

Sulfur-Donor Ligand Ortho-Metalated Complexes Derived from Thiobenzophenones. A Simple Approach to Isobenzothiophene Heterocycles

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Abstract: The first examples of sulfur-donor ligand ortho-metalated complexes were obtained in good to excellent yields by reaction of various thiobenzophenones with diiron enneacarbonyl in benzene at room temperature. The known trinuclear complex $S_2Fe_3(CO)_9$ was a by-product of these reactions, and complexes of the type $(Ar_2C)S_2Fe_2(CO)_6$ were formed in several instances. The structures of these complexes were established on the basis of microanalytical and spectral data as well as by reductive cleavage experiments. Oxidative or photolytic cleavage of the ortho-metalated complexes provides a convenient entry to the little-known isobenzothiophene system.

Since Parshall's¹ review in 1970, a substantial number of papers have appeared in the literature concerning the intramolecular ortho metalation of nitrogen²⁻¹⁹ or phosphorus²⁰⁻²⁸ donor ligands by transition metals. In this new type of aromatic substitution reaction, a metal atom replaces a hydrogen attached to an ortho

position of a benzene ring. The displaced hydrogen may be eliminated as H_2 or H^+ , or may be transferred to another atom (e.g., metal, a different carbon) in the molecule. This paper reports the first examples of a new class of ortho-metalated complexes, sulfur-donor ligand ortho-metalated complexes.

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Complexes having a sulfur and/or carbon atom coordinated to the metal have been isolated from treatment of carbon disulfide with metal carbonyls such as diiron enneacarbonyl $[Fe_2(CO)_9]$,²⁹ dicobalt octacarbonyl,³⁰ and alkylmanganese pentacarbonyls.³¹ There have been no reports on the reactions of thio-carbonyl compounds and simple metal carbonyls. The photochemical ligand substitution reaction of chromium and molybdenum hexacarbonyls with *s*-trithian and 2,4,6-trimethyl-*s*-trithian, cyclic trimers of thioformaldehyde and thioacetaldehyde, respectively, has been reported; however, these organic reactants should be regarded as cyclic sulfides or thioacetals, rather than thioaldehydes.³² This paper describes the reaction of thiobenzophenones with $Fe_2(CO)_9$.³³ When this investigation was undertaken, desulfurization, providing a novel source of free or complexes carbenes, was anticipated, by analogy with the formation of azobenzene by treatment of the corresponding sulfur diimide with iron pentacarbonyl.³⁴

Results and Discussion

Treatment of thiobenzophenone (1, $R_1 = R_2 = H$) and a variety of para mono- or disubstituted derivatives with $Fe_2(CO)_9$ in anhydrous benzene at room temperature gave the ortho-metalated complexes 2-7 in reasonable to excellent yields (Scheme I). Only one ortho-metalated complex can be obtained from a symmetrical thioketone, while more than one such complex may be produced when an unsymmetrical thiobenzophenone is reacted with $Fe_2(CO)_9$. For

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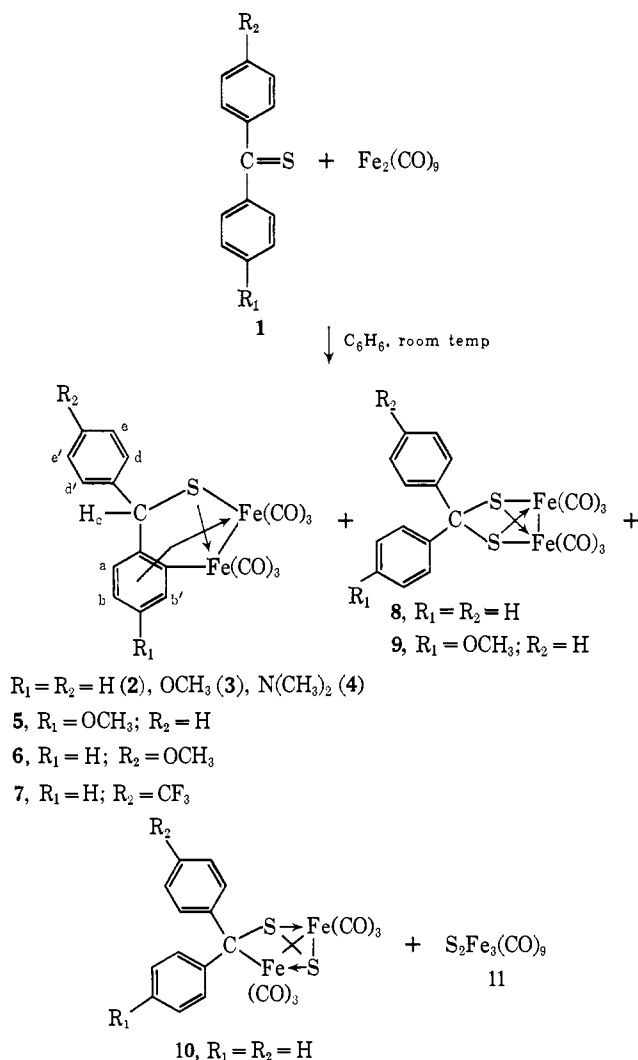
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Table I. Yields, Melting Points, and Analytical Data for Complexes Obtained from Reaction of Thiobenzophenones with Diiron Enneacarbonyl

Thiobenzophenone (1)	Products	Yield, %	Mp, °C ^a	Analyses found (calcd), %			
				C	H	S	Fe
R ₁ = R ₂ = H	2	51.6	85.5–86.0	47.46 (47.74)	2.26 (2.11)	6.45 (6.70)	
	8	< 5		44.80 (44.75)	2.17 (1.98)	12.46 (12.57)	
	10	8.5	160 dec	44.80 (44.75)	2.08 (1.98)	12.35 (12.57)	
R ₁ = R ₂ = OCH ₃	3	89.0	96.0–98.0	47.03 (46.88)	2.55 (2.62)	6.03 (5.96)	21.03 (20.76)
	11	5.8	113.0–114.0				
R ₁ = R ₂ = N(CH ₃) ₂	4	91.5	140.5–143.0	48.64 (48.97)	3.39 (3.57)	6.06 (5.68)	
	11	5.4	113.0–114.5				
R ₁ = H; R ₂ = OCH ₃	5	42.5	130.5–131.0	47.26 (47.28)	2.30 (2.38)	6.24 (6.31)	
	6	15.5	125.0–126.0	47.33 (47.28)	2.34 (2.38)	6.26 (6.31)	
	9	6.6					
	11	5.7	113.0–113.5				
R ₁ = H; R ₂ = CF ₃	7	64.0	108.0–118.0	43.68 (43.98)	1.74 (1.66)	6.23 (5.88)	20.46 (20.46)
	11	11.0	113.0–114.0				

^a In sealed capillary tubes. ^b Lit.³⁶ mp 114°.

Scheme I

example, the major ortho-metalated complex formed from reaction of 4-methoxythiobenzophenone and $Fe_2(CO)_9$ was **5**, which has the iron complexed to the methoxy substituted phenyl group. In contrast, the only ortho-metalated complex arising from 4-trifluoromethylthiobenzophenone has the unsubstituted phenyl group complexed to iron.

No deuterium incorporation was observed when the reaction was conducted in benzene- d_6 . Smaller

amounts of complexes **8–10** were produced in several instances, and the known^{35,36} complex $S_2Fe_3(CO)_9$ (**11**) was a by-product of these reactions. The yields, melting points, and analytical data for the complexes are given in Table I. Pertinent spectral data are listed in Tables II and III.

The structures of the purple red air stable complexes **2–7** were elucidated from analytical and spectral data and by means of decomplexation reactions.

