SYNTHESIS, CHARACTERIZATION AND SOME REACTIONS OF ORGANOMETALLIC COMPLEXES CONTAINING BRIDGING DITHIONITE LIGAND *

CRAIG A. POFFENBERGER, NORMAN H. TENNENT and ANDREW WOJCICKI **

The McPherson Chemical Laboratory, The Ohio State University, Columbus, Ohio 43210 (U.S.A.)

Summary

A novel organometallic dithionite complex, $[\eta^5\text{-}C_5H_5Fe(CO)_2SO_2]_2$, in which the $-S(O)_2S(O)_2-$ ligand bridges two iron atoms has been synthesized by four methods: treatment of $Na[\eta^5\text{-}C_5H_5Fe(CO)_2]$ with a large excess of SO_2, insertion of SO_2 into $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2SO_2$, reaction of $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2Hg$ with SO_2 and irradiation of $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2$ in the presence of SO_2. Of the four preparative routes, photolysis proved to be the most general one and also afforded the analogous complexes $[M(CO)_5SO_2]_2$ (M = Mn or Re) from $[M(CO)_5]_2$ and SO_2. However, irradiation of $[\eta^5\text{-}C_5H_5M(CO)_3]_2$ (M = Mo or W) and SO_2 yielded $[\eta^5\text{-}C_5H_5M(O)S]_2$ instead. The new dithionite complexes were characterized by elemental analysis and infrared and NMR spectroscopy. Photolysis of each of $[\eta^5\text{-}C_5H_5Fe(CO)_2SO_2]_2$ and $[Mn(CO)_5SO_2]_2$ resulted in loss of SO_2 to produce $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2SO_2$ plus $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2$ and $[Mn(CO)_5]_2$, respectively. The complex $[\eta^5\text{-}C_5H_5Fe(CO)_2SO_2]_2$ reacted with alkyl iodides (RI) on heating to give $\eta^5\text{-}C_5H_5Fe(CO)_2I$ and $\eta^5\text{-}C_5H_5Fe(CO)_2[S(O)_2R]$, and underwent alkylation by $(C_2H_5)_3OPF_6$ to yield $\eta^5\text{-}C_5H_5Fe(CO)_2[S(O)_2OC_2H_5]$, among other products. However, no reductive cleavage of $[\eta^5\text{-}C_5H_5Fe(CO)_2\text{-}SO_2]_2$ occurred with KH.

Introduction

It was recently reported from this laboratory that reaction of $Na[\eta^5\text{-}C_5H_5\text{-}Fe(CO)_2]$ with a modest excess (1.5-fold) of SO_2 affords the binuclear complexes $[\eta^5C_5H_5Fe(CO)_2]_2SO_2$ and $[\eta^5\text{-}C_5H_5Fe(CO)]_2(CO)SO_2$ [1,2]. However,

---

* Dedicated to Professor Helmut Behrens on the occasion of his 65th birthday on May 30, 1980.
** Author to whom inquiries about this paper should be addressed.

when a large excess (11-fold) of SO_2 was employed in the above reaction, a novel dithionite complex, $[\eta^5\text{-}C_5H_5Fe(CO)_2SO_2]_2$, formed in addition to the two iron-sulfur dioxide species [2,3]. The synthesis of $[\eta^5\text{-}C_5H_5Fe(CO)_2SO_2]_2$ prompted us to initiate a study with a view first to extending the range of known organometallic dithionite complexes by exploring several viable methods of preparation, and then to examining their chemical behavior. In this paper we describe the experiments that address both of the above points.

Experimental

Reactions were conducted under an atmosphere of dry nitrogen or argon, which were also used routinely in the handling of organometallic compounds. Florisil (60—100 mesh) and Ventron neutral alumina deactivated by the addition of H_2O (6%) were employed in chromatographic separations and purifications. Irradiation experiments were carried out in Pyrex tubes using a Rayonet Model RPR-100 photochemical reactor with sixteen 350 nm lamps. Melting points were obtained on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Elemental analyses were done by Galbraith Laboratories, Inc., Knoxville, Tennessee. ^1H NMR spectra were recorded on Varian Associates A-60A and EM-360L spectrometers using Me_4Si as an internal reference. ^{13}C NMR spectra were obtained on a Bruker HX-90 spectrometer at 22.625 MHz in a Fourier transform mode with the assistance of Dr. C.E. Cottrell. Infrared (IR) spectra were recorded on Beckman IR-9 and Perkin-Elmer Model 337 spectrophotometers using polystyrene film for calibration. Ultraviolet-visible spectra were obtained on a Cary 15 spectrophotometer. Molecular weight determinations in solution were performed on a Mechrolab Model 301-A vapor pressure osmometer. Mass spectra were obtained at 70 eV on an A.E.I. Model MS-9 spectrometer by Mr. C.R. Weisenberger.

Solvents were generally purified as described by Perrin et al. [4]. $W(CO)_6$, $[Co(CO)_4]_2$, $[Mn(CO)_5]_2$, $[Re(CO)_5]_2$, $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2$ and $[\eta^5\text{-}C_5H_5Mo(CO)_3]_2$ were purchased from Strem Chemicals; the four binary metal carbonyls were sublimed in vacuo. The following compounds were prepared by the indicated literature procedures: $\eta^5\text{-}C_5H_5Fe(CO)_2Cl$ [5], $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2SO_2$ [2], $\eta^5\text{-}C_5H_5Fe(CO)_2HgBr$ [6], $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2Hg$ [7], $[\eta^5\text{-}C_5H_5Mo(CO)_3]_2Hg$ [6], $[\eta^5\text{-}C_5H_5W(CO)_3]_2$ [8], $[\eta^5\text{-}C_5H_5W(CO)_3]_2Hg$ [6], $[Co(CO)_4]_2Hg$ [9], $[Co(CO)_3P(n\text{-}C_4H_9)_3]_2Hg$ [10] and $Tl_2S_2O_4$ [11]. Anhydrous grade SO_2 was purified as described previously [12]. $(C_2H_5)_3OPF_6$ was recrystallized from CH_2Cl_2 before use. All other commercially procured chemicals were reagent grade or equivalent quality and were used without further purification.

Preparation of $[\eta^5\text{-}C_5H_5Fe(CO)_2SO_2]_2$ (I)

(A). By reaction of $Na[\eta^5\text{-}C_5H_5Fe(CO)_2]$ with a large excess of SO_2. A THF solution (150 ml) of $Na[\eta^5\text{-}C_5H_5Fe(CO)_2]$, prepared from 3.54 g (10.0 mmol) of $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2$ and freed from excess 1% sodium amalgam and mercury, was cooled to —78°C and treated with 10 ml of liquid SO_2 in 10 ml of THF over a period of 5 min. The cooling bath was removed and the reaction mixture was allowed to warm to 25°C in 1 h. The solution was filtered, the filtrate was

