

biomembranes themselves. The ability of the  $Mg^{2+}$  ion to form anhydrous as well as partly hydrated salt complexes with some of these functions, including the phosphate of phospholipids, especially cardiolipins,<sup>26,27</sup> is an important datum in considerations of biological Mg ionophoresis.

**Supplementary Material Available:** structure factors for the triclinic and orthorhombic crystals (18 pages). Ordering information is given on any current masthead page.

## References and Notes

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## Kinetics and Mechanism of the Alkyl and Aryl Elimination from $\eta^5$ -Cyclopentadienylalkyl (and -aryl)dicarbonyliron(II) Complexes Initiated by Mercury(II) Halides

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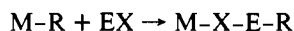
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**Abstract:** The reactions of  $\eta^5$ - $C_5H_5Fe(CO)_2R$  ( $R =$  alkyl and aryl) with  $HgX_2$  ( $X = Cl, Br, \text{ or } I$ ) in organic solvents (usually THF or isopropyl alcohol) were found to proceed by three distinct pathways, affording the following products: (1)  $\eta^5$ - $C_5H_5Fe(CO)_2X$  and  $RHgX$ , (2)  $\eta^5$ - $C_5H_5Fe(CO)_2HgX$  and  $RX$ , and (3)  $Hg_2X_2$  and various substances derived from decomposition of the oxidized  $\eta^5$ - $C_5H_5Fe(CO)_2R$ . The observed pathway(s) for the cleavage of the Fe-R bond depends principally on the ligand  $R$ . Accordingly, primary alkyl and aryl groups cleave mainly via reaction 1; secondary and tertiary alkyl, benzyl, and allyl groups react either exclusively or substantially by path 2; and the good electron releasing groups  $CH(CH_3)_2$  and  $CH_2C(CH_3)_3$  display the redox behavior of path 3. The rates of these cleavage reactions were monitored by infrared and  $^1H$  NMR spectroscopy, mostly at 25 °C. Third-order kinetics, first order in  $\eta^5$ - $C_5H_5Fe(CO)_2R$  and second order in  $HgX_2$ , were found for reactions 1 and 2 in THF or isopropyl alcohol, whereas second-order kinetics, first order in each of  $\eta^5$ - $C_5H_5Fe(CO)_2R$  and  $HgX_2$ , were found for reaction 3. Generally, the rate constants increase with the more negative values of the Taft  $\sigma^*$  of the alkyl group or  $\sigma^+$  of the aryl group, indicative of the electrophilic nature of these cleavages. A positive salt effect and a large solvent effect, THF (1)  $\ll$  isopropyl alcohol or acetone ( $\sim 10^3$ )  $\ll$  nitrobenzene ( $\sim 10^5$ ), were found in all cases. A mechanism is proposed which involves reversible addition of  $HgX_2$  to the metal in  $\eta^5$ - $C_5H_5Fe(CO)_2R$ , followed either by decomposition of the adduct to products (path 3) or by reaction with another molecule of  $HgX_2$  to give  $[\eta^5$ - $C_5H_5Fe(CO)_2(HgX)R]^+HgX_3^-$ . This second intermediate then undergoes reductive elimination of  $RHgX$  (path 1) or dissociation of  $R^+$  (path 2) to afford the observed products. Consistent with the proposed mechanism, the reaction by path 2 between the optically active  $\eta^5$ - $C_5H_5Fe(CO)_2^*CH(CH_3)C_6H_5$  and  $HgCl_2$  yields racemic  $C_6H_5(CH_3)CHCl$ .

Cleavage reactions of transition metal-carbon  $\sigma$  bonds ( $M-R$ ), both eliminative,



and insertion-like,



are processes of great importance in catalysis and stoichiometric synthesis.<sup>2-4</sup> Although the literature abounds in examples of such reactions, there is relatively little known about their mechanisms.