All of the ortho-metalated complexes show three characteristic terminal metal carbonyl stretching bands at 2066.5–2075.0, 2029.5–2037.5, and 1995.0–2000.5 cm^{-1} (CCl_4). The position of the first two bands is significantly dependent on the nature of the substituent(s) with the trifluoromethyl complex **7** exhibiting absorptions at highest wave number, while bands at the low end of the frequency range are observed when dimethylamino groups are present (**4**). These results are consistent with literature data^{37,38} on other complexes which show that, for example, electron donation by a substituent (e.g., $N(CH_3)_2$, OCH_3) to the metal will result in increased back-bonding from the metal to the antibonding orbitals of the carbonyl ligands, and thereby lower ν_{CO} . The two bands for complexes **2** and **3** occur as expected, between those for **4** and **7**. The position of the methoxy group in the monomethoxy complexes **5** and **6** has a negligible effect on the position on the two high frequency carbonyl stretching bands, which is, for unknown reasons, closer to those of **2** than to those of **3**. The carbonyl stretching band at lowest frequency shows no correlation with substituent effects. None of the spectra displayed bands due to bridging carbonyls (1740–1900 cm^{-1}).

Vibrations in the 620–503- cm^{-1} region are assigned to Fe–C–O deformations.^{39–41} Numerous bands were observed in the 475–300- cm^{-1} region, some of which must be due to iron–carbon stretching.

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Table II. Infrared and Electronic Spectral Data for Complexes 2–11

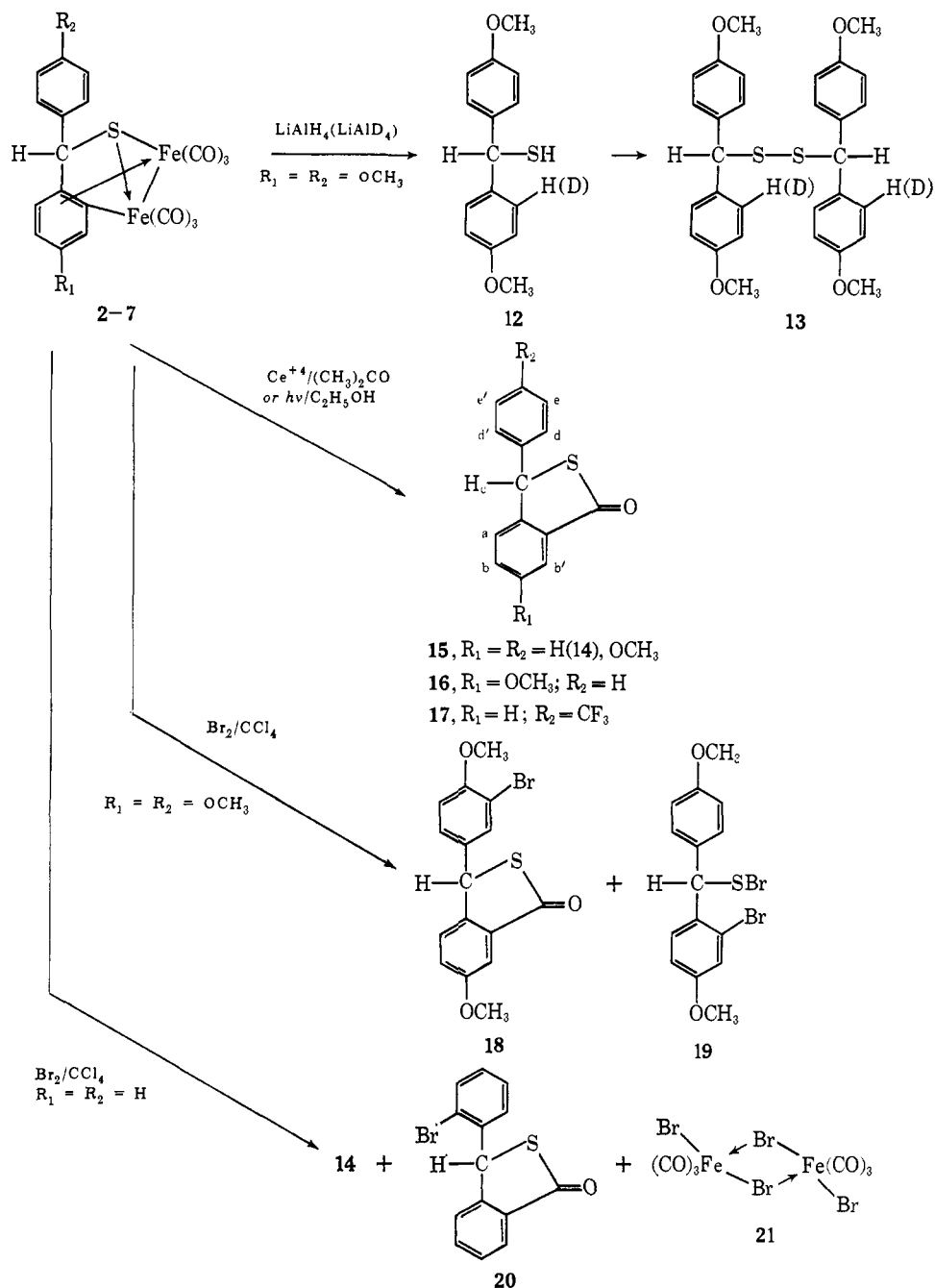
Complex	Infrared		Electronic absorption max ϵ , ^b cm ⁻¹
	ν_{CO} , ^a cm ⁻¹	δ_{FeCO} [solvent], cm ⁻¹	
2	2072 (m), 2034 (s), 1997 (s), 1981 (s, sh)	620 (m), 587 (m), 555 (m) [KBr] 601.5 (w), 580 (wm), 557 (w) [CCl ₄]	40,650 (21,165), 29,280 (8610), 20,830 (2020)
3	2069 (ms), 2033 (s), 1995 (s), 1979 (sh)	610 (w), 582 (w), 574 (w), 554 (w) [CCl ₄]	40,570 (25,700), 29,720 (9438), 21,280 (2390)
4	2066.5 (ms), 2029.5 (s), 2000.5 (s), 1972.0 (sh), 1947.5 (vw)	610 (m), 587 (m), 555 (m) [KBr]	40,650 (27,600), 37,735 (33,200), 29,540 (10,400), 20,830 (3040)
5	2072 (m), 2035 (vs), 2000 (vs), 1980 (sh)		40,485 (20,830), 29,410 (11,725), 20,830 (3510)
6	2072 (m), 2034 (s), 1998 (s), 1980 (sh)		40,485 (21,200), 29,940 (11,425), 21,280 (1780)
7	2100 (w), 2075 (ms), 2037.5 (vs), 2000 (s), 1986 (sh)	580 (w), 552 (w), 503 (vw) [CCl ₄]	40,650 (21,750), 29,325 (8340), 21,290 (2090)
8	2075 (vs), 2064 (m), 2044 (ms), 2035 (vs), 2023 (ms), 2007 (ms), 1981 (w)	597 (w), 579 (w), 562 (w) [CCl ₄]	
9	2081 (vs), 2074 (m), 2045 (s), 2034 (s), 2004 (vs), 1981 (s)	603 (w), 597 (w), 532 (w) [CCl ₄]	
10	2079 (ms), 2042 (s), 2002 (s), 1980 (vs)	618 (m), 560 (ms) [KBr] 620 (w-m), 565 (m) [CCl ₄]	40,240 (6200), 29,850 (7160)
11	2094 (vw), 2086 (vw), 2064.5 (s), 2045.5 (s), 2025 (s)	605 (vs, sh), 565 (vs) [KBr] 600 (w), 580–565 (w) [CCl ₄]	

^a CCl₄ solution: vs = very strong; s = strong; m = medium; w = weak; vw = very weak; vvw = very very weak; sh = shoulder.
^b *n*-Hexane solution.

