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Chemistry of Sulfur-Donor Ligand Ortho-Metalated Iron Carbonyl Complexes and Thiolactones Derived Therefrom

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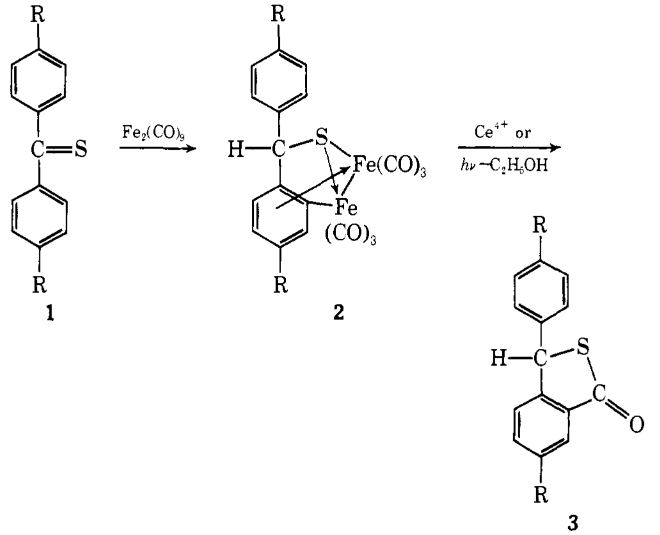
Abstract: Ortho-metalated iron carbonyl complexes can be converted to isobenzothiophenes (thiolactones), in the presence of n-donor ligands such as amines, phosphines, and alcohols. The intermediate in these ligand migration reactions has been isolated. The same transformation can be effected photolytically by use of tetracyanoethylene. Carbonyl insertion and/or desulfurization of the complexes occurred in the presence of anionic reagents (e.g., $^-OC(CH_3)_3$), subject to the nature of the reaction medium. Mercuric acetate cleavage of the complexes results in both ortho-mercuration and desulfurization to give ethers or esters, depending on the reaction conditions. Lactones and/or alkoxy esters resulted when the ortho-metalated complexes were treated with mercuric trifluoroacetate. Lactones were also formed by treatment of the complexes with excess 30% hydrogen peroxide or *m*-chloroperbenzoic acid. Mechanisms are proposed for some of these reactions.

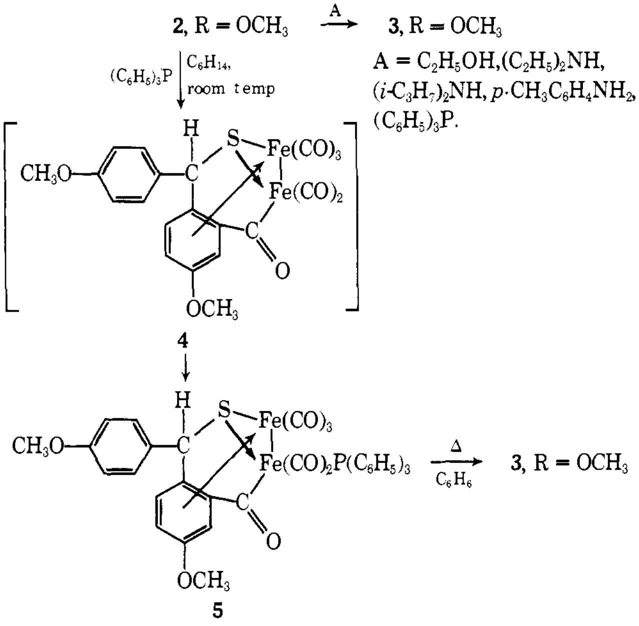
There has been considerable recent interest in the area of transition metal intramolecular ortho-metalation reactions.[1] One of us has reported the first examples of sulfur-donor ligand ortho-metalated complexes (e.g., **2**), formed by reaction of thioketones (**1**) with diiron enneacarbonyl [$Fe_2(CO)_9$]. An initial study of the chemistry of these complexes indicated that they had potential as intermediates for organic synthesis. For instance, oxidative or photolytic cleavage of **2** afforded the relatively little known isobenzothiophene derivatives (**3**) in good yields. This paper describes some new, and synthetically useful, reactions of the ortho-metalated complexes **2**, and of the thiolactones (**3**) derived therefrom.[2]



Results

(i) n-Donor Induced Carbonyl Insertion. Treatment of ortho-metalated complexes (e.g., **2**, R = OCH_3) with a variety of Lewis bases results in carbonyl insertion to give isobenzothiophene derivatives (e.g., **3**, R = OCH_3) in variable yields (Scheme I). Thermolysis of **2**, R = OCH_3, in absolute ethanol for 3 days gave the thiolactone **3**, R = OCH_3, in 13% yield.[1] Reaction of the complex with diethylamine or diisopropylamine in benzene afforded the thiolactone in 49 and 77% yields, respectively. Treatment of **2**, R = OCH_3, with *p*-toluidine gave **3**, R = OCH_3, in 18% yield. The isobenzothiophene derivative was isolated in 42% yield by exposure of the complex to triphenylphosphine in hot benzene.

Scheme I



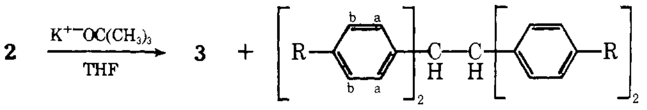
The ortho-metalated complex **2**, R = OCH_3, was treated with triphenylphosphine under gentle conditions (hexane, room temperature) in order to obtain some evidence for the pathway of the n-donor ligand induced reaction. Isolated in 80% yield was an orange, reasonably air-stable complex, **5**, having an infrared (ir) band at 1604 cm^{-1}, assigned to carbonyl stretching of the benzoyl group. The carbonyl absorption for the related $C_6H_5C(=O)Fe(CO)_2C_5H_5$ system occurred at 1603 cm^{-1}.[3] Heating **5** in benzene for 22 hr gave the thiolactone **3** (R = OCH_3), triphenylphosphineiron tetracarbonyl,[4] and an unidentified complex ($\nu_{CO}(CCl_4)$ 2042 s, 1981 s cm^{-1}; no benzoyl absorption).

(ii) **Photolytically Induced Carbonyl Insertion.** It has already been noted that irradiation of **2**, R = OCH_3, in ethanol at 2537 Å affords **3**, R = OCH_3, in 78% yield.[1] We have found the photolytic procedure to be a general one giving thiolactones **3** (R = H, CH_3, C_2H_5) in 82–98% yield.

The ortho-metalated complex **2**, R = OCH_3, was recovered unchanged when the irradiation was effected in benzene. However, if the photolysis was carried out in the presence of added tetracyanoethylene, a 96% yield of the isobenzothiophene **3** could be realized, along with the previously unknown tetracyanoethyleneiron tetracarbonyl. The frequencies of the carbonyl bands (see Experimental Section) for the latter are somewhat higher than those reported for perfluoroolefin iron tetracarbonyl complexes.[5] It should be noted that nonphotolytic reaction of **2**, R = OCH_3, with tetracyanoethylene in benzene for 2 days at room temperature gave the thiolactone in 21% yield.