TABLE 1

SPECTROSCOPIC DATA FOR METAL-DITHIONITE AND RELATED METAL-SULFUR DIOXIDE COMPLEXES

Complex	IR (cm^{-1})		UV-visible (nm) [c]
	$\nu(C\equiv O)$ [a]	$\nu(SO_2)$ [b]	
$[\eta^5\text{-}C_5H_5Fe(CO)_2SO_2]_2$ (I)	2070s, 2059s—vs, 2024vs	1223s, 1040s	318(sh), 438 (7100)
$[\eta^5\text{-}C_5H_5Fe(CO)_2]_2SO_2$ (II)	2027s, 2015vs, 1965s, 1953vs [d]	1135s, 993s [d]	332 (5400), 362 (sh)
$[Mn(CO)_5SO_2]_2$ (V)	2146s, 2090(sh), 2060vs, 2040vs	1224s, 1195w, 1070w, 1037s	383 (1670)
$[Re(CO)_5SO_2]_2$ (VI)	2150s, 2090(sh), 2060vs, 2035vs	1212s, 1190w, 1069w, 1031s	

[a] In CHCl$_3$ (Fe complexes) or CH$_2$Cl$_2$ (Mn and Re complexes) solution. [b] In Nujol mull. [c] In CH$_2$Cl$_2$ solution, 270—600 nm. [e] in parentheses. [d] From ref. 2. Abbreviations: vs, very strong; s, strong; m, medium; w, weak; sh, shoulder.

evaporated to dryness *, the residue was dissolved in minimum CHCl$_3$ and the resulting solution was chromatographed on a 2.5 × 27 cm column of Florisil. Chloroform eluted off a purple band containing 0.350 g (1.00 mmol) of $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2$, 5/1 (v/v) CHCl$_3$/acetone removed an orange band of $[\eta^5\text{-}C_5H_5Fe(CO)_2SO_2]_2$ (I), acetone removed a bright red band containing 0.150 g (3.6% yield) of $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2SO_2$ (II), characterized by IR spectroscopy [2], and finally methanol removed a narrow red band containing a trace amount of $[\eta^5\text{-}C_5H_5Fe(CO)]_2(CO)SO_2$ (III), also characterized by IR spectroscopy [2]. The orange effluent was evaporated to dryness, the residue was dissolved in minimum CHCl$_3$, and the resulting solution was filtered. Slow addition of cyclohexane to the filtrate gave 0.773 g (16% yield based on starting $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2$) of an orange powder, I, m.p. 140—146°C (dec.). Analysis. Found: C, 35.08; H, 2.10; S, 13.20%; mol. wt. (CHCl$_3$ solution), 501. C$_{14}$H$_{10}$Fe$_2$O$_8$S$_2$ calcd.: C, 34.88; H, 2.09; S, 13.30%; mol. wt., 482. Spectroscopic data are presented in Table 1.

(B). By reaction of [η^5-C$_5$H$_5$Fe(CO)$_2$]$_2$Hg with SO$_2$. Sulfur dioxide (20 ml of liquid) was condensed onto 1.61 g (2.91 mmol) of $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2$Hg in a round-bottom flask at —78°C. An acetone-Dry Ice condenser was attached to the flask and the reaction slurry was maintained at reflux for 9 h. As the mixture was allowed to warm to 25°C, the SO$_2$ evaporated to leave an oily residue. This residue was treated with CH$_2$Cl$_2$, and filtration through a sintered glass funnel removed 0.13 g (0.63 mmol) of metallic mercury. The filtrate was chromatographed on Florisil eluting with CH$_2$Cl$_2$ to yield a purple band of $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2$ (0.065 g, 6.3% yield) and a yellow band of unreacted $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2$Hg (0.048 g, 3.0% recovery). Continued elution with 2/1 (v/v) acetone/CH$_2$Cl$_2$ afforded an orange band, from which 0.390 g (23% yield) of $[\eta^5\text{-}C_5H_5Fe(CO)_2SO_2]_2$ (I) was obtained on evaporation of the solvent and crystallization from CH$_2$Cl$_2$/cyclohexane. Finally, elution with methanol

---

* The IR and ^{1}H NMR spectra of this crude material revealed the presence of [η^5-C$_5$H$_5$Fe(CO)$_2$SO$_2$]$_2$ and [η^5-C$_5$H$_5$Fe(CO)$_2$]$_2$SO$_2$.

removed an orange-red band which changed color to yellow on passing through the column. Removal of the solvent furnished 0.524 g of a yellow solid. Analysis. Found: C, 29.21; H, 2.09; S, 10.29% (C/H/S = 7.6/6.5/1.0). IR (Nujol mull, cm^{-1}): 2031s, 1969s, 1085s, 1015m, 976s, 844m, 836m, 634sh, 615s, 579s, 562s. Mass spectrum (80°C): material decomposed (weak isotopic pattern for Hg^+; m/e 186, $(C_5H_5)_2Fe^+$).

(C). By photolysis of $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2$ and SO_2. A solution of 0.333 g (0.941 mmol) of $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2$ in 50 ml of THF was saturated with SO_2 at 25°C and irradiated for 10 min while purging with CO. Sulfur dioxide was then passed through the solution for 10 min and the photolysis under CO was repeated. This cycle was carried out three times for a total photolysis time of 40—45 min. During this period, the solution darkened and an orange-brown precipitate appeared. Solvent was removed from the reaction mixture by rotary evaporation, the residue was extracted into $CHCl_3$ and the extract was chromatographed on Florisil. The elution procedure was identical with that described in (A) above and yielded, in the indicated order after removal of the solvent, 0.125 g of unreacted $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2$, 0.102 g (22.5%) of $[\eta^5\text{-}C_5H_5Fe(CO)_2\text{-}SO_2]_2$ (I) and 0.009 g of $[\eta^5\text{-}C_5H_5Fe(CO)]_2(CO)SO_2$ (III). Substantial amount of a brown non-carbonyl decomposition material remained at the top of the column.

(D). By reaction of $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2SO_2$ (II) with SO_2. Sulfur dioxide (ca. 5 ml of liquid) was introduced into a solution of 0.033 g of II in 10 ml of THF at —78°C. The resulting solution was stirred at —78°C for 2 h and then allowed to warm to ca. 25°C over a period of 1 h. Volatile matter was removed by rotary evaporation, the residue was dissolved in 5 ml of acetone and the solution was chromatographed on Florisil. Elution as described in (A) above yielded, after removal of the solvent, 0.007 g (30%) of $[\eta^5\text{-}C_5H_5Fe(CO)_2SO_2]_2$ (I) and 0.025 g (66% recovery) of unreacted II.

Preparation of $[Mn(CO)_5SO_2]_2$ (V)

In a typical reaction, 1.55 g (4.08 mmol) of $[Mn(CO)_5]_2$ under CO in a Pyrex tube fitted with an acetone-Dry Ice condenser and gas inlet and outlet was treated with 20 ml of liquid SO_2. The resulting solution was photolyzed for 6 h, during which time it changed color from pale yellow to deep red. The SO_2 was evaporated off and the residue was extracted with five 40 ml portions of cyclohexane. The extracts were combined and evaporated to dryness, and the remaining solid was sublimed to give 0.17 g (11% recovery) of unreacted $[Mn(CO)_5]_2$. The residue from the extraction was treated with 150 ml of benzene and filtered to afford a yellow solid and a red filtrate.

The filtrate was evaporated to dryness to yield 0.2 g of a red-purple solid. IR (Nujol mull, cm^{-1}): 2160w, 2115(sh), 2040s, 1985(sh), 1930s, 1160w, 1075w, 975w.