Table III. Nmr and Mass Spectral Data for Complexes 2–10

Complex	Nmr, ^a δ , ppm ^a	Mass spectrum, <i>m/e</i>
2	5.57 (s, H _c), 6.49 (m, H _{dd'}), 6.92–7.70 (m, H _{ee'} , H _a , H _b , R ₁ = R ₂ = H), 8.40 (m, H _{b'})	478 [M] ⁺ , 450 [M – CO] ⁺ , 422 [M – 2CO] ⁺ , 394 [M – 3CO] ⁺ , 366 [M – 4CO] ⁺ , 338 [M – 5CO] ⁺ , 310 [M – 6CO] ⁺ , 254 [M – 6CO – Fe] ⁺ , 144 [Fe ₂ S] ⁺ , 112 [Fe ₂] ⁺ , 56 [Fe] ⁺
3	3.70 (s, R ₂ = OCH ₃), 3.83 (s, R ₁ = OCH ₃), 5.43 (s, H _c), 6.30 (d, H _{dd'} , J _{de} or J _{d'e'} = 8 cps), 6.66 (d, H _{ee'}), 6.86 (dd, H _b , J _{ab} = 9 cps, J _{bb'} = 2 cps), 7.54 (d, H _a), 7.63 (d, H _{b'})	538 [M] ⁺ , ^b 510 [M – CO] ⁺ , 482 [M – 2CO] ⁺ , 454 [M – 3CO] ⁺ , 426 [M – 4CO] ⁺ , 398 [M – 5CO] ⁺ , 370 [M – 6CO] ⁺ , 355 [M – 6CO – CH ₃] ⁺ , 144 [Fe ₂ S] ⁺ , 112 [Fe ₂] ⁺ , 56 [Fe] ⁺
4	2.82 [s, R ₂ = N(CH ₃) ₂], 3.09 [s, R ₁ = N(CH ₃) ₂], 5.37 (s, H _c), 6.24 (d, H _{dd'} , J _{de} or J _{d'e'} = 9.5 cps), 6.59 (d, H _{ee'}), 6.82 (dd, H _b , J _{bb'} = 2.5 cps, J _{ab} = 9.5 cps), 7.31 (d, H _{b'}), 7.51 (d, H _a)	564 [M] ⁺ , 550 [M – CH ₂] ⁺ , 536 [M – CO] ⁺ , 522 [M – CO – CH ₂] ⁺ , 508 [M – 2CO] ⁺ , 494 [M – 2CO – CH ₂] ⁺ , 480 [M – 3CO] ⁺ , 466 [M – 3CO – CH ₂] ⁺ , 452 [M – 4CO] ⁺ , 438 [M – 4CO – CH ₂] ⁺ , 424 [M – 5CO] ⁺ , 410 [M – 5CO – CH ₂] ⁺ , 396 [M – 6CO] ⁺ , 382 [M – 6CO – CH ₂] ⁺ , 144 [Fe ₂ S] ⁺ , 112 [Fe ₂] ⁺ , 56 [Fe] ⁺
5	3.84 (s, R ₁ = OCH ₃), 5.46 (s, H _c), 6.41 (m, H _{dd'}), 6.90 (dd, H _b , J _{ab} = 10 cps, J _{bb'} = 1.5 cps), 7.10 (m, H _{ee'} and R ₂ = H), 7.56 (d, H _a), 7.65 (d, H _{b'})	508 [M] ⁺ , 480 [M – CO] ⁺ , 452 [M – 2CO] ⁺ , 424 [M – 3CO] ⁺ , 396 [M – 4CO] ⁺ , 368 [M – 5CO] ⁺ , 340 [M – 6CO] ⁺ , 325 [M – 6CO – CH ₃] ⁺ , 144 [Fe ₂ S] ⁺ , 112 [Fe ₂] ⁺ , 56 [Fe] ⁺
6	3.69 (s, R ₂ = OCH ₃), 5.54 (s, H _c), 6.38 (d, H _{dd'} , J _{de} or J _{d'e'} = 9 cps), 6.68 (d, H _{ee'}), 6.98–7.62 (m, H _{ab} and R ₁ = H), 8.38 (d, H _{b'})	508 [M] ⁺ , 480 [M – CO] ⁺ , 452 [M – 2CO] ⁺ , 424 [M – 3CO] ⁺ , 396 [M – 4CO] ⁺ , 368 [M – 5CO] ⁺ , 340 [M – 6CO] ⁺ , 325 [M – 6CO – CH ₃] ⁺ , 284 [M – 6CO – Fe] ⁺ , 144 [Fe ₂ S] ⁺ , 112 [Fe ₂] ⁺ , 56 [Fe] ⁺
7	5.55 (s, H _c), 6.49 (d, H _{dd'}), 6.83–7.86 (m, H _{ee'} , H _{ab} , R ₁ = H), 8.63 (s (br), H _{b'})	546 [M] ⁺ , 527 [M – F] ⁺ , 518 [M – CO] ⁺ , 499 [M – CO – F] ⁺ , 490 [M – 2CO] ⁺ , 462 [M – 3CO] ⁺ , 434 [M – 4CO] ⁺ , 406 [M – 5CO] ⁺ , 378 [M – 6CO] ⁺ , 322 [M – 6CO – Fe] ⁺ , 144 [Fe ₂ S] ⁺ , 112 [Fe ₂] ⁺ , 56 [Fe] ⁺
8	7.08 (s)	510 [M] ⁺ , 482 [M – CO] ⁺ , 454 [M – 2CO] ⁺ , 426 [M – 3CO] ⁺ , 398 [M – 4CO] ⁺ , 370 [M – 5CO] ⁺ , 342 [M – 6CO] ⁺ , 198 [(C ₆ H ₅) ₂ CS] ⁺ , 112 [Fe ₂] ⁺ , 56 [Fe] ⁺
9	3.69 (s, OCH ₃), 7.05 (s, C ₆ H ₅)	540 [M] ⁺ , 512 [M – CO] ⁺ , 484 [M – 2CO] ⁺ , 456 [M – 3CO] ⁺ , 428 [M – 4CO] ⁺ , 400 [M – 5CO] ⁺ , 372 [M – 6CO] ⁺ , 228 [<i>p</i> -CH ₃ OC ₆ H ₄ CSC ₆ H ₅] ⁺ , 112 [Fe ₂] ⁺ , 56 [Fe] ⁺
10	7.28 (s)	510 [M] ⁺ , 482 [M – CO] ⁺ , 454 [M – 2CO] ⁺ , 426 [M – 3CO] ⁺ , 398 [M – 4CO] ⁺ , 370 [M – 5CO] ⁺ , 342 [M – 6CO] ⁺ , 112 [Fe ₂] ⁺ , 56 [Fe] ⁺

^a Except for 7 (CCl₄), all spectra were recorded in CDCl₃ with tetramethylsilane as internal standard: s = singlet, d = doublet, dd = doublet of doublets, m = multiplet. For comparative purposes, the nmr data for several thiobenzophenones are given: 1, R₁ = R₂ = OCH₃; δ 3.85 (s, OCH₃), 6.87 (d, J = 9 cps, protons on carbons ortho to methoxy groups), and 7.72 (d, J = 9 cps, protons on carbons ortho to thione group) ppm; 1, R₁ = OCH₃, R₂ = H; δ 3.86 (s, OCH₃), 6.86 (d, J = 9 cps, protons on carbons ortho to the methoxy group), 7.50 (m, protons of the phenyl group), 7.79 (d, J = 9 cps, protons on carbons ortho to the thione group); 1, R₁ = R₂ = N(CH₃)₂; δ 3.03 [s, N(CH₃)₂], 6.58 [d, J = 8.5 cps, protons on carbons ortho to the dimethylamino groups], 7.70 [d, J = 8.5 cps, protons on carbon ortho to the thione function]. Note that several of the assignments for the nmr spectrum of 3, as described in the preliminary communication, are incorrect. ^b Vapor pressure osmometrically determined molecular weight (benzene) was 542 [calcd 538].



The lowest charge transfer band in the electronic spectrum of $\text{Fe}(\text{CO})_5$ is reported to occur at $41,000 \text{ cm}^{-1}$.⁴² Although, as far as we are aware, no data are available in the literature on electronic spectra of organometallic complexes having S-Fe bonds,⁴³ molecular orbital calculations have been carried out and compared with determined electronic spectra for group VI metal hexacarbonyls and their sulfide metal pentacarbonyl derivatives.⁴⁴ Tetrahydrothiophene chromium pentacarbonyl, for example, exhibits three

(42) Footnote 20 of R. A. Levenson, H. B. Gray, and G. P. Cassar, *J. Amer. Chem. Soc.*, **92**, 3653 (1970).

(43) L. Maresca, F. Greggio, G. Sbrignadello, and G. Bor, *Inorg. Chim. Acta*, **5**, 667 (1971), note that the equilibrium ratio of *syn*- and *anti*- $(\mu\text{-RS})_2\text{Fe}_2(\text{CO})_8$ [$\text{R} = \text{CH}_3, \text{C}_2\text{H}_5$] was determined using, among other techniques, ultraviolet spectroscopy; however, such spectra are not presented or discussed.