We have recently been engaged in a systematic investigation of mechanisms of cleavage reactions of  $\eta^5$ - $C_5H_5Fe(CO)LR$  ( $L = CO$  or  $P$  donor ligand) and related complexes with vari-

ous electrophilic reagents. The choice of  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})\text{LR}$  as the substrate complex was dictated by several considerations. First, compounds of this formula are known for a variety of alkyl and aryl groups R when L is CO or a phosphorus donor ligand. They are, on the whole, stable, readily accessible, and inexpensive organometallic derivatives. Second, stereochemical studies at  $\alpha$  carbon have been carried out, principally by Whitesides<sup>5,6</sup> and Baird,<sup>7,8</sup> for several cleavage reactions of  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})\text{LR}$ . These studies furnished useful information on the mechanism of such processes. Third, complexes of the formula  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})\text{LR}$  (or  $\eta^5\text{-cyclopentadienyl}$  ring-substituted analogues) where L is a phosphorus donor ligand contain a chiral metal center and have been shown to exhibit considerable configurational stability.<sup>9-11</sup> Thus they lend themselves well to studies of stereochemical changes at metal in various cleavage reactions. Several such investigations have now been reported.<sup>10-16</sup>

The last two considerations are especially important to our proposed study. This is because the mechanistic approach adopted here entails, whenever possible, complementary examination of the stereochemistry at both  $\alpha$  carbon and metal, as well as kinetics, for the same cleavage reaction of a given type of metal complex.

In our earlier papers described were kinetic studies on the electrophilic insertion reaction of  $\text{SO}_2$  with  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{R}$  and related complexes.<sup>17-19</sup> Stereochemical studies at the iron center for several Fe-R bond cleavage reactions, including that by  $\text{SO}_2$ , were also reported.<sup>10,14-16</sup> The investigation described herein is concerned with another electrophilic scission reaction of the Fe-R bond of  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{R}$ , namely that effected by  $\text{HgX}_2$  (X = Cl, Br, or I).

Since the environmentally important discovery by Wood and co-workers<sup>20</sup> of both enzymatic and nonenzymatic formation of  $\text{CH}_3\text{Hg}^+$  and  $(\text{CH}_3)_2\text{Hg}$  from methylcobalamin and mercury(II) salts, the electrophilic cleavage of transition metal-carbon  $\sigma$  bonds by various mercury(II) species has been the subject of extensive investigations. Several stereochemical<sup>21,22</sup> and kinetic<sup>23-29</sup> studies have been reported, primarily on cobalt(III) and chromium(III) compounds. Invariably a bimolecular interaction was found between the metal-alkyl complex and  $\text{HgX}_2$ , suggestive of an  $\text{S}_{\text{E}}2$  type of mechanism.

Now we describe in detail our kinetic studies of the reaction between various  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{R}$  alkyl and aryl complexes and mercury(II) halides. Based on these results and some complementary stereochemical data,<sup>6,7,15</sup> a mechanism is proposed which differs substantially from those invoked elsewhere.<sup>22-24</sup> A preliminary account of this work was communicated earlier.<sup>30</sup> The stereochemistry of the cleavage of an iron-secondary carbon  $\sigma$  bond is also described.

## Experimental Section

**General Procedures.** An argon atmosphere was employed routinely in all preparative and kinetic aspects of this work. Especially air sensitive solutions and those used for kinetic studies were prepared in a drybox. Ventron alumina, deactivated with distilled water (6-10%), or Florisil (60-100 mesh), from Fisher, were used in chromatographic separations and purifications. Unless otherwise specified ultraviolet irradiations were carried out in a Rayonet Model RPR-100 photochemical reactor using 16 3500-Å lamps. Mass spectra (MS) were recorded by Mr. C. R. Weisenberger on an A.E.I. Model MS-9 spectrometer and by Mr. R. Patterson on a DuPont Instruments 21-490 spectrometer connected to a Perkin-Elmer 990 gas chromatograph. Gas chromatography (GC) was performed on a Varian Associates Aerograph Series 1200 instrument using a 10% SE-30 column. Elemental analyses were done by Galbraith Laboratories, Inc., Knoxville, Tenn.

