to the metal center is important in determining $\delta(^{13}CN)$. This concept seems to be useful in understanding not only our results but also the substantial trans effects observed in substituted cyanocobalamines.[37] Its significance for metal carbonyl complexes has been considered.[28-32] However, we note that a sophisticated analysis of $^{13}CN^-$ and ^{13}CO chemical shifts, such as one given recently for hydrocarbons by Ellis, Maciel, and McIver,[38] is needed.

In Table I, systematic variations can be seen in the splitting between cis and trans cyanide signals. Among the complexes of aromatic N heterocycles (C_{2v} symmetry) this splitting increases as the back-bonding ability of L increases. The effect diminishes abruptly as the series of ligands reaches dimethyl sulfoxide and NO^+. It is evidently related to the fact that the π-acceptor orbitals of the latter two ligands are not prevented by symmetry from interacting simultaneously with all four cis cyano groups.

The known values of ΔE_{CT}, the energy of the metal-to-heterocycle electron-transfer band, and of $\Delta E(^1E(1) \leftarrow {}^1A_1)$, corresponding to the lowest observable d–d transition in each of the complexes, are given in Table I. We find no comprehensive relationship between the energies of either of these electronic transitions and the measured values of $\delta(^{13}CN^-)$ in the complexes. The result can be contrasted with the outcome of a Mössbauer study of several of the complexes[5b] in which a linear relationship was found between the d–d excitation energies and measured isomer shifts. In that instance, the correspondence was expected because, for the set of $Fe(CN)_5L^{n-}$ complexes, d–d transition energies normally increase and isomer shifts decrease according to the ability of the ligand L to augment the ligand field of Fe(II). On the other hand, the factor controlling the measured values of $\delta(^{13}CN)$ in the complexes appears to be the inductive influence of L, transmitted via the iron center. In this case the net effect of σ donation plus π back-donation in the Fe(II)–L bond need not correlate with the position of L in the spectrochemical series.

Acknowledgment. The authors gratefully acknowledge the assistance of Professor R. N. Loeppky in obtaining some of the carbon-13 spectra.

Registry No. $Fe(CN)_5NO^{2-}$, 15078-28-1; $Fe(CN)_5S{=}O(CH_3)_2{}^{3-}$, 56533-28-9; $Fe(CN)_5(NC_4H_4NCH_3)^{2-}$, 40299-79-4; $Fe(CN)_5(NC_4H_4N)^{3-}$, 40299-78-3; $Fe(CN)_5(NC_4H_4N)Fe(CN)_5{}^{6-}$, 56533-29-0; $Fe(CN)_5(NC_4H_4C(C{=}O)NH_2)^{3-}$, 40299-77-2; $Fe(CN)_6{}^{4-}$, 13408-63-4; $Fe(CN)_5(NC_5H_5)^{3-}$, 37475-75-5; $Fe(CN)_5(NC_5H_4\text{-}4\text{-}CH_3)^{3-}$, 37475-65-3; $(H_3N)_5Ru(NC_4H_4NCH_3)Br_3$, 48135-76-8; $Ru(NH_3)_5Cl_3$, 18532-87-1; ^{13}C, 14762-74-4.

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Ortho Metalation and Donor Ligand Complexation Reactions of *O*-Alkyl Thioesters with Diiron Enneacarbonyl

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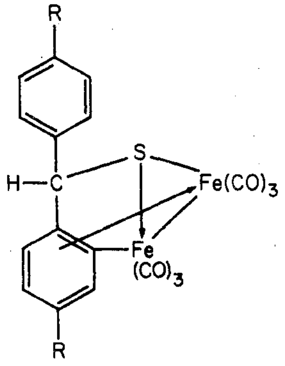
Received April 17, 1975 AIC50270K

Reaction of various *O*-methyl aryl thioesters with diiron enneacarbonyl in benzene at room temperature afforded a sulfur-donor ligand ortho-metalated complex as the minor product, the major component being an isomeric oxygen, sulfur-donor diiron hexacarbonyl complex. For different *O*-alkyl thiobenzoates, increasing the effective bulk of the alkoxy group afforded more of the ortho-metalated complex. The effect of ring strain on the course of these reactions is noted.