(44) P. H. Pettit, Jr., Ph.D. Thesis, Lehigh University, Bethlehem, Pa., 1969.

absorption bands at $25,350$ (ϵ 2700), $39,650$ ($34,000$), and $45,600$ ($40,000$) cm^{-1} . The first band was assigned as a $d \rightarrow d$ transition while the latter two bands were believed to be $d \rightarrow \pi^*$ transitions.⁴⁴ Complexes **2**, **3**, and **5-7** also show three absorptions (Table II), the highest energy band ($\sim 40,600 \text{ cm}^{-1}$) being close to the noted band of $\text{Fe}(\text{CO})_5$ and is likely due to a $d \rightarrow \pi^*$ transition. The band at lowest wave number, and of low extinction coefficient, is assigned as a $d \rightarrow d$ transition. The middle band is at a very different position and has a much lower extinction coefficient than either the middle absorption in $(\text{CH}_2)_4\text{SCr}(\text{CO})_5$ or the higher energy transition in **2-7**. No assignment is made for the middle band in **2**, **3**, and **5-7** or for a fourth absorption in the electronic spectrum of **4** ($37,735 \text{ cm}^{-1}$).

The mass spectra of complexes **2-7** (Table III) are

Table IV. Thiolactones Formed by Reaction of the Ortho-Metalated Complexes with Ceric Ion

Complex	Thio-lactone	Yield, %	Mp, °C	Anal. found (calcd), %			$\nu_{\text{CO}},^a$ cm ⁻¹	Molec-ular ion peak, <i>m/e</i>	Nmr ^b δ , ppm
				C	H	S			
2	14	69	104.5–105.5	74.38 (74.31)	4.77 (4.45)	13.92 (14.17)	1700	226	5.90 (s, H _c), 7.28 (s, H _{dd'} , H _{ee'} , and R ₂ = H), 7.38–8.00 (m, H _{ab} , H _{b'} , and R ₁ = H)
3	15	66	107.0–108.0	67.54 (67.11)	5.25 (4.93)	11.58 (11.20)	1690	286	3.78 (s, R ₂ = OCH ₃), 3.86 (s, R ₁ = OCH ₃), 5.83 (s, H _c), 6.83 (d, H _{ee'} , J _{de} or J _{d'e'} = 9cps), 7.16 (d, H _{dd'}), 7.13 (s, H _{ab}), 7.27 (s, H _{b'})
5	16	78	137.0–137.5	70.27 (70.28)	4.85 (4.72)	12.11 (12.51)	1690	256	3.85 (s, R ₁ = OCH ₃), 5.84 (s, H _c), 7.13 (s, H _{ab}), 7.28 (s, H _{b'} , H _{dd'} , H _{ee'} , and R ₂ = H)
7	17	58		61.34 (61.22)	3.37 (3.08)	10.74 (10.89)	1699	294	5.96 (s, H _c), 7.31 (s, H _{dd'} and H _{ee'}), 7.25–8.17 (m, H _{ab} , H _{b'} and R ₁ = H)
23	25	81	138.0–138.3				1691	261	3.86 (s, OCH ₃), 5.83 (s, methine proton), 7.12 (s, protons ortho to each other), 7.26 (s, isolated hydrogen)

^a CCl₄ solution. ^b CDCl₃ solution with TMS as internal standard.

quite different from those reported for thiobenzophenones.⁴⁵ The following characteristics are common to all the spectra: an abundant molecular ion; successive loss of six carbonyls; a fragment at *m/e* 112 due to [Fe₂]⁺, generally indicative of the presence of a metal-metal bond;⁴⁶ and fragments at *m/e* 144 [Fe₂S]⁺ and 56 [Fe]⁺. An interesting feature of the spectra of complexes not having a substituent on the benzene ring complexed to iron (2, 6, and 7) is the presence of an intense peak due to the fragment [M - 6CO - Fe]⁺. Such a fragment is absent when a substituent is located on the complexed benzene ring [3–5]. Methoxy, dimethylamino, and trifluoromethyl substituents on a benzene ring give characteristic fragmentations.⁴⁷

In the nuclear magnetic resonance (nmr) spectra, the methine proton, H_c, for complexes 2–7, gave a singlet at δ 5.37–5.57 (Table III). Molecular models of these complexes show one of the iron tricarbonyl groups to be capable of shielding the protons of the uncomplexed ring (and of substituents on that ring). Protons a and b, as well as substituent protons on the complexed ring, show similar absorptions to the corresponding signals for the derived thioketone. The signal for H_{b'} in 2–7 is generally deshielded, probably by the ortho σ -bonded iron tricarbonyl group.

The chemistry of complexes 2–7 was of interest for several reasons. First, decomplexation reactions could provide additional evidence for the structures of the ortho-metalated complexes. Second, since the ortho-metalated complexes are preparable in good yields and are easy to handle, it seemed conceivable that such complexes could be important intermediates in the synthesis of organic compounds difficult or impossible to prepare by other means. The reactions studied are presented in Scheme II.

Reduction of 3 by lithium aluminum hydride in tetrahydrofuran gave the mercaptan 12 which, on standing, was oxidized to the disulfide. When lithium

aluminum deuteride was employed as the reducing agent, analogs of 12 and 13 were obtained having a deuterium atom(s) in the ortho position.

Treatment of complexes 2, 3, 5, and 7 with ceric ammonium nitrate in acetone gave the thiolactones 14, 15, 16, and 17, respectively. The yields, melting points, and pertinent spectral data for these compounds are given in Table IV. These thiolactones are dihydro derivatives of the little-known isobenzothiophene heterocycles.^{48,49} Since both the ortho metalation and subsequent oxidative decomplexation reactions proceed in good yields, this two-step sequence is a very convenient and useful entry into the isobenzothiophene ring system.

The ortho-metalated complexes show a great propensity for carbonyl insertion. This is demonstrated by the reactions of 3 under a variety of conditions. For instance, 15 was obtained in 63% yield when 3 was subjected to treatment with ferric chloride in ethanol. When 3 was heated in ethanol at 60° for 3 days, 15 was formed in 13% yield. Irradiation, at 2537 Å, of an absolute ethanol solution of 3 proved to be an excellent alternative source of the thiolactone (78% yield).

When 3 was reacted with bromine in carbon tetrachloride, a trace amount of the anticipated *o*-bromosulfonyl bromide (19) was formed but the predominant product (55%) was a thiolactone, 18, having a bromine substituted ortho to the methoxy group on the benzene ring not containing the thiolactone. Treatment of the unsubstituted complex 2 with the same electrophile gave 14 and a small amount of the bromothiolactone 20 as the organic products. Isolated in good yield was the iron carbonyl bromide 21, which shows carbonyl stretching bands in the ir spectrum at 2120 and 2070 cm⁻¹ and the mass spectrum indicates the presence of six carbonyls as well as four bromine atoms. Complex 21 is related to, but different from, di- μ -bromo-bis(tricarbonyliron), recently isolated from the thermal or

(45) D. Schumann, E. Frese, and A. Schonberg, *Chem. Ber.*, **102**, 3192 (1969).

(46) R. B. King, *Org. Mass Spectrom.*, **2**, 657 (1969), and references contained therein.

(47) See, for instance, F. W. McLafferty, "Interpretation of Mass Spectra," W. A. Benjamin, New York, N. Y., 1966.