**Physical Measurements.** Melting points were obtained on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Specific rotations were measured at the sodium D line (589

nm) or mercury green line (546 nm) on a Perkin-Elmer Model 141 polarimeter using a 1-dm tube. Proton NMR spectra were obtained on a Varian Associates A-60A spectrometer using tetramethylsilane ( $\text{Me}_4\text{Si}$ ) as an internal standard. Infrared (IR) measurements were made on a Beckman IR-9 spectrophotometer using polystyrene film for calibration. The frequencies obtained are accurate to  $\pm 1 \text{ cm}^{-1}$ . Solutions were placed in 0.05-mm  $\text{CaF}_2$  cells, whereas gaseous materials were introduced into a 10-cm KBr cell for these measurements.

**Materials.** Reagent grade  $\text{HgCl}_2$  was used as received; for some reactions it was recrystallized from hot, freshly distilled dioxane and dried at  $100^\circ\text{C}$  ( $\sim 0.1$  Torr) for 24 h. Lithium chloride, also reagent grade, was dried for 24 h at  $100^\circ\text{C}$  ( $\sim 0.1$  Torr) and stored over  $\text{P}_4\text{O}_{10}$ . Reagent grade  $\text{NH}_4\text{PF}_6$  was recrystallized from hot methanol and dried at  $70^\circ\text{C}$  ( $\sim 0.1$  Torr) for 24 h. Tetrahydrofuran (THF), bp  $65\text{-}66^\circ\text{C}$ , and dioxane, bp  $100\text{-}101^\circ\text{C}$ , both reagent grade, were distilled from  $\text{LiAlH}_4$  under Ar immediately before use. Technical grade pentane was distilled from  $\text{CaH}_2$ , bp  $35^\circ\text{C}$ . Reagent grade isopropyl alcohol was saturated with Ar and stored over molecular sieves. All other chemicals and solvents procured commercially were reagent grade or equivalent quality and were used without further purification.

**Molecular Weight and Electrical Conductivity of  $\text{HgCl}_2$  in THF.** Using a Model 301-A Mechrolab osmometer, molecular weight of  $\text{HgCl}_2$  in THF solution was measured over the concentration range 0.02-0.14 M. An average value of 273 g/mol was obtained, with no observable increase at higher concentrations. Calcd for  $\text{HgCl}_2$ : 271.5 g/mol.

Conductivity measurements on 0.002-0.1 M solutions of  $\text{HgCl}_2$  in THF were made on an Industrial Instruments Co. Model RC 16B2 bridge. A molecular conductivity of  $(2.2 \pm 0.2) \times 10^{-3} \text{ cm}^2 \Omega^{-1}$  was obtained, which did not increase at lower concentrations of  $\text{HgCl}_2$ . A 0.001 M solution of  $\text{NH}_4\text{PF}_6$  in THF, measured for comparison, gave a molar conductivity of  $3.5 \text{ cm}^2 \Omega^{-1}$ .