The intramolecular ortho metalation of nitrogen, phosphorus, sulfur, and oxygen ligands is a subject of considerable current interest.[2] For example, treatment of thiobenzophenones with diiron enneacarbonyl $[Fe_2(CO)_9]$ affords sulfur-donor ligand ortho-metalated complexes (**1**) in generally good to excellent yields.[3] If one of the aryl groups of a thiobenzophenone is replaced by an ethoxy group, i.e., *O*-ethyl thiobenzoate (**2a**), then an isomeric oxygen, sulfur-donor ligand diiron hexacarbonyl complex **4a** is isolated as the major product. The ortho-metalated complex **3a** was formed in modest yield, along with a small amount of the trinuclear complex **5**.[4] This result, along with that obtained for *N*,*N*-dimethylthiobenzamide, indicates that the heteroatom has a significant influence on the course of the ortho-metalation reaction.



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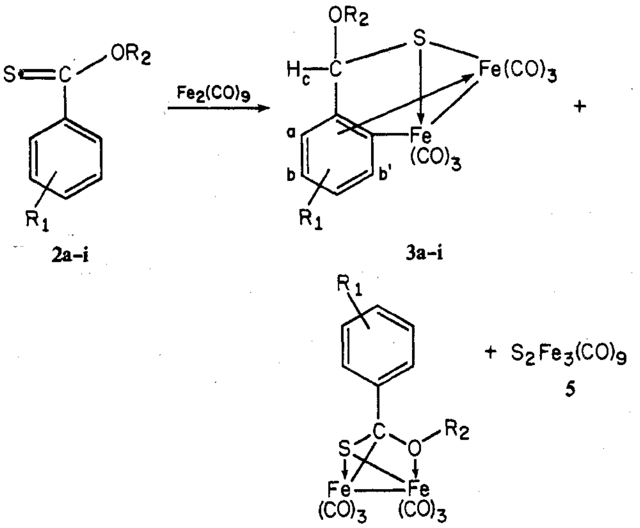
A variety of thioesters were now treated with $Fe_2(CO)_9$ in order to determine what factors affect the product distribution between complexes of structural types **3** and **4**. The results obtained from this study may also contribute to an understanding of the mechanism of the ortho-metalation process.



2a–i **3a–i** **4a–h**

a, $R_1 = H; R_2 = C_2H_5$
b, $R_1 = H; R_2 = CH_3$
c, $R_1 = p\text{-}CH_3; R_2 = CH_3$
d, $R_1 = m\text{-}CH_3; R_2 = CH_3$
e, $R_1 = p\text{-}OCH_3; R_2 = CH_3$
f, $R_1 = p\text{-}CF_3; R_2 = CH_3$
g, $R_1 = p\text{-}Br; R_2 = CH_3$
h, $R_1 = H; R_2 = CH(CH_3)_2$
i, $R_1 = H; R_2 =$ 1-adamantyl

Results and Discussion

Two series of thioesters were reacted with $Fe_2(CO)_9$ in anhydrous benzene at room temperature. One group consisted of *O*-methyl arylthioesters (**2b–g**) with different ring substituents, the other being of various *O*-alkyl thiobenzoates [**2**, $R_1 = H$]. The required thioesters were prepared by one of the following methods: reaction of an ester with phosphorus pentasulfide;[5] treatment of an imido ether with hydrogen sulfide;[6] or reaction of thiobenzoylthioglycolic acid with an alcohol in the presence of imidazole.[7]

The yields, melting points, and analytical data for the products of the thioester–$Fe_2(CO)_9$ reactions are listed in Table I. Pertinent spectral data are given in Table II.

Terminal metal carbonyl stretching absorptions for complexes **3b–i** occurred in the infrared (ir) at 1990–2090 cm^{-1}. Complexes **4b–h** exhibited, in addition to absorptions in the same region, a lower frequency band at 1950–1975 cm^{-1}. A singlet at δ 5.24–5.40 was observed in the nuclear magnetic resonance (NMR) spectra of **3b–i**, assigned to the methine proton H_c. The positions of the ring protons were similar to those reported for the ortho-metalated complexes **1**.[3] The donor ligand complexes **4b–h** lacked a methine proton signal, and displayed the expected signals for a nonmetalated benzene ring. The signal for the methoxy protons of **4b–h** [δ 4.24–4.30] appeared at significantly lower field than the position for the same protons in **3b–i** [δ 3.84–3.88], since in the oxygen, sulfur donor complex, there is withdrawal of electron density from the alkoxy oxygen.

Most of the ortho-metalated complexes gave molecular ion peaks in the mass spectra, followed by successive loss of six carbonyl groups. The highest fragment [*m/e* 416] in the electron impact mass spectrum of the trifluoromethyl derivative **3f** was due to $[M - 3CO]^+$. In most instances, the O,S-donor ligand complexes **4** decomposed on attempted electron impact mass spectral determinations.