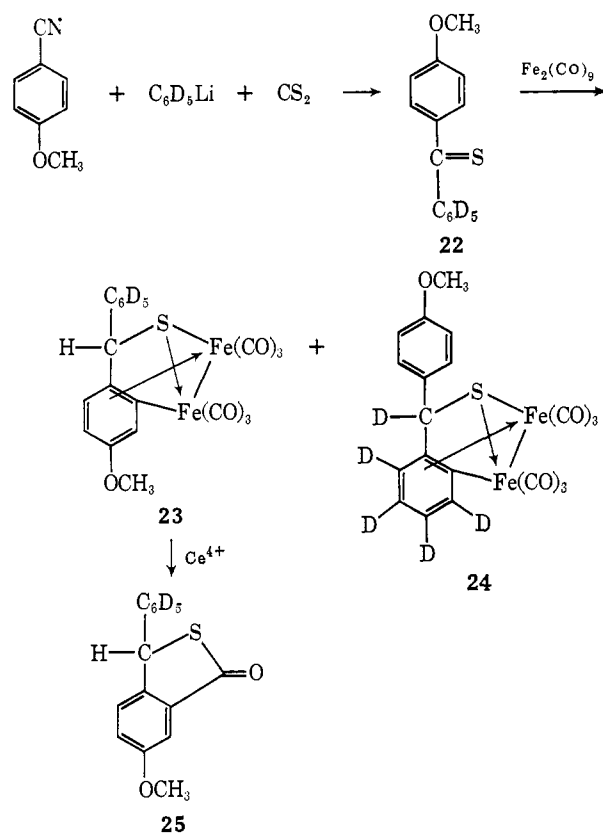
(48) A. Albert, "Heterocyclic Chemistry," The Athlone Press, London, 1959, pp 232–233.

(49) A. R. Katritzky and J. M. Lagowski, "The Principles of Heterocyclic Chemistry," Academic Press, New York, N. Y., 1967.

photochemical reactions of HBr and iron carbonyls.⁵⁰ The difference in behavior of **2** and **3** toward bromine is due, in part, to $R_2 = \text{OCH}_3$ of **3**, which activates that benzene ring toward electrophilic substitution. Since the para position is blocked, bromination occurs ortho to the methoxy group. No reaction occurred when **3** was treated with triphenylcarbenium⁵¹ tetrafluoroborate or with trimethyloxonium hexafluorophosphate.

In order to (i) further confirm the structural assignments for the ortho-metalated complexes, and to (ii) determine whether or not oxidative cyclization occurs onto the benzene ring previously complexed to iron, the pentadeuterated thioketone **22** (Scheme III)

Scheme III



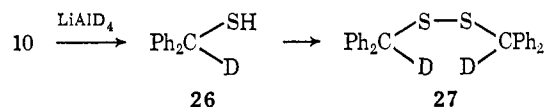
was prepared and reacted with $\text{Fe}_2(\text{CO})_9$ in an identical manner to that used for **1**, $R_1 = \text{H}$, $R_2 = \text{OCH}_3$. Compound **22** was readily obtained by reaction of *p*-methoxybenzonitrile and phenyllithium- d_5 with carbon disulfide. Reaction of **22** with $\text{Fe}_2(\text{CO})_9$ gave the expected mixture of **23** and **24** from which the major complex **23** was isolated in analytically pure form. (No attempt was made to isolate **24** in such a state. The nmr spectrum of crude **24** gave no signals for methine protons but exhibited only a singlet due to the methoxy protons and a quartet for the aromatic protons.) The nmr spectrum of **23** (Experimental Section) was almost identical with that of the non-deuterated complex **5**, except for the absence of unsubstituted benzene ring absorptions in the formed complex. Reaction of **23** with ceric ion gave the thiolactone **25** (Table IV), having the carbonyl group attached to the carbon previously σ -bonded to iron. Therefore, cycli-

(50) E. K. von Gustorf, J. C. Hogan, and R. Wagner, *Z. Naturforsch. B*, **27**, 140 (1972).

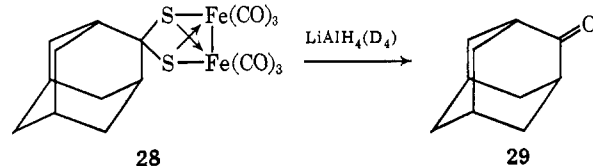
(51) G. Olah, *J. Amer. Chem. Soc.*, **94**, 808 (1972).

zation occurs onto the ring originally complexed to the metal.

As noted earlier, reaction of thiobenzophenone with $\text{Fe}_2(\text{CO})_9$ not only gave **2** and **11** but also the interesting isomeric complexes identified as **8** and **10**. Complex **9**, the analog of **8**, was a by-product of the 4-methoxythiobenzophenone- $\text{Fe}_2(\text{CO})_9$ reaction. Elemental analyses of **8**–**10** clearly indicated the presence of two sulfur and two iron atoms per organic fragment. Only a singlet absorption was observed in the nmr spectra of either **8** or **10** suggesting that neither benzene ring, in each compound, was involved in complexation to a metal atom. Mass spectroscopy indicated the presence of six carbonyl groups and an iron-iron bond in complexes **8**–**10**. Cleavage of the carbon-iron and sulfur-iron bonds of **10** by LiAlD_4 resulted, on work-up, in the formation of **27** (via **26**). The mass spectrum of **27** confirmed the presence of 2.0 deuteriums. Therefore,



10 has a sulfur and an iron atom each σ -bonded to the same carbon atom. Reductive cleavage of **8** or **9** should give, on work-up, the *gem*-dithiol, which in aqueous solution would form the ketone. Insufficient quantities of **8** or **9** were available to react with LiAlH_4 (or LiAlD_4). However, **28**, one of the products of

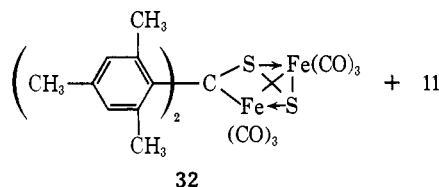
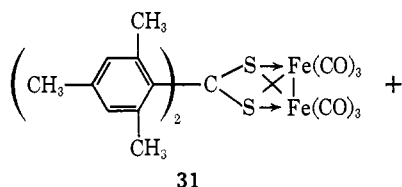
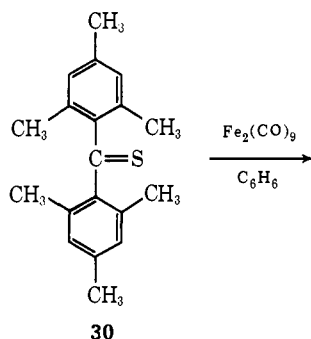


the reaction of adamantanethione and $\text{Fe}_2(\text{CO})_9$, gave adamantanone on treatment with LiAlH_4 or LiAlD_4 .⁵² The carbonyl stretching frequencies for **28** were essentially identical with those for **8** and **9**. It should be noted that complexes analogous to **8** and/or **10** were isolated, in amounts too small for complete characterization (mass spectral identification), from treatment of the other thiobenzophenones with $\text{Fe}_2(\text{CO})_9$.

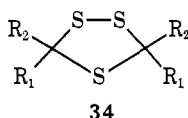
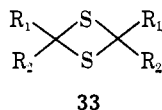
It was of interest to study the reaction of a thiobenzophenone having the ortho positions of the benzene ring substituted, thus blocking ortho metalation. 2,2',-4,4',6,6'-Hexamethylthiobenzophenone (**30**), prepared from the corresponding ketone, gave **31** (major) and **32** (the analogs of **8** and **10**, respectively) on treatment with $\text{Fe}_2(\text{CO})_9$. The trinuclear complex **11** was also isolated from this reaction. Complexes **31** and **32** gave ir and mass spectra analogous to those of **8** and **10**, respectively (Experimental Section). It is worthwhile noting that complexes **8**, **9**, **28**, and **31** gave the corresponding ketone on exposure to air, while no carbonyl compound was formed when **10** or **32** was allowed to come in contact with air. Repeated unsuccessful attempts were made to isolate simple organic by-products (monomer, dimer, or trimer) from the **30**- $\text{Fe}_2(\text{CO})_9$ reaction.

There has been considerable interest in elucidating the mechanism of ortho-metalation reactions.^{1,3} The

(52) H. Alper and A. S. K. Chan, unpublished results.



formation of **5** as the major complex from reaction of 4-methoxythiobenzophenone and $\text{Fe}_2(\text{CO})_9$, and complex **7** from 4-trifluoromethylthiobenzophenone, is clearly indicative of a process involving electrophilic attack. Complexes of type **8–10**, **31**, and **32** do not arise from, nor are sources of, the ortho-metalated complexes. It seemed conceivable that the thioketone might initially dimerize to **33** which would then serve as precursor to the by-products of the $\text{Fe}_2(\text{CO})_9$ reaction. However, compounds of type **33** failed to react with $\text{Fe}_2(\text{CO})_9$ under identical conditions with those used for the thiobenzophenone metal carbonyl reaction.