The yellow solid was extracted with 15 ml of 1/1 (v/v) THF/methanol and the mixture was filtered resulting in the collection of 0.191 g of V. Treatment of the filtrate with 15 ml of cyclohexane and cooling to 0°C gave 0.041 g of additional V, which was collected by filtration. Total yield 0.232 g (11%) of a yellow solid, m.p. (in vacuo) 115—124°C (dec.). Analysis. Found: C, 23.12; H, none or trace; S, 12.28%; mol. wt. (CH$_3$CN solution), 470. $C_{10}Mn_2O_{14}S_2$

calcd.: C, 23.18; H, 0,00; S, 12.38%; mol. wt., 518. Spectroscopic data are presented in Table 1.

Preparation of [Re(CO)₅SO₂]₂ (VI)

Preparation of [Re(CO)$_5$SO$_2$]$_2$ (VI)

In the apparatus used for the preceding synthesis, 1.30 g (2.35 mmol) of [Re(CO)$_5$]$_2$ dissolved in 40 ml of benzene under CO was treated with 30 ml of liquid SO$_2$, and the resulting solution was photolyzed for 8.5 h. During this period the color of the solution slowly changed from light yellow to bright orange. Evaporation of the SO$_2$ resulted in the formation of a white precipitate. The heterogeneous mixture was treated with an additional 80 ml of benzene and filtered to separate the white solid from an orange solution. The filtrate was evaporated to dryness and the residue was sublimed to give 1.15 g (88.3% recovery) of unreacted [Re(CO)$_5$]$_2$.

The white solid was treated with 25 ml of 4/1 (v/v) THF/methanol and the formed suspension was filtered resulting in the collection of 0.055 g (3.5% yield) of VI, m.p. (in vacuo) 168—170°C (dec.). Analysis. Found: C, 15.53; H, none or trace; S, 8.49%. C$_{10}$O$_{14}$Re$_2$S$_2$ calcd.: C, 15.39; H, 0.00; S, 8.21%. Spectroscopic data are furnished in Table 1.

Photolysis of [η^5-C$_5$H$_5$Mo(CO)$_3$]$_2$ and SO$_2$

A solution of 1.00 g (2.00 mmol) of [η^5-C$_5$H$_5$Mo(CO)$_3$]$_2$ in 30 ml of THF under CO was treated with 5 ml of liquid SO$_2$ and then photolyzed at —10°C in the aforementioned apparatus. During the irradiation the solution darkened and a brown precipitate formed. After 2 h, the SO$_2$ was allowed to evaporate and the THF was removed by rotary evaporation. The residue was extracted with CHCl$_3$ and the extract was chromatographed on Florisil. Elution with CHCl$_3$ removed a purple band containing 0.589 g of unreacted [η^5-C$_5$H$_5$Mo-(CO)$_3$]$_2$, and elution with acetone removed an orange band from which 0.077 g (12% yield) of [η^5-C$_5$H$_5$Mo(O)S]$_2$ [13] was obtained on evaporation of the solvent. Mass spectrum (80°C): prominent high m/e peaks at 418 (P^+, 16), 402 (($P-$O)$^+$, 100), 386 (($P-2$O)$^+$, 4), 353 (($P-$C$_5$H$_5$)$^+$, 8), 337 (($P-$C$_5$H$_5$ — O)$^+$, 44), 321 (($P-$C$_5$H$_5-2$O)$^+$, 16) ($P\equiv$[C$_5$H$_5$^{96}Mo(O)S]$_2$, relative intensities in parentheses).

Reaction of [η^5-C$_5$H$_5$Mo(CO)$_2$]$_2$ with SO$_2$

A solution of [η^5-C$_5$H$_5$Mo(CO)$_2$]$_2$ was prepared according to the literature [14] from 0.37 g (0.80 mmol) of [η^5-C$_5$H$_5$Mo(CO)$_3$]$_2$ in 50 ml of toluene. After 24 h of thermolysis, the decarbonylation was substantially more than 50% complete, as indicated by the relative intensities of the respective IR ν(C≡O) bands. The solution was then cooled to 0°C, 1 ml of toluene saturated with SO$_2$ (0.22 g of SO$_2$/ml of toluene [15]) was added and the resulting solution was stirred at 0°C for 45 min. Toluene was removed by rotary evaporation, the red solid was extracted into 10 ml of CHCl$_3$ and the extract was chromatographed on Florisil. Elution as in the preceding reaction and evaporation of the solvent from each effluent afforded 0.181 g of [η^5-C$_5$H$_5$Mo(CO)$_3$]$_2$ and 0.073 g (23% yield based on starting [η^5-C$_5$H$_5$Mo(CO)$_3$]$_2$) of [η^5-C$_5$H$_5$Mo(O)S]$_2$.

Reaction of Na[η^5-C$_5$H$_5$W(CO)$_3$] with SO$_2$

A THF solution (100 ml) of Na[η^5-C$_5$H$_5$W(CO)$_3$], prepared from 1.00 g (1.5

mmol) of $[\eta^5\text{-}C_5H_5W(CO)_3]_2$ and freed from excess 1% sodium amalgam and mercury, was cooled to $-78°C$ and treated with 10 ml of liquid SO_2. Immediately the solution changed color from yellow to purple; it was stirred for 25 min at $-78°C$ and then allowed to warm to ca. $25°C$ over a period of 1 h. The solvent was removed, the residue was treated with 20 ml of CH_2Cl_2 and the mixture was chromatographed on Florisil. Elution with CH_2Cl_2 developed a red-purple band, from which 0.70 g of $[\eta^5\text{-}C_5H_5W(CO)_3]_2$ was obtained on evaporation of the solvent. Continued elution with 1/1 (v/v) CH_2Cl_2/acetone removed an orange band, which on evaporation of the solvent yielded 0.054 g (6.1%) of a solid identified as $[\eta^5\text{-}C_5H_5W(O)S]_2$ (IV). Analysis. Found: C, 20.22; H, 1.43; W, 61.99%. $C_{10}H_{10}O_2S_2W_2$ calcd.: C, 20.09; H, 1.70; W, 61.90%. IR (KBr pellet, cm^{-1}): 3075m, 2082vw, 1500m, 1065m, 1015s, 910s, 851s, 836(sh), 817vs, 675m. Mass spectrum ($140°C$): prominent high m/e peaks at 594 (P^+, 100), 578 $((P-O)^+$, 92), 562 $((P-2\,O)^+$, 10), 529 $((P-C_5H_5)^+$, 32), 513 $((P-C_5H_5-O)^+$, 24), 498 $((P-2\,S-2\,O)^+$, 32), 433 $((P-C_5H_5-2\,S-2\,O)^+$, 12) ($P\equiv[C_5H_5{}^{184}W(O)S]_2$, relative intensities in parentheses).

Finally, elution with methanol removed a yellow band, from which 0.176 g of a yellow solid, m.p. 142–145°C (dec.), was obtained on evaporation to dryness of the effluent. This material decomposed to a white solid during attempts at crystallization from acetone/ether. Analysis of the yellow solid. Found (samples from two different preparations): C, 19.30, 20.80; H, 2.03, 1.90; S, 7.49, 7.17; W, 50.21, 37.88% (C/H/S/W = 6.8/8.6/1.0/1.17, 8.4/9.2/1.09/1.0). IR (Nujol mull, cm^{-1}): 2038s, 1945s, 1895s, 1141s, 1078m, 1063s, 1016w, 974s, 845m, 835m, 634s, 565m, 525m (The white decomposition product showed no $\nu(SO_2)$ bands). Mass spectrum ($120°C$): peaks at m/e corresponding to $(C_5H_5)W(CO)_{3,2,1}{}^+$ (60, 50, 42), $(C_5H_5)_2W^+$ (20), $(C_5H_5)W^+$ (100), $SO_2{}^+$ (>100) (relative intensities in parentheses).