**Metal Alkyls, Aryls, and Related Complexes.** The alkyl complexes  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{R}$  where R =  $\text{CH}_3$ ,<sup>31</sup>  $\text{CD}_3$ ,<sup>31</sup>  $\text{C}_2\text{H}_5$ ,<sup>31</sup>  $\text{CH}(\text{CH}_3)_2$ ,<sup>32</sup>  $\text{C}(\text{CH}_3)_3$ ,<sup>33</sup>  $\text{CH}_2\text{C}(\text{CH}_3)_3$ ,<sup>17</sup>  $\text{CH}_2\text{CH}_2\text{C}(\text{CH}_3)_3$ ,<sup>17</sup>  $\text{CH}_2\text{C}_6\text{H}_5$ ,<sup>34</sup>  $\text{CH}(\text{CH}_3)\text{C}_6\text{H}_5$ ,<sup>35</sup> (+)<sub>546</sub>- $\text{CH}(\text{CH}_3)\text{C}_6\text{H}_5$ ,<sup>35</sup>  $\text{CH}_2\text{Si}(\text{CH}_3)_3$ ,<sup>36</sup> and  $\text{C}(\text{CH}_3)\text{CH}_2\text{C}(\text{CN})_2\text{C}(\text{CN})_2\text{CH}_2$ <sup>37</sup> were prepared by known procedures. The complex with R =  $\text{CH}_2\text{CH}_2\text{C}_6\text{H}_5$  was obtained in 71% yield as yellow-orange crystals, mp  $75^\circ\text{C}$ , by the general method of Piper and Wilkinson<sup>31</sup> using  $\text{Na}[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]$  and  $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{Cl}$ :  $\nu(\text{C}\equiv\text{O})$  (pentane,  $\text{cm}^{-1}$ ) 2011 vs. 1959 vs;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\tau$ ) 2.80 (s, 5 H,  $\text{C}_6\text{H}_5$ ), 5.25 (s, 5 H,  $\text{C}_5\text{H}_5$ ), 7.79 ( $\text{A}_2\text{B}_2\text{m}$ , 4 H,  $\text{CH}_2\text{CH}_2$ ).

Anal. Calcd for  $\text{C}_{15}\text{H}_{14}\text{FeO}_2$ : C, 63.86; H, 5.00. Found: C, 63.93; H, 4.85.

The  $\eta^5\text{-indenyl}$  complex  $\eta^5\text{-C}_9\text{H}_7\text{Fe}(\text{CO})_2\text{CH}_2\text{C}_6\text{H}_5$  was prepared as reported previously.<sup>17</sup> The aryl complexes  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{C}_6\text{H}_5$  and  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{C}_6\text{H}_4\text{OCH}_3$ <sup>p</sup> were synthesized using the general procedure of King and Bisnette.<sup>38</sup>  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{C}_6\text{H}_4\text{Cl}$ <sup>p</sup>, mp  $91^\circ\text{C}$ , was prepared analogously in 26% yield:  $\nu(\text{C}\equiv\text{O})$  (pentane,  $\text{cm}^{-1}$ ) 2026 vs. 1976 vs;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\tau$ ) 2.86 ( $\text{A}_2\text{B}_2\text{m}$ , 4 H,  $\text{C}_6\text{H}_4$ ), 5.20 (s, 5 H,  $\text{C}_5\text{H}_5$ ).

Anal. Calcd for  $\text{C}_{13}\text{H}_9\text{ClFeO}_2$ : C, 54.12; H, 3.14. Found: C, 54.26; H, 2.96.

The complexes  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{Cl}$ <sup>39</sup> and  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{HgCl}$ <sup>40</sup> were made by known methods. The organochromium compounds  $\eta^5\text{-C}_5\text{H}_5\text{Cr}(\text{NO})_2\text{CH}_3$  and  $\eta^5\text{-C}_5\text{H}_5\text{Cr}(\text{NO})_2\text{Cl}$  were supplied by Ms. N. DeLuca.

**Reactions of Metal Alkyls and Aryls with Mercury(II) Halides.** Cleavage reactions between the metal-alkyl or -aryl complexes and  $\text{HgX}_2$  (X = Cl, Br, or I) were generally carried out in THF, and less frequently in isopropyl alcohol or acetone. All of the organometallic starting compounds were chromatographed immediately before use. Equimolar amounts of reactants, sometimes in higher concentrations than those used for the kinetic studies (vide infra), were generally employed to facilitate separation and identification of products. Metal carbonyl and nitrosyl products were characterized by a comparison of their melting points,  $^1\text{H}$  NMR spectra, and IR  $\nu(\text{C}\equiv\text{O})$  or  $\nu(\text{N}\equiv\text{O})$  with the corresponding literature data.