For the *O*-methyl arylthioesters [**2b–g**], the major product was the O,S-donor complex [**4b–g**] in all cases. *O*-Methyl *m*-thiotoluate (**2d**) gave the ortho-metalated complex having the methyl group para to the iron containing carbon. The ratios of ortho-metalated to O,S-donor complex were as follows:

Thioester	3/4	Thioester	3/4
2b	0.26	**2e**	0.79
2c	0.29	**2f**	0.13
2d	0.38	**2g**	0.33

There is a marked increase in the proportion of ortho-metalated complex formed in going from a thioester containing the electron-withdrawing trifluoromethyl group (**2f**) to that having the electron-donating methoxy substituent (**2e**). This trend is indicative of an electrophilic type process. In addition, the ratio of **3**/**4** is significantly greater for the meta (**2d**) than for the para thiotoluate. It is the meta rather than the para methyl group which can directly activate the position ortho to the thioester group to electrophilic attack.

Increase in the effective bulk of the alkoxy group of the *O*-alkyl thiobenzoates has a dramatic effect on the product distribution. The ratios of **3**/**4** are:

Thioester	3/4	Thioester	3/4
2b	0.26	**2h**	1.46
2a	0.29[3]	**2i**	**3i** only

Only the ortho-metalated complex **3i** was isolated using the 1-adamantylmethyl thioester **2i**.

A rationale for the above results can be given on the basis of the pathway outlined in Scheme I. Initial attack of a lone pair of sulfur at the metal carbonyl would give **6**, with loss of carbon monoxide. This complex has at least two reaction paths available to it: (i) iron insertion at an ortho carbon to give **7**, which on hydride transfer to iron (**8**) and then to the sulfur containing carbon would give **9**, and carbon monoxide loss from the latter would afford the ortho-metalated complex (**3**); (ii) coordination of the alkoxy oxygen to an iron atom (**10**), followed by bond reorganization (**11**) and carbon monoxide loss, would give the O,S-donor ligand complex **4**.

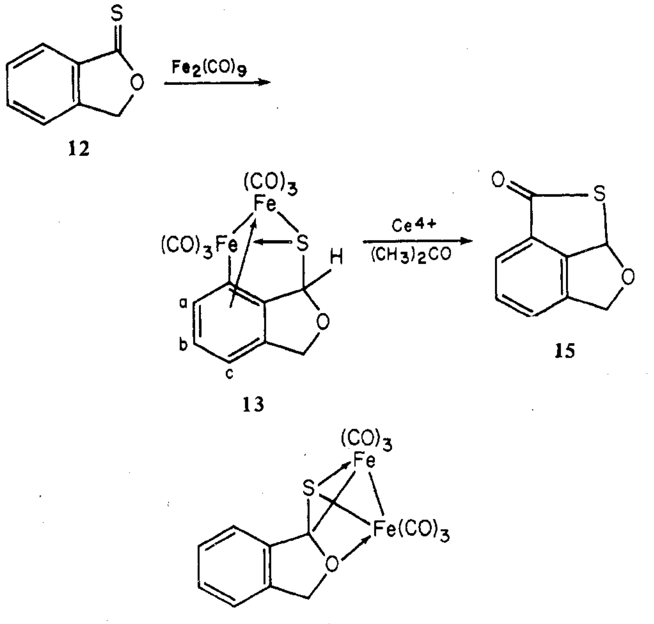
Table I. Yields, Melting Points, and Analytical Data for Complexes Obtained from Reaction of Thioesters with $Fe_2(CO)_9$

Thiobenzoate	Products	Yield,[a] %	Mp dec, °C	Anal. found (calcd) C	H	S	Fe
2b	**3b**	10	65	39.39 (38.93)	2.11 (1.87)	7.40 (7.42)	26.12 (25.86)
	4b	38	60	38.61 (38.93)	1.95 (1.87)	7.76 (7.42)	25.31 (25.86)
	5	3.4	114[2,3]				
2c	**3c**	15	105	40.13 (40.38)	2.41 (2.24)		
	4c	52	90	41.05 (40.38)	2.61 (2.24)		
	5	7.5	114				
2d	**3d**	15	88	39.87 (40.38)	2.42 (2.24)		
	4d	40	oil	40.87 (40.38)	2.42 (2.24)		
	5	1.8	114				
2e	**3e**	33	90	39.17 (38.98)	2.19 (2.18)	7.03 (6.94)	23.89 (24.19)
	4e	42	110	38.31 (38.98)	2.00 (2.18)	7.22 (6.94)	
	5	3.1	114				
2f	**3f**	2.4	85	37.05 (36.04)	1.86 (1.41)	6.73 (6.41)	21.67 (22.34)
	4f	18	105	36.77 (36.04)	1.44 (1.41)	7.02 (6.41)	
	5	1.4	114				
2g	**3g**	18	47	33.38 (32.90)	1.34 (1.37)	6.61 (6.27)	
	4g	54	55	32.93 (32.90)	1.21 (1.37)		
	5	3.6	114				
2h	**3h**	32	57	42.02 (41.80)	2.17 (2.61)	7.31 (6.98)	24.90 (24.35)
	4h	22	oil	41.52 (41.80)	2.44 (2.61)	6.82 (6.98)	24.60 (24.35)
	5	1.1	114				
2i	**3i**	55	93	51.38 (50.91)	4.11 (3.88)		
	5	2.3	114				
12	**13**	39	110	39.64 (39.14)	1.67 (1.3°)	8.08 (7.45)	
	5	0.7	114				