Photolysis of $[\eta^5\text{-}C_5H_5W(CO)_3]_2$ and SO_2

The apparatus used for this photoreaction was that described earlier for the irradiation of $[Mn(CO)_5]_2$ and SO_2; it was modified, however, by the additional attachment of an evacuated gas bulb.

A solution of 0.203 g (3.05 mmol) of $[\eta^5\text{-}C_5H_5W(CO)_3]_2$ in 50 ml of THF under CO, treated with 5 ml of liquid SO_2, was photolyzed at $-10°C$ in the above closed system. During the irradiation the color of the solution changed from red-purple to orange, and a brown solid precipitated. The evacuated bulb was opened to the reaction system and a gas sample was collected. After 2 h, the SO_2 and THF were removed, the residue was extracted with 15 ml of CH_2Cl_2 and the extract was chromatographed on Florisil. Elution and subsequent workup as in the preceding reaction yielded 0.038 g (19% recovery) of unreacted $[\eta^5\text{-}C_5H_5W(CO)_3]_2$, 0.034 g (19%) of $[\eta^5\text{-}C_5H_5W(O)S]_2$ (IV) and 0.03 g of the yellow, unidentified material. The gas in the bulb was shown to contain CO_2 (in addition to SO_2) by IR spectroscopy ($\nu_3(CO_2)$ 2350 cm^{-1} [16]) and mass spectrometry (m/e 44, $CO_2{}^+$).

Photolysis of $[\eta^5\text{-}C_5H_5Fe(CO)_2SO_2]_2$ (I)

A solution of 0.10 g (0.21 mmol) of I in 45 ml of THF was irradiated for 15

min while slowly purging with CO. The color of the solution changed from orange to red-brown. Solvent was removed by rotary evaporation, the residue was dissolved in minimum CHCl$_3$ and the resulting solution was chromatographed on Florisil. Elution and workup as described earlier yielded 0.010 g (13%) of [η^5-C$_5$H$_5$Fe(CO)$_2$]$_2$, trace unreacted I and 0.023 g (26%) of [η^5-C$_5$H$_5$Fe(CO)$_2$]$_2$SO$_2$ (II).

Irradiation under comparable conditions for 1 h led to the formation of un-identified decomposition materials. None of [η^5-C$_5$H$_5$Fe(CO)$_2$]$_2$, I or II was detected on chromatography of the reaction mixture.

Photolysis of [Mn(CO)$_5$SO$_2$]$_2$ (V)

A solution of 0.09 g (0.2 mmol) of V in 40 ml of THF was irradiated for 10 min while slowly purging with CO. The color of the solution changed from light yellow to orange. Solvent was removed under reduced pressure and the yellow-brown residue was extracted with ca. 20 ml portions of benzene until the extract was colorless. The extracts were combined and the benzene was removed by rotary evaporation to leave 0.02 g (20% yield) of [Mn(CO)$_5$]$_2$.

The yellow-brown residue from the above extraction was treated with 10 ml of CH$_3$CN, and the resulting mixture was filtered to separate an orange solution from a small amount of a white solid. Evaporation to dryness of the filtrate afforded 0.045 g (50% recovery) of unreacted V.

Irradiation of 0.08 g of V under comparable conditions for 1 h led to the isolation of 0.018 g (30% yield) of [Mn(CO)$_5$]$_2$ and 0.024 g of a brown solid, IR (Nujol mull, cm^{-1}): 2150w, 2050s, 2040s, 1990s, 1940s, 1180—980w(br), 630s.

Thermolysis of [Mn(CO)$_5$SO$_2$]$_2$ (V)

Heating V at 74°C (1 Torr) for 2 h produced no change in color. However, on thermolysis at 97°C (1 Torr) for 2 h the solid slowly darkened from yellow to orange. IR (Nujol mull, cm^{-1}): 2100m, 2025s, 2010s, 1970m, 1175m(br), 910m(br), 635s, 615s. The resultant material was insufficiently volatile at 100°C for a mass spectrum to be obtained.

Reactions of [η^5-C$_5$H$_5$Fe(CO)$_2$SO$_2$]$_2$ (I) with alkyl halides

Generally, a solution of I and a large excess of the alkyl halide in 30 ml of THF was maintained at reflux for 3 h. After the reaction solution had cooled to room temperature, a small amount of insoluble material was removed by filtration. The filtrate was evaporated to a red oil *, which was dissolved in 10 ml of CHCl$_3$ and chromatographed on alumina using CHCl$_3$ for elution. Experimental details and results are summarized in Table 2. The products were identified by IR spectroscopy by comparison either with the spectra of authentic samples or with those reported in the literature (for η^5-C$_5$H$_5$Fe(CO)$_2$[S(O)$_2$R] [17]).

---

* When the alkyl halide was CH$_3$I, the ^{1}H NMR spectrum of the oil revealed the presence of η^5-C$_5$H$_5$Fe(CO)$_2$I and η^5-C$_5$H$_5$Fe(CO)$_2$[S(O)$_2$CH$_3$].

TABLE 2

REACTIONS OF $[\eta^5\text{-}C_5H_5Fe(CO)_2SO_2]_2$ (I) WITH ALKYL HALIDES

Alkyl halide	Amounts of reactants (mmol) ^{a}	Products ^{b}, yield (%)
CH_3I	0.43, 55.8	$\eta^5\text{-}C_5H_5Fe(CO)_2I$, 57
		$\eta^5\text{-}C_5H_5Fe(CO)_2[S(O)_2CH_3]$, 22
		$[\eta^5\text{-}C_5H_5Fe(CO)]_2(CO)SO_2$ (III), 1
C_2H_5I	0.43, 31	$\eta^5\text{-}C_5H_5Fe(CO)_2I$, 56
		$\eta^5\text{-}C_5H_5Fe(CO)_2[S(O)_2C_2H_5]$, 20
$2\text{-}C_3H_7I$	0.34, 26	$\eta^5\text{-}C_5H_5Fe(CO)_2I$, 60
		$\eta^5\text{-}C_5H_5Fe(CO)_2[S(O)_2C_3H_7\text{-}2]$, 8
C_2H_5Br	0.25, 39	$[\eta^5\text{-}C_5H_5Fe(CO)_2]_2$, 77
		$[\eta^5\text{-}C_5H_5Fe(CO)]_2(CO)SO_2$ (III), 15
$2\text{-}C_3H_7Br$	0.30, 35	$[\eta^5\text{-}C_5H_5Fe(CO)_2]_2$, 62
		$[\eta^5\text{-}C_5H_5Fe(CO)]_2(CO)SO_2$ (III), 9

^{a} First $[\eta^5\text{-}C_5H_5Fe(CO)_2SO_2]_2$, then the alkyl halide (in excess). ^{b} Listed in the order of elution from the column.