(iii) **Carbonyl Insertion Effected by Anionic Reagents. Desulfurization of the Resultant Thiolactones.** Treatment of the ortho-metalated complexes **2**, R = OCH_3 and/or R = CH_3, with hydroxide, methoxide, azide, or thiocyanate ion, as well as cyanogen bromide, afforded the thiolactones in generally high yield (Experimental Section). Reaction of potassium *tert*-butoxide with **2**, R = CH_3, in benzene gave **3**, R = CH_3, in 95% yield.

Reaction of **2**, R = OCH_3, with potassium *tert*-butoxide in tetrahydrofuran (THF) afforded the desulfurized product **6**, R = OCH_3, and the thiolactone **3**, R = OCH_3, in 4 and 61% yields, respectively. The tetraarylethane was obtained as the only product (28% yield) when the reaction was effected in *tert*-butyl alcohol. Similar reaction of the *p*-tolyl-substituted complex **2**, R = CH_3, with $K^{+}{}^{-}OC(CH_3)_3$ in the THF gave **3**, R = CH_3, and the tetraarylethane **6**, R = CH_3, in 78 and 1.7% yields, respectively. Changing the solvent for this reaction to *tert*-butyl alcohol afforded **3** and **6** (R = CH_3) in 18 and 15% yields, respectively.



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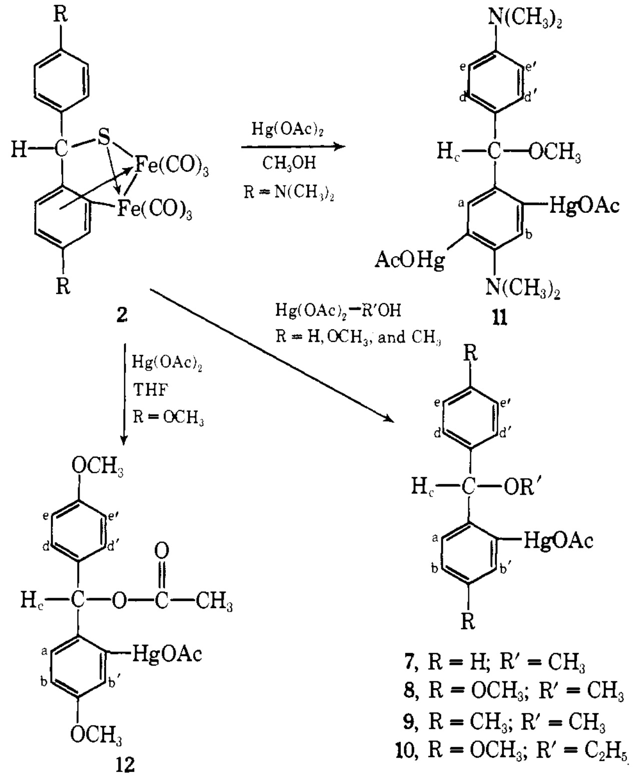
Grignard reagents reacted with the complexes in a similar manner to that observed with alkoxides. Treatment of methylmagnesium iodide with **2**, R = OCH_3, in diethyl ether resulted in formation of **3**, R = OCH_3, and **6**, R = OCH_3, as well as *S*-methyl thioacetate.[6] The use of ethylmagnesium bromide as the reagent gave the thiolactone in 17% yield and the substituted ethane in 18% yield. That the thiolactone is the precursor to the tetraarylethane was demonstrated by conversion of **3**, R = OCH_3, to **6**, R = OCH_3, using $K^{+}{}^{-}OC(CH_3)_3$ in *tert*-butyl alcohol as the reagent. No reaction occurred when **2**, R = OCH_3, was treated with methyl iodide.

Table I. Yields, Melting Points, and Analytical Data for Ortho-Mercurated Compounds 7–12

2, R =	Solvent	Product[a]	Yield (%)	Mp (°C)
H	CH_3OH	7	68	Oil
OCH_3	CH_3OH	8	59	73–74
	C_2H_5OH	10	69	Oil
	THF	12	81	41–45
$N(CH_3)_2$	CH_3OH	11	39	95–98
CH_3	CH_3OH	9	36	114.5–115.0

[a] All products gave satisfactory C and H analyses and the analytical data were made available to the editors and referees.

Scheme II



7, R = H; R' = CH_3
8, R = OCH_3; R' = CH_3
9, R = CH_3; R' = CH_3
10, R = OCH_3; R' = C_2H_5

(iv) **Mercuric Acetate Cleavage Reactions.** Cleavage of the ortho-metalated complexes by mercuric acetate results in both ortho-mercuration and desulfurization. For example, when **2**, R = H, OCH_3, CH_3, was treated with a 4–5 mol excess of mercuric acetate in methanol, the corresponding methyl ethers **7–9** were obtained in good yields (Table I and Scheme II). The ethoxy analog **10** was formed in 69% yield when **2**, R = OCH_3, was treated with mercuric acetate in ethanol. Use of the dimethylamino substituted complex **2**, R = $N(CH_3)_2$, as the reactant gave the bismercuric acetate **11**.

Solvents have an important influence on the course of the reaction. Mercuric acetate cleavage of **2**, R = OCH_3, in the aprotic solvent THF gave the acetate **12** rather than an ether. Methyl mercuric acetate failed to react with the ortho-metalated complexes. Pertinent spectral data for the organomercurials are listed in Table II.

(v) **Lactone and Ester Synthesis via Mercuric Trifluoroacetate.** Mercuric trifluoroacetate reacted differently than $Hg(OAc)_2$ toward the ortho-metalated complexes. Treatment of **2**, R = H, CH_3, OCH_3, with mercuric trifluoroacetate in methanol gave the corresponding lactones **13** (R = H, OCH_3, CH_3) and esters **14** (R = H, OCH_3, CH_3) in good combined yields (Scheme III). In the aprotic solvent THF, mercuric trifluoroacetate cleavage of **2**, R = OCH_3, gave only the lactone **13**, R = OCH_3, in 77% yield. The yields, melting points, and analytical data for the products are given in Table III, and spectral data are listed in Table IV.