[a] Yields are based on thioester.

For all ring substituted *O*-methyl thioesters, the major product is the O,S-donor complex **4**, suggesting that coordination of oxygen to iron is more facile than the attachment of an iron to an ortho carbon (even though there are two possible ortho positions). The increase in the proportion of ortho-metalated complexes with an increase in the effective bulk of the R_2 group of the *O*-alkyl thiobenzoates is probably a consequence of steric hindrance to coordination of oxygen to iron, the steric effect arising from repulsion between R_2 and the iron carbonyl groups.

It was of considerable interest to determine whether oxygen coordination to iron could be inhibited by ring strain, as well as by the already demonstrated effect of the size of R_2. Reaction of the five-membered ring thiolactone, thiophthalide (**12**), with $Fe_2(CO)_9$ gave the ortho-metalated complex **13** in 39% yield and less than 1% of $S_2Fe_3(CO)_9$, but no O,S-donor complex (**14**). Complex **13** is less strained than **14**. Since thiophthalide is, in a sense, the cyclic analog of *O*-methyl thiobenzoate (**2b**), these results show that ring strain has an important effect on the reaction course.



14

Oxidative cyclization of **13** by ceric ion in acetone gave the novel tricyclic α-alkoxy thiolactone **15**.

Experimental Section

General. Solvents were purified and dried by standard methods. Melting points were determined on a Fisher-Johns melting point apparatus, and are uncorrected. Infrared spectra were recorded on Perkin-Elmer 457 and Beckman IR-20A spectrometers. Nuclear magnetic resonance spectra were recorded on a Varian A-60 or T-60 spectrometer. Mass spectra were determined using a Varian MS902 mass spectrometer. Elemental analyses were carried out by Galbraith Laboratories, Inc., Knoxville, Tenn. and by Instranal Laboratory, Rensselaer, N.Y.

All reactions were effected under an atmosphere of dry nitrogen.

***O*-Alkyl Thioesters. (i) *O*-Methyl Thiobenzoate (2b) and *O*-Methyl *p*-Thiotoluate (2c).** These thioesters were synthesized by heating a mixture of methyl benzoate or methyl *p*-toluate and phosphorus pentasulfide in the presence of a catalytic amount of sodium bicarbonate for 24 hr at 80°.[5]

(ii) *O*-Methyl *m*-Thiotoluate (2d), *O*-Methyl *p*-Methoxythiobenzoate (2e), *O*-Methyl *p*-Trifluoromethylthiobenzoate (2f), and *O*-Methyl *p*-Bromothiobenzoate (2g). These thioesters were prepared by treating the appropriate nitrile first with methanol and dry hydrogen chloride gas to give the imido ether, which was subsequently reacted with H_2S.[6,8]

(iii) *O*-Isopropyl Thiobenzoate (2h). The method of Barton et al.[7] was used to prepare this thioester. Sodium hydride (2.35 g) was added to thiobenzoylthioglycolic acid (5.0 g) in dry tetrahydrofuran (75 ml). When effervescence ceased, imidazole (3.2 g) was added in small portions. The mixture was refluxed for 15 min and absolute 2-propanol (1.41 g) added, and the resulting mixture was refluxed for 15 min more. The mixture was poured into water and extracted with ether, and the ether extract (dried over $MgSO_4$) was evaporated in vacuo. The resulting solid was dissolved in the minimum amount of petroleum ether and then chromatographed on Florisil. Elution with petroleum ether gave the thioester as a yellow oil in 54% yield: ir (neat) ν_{CS} 1225 cm^{-1}; NMR ($CDCl_3$) δ 1.47 (d, 6 H, CH_3), 5.90 (m, 1 H, $CH(CH_3)_2$), 7.15–8.20 (m, 5 H, aromatic protons).