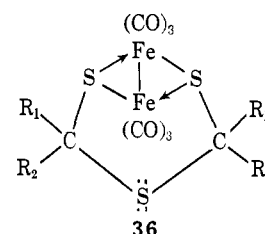
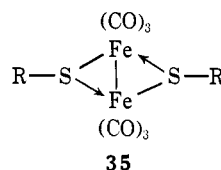


Another possible intermediate was the trithiolan **34**. Tetraphenyltrithiolan (**34**, $\text{R}_1 = \text{R}_2 = \text{C}_6\text{H}_5$) did react with $\text{Fe}_2(\text{CO})_9$ giving **8** (6.2%), **10** (14.2%), and **11** (24.6%) in substantially higher yield and **2** (29.6%) in much lower yield than obtained from reaction of **1** ($\text{R}_1 = \text{R}_2 = \text{H}$) and $\text{Fe}_2(\text{CO})_9$. Note that the relative yields of **8**, **10**, and **11** are in the same order for reaction of **1** ($\text{R}_1 = \text{R}_2 = \text{H}$) or **34** ($\text{R}_1 = \text{R}_2 = \text{C}_6\text{H}_5$) with $\text{Fe}_2(\text{CO})_9$. Hence, it seems likely that a trithiolan, or a similar reaction species, is involved in the formation of **8–10**, **31**, and **32**. Trithiolan **34** contains a disulfide linkage, and disulfides have been shown to react with iron carbonyls to form complexes of type **35**.^{53,54} Similarly, **34** would give **36** which may be the key precursor to the by-products (and to regenerated thioketone).

In summary, this paper has described the first examples of sulfur-donor ligand ortho-metalated complexes. These complexes, on the basis of a limited chemical investigation, show considerable promise as

(53) J. Cooke, M. Green, and F. G. A. Stone, *J. Chem. Soc. A*, 170 (1968), and references contained therein.

(54) H. Alper, unpublished results.



intermediates for organic synthesis. Attempts have been made to gain some insight into the mechanism of complex formation. We are currently further investigating the chemistry of the complexes reported here as well as the preparation of sulfur-donor ligand ortho-metalated complexes involving other transition metals (*e.g.*, cobalt) and other organic moieties (*e.g.*, thionbenzoates).

Experimental Section

Melting points were measured in sealed capillary tubes using a Gallenkamp apparatus and are corrected. Microanalyses were performed by: A. Bernhardt, Fritz-Pregl-Straße, West Germany; Par-Alexander Labs, S. Daytona, Fla; and Meade Microanalytical Laboratory, Amherst, Mass. Infrared spectra were obtained on a Perkin-Elmer 457 grating spectrophotometer. A Perkin-Elmer 521 spectrophotometer was used to more precisely ($\pm 1.0 \text{ cm}^{-1}$) locate the positions of the bands associated with the iron carbonyl groups. All ir determinations were calibrated using polystyrene film. Nuclear magnetic resonance spectra were determined on Varian A-60 (TMS as internal standard) and/or HA-100 spectrometers. Mass spectra were recorded on Atlas CH-4 or Varian MS 9 spectrometers. Ultraviolet spectra were determined on a Perkin-Elmer 202 spectrophotometer.

Diiron enneacarbonyl and iron pentacarbonyl were purchased from Pressure Chemical Co. and used as received. Solvents were dried and purified by standard techniques. All reactions were run and worked up under a dry nitrogen atmosphere.

Reaction of $\text{Fe}_2(\text{CO})_9$ with: (i) Thiobenzophenone. A mixture of thiobenzophenone (Columbia Organics; 1.00 g, 5.05 mmol) and $\text{Fe}_2(\text{CO})_9$ (2.77 g, 7.62 mmol) in benzene (40 ml) was stirred at room temperature for 30 hr. The solution was filtered through Celite 545 (Fisher Scientific Co.), and the filtrate was flash evaporated *in vacuo*. The residue from flash evaporation was dissolved in petroleum ether (bp 38–52°, *ca.* 3.5 ml) and chromatographed on acidic alumina (Woelm activity grade 1). Elution with petroleum ether gave a mixture of **10** and **11** (fraction A). Elution with 4–6% ether–petroleum ether (v/v) gave **2**, contaminated with trace amounts of **10** (fraction B). Elution with ether or ether–methylene chloride gave **8**. Fraction A was rechromatographed on Florisil (60–100 mesh). The trinuclear complex **11** was eluted first off the column with petroleum ether followed by **10**. Analytically pure **2** was obtained by rechromatography of fraction B on acidic alumina and elution with light petroleum. See Table I for characterization data.

(ii) **4,4'-Dimethoxythiobenzophenone.** A mixture of **1**, $\text{R}_1 = \text{R}_2 = \text{OCH}_3$ (Aldrich Chemical Co., 1.29 g, 5.00 mmol), $\text{Fe}_2(\text{CO})_9$ (2.79 g, 7.68 mmol) and benzene (40 ml) was stirred at room temperature for 36 hr. After the mixture was filtered and flash evaporated as above, the residue from *in vacuo* evaporation was dissolved in pentane and chromatographed on Florisil. Elution with pentane gave **11** followed by the ortho-metalated complex **3**. Identical results were obtained when the reaction was effected in benzene-*d*₆.

(iii) **4,4'-Bis(dimethylamino)thiobenzophenone** (Alfred Bader Co.). Using essentially the same conditions as ii, the residue from flash evaporation was washed with petroleum ether to remove a small quantity of unreacted thioketone. The red solid was dissolved in 1–2 ml of ether and chromatographed on either silica gel or Florisil. Elution with petroleum ether gave **11** and elution with ether–petroleum ether gave **4**.

(iv) **4-Methoxythiobenzophenone.** A mixture of 4-methoxythiobenzophenone⁵⁵ (3.442 g, 15.0 mmol) and $\text{Fe}_2(\text{CO})_9$ (6.20 g, 17.0 mmol) in benzene (50 ml) was stirred at room temperature for 36 hr. The solution was filtered through Celite, and flash evapora-

(55) A. Schonberg and E. Frese, *Chem. Ber.*, 101, 701 (1968).

tion of the filtrate gave a red residue which was dissolved in petroleum ether (bp 38–50°) and chromatographed on Florisil. Elution with petroleum ether gave **11** followed by the pure brick-red complex **5**. Elution with ether gave first a mixture of **5** and **6** (fraction A), then **9** (fraction B), and finally *p*-methoxybenzophenone, formed by oxidation of unreacted thioetone during chromatographic work-up. Fraction A, upon rechromatography on acidic alumina (Woelm activity grade I) with petroleum ether or petroleum ether-ether as eluent, gave **5** followed by the ruby-red complex **6**. Pure **9** was obtained by rechromatography of fraction B on Florisil using petroleum ether-ether as the eluent.

(v) **4-Trifluoromethylthiobenzophenone**. The thioetone (ν_{CS} 1260 cm^{-1}), an intense blue oil, was obtained in 39% yield by treating carbon disulfide with the lithium salt of the ketimine formed by reaction of phenyllithium (Alfa Inorganics, Inc.) with *p*-trifluoromethylbenzotrile (PCR, Inc.).⁵⁶ Using the same reaction conditions as described for ii, the residue from *in vacuo* evaporation was dissolved in carbon tetrachloride and chromatographed on neutral alumina (Woelm activity grade I). Elution with carbon tetrachloride first gave **11**, followed by **7**, which was contaminated with a little of the trinuclear complex. Analytically pure **7** was obtained by rechromatography on Florisil using petroleum ether as the eluent.

Metal Hydride Reduction of 3. (i) **Lithium Aluminum Hydride (LiAlH₄)**. A tetrahydrofuran (THF) solution (20 ml) of **3** (0.964 g, 1.79 mmol) was added dropwise to a suspension of LiAlH₄ (Alfa Inorganics, Inc., 0.177 g, 4.66 mmol) in THF (10 ml) at 0°. The reaction mixture was stirred for 2 hr at 0°, more LiAlH₄ (0.177 g) was added, and stirring was continued for an additional 2 hr at 0°. Ethyl acetate was added and the solution was filtered. A viscous tan residue, obtained by flash evaporation of the filtrate, was dissolved in ether and chromatographed on Florisil. Elution with ether gave 0.178 g (38%) of the mercaptan **12** [ir (KBr) ν_{SH} 2540 (w) cm^{-1}]. On standing, **12** converted to **13**: mp 186–187°; nmr (CDCl₃) δ 3.61 (s, 12 H, OCH₃), 4.67 (s, 2 H, H-C-S-), 6.61 (d, 8 H, *J* = 9 cps, protons on carbons ortho to methoxy groups), 7.04 (d, 8 H, *J* = 9 cps, protons on carbons meta to methoxy groups).