Reaction of $[\eta^5\text{-}C_5H_5Fe(CO)_2SO_2]_2$ (I) with $(C_2H_5)_3OPF_6$

A solution of 0.24 g (0.50 mmol) of I and 0.12 g (0.50 mmol) of $(C_2H_5)_3$-OPF_6 in 30 ml of CH_2Cl_2 was stirred at 25°C for 1.5 h, during which time it changed color from orange to red purple. The solution was then concentrated to 15 ml, resulting in the formation of a red precipitate, which was collected by filtration, 0.03 g. IR (Nujol mull, cm^{-1}): 2070s, 2010s, 840—820s. ^{1}H NMR (CD_3CN solution, τ): 4.55s ($\eta^5\text{-}C_5H_5$).

The filtrate was evaporated to a red oil, which showed the following signals in the ^{1}H NMR spectrum ($CDCl_3$ solution, τ): 4.42 s, 4.66 s, 4.71 s, 4.77 s ($\eta^5\text{-}C_5H_5$), 5.66 q ($J = 7$ Hz, CH_2), 8.77 t ($J = 7$ Hz, CH_3). The oil was dissolved in 15 ml of $CHCl_3$ and chromatographed on Florisil. Elution with 5/1 (v/v) $CHCl_3$/acetone developed a yellow band, which after removal from the column and evaporation to dryness afforded 0.038 g (17% yield) of known [18] $\eta^5\text{-}C_5H_5Fe(CO)_2[S(O)_2OC_2H_5]$, characterized by IR and ^{1}H NMR spectroscopy.

Attempted reaction of $[\eta^5\text{-}C_5H_5Fe(CO)_2SO_2]_2$ (I) with KH

To 0.44 g (0.90 mmol) of I and 0.063 g (1.6 mmol) of KH (93%) at —78°C, 15 ml of THF was added on the vacuum line. No evolution of H_2 was observed as the solution was stirred for 1 h. The reaction mixture was allowed to warm to —30°C (1,2-dichloroethane slush bath) and was stirred at that temperature for 1 h, again without any observable evolution of H_2. Finally, stirring at 23°C for 5.5 h also failed to produce H_2. Solvent was then removed and an IR spectrum of the residue showed unreacted I.

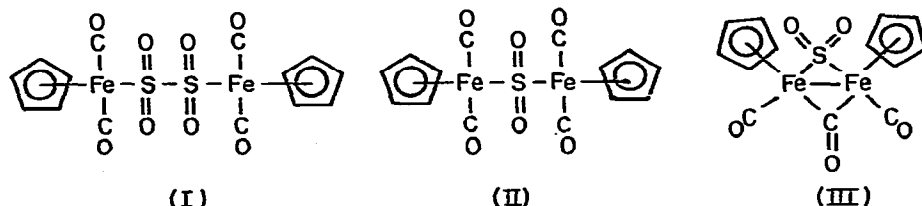### Results and discussion

Synthesis

Reaction of $Na[\eta^5\text{-}C_5H_5Fe(CO)_2]$ with a large excess of SO_2 in THF solution afforded the novel dithionite complex $[\eta^5\text{-}C_5H_5Fe(CO)_2SO_2]_2$ (I) in 16% yield,

in addition to $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2$, $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2SO_2$ (II) and $[\eta^5\text{-}C_5H_5\text{-}Fe(CO)]_2(CO)SO_2$ (III).


(I)   (II)   (III)

An examination by ^1H NMR and IR spectroscopy of the crude reaction mixture before workup revealed the presence of both I and II. Thus these complexes are formed during the reaction, and are not artifacts of the subsequent manipulations. Since previous work [2] has shown that reaction of $Na[\eta^5\text{-}C_5H_5\text{-}Fe(CO)_2]$ with a slight excess of SO_2 produces only $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2$, II and III, it appeared that the formation of I may result from insertion of SO_2 into II. In support of this proposal, I was indeed isolated when II and SO_2 reacted in THF solution.

The aforementioned reactions are thought to proceed by the thermal pathways depicted in Scheme 1. A considerable portion of this scheme has already been discussed [2].

SCHEME 1
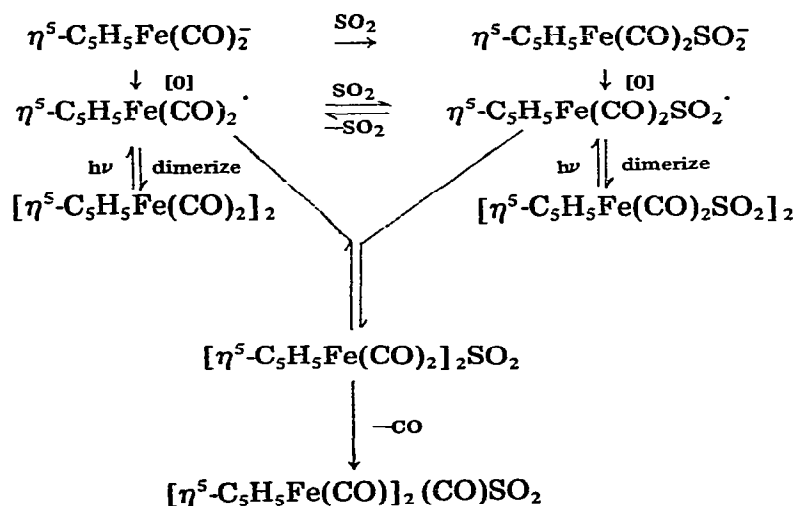
In an attempt to extend the range of organometallic dithionite complexes, reactions of each of $Na[\eta^5\text{-}C_5H_5Mo(CO)_3]$ and $Na[\eta^5\text{-}C_5H_5W(CO)_3]$ with SO_2 were examined. However, no characterizable SO_2-containing compounds were isolated. The reaction of the molybdenum carbonyl anion afforded $[\eta^5\text{-}C_5H_5\text{-}Mo(CO)_3]_2$, whereas that of the tungsten carbonyl anion yielded $[\eta^5\text{-}C_5H_5W\text{-}(CO)_3]_2$, $[\eta^5\text{-}C_5H_5W(O)S]_2$ (IV) and a yellow solid. The characterization of complex IV is detailed in the Experimental section; its structure has been assigned in analogy to the known structure [19] of the corresponding molyb-

(IV)
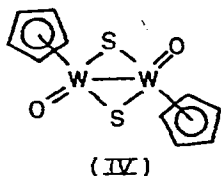
denum compound [13]. A possible mechanism leading to the formation of IV is presented later in this subsection. The yellow solid exhibited IR $\nu(C{\equiv}O)$ absorptions as well as the $\nu(SO_2)$ bands at 1141 and 1063 cm^{-1}. The elemental analysis showed a large variation in tungsten content (38—50%), although the W/S ratio was approximately 1/1. A facile decomposition to a white solid, showing no IR $\nu(SO_2)$ bands, during attempts at crystallization precluded full characterization of this yellow material. On the basis of the criteria set out by Kubas [20], the position of the $\nu(SO_2)$ bands best fits a structure in which SO_2 bridges two tungsten atoms.

Ligand substitution reactions were explored as an alternative, more direct route to I. However, reactions of η^5-$C_5H_5Fe(CO)_2Cl$ with each of $Na_2S_2O_4$ and $Tl_2S_2O_4$ in CH_3OH at 25°C for 24 and 17 h, respectively, afforded very small quantities of II, III and other unidentified products, but no complex I.