Anal. Calcd for $C_{10}H_{12}OS$: C, 66.63; H, 6.71. Found: C, 66.06; H, 7.01.

Table II. Pertinent Ir, NMR, and Mass Spectra for **3b**-**i**, **4b**-**h**, and **13**

Complex	ν(CO),[a] cm^{-1}	NMR δ,[b] ppm	*m/e*
3b	2074, 2040, 1990	3.84 (s, 3 H, OCH$_3$), 5.34 (H$_c$), 6.78–8.30 (m, 4 H, aromatic H's)	432 M$^+$, 348 (M – 3CO)$^+$, 320 (M – 4CO)$^+$, 264 (M – 6CO)$^+$
3c	2070, 2040, 1990	2.49 (s, 3 H, CH$_3$), 3.88 (s, 3 H, R$_2$ = CH$_3$), 5.29 (s, 1 H, H$_c$), 7.10–7.65 (m, 2 H, H$_a$, H$_b$), 8.18 (s (br), 1 H, H$_{b'}$)	446 M$^+$, 390 (M – 2CO)$^+$, 362 (M – 3CO)$^+$, 334 (M – 4CO)$^+$, 306 (M – 5CO)$^+$, 278 (M – 6CO)$^+$
3d	2075, 2050, 1990	2.26 (s, 3 H, CH$_3$), 3.87 (3, 3 H, R$_2$ = CH$_3$), 5.35 (H$_c$), 6.89 (dd, 1 H, proton para to H$_c$C<, J_{ortho} = 8 Hz, J_{meta} = 2.0 Hz), 7.36 (d, 1 H, H$_a$, J_{meta} = 2.0 Hz), 8.12 (d, 1 H, H$_{b'}$)	446 M$^+$, 418 (M – CO)$^+$, 390 (M – 2CO)$^+$, 362 (M – 3CO)$^+$, 334 (M – 4CO)$^+$, 306 (M – 5CO)$^+$, 278 (M – 6CO)$^+$
3e	2070, 2040, 2030, 2000	3.80 (s, 3 H, R$_1$ = OCH$_3$), 3.85 (s, 3 H, R$_2$ = CH$_3$), 5.40 (s, 1 H, H$_c$), 6.86 (dd, 1 H, H$_b$, J_{ab} = 9 Hz, $J_{bb'}$ = 2 Hz), 7.26 (d, 1 H, H$_b$), 7.60 (d, 1 H, H$_a$)	
3f	2080, 2042, 2000	3.83 (s, 3 H, R$_2$ = CH$_3$), 5.38 (s, 1 H, H$_c$), 7.3–8.5 (m, 3 H, H$_a$, H$_b$, H$_{b'}$)	416 [M – 3CO]$^+$, 360 [M – 5CO)$^+$, 332 [M – 6CO]$^+$
3g	2060, 2050, 2000, 1990	3.86 (s, 3 H, R$_2$ = CH$_3$), 5.24 (s, 1 H, H$_c$), 7.58 (dd, 1 H, H$_b$, J_{ab} = 9.0 Hz, $J_{bb'}$ = 2.5 Hz), 7.87 (d, 1 H, H$_a$), 8.41 (d, 1 H, H$_{b'}$)	511 [M]$^+$, 455 [M – 2CO]$^+$, 427 [M – 3CO]$^+$, 399 [M – 4CO]$^+$, 371 [M – 5CO]$^+$, 343 [M – 6CO]$^+$
3h	2080, 2040, 1995	1.12 (d), 1.15 (d) (2 nonequivalent methyls), 3.88 (m, 1 H, CH(CH$_3$)$_2$), 5.53 (s, 1 H, H$_c$), 7.08 (t, 1 H, H$_{\text{para}}$ to H$_c$C< 7.23 (t, 1 H, H$_b$), 7.70 (d, 1 H, H$_a$, J_{ab} = 9 Hz), 8.25 (d, 1 H, H$_{b'}$, J_{ortho} = 9 Hz)	460 [M]$^+$, 432 [M – CO]$^+$, 404 [M – 2CO]$^+$, 376 [M – 3CO]$^+$, 348 [M – 4CO]$^+$, 320 [M – 5CO]$^+$, 292 [M – 6CO]$^+$