(vi) **Lactone Synthesis via 30% Hydrogen Peroxide or *m*-Chloroperbenzoic Acid.** Treatment of complex **2**, R =

Table II. Pertinent Infrared, NMR, and Mass Spectral Data for 7–12

Product	Irν_{CO}, cm^{-1} (Phase)[a]	NMR, ppm[b]	MS, M$^+$, *m/e*
7	1595(neat)	2.04 (s, 3 H, $HgOCOCH_3$), 3.38 (s, 3 H, OCH_3), 5.43 (s, 1 H, H_c), 6.92–7.34 (m, 9 H, aromatic protons)	457
8	1585(KBr)	2.04 (s, 3 H, $HgOCOCH_3$), 3.36 (s, 3 H, $CHOCH_3$), 3.78 (s, 6 H, OCH_3), 5.26 (s, 1 H, H_c), 6.81 (d, 1 H, H_b, J_{ab} = 8.0 Hz, $J_{bb'}$ = 2.5 Hz), 6.84 (d, 2 H, $H_{ee'}$, $J_{de} = J_{d'e'}$ = 8.5 Hz), 6.94 (d, 1 H, H_b), 7.22 (d, 1 H, H_a), 7.24 (d, 2 H, $H_{dd'}$)	517
9	1580(KBr)	2.05 (s, 3 H, $HgOCOCH_3$), 2.30 (s(br), 6 H, CH_3), 3.38 (s, 3 H, OCH_3), 5.28 (s, 1 H, H_c), 7.24 (m, 7 H, aromatic protons)	485
10	1590(CCl_4)	1.28 (t, 3 H, CH_3), 2.07 (s, 3 H, $HgOCOCH_3$), 3.62 (q, 2 H, OCH_2), 3.81 (s(br), 6 H, OCH_3), 5.40 (s, 1 H, H_c), 6.84 (dd, 1 H, H_b, J_{ab} = 8.0 Hz, $J_{bb'}$ = 2.5 Hz), 6.87 (d, 2 H, $H_{ee'}$, $J_{d'e'}$ = 8.5 Hz), 6.95 (d, 1 H, $H_{b'}$), 7.26 (d, 1 H, H_a), 7.28 (d, 2 H, $H_{dd'}$)	
11	1586(KBr)	2.00 (s, 6 H, $HgOCOCH_3$), 2.77 (s, 12 H, $N(CH_3)_2$), 3.35 (s, 3 H, OCH_3), 5.19 (s, 1 H, H_c), 6.69 (d, 2 H, $H_{ee'}$, $J_{de'}$ = 8.0 Hz), 7.14 (d, 2 H, $H_{dd'}$), 7.16 (s, 1 H, H_b), 7.33 (s, 1 H, H_a)	802
12	1585(KBr)	2.09 (s, 3 H, $HgOCOCH_3$), 2.15 (s, 3 H, $OCOCH_3$), 3.79 (s, 6 H, OCH_3), 6.30 (s, 1 H, H_c), 6.84 (d, 2 H, $H_{ee'}$, $J_{de'}$ = 9.0 Hz), 6.89 (dd, 1 H, H_b, J_{ab} = 8.0 Hz, $J_{bb'}$ = 2.0 Hz), 6.89 (d, 1 H, $H_{b'}$), 7.24 (d, 2 H, $H_{dd'}$), 7.49 (d, 1 H, H_a)	545

[a] Carbonyl of mercuric acetate group.[7] [b] Chloroform-*d* was used as the solvent and tetramethylsilane (TMS) as the internal standard.

Table III. Products Formed by Reaction of the Ortho-Metalated Complexes with $Hg(OCOCF_3)_2$

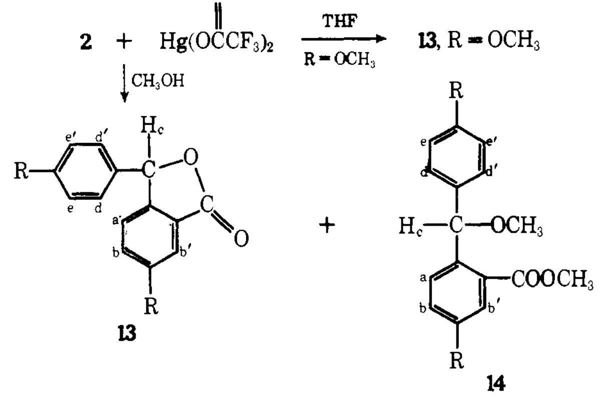
2, R =	Product[a]	Yields (%)	Mp (°C)
H	13, R = H	30	103.0–104.5
	14, R = H	33	Oil
OCH_3	13, R = OCH_3	41	133–135
	14, R = OCH_3	49	Oil
CH_3	13, R = CH_3	25	109–110
	14, R = CH_3	35	Oil

[a] All products gave satisfactory C and H analyses and the analytical data were made available to the editors and referees.

OCH_3, with *m*-chloroperbenzoic acid afforded **3**, R = OCH_3, and **13**, R = OCH_3, in 22 and 33% yields, respectively. The oxidation of ortho-metalated complexes **2**, R = H, OCH_3, CH_3, with excess of 30% hydrogen peroxide gave the lactones **13**, R = H, OCH_3, CH_3, in 49, 73, and 45% yields, respectively.

Use of equimolar quantities of reactants, or a slight excess of oxidizing agent, resulted in the generation of a mixture of lactone and thiolactone. However, thiolactones can be completely converted to the corresponding lactones by the use of a large excess of hydrogen peroxide in acetic anhydride. No reaction occurred when the lactone was exposed to 30% H_2O_2 in acetic anhydride.

Scheme III



Discussion

The thermal conversion of **2** to **3**, using Lewis bases, proceeds in good yields via initial ligand migration of the aro-

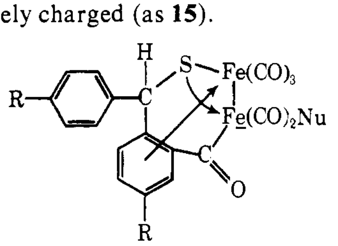
Table IV. Pertinent Spectral Data for Lactones 13 and Esters 14