Anal. Calcd for C₃₀H₃₀O₅S₂: C, 69.47; H, 6.07; S, 12.42. Found: C, 69.47; H, 5.83; S, 12.36; mol wt calcd 518; found (osmometry) 499.

(ii) **Lithium Aluminum Deuteride (LiAlD₄)**. Using essentially the identical procedure with that described above, LiAlD₄ (Norell Chemical Corp.) reduction gave 37% of **12-d₁** [ir (KBr) ν_{SH} 2540 (w), $\nu_{\text{C-D}}$ 2260 (w-m) cm^{-1}]. On standing, **12-d₁** oxidized to **13-d₂**: nmr (CDCl₃) δ 3.63 (s, 12 H, OCH₃), 4.59 (s, 2 H, H-C-S-), 6.63 (d (broad), 8 H, protons on carbons ortho to methoxy group), and 7.03 (d, 6 H, *J* = 9 cps, protons on carbons meta to methoxy group). The highest peak in the mass spectrum occurred at *m/e* 456 [(4-CH₃OC₆H₄-)(2-D-4-CH₃OC₆H₃-)CH]₂⁺ and corresponds to loss of S₂ from the molecular ion. The base peak in the spectrum was at *m/e* 228 [(4CH₃OC₆H₄-)(2-D-4-CH₃OC₆H₃-)CH]⁺. The mass spectrum indicated >97% deuterium at the two ortho carbons of **13-d₂**.

Oxidative Cleavage of 2, 3, 5, and 7 by Ceric Ion. To an acetone solution (10–30 ml) of the ortho-metalated complex (~0.75 mmol) was added, in small portions, ceric ammonium nitrate (3.2–4.0 mmol). After addition was complete, the reaction mixture was stirred for 2 hr at room temperature. Ether was added, the solution filtered, and the filtrate evaporated *in vacuo*. The residue was dissolved in the minimum amount of benzene and chromatographed on Florisil. Elution with benzene or ether-benzene gave the thiolactone (pertinent physical data for **14–17** are listed in Table IV).

Alternative Methods for Effecting Conversion of 3 to 15. (i) **Oxidative Cleavage by Ferric Chloride.** A solution of anhydrous ferric chloride (0.60 g, 3.7 mmol) in absolute ethanol (20 ml) was added dropwise to a stirred ethanol solution (30 ml) containing **3** (0.763 g, 1.42 mmol). The reaction mixture was heated with stirring at 60° for 7 hr. The solution was cooled and filtered, and the filtrate was added to methylene chloride (100–200 ml). The solution was washed repeatedly with water until the aqueous phase was clear. The dried organic fraction was flash evaporated; the residue was dissolved in benzene and chromatographed on Florisil. Elution with benzene-ether gave a semisolid which was crystallized from ether. The yield of pure **15** was 0.255 g (63%).

(ii) **Thermal Reaction.** A solution of **3** (0.140 g, 0.26 mmol) in

absolute ethanol (20 ml) was stirred for 72 hr at 60°. Work-up as above gave 10 mg (13%) of **15**.

(iii) **Photochemical Conversion.** A degassed solution of **3** (0.300 g, 0.557 mmol) in absolute ethanol (100 ml) was irradiated at 2537 Å for 4–6 days. The solution was filtered and crystallization (ether) of the semisolid residue obtained from solvent evaporation gave 0.120 g (78%) of pure thiolactone (**15**).

Bromination of 3. Bromine (2.0 ml) in carbon tetrachloride (CCl₄) (20 ml) was added to a stirred CCl₄ (20 ml) solution containing 0.682 g (1.27 mmol) of complex **3**. After the mixture was stirred for 2 hr at room temperature, excess bromine and the solvent were removed by evaporation *in vacuo*. The residue was dissolved in methylene chloride and washed several times with water (until the aqueous layer was clear). Crystallization with acetone gave **18**, contaminated by trace amounts of **19**, the latter detected by mass spectral analysis which gave a molecular ion peak at *m/e* 418 (two bromines present). Recrystallization afforded 0.201 g (55% yield) of pure **18**: mp 217.5–218.5°; ir (KBr) ν_{CO} 1666 (s) cm^{-1} ; nmr (CDCl₃) δ 3.96 (s, 3 H, methoxy protons of thiolactone fused benzene ring), 4.06 (s, 3 H, methoxy protons of bromo substituted ring), 7.18 (s, 2 H, protons ortho to each other in thiolactone fused benzene ring), 7.28 (dd, 1 H, *J_o* = 8.5 cps, *J_m* = 2.5 cps, proton para to bromine substituent), 7.37 (s, 1 H, isolated aromatic proton of benzene ring fused to the thiolactone), 7.67 (s, 1 H, HCS), 8.21 (d, 1 H, *J_o* = 8.5 cps, proton meta to bromine), 8.42 (d, 1 H, *J* = 2.5 cps, proton ortho to bromine). *Anal.* Calcd for C₁₆H₁₃BrO₃S: C, 52.61; H, 3.59; S, 8.78; Br, 21.88. Found: C, 52.23; H, 3.31; S, 8.90; Br, 22.10; mol wt calcd 365; found (osmometry) 357.

Bromination of 2. To a solution of **2** (0.888 g, 1.86 mmol) in CCl₄ (20 ml) was added, dropwise, 0.75 ml (13.8 mmol) of bromine in CCl₄ (10 ml). The solution was stirred for 3 hr at room temperature, during which time a red suspension formed as well as a gluey reddish mass which accumulated at the bottom of the reaction flask. The solution was filtered to give 0.248 g of the bromine iron carbonyl complex **21**. The reddish mass in the reaction flask was insoluble in CCl₄ or ether but soluble in methylene chloride. The mass was dissolved in methylene chloride, combined with the CCl₄ filtrate above, and evaporated at room temperature under a stream of nitrogen. The residue was then triturated with ether to give an additional 0.450 g of **21**. The ether extract was evaporated *in vacuo*, and then the residue was vacuum dried for 15 hr. This residue, upon treatment with a few milliliters of ether, crystallized 0.115 g of **21**. Total yield of air-sensitive **21** was 0.831 g, mp >90° dec; ir (KBr) ν_{CO} 2120 (ms), 2070 (vs) cm^{-1} (other absorptions at 610 (s), 560 (vs), 482 (w), 465 (w), 445 (w), and 415 (w)); mass spectrum gives a molecular ion peak at *m/e* 599 followed by loss of six carbonyls (appearance pattern indicates four bromines). *Anal.* Calcd for C₆Br₄Fe₂O₆: Br, 53.33; Fe, 18.63. Found: Br, 53.82; Fe, 17.88. Slow crystallization of the ether soluble portion afforded 35 mg of crude bromothiolactone **20**. Recrystallization from acetone gave 12 mg of pure **20**: mp 117° dec; ir (KBr) ν_{CO} 1672 (s) cm^{-1} ; the nmr spectrum showed an ABCD pattern as in *o*-bromoaniline,⁵⁷ for the four protons on the bromine substituted ring. If bromine was located on the benzene ring fused to the thiolactone, then the other benzene ring protons should appear as a singlet as was observed for **14** and **16**.

The remaining ether solution was chromatographed on Florisil. Elution with ether gave 123 mg of a viscous oil. Mass spectrometry (and nmr) indicated a 9:1 ratio of thiolactone **14** to what is believed to be the corresponding lactone (ν_{CO} 1775 cm^{-1}).