A Beer's law plot for the  $\nu_s(\text{C}\equiv\text{O}) = 2048 \text{ cm}^{-1}$  absorption of  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{Cl}$  in THF was found to be linear in the concentration range  $5 \times 10^{-3}$  to  $5 \times 10^{-2} \text{ M}$ . A similar plot for  $\nu_{\text{as}}(\text{C}\equiv\text{O}) = 1959 \text{ cm}^{-1}$  of  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{HgCl}$  in THF exhibits linearity over the concentrations  $2 \times 10^{-3}$  to  $2 \times 10^{-2} \text{ M}$ . These plots were often

employed in a direct determination of the yields of the appropriate iron carbonyl product in the reaction solution, since workup of such mixtures generally resulted in some decomposition.

The organomercury products  $\text{RHgX}$  were characterized by reference to their known melting points<sup>41-45</sup> and/or  $^1\text{H}$  NMR spectra.<sup>46</sup> Organic compounds formed in some reactions were removed with the solvent under reduced pressure ( $\sim 0.1$  Torr) from the metal-containing species and trapped at  $-196^\circ\text{C}$ . These solutions were then analyzed by GC-MS and/or by  $^1\text{H}$  NMR spectroscopy. The  $\text{Hg}_2\text{Cl}_2$  precipitate was characterized by its mass spectrum, consisting only of the ions  $\text{Hg}^+$ ,  $\text{HgCl}^+$ , and  $\text{HgCl}_2^+$ , and by its reaction with aqueous  $\text{OH}^-$ .<sup>47</sup> Liberated CO was identified by its characteristic IR absorption at  $2146\text{ cm}^{-1}$ .

**A.  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{R}$ , Where  $\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, \text{CH}_2\text{C}(\text{CH}_3)_3, \text{CH}_2\text{CH}_2\text{C}(\text{CH}_3)_3, \text{CH}_2\text{CH}_2\text{C}_6\text{H}_5, \text{ or } \text{CH}_2\text{Si}(\text{CH}_3)_3$ , with  $\text{HgCl}_2$ .** To  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{R}$  ( $\sim 0.5$  g) in 1–2 mL of THF was added an equimolar amount of  $\text{HgCl}_2$  dissolved in 1–3 mL of THF. The flask was stoppered and maintained at  $25^\circ\text{C}$  for 12 h, at which time the reaction was found by IR spectroscopy to be  $>95\%$  complete, with the only detectable metal carbonyl product being  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{Cl}$ . The solution was concentrated to  $\sim 1$  mL, treated with 5 mL of benzene, and chromatographed on a  $3 \times 20\text{-cm}$  column of Florisil. Pentane eluted any unreacted  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{R}$  (trace), then benzene removed colorless  $\text{RHgCl}$  (86–96%), and finally 3:1 (v/v)  $\text{CH}_2\text{Cl}_2$ /acetone eluted a red band containing  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{Cl}$  (82–94%). Some decomposition of the products occurred upon workup.

Based on the absorbance of the IR  $\nu(\text{C}\equiv\text{O})$  band of the  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{Cl}$ , yields of  $\geq 97\%$  were obtained in the reaction of  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{R}$  (0.5 mmol), where  $\text{R} = \text{CH}_3, \text{C}_2\text{H}_5$ , and  $\text{CH}_2\text{CH}_2\text{C}(\text{CH}_3)_3$  with ca. tenfold excess  $\text{HgCl}_2$  in THF (25 mL) at  $25^\circ\text{C}$ .