Product	Irν_{CO}, cm^{-1} (Phase)[a]	NMR, ppm	MS, *m/e*
13, R = H	1758(KBr)	6.39 (s, 1 H, H_c), 7.94 (d, 1 H, $H_{b'}$, $J_{bb'}$ = 8.0 Hz), 7.20–7.70 (m, 8 H, other aromatic protons)	270, 226, 195
13, R = OCH_3	1762(KBr)	3.77 (s, 3 H, $R_2 = OCH_3$), 3.86 (s, 3 H, $R_1 = OCH_3$), 6.03 (s, 1 H, H_c), 6.82 (d, 2 H, $H_{ee'}$, $J_{de} = J_{d'e'}$ = 9.0 Hz), 6.85 (dd, 1 H, H_b, J_{ab} = 9.0 Hz, $J_{bb'}$ = 1.5 Hz), 7.01 (d, 2 H, $H_{dd'}$), 7.36 (d, 1 H, $H_{b'}$), 7.80 (d, 1 H, H_a)	
13, R = CH_3	1760(KBr)	2.32 (s, 3 H, $R_2 = CH_3$), 2.45 (s, 3 H, $R_1 = CH_3$), 6.32 (s, 1 H, H_c), 6.95–7.20 (m, 5 H, $H_{dd'}$, $H_{ee'}$, H_b), 7.41 (d, 1, H, H_a, J_{ab} = 7.5 Hz), 7.68 (s(br), 1 H, $H_{b'}$)	
14, R = H	1730(CCl_4)	3.38 (s, 3 H, OCH_3), 3.82 (s, 3 H, $OCOCH_3$), 7.18 (m, 9 H, aromatic protons)	256, 225, 198
14, R = OCH_3	1729(CCl_4)	3.32 (s, 3 H, OCH_3), 3.72 (s, 3 H, $R_2 = OCH_3$), 3.76 (s, 3 H, $R_1 = OCH_3$), 3.86 (s, 3 H, $OCOCH_3$), 6.08 (s, 1 H, H_c), 6.81 (d, 2 H, $H_{ee'}$, $J_{de} = J_{d'e'}$ = 8.5 Hz), 6.92 (dd, 1 H, H_b, J_{ab} = 8.0 Hz, $J_{bb'}$ = 2.5 Hz), 7.28 (d, 2 H, $H_{dd'}$), 7.36 (d, 1 H, $H_{b'}$), 7.50 (d, 1 H, H_a)	
14, R = CH_3	1722(neat)	2.28 (s, 3 H, $R_2 = CH_3$), 2.31 (s, 3 H, $R_1 = CH_3$), 3.33 (s, 3 H, OCH_3), 3.82 (s, 3 H, $OCOCH_3$), 6.11 (s, 1 H, H_c), 7.04 (d, 2 H, $H_{ee'}$, $J_{de} = J_{d'e'}$ = 8.0 Hz), 7.06 (dd, 1 H, J_{ab} = 7.5 Hz, $J_{bb'}$ = 2.0 Hz, H_b), 7.25 (d, 2 H, $H_{dd'}$), 7.37 (d, 2 H, H_a), 7.62 (s(br), 1 H, $H_{b'}$)	284, 269, 253

[a] Reference 8.

matic carbon-iron σ-bond of **2** to a terminal carbonyl carbon to give **4** (Scheme I). Alkyl and aryl manganese pentacarbonyls undergo a similar type of reaction with n-donor ligands.[9] Addition of the ligand (e.g., $P(C_6H_5)_3$) to the 16-electron iron atom of **4** would give **5** which collapses, at elevated temperatures, to the thiolactone. Iron-iron bond cleavage or carbon monoxide loss may compete with C-Fe σ-bond migration when ultraviolet light is used to convert **2** to **3**.

The mechanism for the high yield conversion of **2** to **3** by anionic reagents is probably very similar to that outlined in Scheme I, except for complex **5**, which, in these reactions, would be negatively charged (as **15**).



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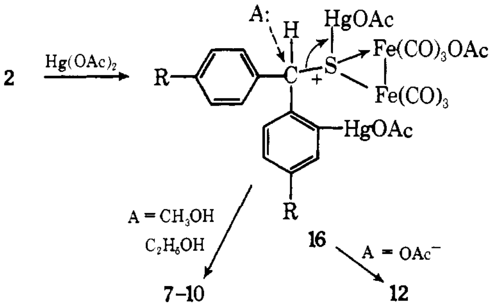
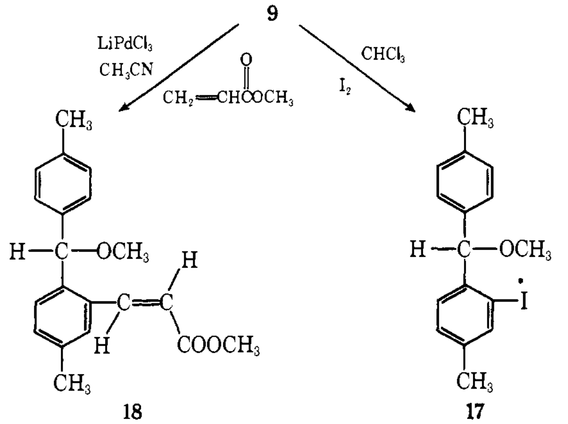
$Nu^- = OH^-, OCH_3^-, Br^-, N_3^-, OC(CH_3)_3^-, NCS^-$

Mercuric acetate probably serves two functions in reactions with the ortho-metalated complexes (Scheme IV)—cleavage of the iron-carbon σ-bond (rather than ligand migration to give the carbonyl inserted product) and mercuration at sulfur to give **16**. In an alcohol medium, the ether arises from attack by the solvent at the benzylic carbon of **18**, followed by proton loss. In THF, attack of acetate ion on **18** would afford the ester. Reaction of thiobenzophenones with $Fe_2(CO)_9$, and subsequent mercuric acetate treatment, thus results in transformation of a thione group to an ether or ester, with concurrent ortho-mercuration, in good overall yield. Since it is well recognized that the mercuric acetate group can be readily displaced under mild conditions, using a wide range of reagents,[10] the reactions described above represent a simple and convenient approach to aromatics which are otherwise difficult to impossible to synthesize. For example, treatment of **9** with iodine in chloroform affords the iodide **17** in 74% yield, while the cinnamate ester **18** was isolated in 54% yield by coupling of methyl acrylate with the aryl palladium chloride derived from **9**.[11]

Scheme IV





No analog of the mercuric acetate cleavage products was isolated using $Hg(OCOCF_3)_2$. The mercuric trifluoroacetate reaction may proceed via the thiolactone, since exposure of **3**, R = CH_3, to the reagent afforded **13** and **14**, R = CH_3. It seems likely that the critical step in the ortho-metalated complex-$Hg(OCOCF_3)_2$ reaction is a ligand migration process identical with that described earlier (with mercuration probably occurring simultaneously at sulfur) to give **19** (Scheme V). Oxidative addition of the reagent at the 16-electron iron atom of **19** would afford **20** which may then collapse to **21**, **21** simply being the S-mercurated thiolactone. Ring-opening of **21** would give **22**, the driving force being the stability of the resulting diarylmethyl carbonium ion. Ion **22** can react with methanol to afford the methoxy ester. An alternative pathway—the only pathway available when tetrahydrofuran is used as the solvent—is the addition of trifluoroacetate ion to give **23**. Cyclization of the latter would afford the oxonium ion **24**. The lactone could then be generated by elimination of the trifluoroacetyl group.

It is worthwhile noting that mercuric chloride can transform **2** to the thiolactones **3**. Further reaction does not occur, however, perhaps because mercuric chloride is less electrophilic than mercuric trifluoroacetate. It is not clear why $Hg(OCOCH_3)_2$ behaves so uniquely (i.e., C-Fe σ-bond cleavage occurs in preference to ligand migration).

