. 60–80°) gave reddish-brown crystals of (B)

(1.93 g, 2.45 mmole, 22%) decompn. ca. 175°. (Found: C, 36.38; H, 2.47; S, 12.21; Residue, 32.32. $C_{24}H_{20}Fe_4O_{10}S_3$ calcd.: C, 36.59; H, 2.56; S, 12.21; Fe_2O_3, 40.54%.)

The residue which was insoluble in acetone was treated with hot ethanol (3 × 40 ml); a brownish solid was filtered (0.365 g) but not identified. Evaporation of the filtrate gave a light brown solid which recrystallised from ethanol/petroleum ether (b.p. 60–80°) as a yellowish-brown powdery solid $CpFe(CO)_2FeSO_3H{\cdot}H_2O$ (4.29 g, 12.9 mmole 57%) decompn. ca. 180°. (Found: C, 25.60; H, 2.82; S, 10.03; Residue, 38.18; mol.wt. osmometric in methanol, 359. $C_7H_8Fe_2SO_6$ calcd.: C, 25.34; H, 2.43; S, 9.93; Fe_2O_3, 48.13%; mol.wt., 332.)

λ_{max} (KBr), 3380 m, 3115 w, 2977 vw, 2934 vw, 2054 vs, 2002 vs, 1628 w, 1429 m, 1423 (sh), 1244 m, 1182 vw, 1101 (sh), 1038 (sh), 976 s, 854 w, 836 vw, 621 m, 606 m, 576 s, 653 m, 495 m cm^{-1}.

Conversion of (B) into (A). (B) (0.33 g) was dissolved in methylene chloride (30 ml); petroleum ether (b.p. 60–80°) (1 ml) was added and the solution left at 0° overnight. The dark reddish crystals of (A) (0.018 g) were filtered and the filtrate evaporated to yield a further amount of (A) as a reddish powder (0.300 g) decompn. ca. 160°. (Found: C, 36.46; H, 2.45; S, 12.29; Residue, 33.34; mol.wt. osmometric in methanol, 781. $C_{24}H_{20}Fe_4O_{10}S_3$ calcd.: C, 36.59; H, 2.56; S, 12.21; Fe_2O_3, 40.54%; mol.wt., 788.)

It was also found that evaporation of a pure acetone solution of (B) afforded (A) as a reddish solid.

Conversion of A into B. (A) (ca. 0.1 g) was dissolved in acetone (50 ml); petroleum ether (b.p. 60–80°) was added and the solution evaporated to yield (B) as a reddish brown solid.

(6). *Dimanganese decacarbonyl*

Sulphur dioxide (ca. 20 ml) and dimanganese decacarbonyl (1.43 g, 3.68 mmole) were sealed *in vacuo* in a 100 ml thick-walled pyrex ampoule and placed in an oven at 50° for 45 h. The dimanganese decacarbonyl dissolved to form a dark solution. The volatile material was removed under reduced pressure leaving a yellow solid which sublimed *in vacuo* at 50° to yield dimanganese decacarbonyl (1.42 g, 3.64 mmole 99% recovery).

A similar experiment carried out at 22° for 24 h was also unsuccessful.

(7). *Bis(tricarbonyl-π-cyclopentadienylmolybdenum)*

Bis(tricarbonyl-π-cyclopentadienylmolybdenum) (4.20 g, 8.57 mmole) and sulphur dioxide (ca. 25 ml) were sealed *in vacuo* in a 100 ml pyrex ampoule and placed in an oven at 50° for 48 h. Very little of the purple solid appeared to dissolve. The sulphur dioxide was removed under reduced pressure and the residue extracted with acetone (ca. 50 ml) to yield bis(tricarbonyl-π-cyclopentadienylmolybdenum) (4.04 g, 8.24 mmole, 96% recovery).

Similar reactions in refluxing benzene and in methylene chloride at 28°, 54 h were unsuccessful. The starting material was recovered in good yield.

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