A solution of  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CH}_2\text{C}(\text{CH}_3)_3$  (0.06 g, 0.25 mmol) and  $\text{HgCl}_2$  (0.68 g, 2.5 mmol) in THF (25 mL) was stirred for 3 days. IR spectroscopy showed  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{Cl}$  (10%) to be the only iron carbonyl product. In addition, appreciable amounts of each of the following compounds were formed:  $\text{Hg}_2\text{Cl}_2$  as a gray-white precipitate, cyclopentadiene, neopentyl chloride, CO, and a THF-soluble iron-containing material free of CO or organic ligands, which was not characterized.

**B.  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CH}_3$  with  $\text{HgX}_2$ , Where  $\text{X} = \text{Br}$  or  $\text{I}$ .** Acetone solutions (10 mL) of approximately equimolar ( $\sim 1$  mmol)  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CH}_3$  and  $\text{HgX}_2$  were stirred for 12 h at  $25^\circ\text{C}$ . The solvent was removed, the residue was extracted with  $\text{CDCl}_3$ , and the extracts were filtered.  $^1\text{H}$  NMR spectra of the filtrate revealed the  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{X}$ <sup>48</sup> and  $\text{RHgX}$ .

**C.  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CH}_2\text{CH}_2\text{C}_6\text{H}_5$  with  $\text{HgX}_2$ , Where  $\text{X} = \text{Br}$  or  $\text{I}$ .** THF solutions (5 mL) of  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CH}_2\text{CH}_2\text{C}_6\text{H}_5$  ( $\sim 0.25$  mmol) and  $\text{HgX}_2$  (2.5 mmol) were stored for 48 h ( $\text{X} = \text{Br}$ ) and 2 weeks ( $\text{X} = \text{I}$ ) at  $25^\circ\text{C}$ . Only the  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{X}$  was detected by IR spectroscopy in the  $\nu(\text{C}\equiv\text{O})$  region.<sup>48</sup>

**D.  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CH}_2\text{C}_6\text{H}_5$  with  $\text{HgCl}_2$ .** A solution of the benzyl complex (0.15 g, 0.56 mmol) and  $\text{HgCl}_2$  (1.75 g, 6.45 mmol) in isopropyl alcohol (25 mL) was stirred for 3 h at  $25^\circ\text{C}$ , at which time IR spectroscopy showed the yield of  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{Cl}$  to be  $>50\%$ . A trace amount of  $\text{Hg}_2\text{Cl}_2$  along with an orange precipitate were filtered off, dissolved in  $\text{CHCl}_3$ , and chromatographed on a Florisil column. Elution with benzene removed  $\text{C}_6\text{H}_5\text{CH}_2\text{HgCl}$  (0.039 g, 22%) and elution with  $\text{CHCl}_3$  yielded yellow-orange  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{HgCl}$  (0.083 g, 36%).

Reaction between  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CH}_2\text{C}_6\text{H}_5$  (0.12 g, 0.45 mmol) and  $\text{HgCl}_2$  (0.66 g, 2.43 mmol) in THF ( $\sim 0.3$  mL) for 2 h at  $25^\circ\text{C}$  afforded 0.15 g (80%) of  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{HgCl}$  and 0.02 g (21%) of  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{Cl}$ .

**E.  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CH}(\text{CH}_3)_2$  with  $\text{HgCl}_2$ .** A solution of  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CH}(\text{CH}_3)_2$  (3.38 g, 15.7 mmol) and  $\text{HgCl}_2$  (2.72 g, 10.0 mmol) in THF (25 mL) under Ar was frozen, the Ar was pumped off on a vacuum line, and the reaction mixture was allowed to warm back to  $25^\circ\text{C}$ , at which temperature it was maintained for 27 h. The following materials were found to be present: (a) precipitated  $\text{Hg}_2\text{Cl}_2$ ,  $>95\%$  based on the  $\text{HgCl}_2$ ; (b) unreacted  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CH}(\text{CH}_3)_2$  (1.0 g, 4.5 mmol); (c)  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{HgCl}$  ( $<5\%$ ) and  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{Cl}$  (trace); (d) CO; and (e) propene, isopropyl chloride, and cyclopentadiene in the approximate ratio 0.4:0.8:1.0 (GC-MS analysis). In addition there were trace quantities of unidentified iron carbonyls, a species with  $\nu(\text{C}\equiv\text{O}) \sim 1750\text{ cm}^{-1}$  (probably  $(\text{CH}_3)_2\text{CHCOCl}$ ), and iron-containing de-

composition impurities. No  $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$  was detected.