The inexpensive reagent, 30% H_2O_2, can effect a novel synthesis of lactones from **2** (or thioketones derived therefrom). The initial formation of **3** probably occurs in the same manner as for the ceric ion reaction with **2**.[1]

In conclusion, this research has resulted in several important synthetic applications of intraligand aryl migration and other carbon-metal bond cleavage reactions of ortho-metalated complexes. These include a simple synthesis of aromatics not readily accessible by other means and high yield conversions of ortho-metalated complexes to thiolactones. Thiolactones (thiophthalides), previously little investigated,[12] undergo interesting ring-opening (e.g., desulfurization) and oxidation reactions.

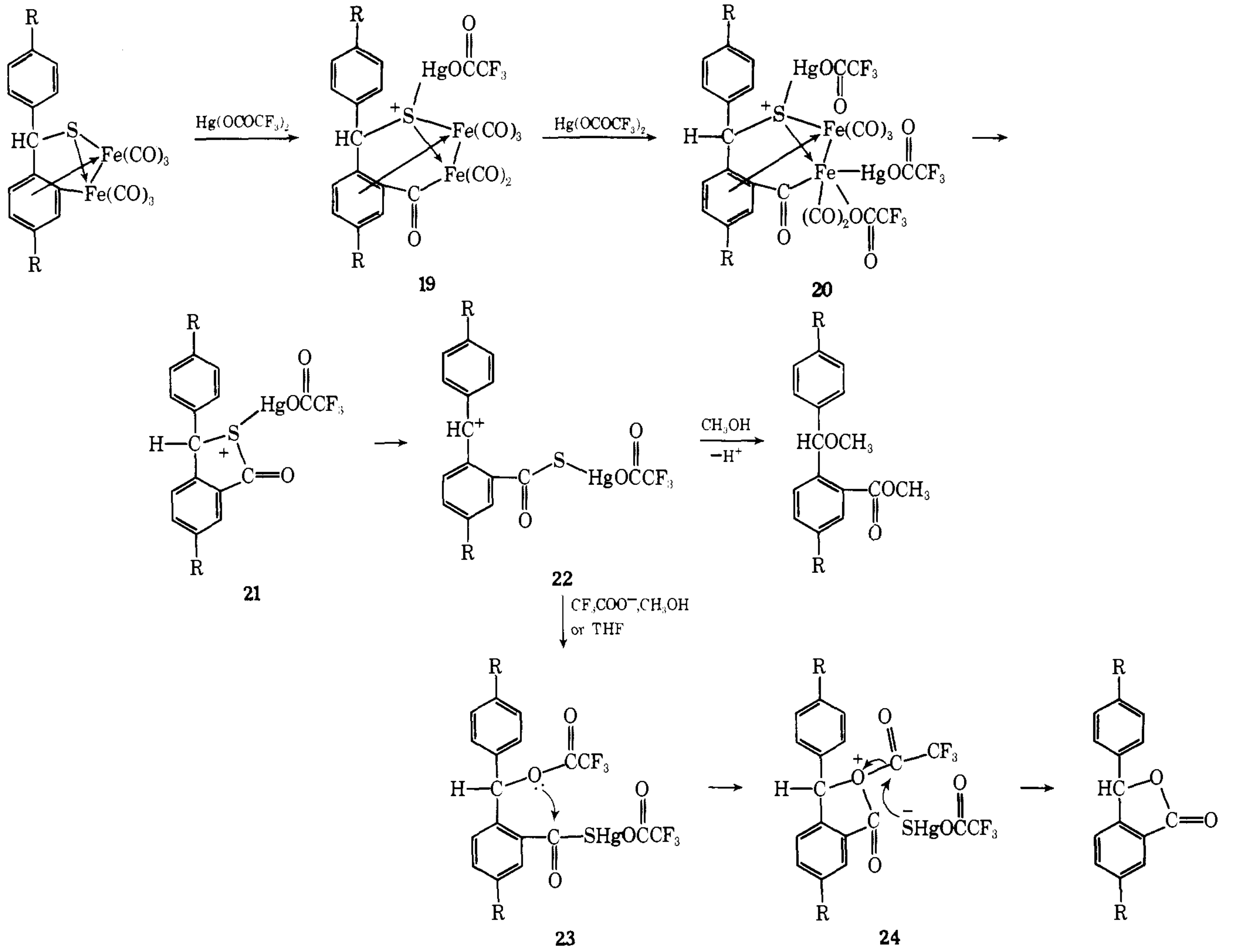
Experimental Section

General Procedure. Melting points were determined on a Fisher-Johns apparatus and are uncorrected. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn., Hoffman La Roche, Inc., Nutley, N.J., and by Instranal Laboratory, Inc., Rensselaer, N.Y. Infrared spectra were recorded on a Perkin-Elmer 457 grating spectrophotometer. Nuclear magnetic resonance spectra were determined using Varian A-60 and/or HA-100 spectrometers. Mass spectra were recorded on a Varian MS902 spectrometer.

All reactions were run under an atmosphere of dry nitrogen. Solvents were dried and purified by standard techniques.

Starting Materials. Diiron enneacarbonyl, $Fe_2(CO)_9$, was obtained from Pressure Chemical Co., Pittsburgh, Pa. 4,4′-Dimethoxythiobenzophenone was purchased from Aldrich Chemical Co., Milwaukee, Wis. All other thiobenzophenones were synthesized according to literature procedures.[13] The ortho-metalated complexes **2** (R = H, OCH_3, CH_3) were prepared according to the method of Alper and Chan.[1] The ortho-metalated complex **2**, R = CH_3, was prepared as follows. A mixture of 4,4′-dimethylthiobenzophenone (2.00 g, 8.80 mmol) and $Fe_2(CO)_9$ (4.90 g, 13.50 mmol) in benzene (70 ml) was stirred at room temperature for 36 hr. The reaction mixture was filtered through Celite 545 and the filtrate was flash evaporated under reduced pressure. The residue from flash evaporation was dissolved in the minimum amount of pentane and chromatographed on neutral alumina. Elution with pentane first gave a trace amount of $S_2Fe_3(CO)_9$, followed by **2**, R

Scheme V



= CH_3, in 73% yield: mp 104° dec; ir(CCl_4) ν_{CO} 2071 (m), 2039 (s), 1980 (s), and 1955 (s, sh) cm^{-1}; NMR ($CDCl_3$) 2.23 (s, CH_3 of uncomplexed benzene ring), 2.35 (s, CH_3 of complexed benzene ring), 5.52 (s, H_c), 6.36 (d, $H_{dd'}$, J_{de} or $J_{d'e'}$ = 8 Hz), 6.88-7.23 (m, H_b, $H_{ee'}$), 7.49 (d, H_a, J_{ab} = 8.5 Hz), 8.18 (s(vb), $H_{b'}$).

Anal. Calcd for $C_{21}H_{14}SFe_2O_6$: C, 49.85; H, 2.77. Found: C, 49.60; H, 2.78.