Since $SnCl_2$ is capable of displacement of Hg in $[\eta^5$-$C_5H_5Fe(CO)_2]_2Hg$ to yield $[\eta^5$-$C_5H_5Fe(CO)_2]_2SnCl_2$ [10], it was thought that SO_2, possessing amphoteric properties and a carbene-like structure in common with $SnCl_2$, might react in an analogous fashion with $[\eta^5$-$C_5H_5Fe(CO)_2]_2Hg$, first to yield II and then I. Indeed, reaction of $[\eta^5$-$C_5H_5Fe(CO)_2]_2Hg$ with a large excess of SO_2 afforded the desired I in 23% yield, in addition to $[\eta^5$-$C_5H_5Fe(CO)_2]_2$ and another product which has not been fully characterized (see the Experimental section). However, attempts at extending this reaction to other mercury derivatives of the metal carbonyls with a view to synthesizing dithionite complexes have again proved fruitless. Thus, interaction of each of $[\eta^5$-$C_5H_5Mo(CO)_3]_2Hg$, $[\eta^5$-$C_5H_5W(CO)_3]_2Hg$, $[Co(CO)_4]_2Hg$ and $[Co(CO)_3P(n$-$C_4H_9)_3]_2Hg$ with a large excess of SO_2 in THF at —10°C for at least 14 h resulted in a recovery of 82—96% of the starting metal carbonyl. By contrast, all of the aforementioned compounds react with $SnCl_2$ in a manner analogous to $[\eta^5$-$C_5H_5Fe(CO)_2]_2Hg$ [10]. It is also noteworthy that no reaction was observed between η^5-C_5H_5Fe-$(CO)_2HgBr$ and neat SO_2 at reflux in 3 h, indicating that the coordination environment of mercury can markedly influence reactivity toward SO_2.

The reactions leading to the formation of I and II in Scheme 1 are thought to involve metal-centered radicals. Thus, irradiation of $[\eta^5$-$C_5H_5Fe(CO)_2]_2$, which produces η^5-$C_5H_5Fe(CO)_2{}^\cdot$ [21], may be expected to furnish the desired dithionite complex in the presence of SO_2 by the route depicted in Scheme 1. The report that a prolonged thermal treatment of $[\eta^5$-$C_5H_5Fe(CO)_2]_2$ with SO_2 affords products other than I or II [22] does not militate against this expectation, since neither of these compounds would survive the conditions employed in the thermolysis. Besides η^5-$C_5H_5Fe(CO)_2{}^\cdot$, a large number of other metal-centered radicals have been generated by irradiation of the corresponding binuclear metal carbonyls at the frequency of the $\sigma \rightarrow \sigma^*$ transition of the metal—metal bond [21,23,24]. Therefore, photolysis of such carbonyl dimers in the

presence of SO_2 promised to represent a general approach to the synthesis of organometallic dithionite complexes.

Irradiation of $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2$ and SO_2 in THF solution indeed produced I, in a yield comparable to that from the reaction of $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2Hg$ with SO_2. Likewise, photolysis of $[M(CO)_5]_2$ (M = Mn or Re) and SO_2 afforded small amounts (11 and 3.5% yield, respectively) of the desired dithionite complexes, $[M(CO)_5SO_2]_2$ (V, M = Mn; VI, M = Re).

$$(OC)_5Mn-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}-Mn(CO)_5 \qquad\qquad (OC)_5Re-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}-Re(CO)_5$$

$$(\text{V}) \qquad\qquad\qquad\qquad\qquad\qquad (\text{VI})$$

No corresponding $[M(CO)_5]_2SO_2$ were observed in these reactions. The low yields may be ascribed to a photochemically induced extrusion of SO_2 from these three products to regenerate the respective metal carbonyl dimers. The absorption maxima in the UV-visible spectra of I and V, as well as of II (Table 1), occur at frequencies similar to those for the parent dimers, $[\eta^5\text{-}C_5H_5\text{-}Fe(CO)_2]_2$ [21] and $[Mn(CO)_5]_2$ [23]. The lamps employed in the irradiation supplied a sufficiently broad range of energy to cover these maxima and thus to promote both the forward and the reverse processes in eq. 1.

$$M-M \underset{\underset{-SO_2}{h\nu}}{\overset{\overset{h\nu}{SO_2}}{\rightleftharpoons}} M-S(O)_2-M \underset{\underset{-SO_2}{h\nu}}{\overset{\overset{h\nu}{SO_2}}{\rightleftharpoons}} M-S(O)_2S(O)_2-M \qquad\qquad (1)$$
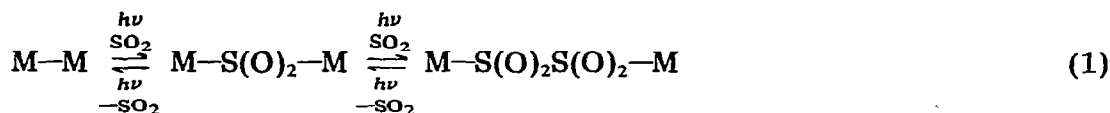
As described later in this paper, photolysis of I affords both II and $[\eta^5\text{-}C_5H_5\text{-}Fe(CO)_2]_2$, whereas photolysis of II yields $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2$. Furthermore, V decomposes under irradiation to give $[Mn(CO)_5]_2$.

Entirely different results were obtained when SO_2-saturated THF solutions of $[\eta^5\text{-}C_5H_5M(CO)_3]_2$ (M = Mo or W) were irradiated. In each case $[\eta^5\text{-}C_5H_5\text{-}M(O)S]_2$ was isolated, there being no evidence of formation of a dithionite complex.

Reaction of $[\eta^5\text{-}C_5H_5Mo(CO)_2]_2$, generated in situ, with SO_2 in toluene at $0°C$ also yielded $[\eta^5\text{-}C_5H_5Mo(O)S]_2$, thus suggesting that the photochemical reactions may well proceed as depicted in Scheme 2.

The metal—metal triple bond in $[\eta^5\text{-}C_5H_5M(CO)_2]_2$ has been reported to add unsaturated molecules, such as allenes [25] and acetylenes [26]. The bridging SO_2 is expected to possess very polar S—O bonds and may behave similarly to $(CH_3)_3NO$ [27] in oxidizing coordinated CO to CO_2. Carbon dioxide has, in fact, been isolated from the photochemical reaction of $[\eta^5\text{-}C_5H_5W(CO)_3]_2$ with SO_2. Scheme 2 also accounts for the formation of IV from $Na[\eta^5\text{-}C_5H_5W(CO)_3]$ and SO_2, as SO_2 can oxidize the carbonyl anion to $\eta^5\text{-}C_5H_5W(CO)_3{}^{\cdot}$, which would then enter the depicted sequence of reactions.