When  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CH}(\text{CH}_3)_2$  (0.23 g, 1.0 mmol) and  $\text{HgCl}_2$  (5.53 g, 20.4 mmol) were allowed to react in the presence of 2,2-diphenyl-1-picrylhydrazyl (DPPH) (0.42 g, 1.1 mmol) in 25 mL of THF for 48 h at  $25^\circ\text{C}$ , the organic products were again propene, isopropyl chloride, and cyclopentadiene, but in the ratio 0.5:0.7:0.04 (GC-MS analysis). Also recovered from the reaction solution was a dark red crystalline compound characterized as 2,2-diphenyl-1-picrylhydrazine (0.31 g, 72%): mp  $171^\circ\text{C}$  (lit.<sup>49</sup> mp  $172\text{--}173^\circ\text{C}$ ); MS (70 eV, source temp  $90^\circ\text{C}$ )  $\text{P}^+ m/e$  395, no Fe or Hg;  $^1\text{H}$  NMR ( $\text{CDCl}_3, \tau$ )  $-0.33$  (s, br), 2.78 (c, br); IR spectrum (KBr pellet,  $\text{cm}^{-1}$ ) similar to that of DPPH, but shifted to lower frequency by  $5\text{--}55\text{ cm}^{-1}$  plus absorptions at 3290 m, 3110 w.

Anal. Calcd for  $\text{C}_{18}\text{H}_{13}\text{N}_5\text{O}_6$ : C, 54.68; H, 3.29; N, 17.72. Found: C, 54.78; H, 3.59; N, 14.56.

No other species was trapped.  $\text{Hg}_2\text{Cl}_2$  and unreacted  $\text{HgCl}_2$  were also isolated. Other metal-containing products were not examined.

**F.  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CH}(\text{CH}_3)\text{C}_6\text{H}_5$  and  $(+)\text{-}_{546}\text{-}\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CH}(\text{CH}_3)\text{C}_6\text{H}_5$  with  $\text{HgCl}_2$ .** A solution of  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CH}(\text{CH}_3)\text{C}_6\text{H}_5$  (0.087 g, 0.31 mmol) and  $\text{HgCl}_2$  (2.71 g, 10.0 mmol) in 25 mL of THF was stirred for 2 h at  $25^\circ\text{C}$ . A slight cloudiness was observed owing to the formation of trace  $\text{Hg}_2\text{Cl}_2$ . IR spectroscopy showed  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{HgCl}$  (91%) to be the only carbonyl-containing product.

To a solution of  $(+)\text{-}_{545}\text{-}\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CH}(\text{CH}_3)\text{C}_6\text{H}_5$  (0.16 g, 0.57 mmol),  $[\alpha]^{25}_{546} = +68^\circ$  ( $\text{CHCl}_3$  solution), in 1 mL of acetone was added  $\text{HgCl}_2$  (0.16 g, 0.59 mmol) dissolved in 4 mL of acetone. An immediate reaction was observed with the formation of  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{HgCl}$ . The mixture was stirred for 1 h at  $25^\circ\text{C}$  and the solvent and other volatile matter were removed at ca. 0.1 Torr and collected at  $-196^\circ\text{C}$ . After warming to  $25^\circ\text{C}$  the acetone was pumped off at ca. 20 Torr and the remaining clear liquid (0.034 g, 42%) was identified as  $\text{C}_6\text{H}_5(\text{CH}_3)\text{CHCl}$ : calculated MS  $\text{P}^+$  for  $\text{C}_8\text{H}_9\text{S}^{35}\text{Cl}$ ,  $m/e$  140.039 27; found  $m/e$  140.039 49 (70 eV, source temp  $120^\circ\text{C}$ ). A  $\text{CHCl}_3$  solution of this liquid showed  $[\alpha]^{25}_{589} = 0^\circ$ .<sup>50</sup>