(i) **n-Donor Induced Carbonyl Insertion. (a) Reaction of 2, R = OCH_3, with Diethylamine, Diisopropylamine, *p*-Toluidine, or Triphenylphosphine.** To a benzene solution (50 ml) of the complex (0.717 g, 1.34 mmol) was added, drop-by-drop, excess diethylamine. The reaction mixture was heated in benzene at 60° for 2 days. The solution was cooled and filtered, and the filtrate was evaporated in vacuo to remove benzene and diethylamine. The residue resulting from evaporation was dissolved in the minimum amount of benzene and chromatographed on Florisil. Elution with 3:1 benzene-ether gave 0.186 g (49%) of the thiolactone **3**, R = OCH_3, mp 107-108° (lit.[1] mp 107-108°).

The thiolactone was formed in 77% yield when diisopropylamine was used instead of diethylamine as the reagent. *p*-Toluidine reacted with the complex, under identical conditions, to give **3**, R = OCH_3, in 18% yield. If triphenylphosphine was employed as the Lewis base, and the reaction mixture was refluxed in benzene for 24 hr, then a 42% yield of the thiolactone resulted.

(b) Reaction of 2, R = OCH_3, with Triphenylphosphine at Room Temperature. A mixture of **2**, R = OCH_3 (0.57 g, 1.06 mmol), and triphenylphosphine (1.70 g, 6.42 mmol) in hexane (100 ml) was stirred at room temperature for 12 hr. The mixture was then filtered and the solid product was washed thoroughly with hexane and dried in vacuo to give **5** in 80% yield: mp 125-127° dec; ir (KBr) ν_{CO} 2062 (s), 2021 (s), 1990 (vs), 1962 (vs), and 1946 (ms) cm^{-1}; NMR ($CDCl_3$) δ 3.78 (s, 3 H, OCH_3 of disubstituted ring), 3.81 (s, 3 H, OCH_3 of trisubstituted ring), 6.18 (s, 1 H, H_c), and 6.48-7.80 (aromatic protons).

Anal. Calcd for $C_{39}H_{29}Fe_2O_8PS$: C, 58.52; H, 3.65; Fe, 13.95; S, 4.00; mol wt, 800.4. Found: C, 58.87; H, 4.01; Fe, 14.25; S, 3.62, mol wt, 781.

(c) **Thermolysis of 5.** Complex **5** (0.11 g, 0.18 mmol), dissolved in benzene (50 ml), was refluxed for 22 hr. The solution was cooled and filtered, and the filtrate was flash evaporated under reduced pressure to give an oil. The latter was dissolved in benzene and chromatographed on Florisil. Elution with benzene gave triphenylphosphineiron tetracarbonyl, identified by comparison of spectral data with an authentic sample.[4] Further elution with benzene gave a small amount of an unidentified complex: ir (CCl_4) ν_{CO} 2042 (s), 1981 (s) cm^{-1}. Elution with ether or benzene-ether afforded the thiolactone **3**, R = OCH_3, in 57% yield.

(ii) **Photolytically Induced Carbonyl Insertion.** A mixture of **2**, R = OCH_3 (0.68 g, 1.26 mmol), and tetracyanoethylene (0.16 g, 1.26 mmol) in benzene (100 ml) was irradiated at 2537 Å for 5 hr. The mixture was filtered, and the filtrate was evaporated under reduced pressure. The residue was treated with hexane and filtered to give tetracyanoethyleneiron tetracarbonyl in 23% yield: mp 140° dec; ir (KBr) ν_{CN} 2220 (s) cm^{-1}; ν_{CO} 2164 (s), 2107 (m), 2055 (m) cm^{-1}; ir ($CHCl_3$) ν_{CN} 2220 (s) cm^{-1}; ν_{CO} 2155 (s), 2105 (s), 2050 (s) cm^{-1}.

Anal. Calcd for $C_{10}FeN_4O_4$: C, 40.50; H, 0.00; N, 19.00. Found: C, 39.54; H, 0.16; N, 20.18.

The filtrate, which contained a mixture of unreacted complex and the thiolactone (**3**, R = OCH_3) was flash evaporated under reduced pressure. The residue was dissolved in pentane and chromatographed on Florisil. Elution with pentane gave unreacted complex and elution with benzene afforded **3**, R = OCH_3, in 96% yield. No reaction occurred when **2**, R = OCH_3 (0.70 g, 1.30

mmol) was irradiated at 2537 Å in benzene (70 ml) for 17 hr.

(iii) Carbonyl Insertion Effected by Anionic Reagents. Desulfurization of the Resultant Thiolactones. (a) Reaction of 2, R = OCH_3, with NaSCN. A mixture of **2**, R = OCH_3 (0.50 g, 0.93 mmol), and NaSCN (0.42 g, 5.25 mmol) was dissolved in benzene (50 ml) and methanol (10 ml), and then stirred at reflux for 24 hr. The reaction mixture was cooled and filtered and the filtrate was flash evaporated in vacuo. The residue from flash evaporation was dissolved in the minimum amount of benzene and chromatographed on Florisil. Elution with benzene gave **3**, R = OCH_3, in quantitative yield, identified by comparison with an authentic sample.[1]

(b) Reaction of 2, R = OCH_3, with NaN_3. A mixture of **2**, R = OCH_3 (0.52 g, 0.96 mmol) and NaN_3 (0.39 g, 600 mmol) in absolute methanol (60 ml) was refluxed with stirring for 48 hr. Work-up as described for (a) gave **3**, R = OCH_3 in 72% yield.

(c) Reaction of 2, R = CH_3, with Cyanogen Bromide. A mixture of **2**, R = CH_3 (0.50 g, 0.93 mmol), and cyanogen bromide (0.59 g, 5.58 mmol) in benzene (70 ml) was stirred at reflux temperature for 3 days. The reaction mixture was filtered and the filtrate was flash evaporated under reduced pressure. The reaction solid contained a small amount of what may be $Fe(CO)_4CN$: ir (KBr) ν_{CN} 2200 (m); ν_{CO} 2130 (w), 2075 (s), and 2030 (m) cm^{-1}. Attempts to isolate this material in analytically pure form were unsuccessful. The red oil from flash evaporation of the filtrate was dissolved in hexane and filtered. The hexane solution was reduced in volume and cooled to give the thiolactone, **3**, R = CH_3, in 90% yield: mp 112–113°; ir (CCl_4) ν_{CO} 1685 cm^{-1}; NMR ($CDCl_3$) δ 2.32 (s, 3 H, CH_3 of the disubstituted benzene ring), 2.43 (s, 3 H, CH_3 of the trisubstituted benzene ring, 5.82 (s, 1 H, >CH), and 7.12 (m, 7 H, aromatic protons). The mother liquor was flash evaporated to give 0.07 g of an unidentified compound: mp 198° dec; ir (KBr) ν_{CO} 2089 (s), 2050 (m), 1995 (w), 1975 (s), and 1955 (m) cm^{-1}.