Characterization

The iron complex I was obtained as a bright orange solid which possesses

SCHEME 2
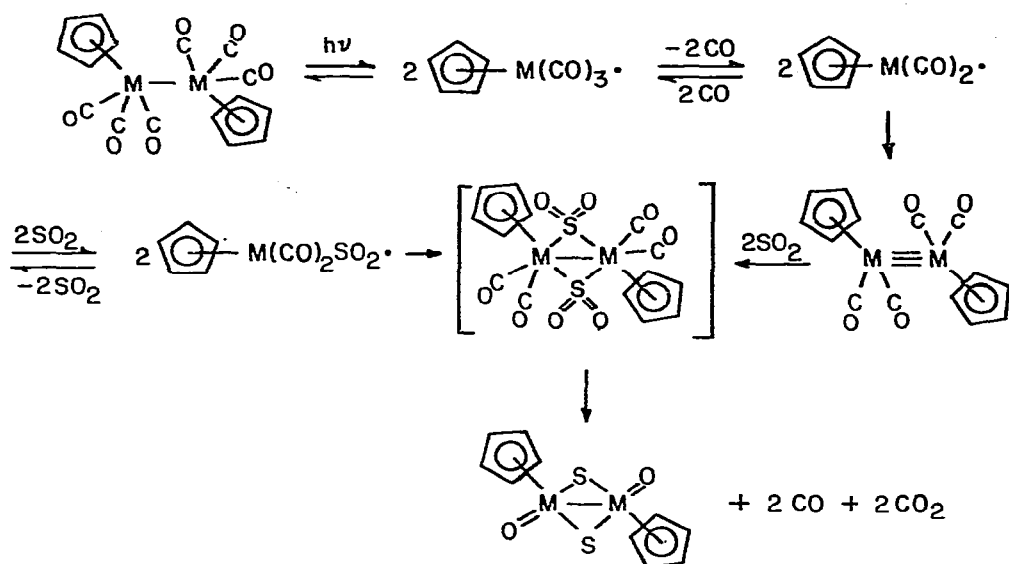
good stability to air. However, it slowly decomposes to III on storage in solution. The corresponding manganese and rhenium complexes, yellow V and white VI, respectively, also are stable to air in the solid. They (especially VI) exhibit much lower solubility in organic solvents than does complex I. All three dithionite compounds were characterized by elemental analysis, and the binuclear formulations of I and V are supported by molecular weight determinations in solution. However, attempts at measurement of the mass spectra of I, V and VI at 80°C proved unsuccessful. The recorded fragmentation patterns were those of the parent metal carbonyl dimers, along with peaks due to SO_2.

The ^1H NMR spectrum of I in $CDCl_3$ solution at 25°C shows a single η^5-C_5H_5 resonance at τ 4.64 ppm, whereas the ^{13}C NMR spectrum, also in $CDCl_3$ solution at 25°C, exhibits a CO resonance at 208.381 and an η^5-C_5H_5 resonance at 86.176 ppm downfield from Me_4Si. The η^5-C_5H_5 signal in both the ^1H and the ^{13}C NMR spectra remains sharp on lowering the temperature to —40 and —70°C, respectively, of the acetone-d_6 solutions. These data accord with the assigned dithionite structure I and rule out dissociation of this binuclear species into the η^5-C_5H_5Fe(CO)$_2$SO$_2^{\cdot}$ radicals in solution. By contrast, dithionite ion, $S_2O_4^{2-}$, undergoes some dissociation to SO_2^{-} when $Na_2S_2O_4$ dissolves in H_2O [28].

In the IR spectra of I, V and VI in Nujol mull, $\nu(SO_2)$ absorptions are observed at 1224—1212 and 1040—1031 cm^{-1}. These bands occur at considerably higher frequencies than those of the SO_2-bridged complex II (1135 and 993 cm^{-1}). In addition to supporting the same type of structure of the SO_2 groups in all three compounds, the positions of these absorptions reflect more sulfur—oxygen double bonding in I than in II. This presumably results from each Fe atom π-bonding to the empty $3d$ orbitals of the same S atom in II, but of a different S atom in I. As a further consequence, the extent of each Fe—S π-bonding interaction in II is more limited than in I, and more electron density is

shifted from the metal to the π^* orbitals of CO in II than in I. As shown in Table 1, $\nu(C\equiv O)$ absorptions of II indeed occur at considerably lower frequencies than those of I. It is noteworthy in this context that diphenyl-α-disulfone, $C_6H_5S(O)_2S(O)_2C_6H_5$, exhibits $\nu(SO_2)$ absorptions at substantially higher frequencies than either I, V and VI or II, 1325 and 1150 cm^{-1} [29], presumably because of little C_6H_5-S π-bonding therein.

The IR spectrum of I in CHCl$_3$ solution shows 3 $\nu(C\equiv O)$ bands; simple group theoretical considerations predict 2, 3 or 4 IR-active absorptions for complexes of the type η^5-C$_5$H$_5$(CO)$_2$Fe—X—Fe(CO)$_2$(η^5-C$_5$H$_5$), depending on the conformation. The number of observed bands points to C_{2v} molecular symmetry of I in solution. Both V and VI exhibit 4 IR $\nu(C\equiv O)$ absorptions in CH$_2$Cl$_2$ solution which may be assigned as follows in slightly perturbed C_{4v} local symmetry at metal [30]: 2146 (Mn) and 2150 (Re), A_1 (equatorial); 2090 (Mn, Re), B_1; 2060 (Mn, Re), E; and 2040 (Mn) and 2035 (Re), A_1 (axial). Thus, these solution spectra are in full agreement with the assigned structures.

Reactions

Several reactions of complexes I and V were investigated; they included thermolysis, photolysis and interaction with electrophilic and nucleophilic reagents. In addition to furnishing information on the chemistry of ligated dithionite, some of these studies provide results that strengthen the proposed structural formulations.

Thermolysis of I in THF solution at reflux for 3 h led to the isolation of [η^5-C$_5$H$_5$Fe(CO)$_2$]$_2$ (77%) and III (15%), which is known to arise from thermal decomposition of II. By contrast, heating V at 97°C (1 Torr) afforded an orange solid with broad IR bands at 1175—910 cm^{-1}, indicative of a sulfite or sulfate structure [31]. There was no evolution of SO$_2$ during the latter thermolysis. The different behaviors of I and V appear to reflect a stronger S—S bond and, possibly, M—S bonds in V than in I. Thermal decomposition of I most likely proceeds by homolysis of the S—S bond (eq. 2)

$$[\eta^5\text{-C}_5\text{H}_5\text{Fe(CO)}_2\text{SO}_2]_2 \rightarrow 2\ \eta^5\text{-C}_5\text{H}_5\text{Fe(CO)}_2\text{SO}_2^{\bullet} \qquad (2)$$

and subsequent reactions of the η^5-C$_5$H$_5$Fe(CO)$_2$SO$_2^{\bullet}$ radicals as depicted in Scheme 1. However, complex V may undergo decomposition by a redox process, the details of which cannot be elucidated from the present work.

Photolysis of I and V in THF solution led to the extrusion of SO$_2$ and the formation of [η^5-C$_5$H$_5$Fe(CO)$_2$]$_2$ and II from I, and of [Mn(CO)$_5$]$_2$ from V. As mentioned earlier in the paper, these reactions are thought to proceed via light induced homolysis of the S—S bond. It is of interest that the photolysis [32] and the thermolysis [33] of C$_6$H$_5$S(O)$_2$S(O)$_2$C$_6$H$_5$ proceed by the initial generation of C$_6$H$_5$SO$_2^{\bullet}$, and dissolution of Na$_2$S$_2$O$_4$ in water furnishes the radical anion SO$_2^{\bar{}}$ [28].