3i	2075, 2040, 1990	1.27–2.00 (m, 15 H, adamantyl protons), 3.93 (2 H, CH$_2$O), 5.38 (s, 1 H, H$_c$), 7.14 (t, 1 H, H$_{\text{para}}$ to H$_c$C<), 7.34 (t, 1 H, H$_b$), 7.63 (d, 1 H, H$_a$, J_{ab} = 9 Hz), 8.20 (d, 1 H, H$_{b'}$ = 9 Hz)	566 [M]$^+$, 482 [M – 3CO]$^+$, 454 [M – 4CO]$^+$, 398 [M – 6CO]$^+$
4b	2074, 2060, 2040, 1992, 1975, 1962	4.30 (s, 3 H, R$_2$ = CH$_3$), 7.00–8.05 (m, 5 H, aromatic protons)	
4c	2075, 2055, 2040, 1995, 1965	2.37 (s, 3 H, R$_1$ = CH$_3$), 4.25 (s, 3 H, R$_2$ = CH$_3$), 7.13 (d, 2 H, protons *ortho* to methyl group, J_{ortho} = 9 Hz), 8.06 (d, 2 H, protons meta to methyl group)	446 [M]$^+$, 418 [M – CO]$^+$, 390 [M – 2CO]$^+$, 362 [M – 3CO]$^+$, 278 [M – 6CO]$^+$
4d	2080, 2058, 2040, 2000, 1960	2.35 (s, 3 H, R$_1$ = CH$_3$), 4.27 (s, 3 H, R$_2$ = CH$_3$), 7.23–8.00 (m, 3 H, aromatic protons)	
4e	2080, 2058, 2038, 1998, 1985, 1973, 1963	3.82 (s, 3 H, R$_1$ = OCH$_3$), 4.26 (s, 3 H, R = CH$_3$), 6.32 (d, 2 H, protons *ortho* to the methoxy group, J_{ortho} = 9 Hz), 8.02 (d, 2 H, protons meta to the methoxy group)	462 [M]$^+$, 406 [M – 2CO]$^+$ 378 [M – 3CO]$^+$, 294 [M – 6CO]$^+$
4f	2080, 2065, 2045, 2003, 1968	4.30 (s, 3 H, R$_2$ = CH$_3$), 7.67 (d, 2 H, protons *ortho* to the CF$_3$ group, J_{ortho} = 8.5 Hz), 8.11 (d, 2 H, protons meta to CF$_3$)	
4g	2080, 2060, 2040, 2010, 1986, 1958	4.24 (s, 3 H, R$_2$ = CH$_3$), 7.46 (d, 2 H, protons *ortho* to Br, J = 8.5 Hz), 8.06 (d, 2 H, protons meta to Br)	
4h	2080, 2060, 2039, 1990, 1969, 1956		460 [M]$^+$, 404 [M – 2CO]$^+$, 376 [M – 3CO]$^+$, 292 [M – 6CO]$^+$
13	2070, 2040, 2020, 1996	5.52 (s, 1 H, CHS), 5.58 (s, 2 H, CH$_2$), 7.30–7.70 (m, 2 H, H$_b$, H$_c$), 8.09 (dd, 1 H, H$_a$, J_{ab} = 9.5 Hz, J_{ac} = 2.0 Hz)	