(d) Attempted Reaction of 2, R = OCH_3, with Methyl Iodide. A mixture of CH_3I (1.44 g, 8.05 mmol) and the complex (9.77 g, 1.43 mmol) in absolute methanol (60 ml) was stirred for 74 hr at 50°. Work-up gave recovered complex.

(e) Reaction of 2, R = OCH_3, with Sodium Hydroxide. A mixture of **2**, R = OCH_3 (0.70 g, 1.30 mmol), and NaOH (0.07 g, 1.75 mmol) in 95% ethanol (80 ml) was stirred at room temperature for 23 hr. The mixture was filtered and the filtrate was flash evaporated under reduced pressure. The resulting red oil was dissolved in benzene and chromatographed on neutral alumina. Elution with benzene gave unreacted **2**, R = OCH_3. Further elution afforded **3**, R = OCH_3, in 28% yield.

(f) Reaction of 2, R = OCH_3, with Sodium Methoxide. A mixture of **2**, R = OCH_3 (0.60 g, 1.11 mmol), and $NaOCH_3$ (0.07 g, 1.30 mmol) in tetrahydrofuran (70 ml) was stirred at room temperature for 45 hr. Work-up as described for (a) gave the thiolactone **3**, R = OCH_3, in 88% yield.

(g) Reaction of 2, R = OCH_3, with Potassium *tert*-Butoxide. Potassium *tert*-butoxide (0.51 g, 4.59 mmol) was added to **2**, R = OCH_3 (0.52 g, 0.98 mmol) in tetrahydrofuran (50 ml) at 0°. The reaction mixture was vigorously stirred for 2 hr. The mixture was filtered and the filtrate was flash evaporated under reduced pressure. The residue from flash evaporation was taken up in the minimum amount of benzene and chromatographed on Florisil. Elution with benzene first gave unreacted complex, followed by a mixture of **3**, R = OCH_3, and **2**, R = OCH_3. The latter mixture was rechromatographed on neutral alumina. Elution with benzene first afforded 1,1,2,2-tetra-*p*-methoxyphenylethane (**6**, R = OCH_3) as a yellow oil in 4% yield: NMR ($CDCl_3$) δ 3.67 (s, 12 H, R = OCH_3), 4.67 (s, 2 H, CH), 6.63 (d, 8 H, H_a, J_{ab} = 9 Hz), and 7.08 (d, 8 H, H_b). Further elution gave **3**, R = OCH_3, in 61% yield. When a mixture of **2**, R = OCH_3 (1.02 g, 9.90 mmol) and $KOC(CH_3)_3$ (1.28 g, 11.4 mmol) in *tert*-butyl alcohol (50 ml) was stirred at room temperature for 22 hr, only the ethane was formed in 28% yield. The product was purified as noted above (chromatography on neutral alumina). Reaction of **3**, R = OCH_3 (0.46 g, 1.60 mmol), with $KOC(CH_3)_3$ (1.07 g, 9.60 mmol) in *tert*-butyl alcohol (50 ml) at room temperature for 24 hr afforded **6**, R = OCH_3, in 16.3% yield. Work-up used was that described previously.

(h) Reaction of 2, R = CH_3, with Potassium *tert*-Butoxide in Benzene. Potassium *tert*-butoxide (0.19 g, 1.60 mmol) was added to **2**, R = CH_3 (0.61 g, 1.12 mmol) in benzene (70 ml) at 0°. The solution was allowed to warm to room temperature and then stirred for 44 hr. The reaction mixture was filtered, and the filtrate was flash evaporated under reduced pressure. The residue from flash evaporation was dissolved in benzene and chromatographed on neutral alumina. Elution with benzene gave a small amount of unreacted complex followed by the thiolactone, **3**, R = CH_3, in 95% yield.

In Tetrahydrofuran. Potassium *tert*-butoxide (0.80 g, 7.12 mmol) was added to **2**, R = CH_3 (0.60 g, 1.18 mmol) in tetrahydrofuran (80 ml) at 0°. The mixture was allowed to warm to room temperature and then was stirred for 22 hr. The reaction mixture was filtered and the filtrate was flash evaporated under reduced pressure. The residue from flash evaporation was triturated with pentane. The pentane solution was concentrated to a small volume and then chromatographed on Florisil. Elution with pentane gave **6**, R = CH_3, in 1.7% yield as a yellow oil: NMR ($CDCl_3$) δ 2.20 (s, 12 H, CH_3), 4.75 (s, 2 H, CH) and 7.17 (m, 16 H, aromatic protons).

In *tert*-Butyl Alcohol. A mixture of **2**, R = CH_3 (1.57 g, 3.11 mmol) and $KOC(CH_3)_3$ (2.10 g, 18.7 mmol) in *tert*-butyl alcohol (100 ml) was stirred for 20 hr. The reaction mixture was filtered and the filtrate was flash evaporated under reduced pressure. The residue from flash evaporation was dissolved in the minimum amount of benzene and chromatographed on neutral alumina. Elution with benzene first gave the tetraarylethane, **6**, R = CH_3, in 15% yield. Further elution with benzene and diethyl ether afforded the thiolactone, **3** (R = CH_3), in 18% yield.

(i) Reaction of 2, R = OCH_3 with Methylmagnesium Iodide. Methylmagnesium iodide (1.99 g, 12.00 mmol) in diethyl ether (50 ml) was added, drop-by-drop, to the complex (0.74 g, 1.38 mmol) in diethyl ether (40 ml). The reaction mixture was stirred at room temperature for 21 hr. The mixture was filtered and the filtrate was flash evaporated under reduced pressure at room temperature. The residue was dissolved in the minimum amount of benzene and chromatographed on neutral alumina. Elution with benzene afforded **6**, R = OCH_3, in 9.5% yield and then the volatile *S*-methyl thioacetate (NMR ($CDCl_3$) δ 2.25 (s, 3 H, CH_3 attached to sulfur) and 2.35 (s, 3 H, CH_3 adjacent to the carbonyl function)). The thioacetate was identified by comparison with spectral results of an authentic sample.[7] Further elution with benzene afforded **3**, R = OCH_3, in 22.5% yield.

(j) Reaction of 2, R = OCH_3, with Ethylmagnesium Bromide. Ethylmagnesium bromide (1.58 g, 12.00 mmol) in diethyl ether (50 ml) was added, drop-by-drop, to **2**, R = OCH_3 (0.88 g, 1.65 mmol), in diethyl ether (40 ml). The reaction mixture was stirred at room temperature for 19 hr. Work-up as described for (g) gave the ethane **6**, R = OCH_3, in 18% yield and the thiolactone **3**, R = OCH_3, in 17% yield.