Reactions of I with alkyl iodides, RI, in THF at reflux afforded η^5-C$_5$H$_5$Fe-(CO)$_2$I and η^5-C$_5$H$_5$Fe(CO)$_2$[S(O)$_2$R], as summarized in Table 2. Under comparable conditions, there was no reaction between I and alkyl bromides, and only [η^5-C$_5$H$_5$Fe(CO)$_2$]$_2$ and III, both obtained previously from the thermolysis of I in THF, were isolated. This general behavior, coupled with the results of the alkylation of I by (C$_2$H$_5$)$_3$OPF$_6$ (vide infra), points to a free radical pathway

for the reaction between I and RI, with η^5-$C_5H_5Fe(CO)_2{}^\bullet$ (or, less likely, η^5-$C_5H_5Fe(CO)_2SO_2{}^\bullet$) abstracting iodine from RI. Metal-centered carbonyl radicals readily react with alkyl iodides to yield the corresponding metal carbonyl iodides [34]. The difference in behavior toward I of RBr and RI is presumably a manifestation of the lower rate of abstraction of bromine compared to iodine by radicals; for example, the reactions of methyl halides with Na atom show the same effect [35].

Thermolysis of V and CH_3I in a sealed tube at 80°C for 3 h led to a recovery of most of the dithionite complex (83%) and the isolation of trace unidentified brown solid. This result provides further indication that the S—S bond is more stable in V than in I.

Treatment of I with $(C_2H_5)_3OPF_6$ in CH_2Cl_2 solution at room temperature resulted in the formation of several products, as indicated by the presence of 4 η^5-C_5H_5 ^1H NMR resonances of the reaction mixture. Of these, only η^5-C_5H_5-$Fe(CO)_2[S(O)_2OC_2H_5]$ could be isolated after separation by column chromatography. The other compounds, which remained at the top of the column, have not been characterized, but they do not include any of the previously reported [2,17,18,36,37] η^5-$C_5H_5Fe(CO)_2$-containing complexes with sulfur-oxygen ligands. The formation of η^5-$C_5H_5Fe(CO)_2[S(O)_2OC_2H_5]$ would seem to point to an electrophilic attack of $C_2H_5{}^+$ at one of the oxygen atoms of the dithionite linkage of I.

Attempts at reductive cleavage of the S—S bond in I to form η^5-C_5H_5Fe-$(CO)_2SO_2{}^-$ proved unsuccessful. No reaction was observed when I was treated with KH in THF at 25°C. A reaction that occurred between I and $Na/K_{2.8}$ did not yield known [36] $K[\eta^5$-$C_5H_5Fe(CO)_2SO_2]$.

Acknowledgment

References

1 M.R. Churchill, B.G. DeBoer, K.L. Kalra, P. Reich-Rohrwig and A. Wojcicki, J. Chem. Soc., Chem. Commun., (1972) 981.
2 P. Reich-Rohrwig, A.C. Clark, R.L. Downs and A. Wojcicki, J. Organometal. Chem., 145 (1978) 57.
3 N.H. Tennent, S.R. Su, C.A. Poffenberger and A. Wojcicki, J. Organometal. Chem., 102 (1975) C46.
4 D.D. Perrin, W.L.F. Armarego and D.R. Perrin, Purification of Laboratory Chemicals, Pergamon Press, Oxford, 1966.
5 T.S. Piper, F.A. Cotton and G. Wilkinson, J. Inorg. Nucl. Chem., 1 (1955) 165.
6 M.J. Mays and J.D. Robb, J. Chem. Soc. A, (1968) 329.
7 E.O. Fischer and R. Böttcher, Z. Naturforsch., 10b (1955) 600.
8 R.B. King and F.G.A. Stone, Inorg. Synth., 7 (1963) 107.
9 W. Hieber, E.O. Fischer and E. Böckly, Z. Anorg. Allgem. Chem., 269 (1952) 308.
10 F. Bonati, S. Cenini and R. Ugo, J. Chem. Soc. A, (1957) 932.
11 P.W. Schenk and W. Müller, Angew. Chem., 69 (1957) 779.
12 J.E. Thomasson, P.W. Robinson, D.A. Ross and A. Wojcicki, Inorg. Chem., 10 (1971) 2130.
13 P.M. Treichel and G.R. Wilkes, Inorg. Chem., 5 (1966) 1182.
14 D.S. Ginley and M.S. Wrighton, J. Amer. Chem. Soc., 97 (1975) 3533; R.J. Klingler, W. Butler and M.D. Curtis, J. Amer. Chem. Soc., 97 (1975) 3535.
15 A. Seidell, Solubilities of Inorganic and Metal-Organic Compounds, Vol. II, 4th Ed., American Chemical Society, Washington, D.C., 1965, p. 1405.

16 K. Nakamoto, Infrared Spectra of Inorganic and Coordination Compounds, 2nd Ed., Wiley-Interscience, New York, 1970, p. 77.
17 J.P. Bibler and A. Wojcicki, J. Amer. Chem. Soc., 88 (1966) 4862.
18 C.A. Poffenberger and A. Wojcicki, J. Organometal. Chem., 165 (1979) C5.
19 D.L. Stevenson and L.F. Dahl, J. Amer. Chem. Soc., 89 (1967) 3721.
20 G.J. Kubas, Inorg. Chem., 18 (1979) 182.
21 H.B. Abrahamson, M.C. Palazzotto, C.L. Reichel and M.S. Wrighton, J. Amer. Chem. Soc., 101 (1979) 4123.
22 D.S. Field and M.J. Newlands, J. Organometal. Chem., 27 (1971) 221.
23 M.S. Wrighton and D.S. Ginley, J. Amer. Chem. Soc., 97 (1975) 2065.
24 M.S. Wrighton and D.S. Ginley, J. Amer. Chem. Soc., 97 (1975) 4246.
25 W.I. Bailey, Jr., M.H. Chisholm, F.A. Cotton, C.A. Murillo and L.A. Rankel, J. Amer. Chem. Soc., 100 (1978) 802.
26 W.I. Bailey, Jr., M.H. Chisholm, F.A. Cotton and L.A. Rankel, J. Amer. Chem. Soc., 100 (1978) 5764.
27 D.J. Blumer, K.W. Barnett and T.L. Brown, J. Organometal. Chem., 173 (1979) 71.
28 F.A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, 3rd Ed., Wiley-Interscience, New York, 1972, p. 451.
29 J.M. Squire and W.A. Waters, J. Chem. Soc., (1962) 2068.
30 C.S. Kraihanzel and F.A. Cotton, Inorg. Chem., 2 (1963) 533.
31 Ref. 16, pp. 87 and 107—110.
32 J.L. Kice and N.A. Favstritsky, J. Org. Chem., 35 (1970) 114.
33 M. Kobayashi, K. Tanaka and H. Minato, Bull. Chem. Soc. Jap., 45 (1972) 2906.
34 H.B. Abrahamson and M.S. Wrighton, J. Amer. Chem. Soc., 99 (1977) 5510.
35 H. Von Hartel and M. Polanyi, Z. Phys. Chem. (Frankfurt/Main), 11b (1930) 97.
36 C.R. Jablonski, J. Organometal. Chem., 142 (1977) C25.
37 C.A. Poffenberger and A. Wojcicki, manuscript in preparation.