[a] CCl$_4$ solution. [b] CDCl$_3$ solution with (CH$_3$)$_4$Si as internal standard.

(iv) *O*-Adamantylmethyl Thiobenzoate (2i). The method of Barton et al.[7] was used here. 1-Adamantanemethanol (3.9 g) was reacted with sodium hydride (2.35 g) and thiobenzoylthioglycolic acid (5.0 g) in dry tetrahydrofuran. Work-up as described for *O*-isopropyl thiobenzoate gave 4.3 g (63.5%) of a yellow crystalline thioester: mp 73–78°; ir (neat) ν_{CS} 1230 cm^{-1}; NMR (CDCl$_3$) δ 1.73 (m, 15 H, adamantyl protons), 4.23 (s, 2 H, CH$_2$O), 7.30–8.20 (m, 5 H, aromatic protons).

Anal. Calcd for C$_{17}$H$_{20}$OS: C, 75.52; H, 7.76. Found: C, 74.99; H, 8.07.

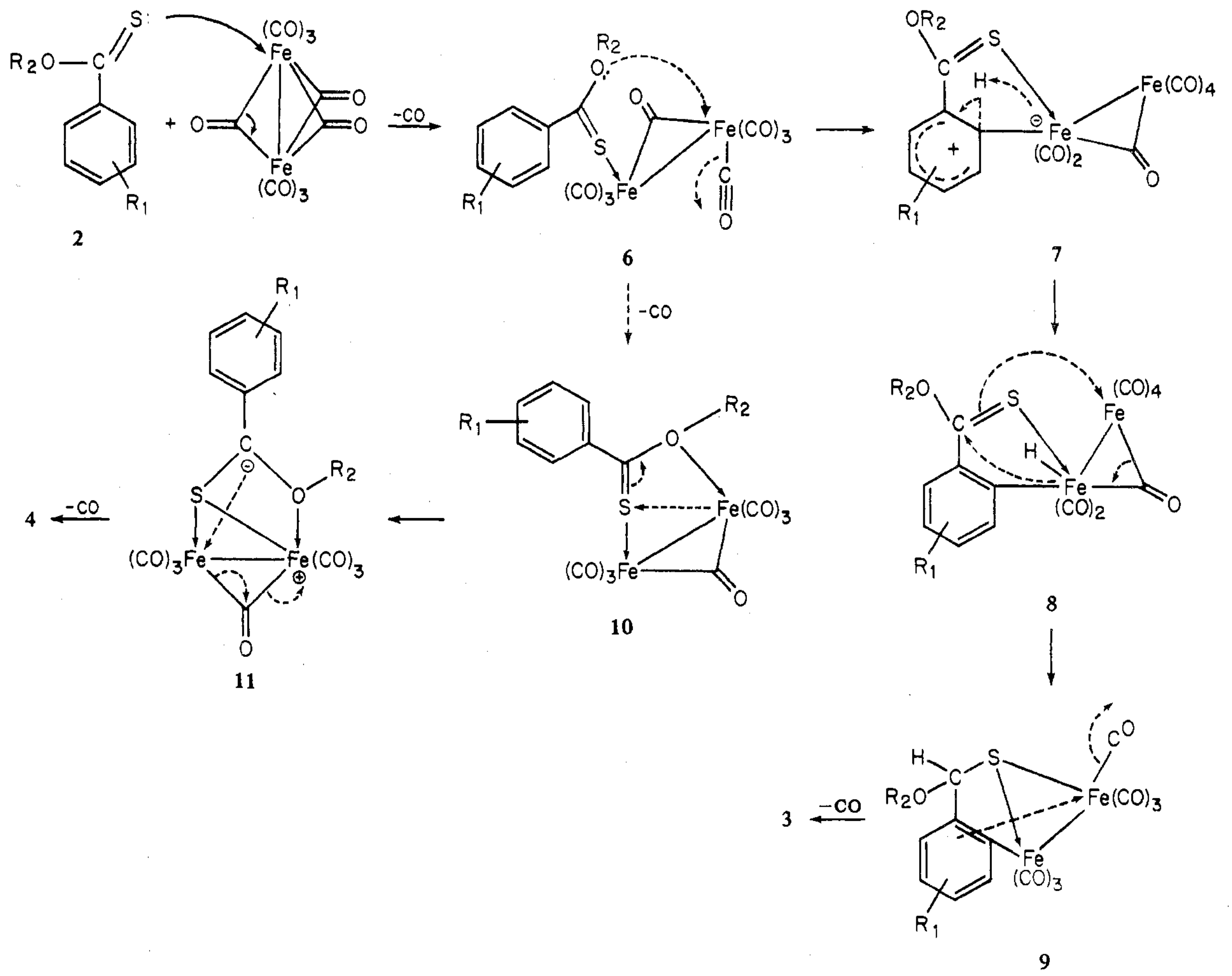
(v) Thiophthalide (12). Thiophthalide was prepared according to the procedure of Renson and Collienne.[9] The melting point was 114–117° (lit.[9] m.p. 110°); ir (ν_{CS}) 1280 cm^{-1}.

Reactions of Thioesters with Fe$_2$(CO)$_9$. (i) *O*-Methyl Thiobenzoate (2b). A mixture of *O*-methyl thiobenzoate (2.5 g, 16.4 mmol) and Fe$_2$(CO)$_9$ [9.0 g, 24.7 mmol] in dry benzene (80 ml) was stirred at room temperature for 36 hr. The solution was filtered, and the filtrate was flash evaporated. The resulting solid was dissolved in the minimum amount of petroleum ether (bp 40–60°) and then chromatographed on Florisil. Elution with petroleum ether gave S$_2$Fe$_3$(CO)$_9$ (**5**), followed by the oxygen, sulfur donor complex **4b**. Elution with ether gave the crude ortho-metalated complex **3b**. Analytically pure **3b** and **4b** were obtained by rechromatographing each on Florisil. Pertinent analytical and physical data are listed in Tables I and II.