(iv) Mercuric Acetate Cleavage Reactions. (a) General Procedure for the Reaction of the Ortho-Metalated Complexes with Mercuric Acetate in Methanol. Mercuric acetate (2.06 g, 6.48 mmol) was slowly added with stirring to the complex (1.15 mmol) dissolved in absolute methanol (80 ml). The mixture was stirred at room temperature for 24 hr. The reaction mixture was then filtered and the filtrate was flash evaporated under reduced pressure. The residue was treated with benzene and filtered and the filtrate was flash evaporated. The oil obtained from flash evaporation was crystallized from carbon tetrachloride and hexane to give pure aryl mercuric acetate. Pertinent physical and spectral data for the orthomercurated compounds may be found in Tables I and II.

(b) Reaction of 2, R = OCH_3, with Mercuric Acetate in 95% Ethanol. Reaction and work-up was effected in the same manner as in (a), except that 95% ethanol was used as the solvent.

(c) Reaction of 2, R = OCH_3, with Mercuric Acetate in Tetrahydrofuran. Reaction was effected in the same manner as in (a) except that tetrahydrofuran was used as the solvent. Work-up was effected as described in (a), except that recrystallization was carried out at −78° (Dry Ice-acetone).

(d) Reaction with Methyl Mercuric Acetate. A mixture of **2**, R = OCH_3 (0.70 g, 1.30 mmol) and methyl mercuric acetate (1.69 g, 6.15 mmol) in methanol (60 ml) was stirred at room temperature for 24 hr. Work-up gave recovered starting materials.

(e) Reaction of the Aryl Mercuric Acetate 9 with Iodine. Iodine (0.51 g, 2.0 mmol) was added to 0.97 g (2.0 mmol) of **9** dissolved in 20 ml of chloroform. After stirring at room temperature for 6 hr, the solution was filtered, and the filtrate was evaporated in vacuo. The resulting oil was treated with 5 ml of benzene and filtered, and the filtrate was chromatographed on neutral alumina.

Elution with benzene–chloroform gave 0.524 g (74% yield) of the aryl iodide **17** as an oil: mass spectrum (*m/e*) 352.

Anal. Calcd for $C_{16}H_{17}IO$: C, 54.57; H, 4.98. Found: C, 54.55; H, 5.03.

(f) Reaction of 9 with Methyl Acrylate and $LiPdCl_3$. A mixture of **9** (0.97 g, 2.0 mmol), methyl acrylate (1.03 g, 12 mmol), and 60 ml of 0.1 *M* $LiPdCl_3$ in acetonitrile was stirred for 2 days at room temperature. The solution was filtered, and flash evaporation of the filtrate gave an oil which was crystallized from hexane at −78°. Recrystallization from hexane or hexane–benzene gave 0.33 g (54%) of pure cinnamate ester **18**: mp 98–100°; ir (ν_{CO}) 1720, $\nu_{C=C}$ 1645 cm^{-1}; mass spectrum (*m/e*) 310.

Anal. Calcd for $C_{20}H_{22}O_3$; C, 77.37; H, 7.14. Found: C, 77.48; H, 6.97.

(v) Lactone and Ester Synthesis via Mercuric Trifluoroacetate. (a) General Procedure for Reaction of the Ortho-Metalated Complexes (2, R = H, OCH_3, CH_3) with Mercuric Trifluoroacetate in Methanol. A mixture of mercuric trifluoroacetate (5.36 g, 12.60 mmol), ortho-metalated complex (2.10 mmol), and absolute methanol (80 ml) was stirred at room temperature for 24 hr. The mixture was filtered and the filtrate was flash evaporated under reduced pressure. The residue from flash evaporation was dissolved in the minimum amount of benzene and chromatographed on silica gel. Elution with benzene–ether gave a mixture of lactone and alkoxy ester. The mixture was then taken up in the minimum amount of methanol, and hexane was added. The lactone **13** crystallized upon cooling and was filtered. Flash evaporation of the filtrate gave the ester **14.** See Tables III and IV for pertinent data for **13** and **14.**

(b) Reaction of 2, R = OCH_3, with $Hg(CF_3COO)_2$ in THF. A mixture of $Hg(OCOCF_3)_2$ (4.55 g, 10.70 mmol), **2,** R = OCH_3 (0.96 g, 1.78 mmol), and tetrahydrofuran (100 ml) was stirred at room temperature for 24 hr. The reaction mixture was filtered and the filtrate was flash evaporated under reduced pressure. The residue from flash evaporation was dissolved in benzene and filtered. This filtrate was flash evaporated under reduced pressure to give **13,** R = OCH_3, which was recrystallized from methanol–hexane. The yield was 77%.

(c) Reaction of 2, R = OCH_3, with Mercuric Chloride. A mixture of **2,** R = OCH_3 (0.61 g, 1.13 mmol), and $HgCl_2$ (1.74 g, 6.42 mmol) in absolute methanol (80 ml) was stirred for 72 hr at room temperature. Work-up as described in section ii-e gave **3,** R = OCH_3, in 60% yield.

(vi) Lactone Synthesis via 30% H_2O_2 or *m*-Chloroperbenzoic Acid. (a) *m*-Chloroperbenzoic Acid. A solution of *m*-chloroperbenzoic acid (4.43 g, 25.70 mmol) in benzene (100 ml) was added, drop-by-drop, to a solution of **2,** R = OCH_3 (0.60 g, 1.12 mmol), in benzene (50 ml) at 0°. The mixture was stirred for 2.5 hr and then filtered. The filtrate was washed successively with 5% $NaHSO_3$ (100 ml), 5% $NaHCO_3$ (100 ml), and finally with water (100 ml). The benzene extract was filtered through $MgSO_4$ and then flash evaporated under reduced pressure. The residue resulting from flash evaporation was taken up in the minimum amount of benzene and chromatographed on silica gel. Elution with benzene gave **3,** R = OCH_3 in 22% yield followed by **13,** R = OCH_3 (33% yield).

(b) Hydrogen Peroxide—General Procedure for Reaction with 2, R = H, OCH_3, CH_3. Hydrogen peroxide (0.96 ml, 11.16 mmol) was added dropwise to a stirred ice-cold solution of **2,** R = OCH_3 (1.00 g, 1.86 mmol) in acetic anhydride (40 ml). After addition was complete, the mixture was allowed to warm to room temperature and then stirred for 1–5 days. The mixture was filtered and the filtrate was flash evaporated under reduced pressure. The residue from flash evaporation was dissoved in the minimum amount of benzene and chromatographed on neutral alumina. Elution with benzene gave unreacted complex followed by a mixture of lactone and thiolactone. This latter mixture was rechromatographed on silica gel and elution with benzene gave thiolactone followed by lactone. Thiolactone can be completely converted to lactone using a large excess of H_2O_2 in acetic anhydride. No reaction occurred when the lactone was exposed to 30% H_2O_2. Yields and pertinent spectral data for the lactones are given in Tables III and IV.

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