Reaction of 4-Methoxythiobenzophenone-d₅ (22) with Fe₂(CO)₉. (i) **Preparation of 4-Methoxythiobenzophenone-d₅ (22).** (a) **Phenyllithium-d₅.** Bromobenzene-d₅ (Stohler Isotope Chemicals; 5.0 g, 31 mmol) in ether (16 ml) was added dropwise to lithium ribbon (0.94 g, 136 mmol) in ether (8 ml). After stirring for 1 hr, the solution was filtered to remove excess lithium. The phenyllithium-d₅ filtrate was used immediately for reaction with *p*-methoxybenzotrile.

(b) **4-Methoxythiobenzophenone-d₅.** The thioetone was prepared by an essentially identical procedure (*p*-methoxybenzotrile-phenyllithium-d₅-CS₂) with that described by Ahmed and Lwowski⁵⁶ for the synthesis of thiobenzophenone (3.5 hr reaction time). The nmr spectrum (CDCl₃) of **22** gave the following signals: δ 3.83 (s, 3 H, OCH₃), 6.85 (d, 2 H, *J* = 9 cps, protons on carbons ortho to the methoxy group), and 7.79 (d, 2 H, *J* = 9 cps, protons on carbons meta to the methoxy group). A molecular ion peak was observed in the mass spectrum at *m/e* 233.

(56) R. Ahmed and W. Lwowski, *Org. Prep. Proced. Int.*, **3**, 135 (1971).

(57) S. Clough, *Mol. Phys.*, **2**, 349 (1959).

(ii) **Reaction of 22 with Fe₂(CO)₉.** Identical reaction and work-up as those described for **1** (R₁ = H, R₂ = OCH₃), gave pure **23** (no attempt was made to isolate pure **24**, see text): mp 131.5–132.5°; nmr (CDCl₃) δ 3.83 (s, 3 H, OCH₃), 5.47 (s, 1 H, -CHS-), 6.88 (dd, 1 H, J_o = 8.5 cps, J_m = 2.0 cps, proton ortho to the methoxy group and coupled to protons both ortho and meta to it), 7.57 (d, 1 H, J = 8.5 cps, proton meta to the methoxy group), 7.65 (d, 1 H, J = 2.0 cps, isolated aromatic proton); mass spectrum *m/e* 513 [M]⁺, 485 [M - CO]⁺, 457 [M - 2CO]⁺, 429 [M - 3CO]⁺, 401 [M - 4CO]⁺, 373 [M - 5CO]⁺, 345 [M - 6CO]⁺, 330 [M - 6CO - CH₃]⁺, 144 [Fe₂S]⁺, 112 [Fe₂]⁺, 56 [Fe]⁺.

Oxidative Cleavage of 23 by Ceric Ion. Using identical conditions as described for reaction of **5** with ceric ammonium nitrate, **23** gave **25** in 81% yield (data given in Table IV).

Reductive Cleavage of 10 by Lithium Aluminum Deuteride (LiAlD₄). Complex **10** (0.173 g, 0.340 mmol) in THF (10 ml) was added dropwise to a suspension of LiAlD₄ (0.225 g, 5.40 mmol) in THF (5 ml) at 0°. The solution was stirred for 100 min at 0°, followed by addition of ethyl acetate. The solution was filtered and the filtrate was evaporated *in vacuo* to give a residue which was dissolved in benzene (1 ml) and chromatographed on a short column (3 × 1 cm) of Florisil. Elution with benzene gave 0.025 g (37%) of diphenyldeuteriomethyl disulfide (**27**, the mercaptan **26** was first obtained but was rapidly oxidized to disulfide): ir (KBr) 740 (s), 695 (vs) cm⁻¹; nmr (CDCl₃) δ 7.25 (s, aromatic protons). The highest peak occurred in the mass spectrum at *m/e* 336 [(C₆H₅)₂CD]₂⁺ and corresponds to loss of S₂ from the molecular ion. The base peak in the spectrum appeared at *m/e* 168 [(C₆H₅)₂CD]⁺. The mass spectrum indicated >98% d₂.

Reaction of 2,2',4,4',6,6'-Hexamethylthiobenzophenone (30) with Fe₂(CO)₉. (i) **2,2',4,4',6,6'-Hexamethylthiobenzophenone (30).** **2,2',4,4',6,6'-Hexamethylbenzophenone** (10.0 g, 37.5 mmol, Aldrich Chemical Co.) in xylene (420 ml) was refluxed with phosphorus pentasulfide (4.0 g; British Drug Houses, Inc.). After 4 hr, the solution was cooled somewhat (to ~80°), another 3.0-g portion of P₄S₁₀ added, and refluxing continued for 7 hr. A further 3 g of P₄S₁₀ was then added and refluxing was carried out for 1 additional day. After the xylene was removed by flash evaporation *in vacuo*, the residue was dissolved in benzene and chromatographed on alumina (Fisher 80–200 mesh). Elution with benzene-petroleum ether gave a blue-green solid which was now chromatographed on neutral alumina (Woelm activity grade I). Elution with petroleum ether gave 1.88 g of blue thio-ketone (**30**), contaminated by the reactant ketone. Further chromatography on acidic alumina (Woelm activity grade I) using benzene-petroleum ether as eluent failed to remove the ketone contaminant from **30** and the latter was used as such for reaction

with Fe₂(CO)₉. Spectral properties: ir (KBr) ν_{CS} 1240 cm⁻¹; nmr (CDCl₃) δ 2.12 (s, 12 H, protons on methyl groups ortho to the thione function), 2.28 (s, 6 H, protons of methyl groups para to thione), and 6.83 (s, 4 H, aromatic protons); mass spectrum *m/e* 282.

(ii) **Reaction of 30 with Fe₂(CO)₉.** A mixture of **30** (0.55 g, 1.77 mmol) and Fe₂(CO)₉ (1.50 g, 4.13 mol) in benzene (30 ml) was stirred at room temperature for 48 hr. The solution was filtered and the filtrate concentrated *in vacuo*. The residue was dissolved in petroleum ether (3 ml) and chromatographed on Florisil. Elution with petroleum ether (bp 38–52°) gave 49.6 mg of the trinuclear complex **11**. Eluted immediately after **11** was the orange-red complex **32** (22 mg): ir (CCl₄) ν_{CO} 2086 (s), 2041 (s), 2000.5 (s), 1981 (s, sh) cm⁻¹; δ_{FeCO} 613 (w), 582 (w), 562 (m) cm⁻¹; mass spectrum *m/e* 594 [M]⁺, 566 [M - CO]⁺, 538 [M - 2CO]⁺, 510 [M - 3CO]⁺, 482 [M - 4CO]⁺, 454 [M - 5CO]⁺, 426 [M - 6CO]⁺, 112 [Fe₂]⁺, 56 [Fe]⁺.

Further elution with petroleum ether gave 138.5 mg of the red-purple complex **31**, mp 76–80°; ir (CCl₄) ν_{CO} 2075 (vs), 2058 (w), 2044 (wm), 2035.4 (vs), 2024.5 (s), 2009 (s), 1982 (s) cm⁻¹; δ_{FeCO} 613 (w), 582 (wm), 562 (wm) cm⁻¹; nmr (CDCl₃) δ 2.11 (s, 12 H, protons on methyl groups ortho to benzylic carbon), 2.18 (s, 6 H, protons of methyl group para to benzylic carbon), and 6.77 (s, 4 H, aromatic protons); mass spectrum *m/e* 594 [M]⁺, 566 [M - CO]⁺, 538 [M - 2CO]⁺, 510 [M - 3CO]⁺, 482 [M - 4CO]⁺, 454 [M - 5CO]⁺, 426 [M - 6CO]⁺, 282 [30]⁺, 112 [Fe₂]⁺, 56 [Fe]⁺.

Anal. Calcd for C₂₅H₂₂S₂Fe₂O₈: C, 51.32; H, 4.12; S, 11.91; Fe, 20.75. Found: C, 51.29; H, 4.57; S, 12.24; Fe, 20.65.

Reaction of Tetraphenyltrithiolan with Fe₂(CO)₉. A mixture of tetraphenyltrithiolan⁸⁸ (0.412 g, 0.965 mmol) and Fe₂(CO)₉ (1.57 g, 4.35 mmol) in benzene (30 ml) was stirred at room temperature for 36 hr. Work-up as described for the reaction of thiobenzophenone and Fe₂(CO)₉ gave **2** (29.6%), **8** (6.2%), **10** (14.2%), and **11** (24.6%).

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