(ii) *O*-Methyl *p*-Thiotoluate (2c). A mixture of **2c** (2.88 g, 17.3 mmol) and Fe$_2$(CO)$_9$ (8.40 g, 23.1 mmol) in dry benzene (80 ml) was stirred at room temperature for 36 hr. After filtration and subsequent flash evaporation, the oil was dissolved in the minimum amount of petroleum ether and chromatographed on Florisil. Elution with petroleum ether gave **5** followed by **4c** and then the ortho-metalated complex **3c**. The O,S-donor complex **4c** was purified by repeated chromatography on neutral alumina (Woelm activity grade I) using petroleum ether as the eluant. Complex **3c** was purified further by chromatography on silica gel with petroleum ether employed as eluant.

(iii) *O*-Methyl *m*-Thiotoluate (2d). The thioester (4.20 g, 25.3 mmol) and Fe$_2$(CO)$_9$ (15.0 g, 41.2 mmol) were reacted, and the reaction mixture was then worked-up, as described for **2c**.

Scheme I



(iv) *O*-Methyl *p*-Methoxythiobenzoate (2e). The thioester (1.97 g, 10.8 mmol) and $Fe_2(CO)_9$ [5.70 g, 15.7 mmol] were reacted as described for **2b**. Work-up by chromatography on Florisil gave $S_2Fe_3(CO)_9$ on elution with petroleum ether, the O,S-donor complex **4e** on elution with 9:1 petroleum ether–ether, and **3e** on elution with ether. Complex **4e** was further purified by chromatography on neutral alumina, using benzene as the eluant.

(v) *O*-Methyl *p*-Trifluoromethylthiobenzoate (2f). The thioester (0.69 g, 3.14 mmol) and $Fe_2(CO)_9$ (1.75 g, 4.81 mmol) were reacted, and the reaction mixture was then worked-up, as described for **2b**.

(vi) *O*-Methyl *p*-Bromothiobenzoate (2g). The thioester (3.81 g, 16.5 mmol) and $Fe_2(CO)_9$ (12.7 g, 34.6 mmol) were reacted, and the reaction mixture was then worked-up, as described for **2b**.

(vii) *O*-Isopropyl Thiobenzoate (2h). The thioester (0.92 g, 5.47 mmol) and $Fe_2(CO)_9$ [2.98 g, 8.20 mmol] were reacted, and the reaction mixture was then worked-up, as described for **2b**.

(viii) *O*-Adamantylmethyl Thiobenzoate (2i). The thioester (2.50 g, 7.76 mmol) and $Fe_2(CO)_9$ (9.25 g, 11.7 mmol) were reacted as described for **2b**. Work-up by chromatography on Florisil gave $S_2Fe_3(CO)_9$ on elution with petroleum ether, and the ortho-metalated complex **3i** on elution with benzene. Complex **3i** decomposed on attempted chromatography on alumina or silica gel.

(ix) Thiophthalide (12). The thioester (1.08 g, 7.20 mmol) and $Fe_2(CO)_9$ (5.40 g, 14.8 mmol) were reacted, and the reaction mixture was then worked-up, as described for **2b**.

Reaction of the Ortho-Metalated Complex 13 with Ceric Ion. Ceric ammonium nitrate (6.48 g, 12.0 mmol) was added, in small portions, to an acetone (40 ml) solution of the ortho-metalated complex **13** (1.0 g, 2.3 mmol). The reaction mixture was stirred at room temperature for 5.5 hr, and ether (20 ml) was then added. The reaction mixture was filtered, and the filtrate was evaporated in vacuo to give a yellow solid. Recrystallization of the latter from CCl_4/petroleum ether gave the tricyclic thiolactone **15** as a cream-white solid: mp 95–98°; ir (KBr) ν_{CO} 1700 cm^{-1}; mass spectrum (*m*/*e*) 178 (M^+).

Anal. Calcd for $C_9H_6O_2S$: C, 60.66; H, 3.39; S, 17.97. Found: C, 60.61; H, 3.23; S, 18.06.

Acknowledgment. We are grateful to the National Institutes of Health, the National Research Council of Canada, and the University of Ottawa (Rector's Fund) for support of this research.

Registry No. **3b**, 55669-09-5; **3c**, 55669-11-9; **3d**, 55669-13-1; **3e**, 55669-15-3; **3f**, 55669-17-5; **3g**, 55669-19-7; **3h**, 55669-21-1; **3i**, 55669-23-3; **4b**, 55669-10-8; **4c**, 55669-12-0; **4d**, 55669-14-2; **4e**, 55669-16-4; **4f**, 55669-18-6; **4g**, 55669-20-0; **4h**, 55669-22-2; **5**, 22309-04-2; **13**, 55669-24-4; **15**, 55669-08-4; $Fe_2(CO)_9$, 15321-51-4.

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