**G.  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{C}(\text{CH}_3)_3$  with  $\text{HgX}_2$ , Where  $\text{X} = \text{Cl}, \text{Br}$ , or  $\text{I}$ .** A solution of  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{C}(\text{CH}_3)_3$  (0.12 g, 0.51 mmol) and  $\text{HgCl}_2$  (0.14 g, 0.51 mmol) in 1–2 mL of THF was stirred for 15 h at  $25^\circ\text{C}$ . Removal of the volatiles ( $\sim 0.1$  Torr) left 0.20 g (96%) for the yellow-orange  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{HgCl}$ . Analysis of the collected liquid revealed the presence of  $(\text{CH}_3)_3\text{CCl}$  characterized by MS and  $^1\text{H}$  NMR spectroscopy.<sup>51</sup>

A slurry of  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{C}(\text{CH}_3)_3$  (0.5–0.6 mmol) and  $\text{HgX}_2$  ( $\text{X} = \text{Br}$  or  $\text{I}$ ) (0.7–0.9 mmol) in ca. 0.5 mL of acetone- $d_6$  was allowed to react for 1 h at  $25^\circ\text{C}$ , additional solvent (2 mL) was introduced, and the solution was filtered.  $^1\text{H}$  NMR analysis of the filtrate revealed the  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{HgX}$ <sup>40</sup> and  $(\text{CH}_3)_3\text{CX}$ .<sup>51</sup>

**H.  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{R}$ , Where  $\text{R} = \text{C}_6\text{H}_5, p\text{-C}_6\text{H}_4\text{Cl}$ , and  $p\text{-C}_6\text{H}_4\text{OCH}_3$ , with  $\text{HgCl}_2$ .** The title aryl complexes (0.2–0.7 g) reacted with excess  $\text{HgCl}_2$  in ca. 5 mL of THF, acetone, or isopropyl alcohol at  $25^\circ\text{C}$  to afford  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{Cl}$  ( $>95\%$  by IR  $\nu(\text{C}\equiv\text{O})$  absorbance) and  $\text{RHgCl}$  ( $>85\%$ ) as the major products. Some  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{HgCl}$  ( $<5\%$ ) was detected by IR and  $^1\text{H}$  NMR spectroscopy for the reactions of the  $\text{R} = \text{C}_6\text{H}_5$  and  $p\text{-C}_6\text{H}_4\text{OCH}_3$  complexes in all three solvents.  $\text{Hg}_2\text{Cl}_2$  was observed, in trace amount, only in the reactions of the  $\text{R} = p\text{-C}_6\text{H}_4\text{OCH}_3$  complex.

**I.  $\eta^5\text{-C}_9\text{H}_7\text{Fe}(\text{CO})_2\text{CH}_2\text{C}_6\text{H}_5$  with  $\text{HgCl}_2$ .** The reaction of  $\eta^5\text{-C}_9\text{H}_7\text{Fe}(\text{CO})_2\text{CH}_2\text{C}_6\text{H}_5$  (0.0081 g, 0.025 mmol) with  $\text{HgCl}_2$  (0.91 g, 3.3 mmol) in THF (25 mL) for 12 h at  $25^\circ\text{C}$  yielded a red solution showing IR  $\nu(\text{C}\equiv\text{O})$  absorptions of  $\eta^5\text{-C}_9\text{H}_7\text{Fe}(\text{CO})_2\text{Cl}$  (2044 and 2000  $\text{cm}^{-1}$ ). No precipitate was formed.

**J.  $\eta^5\text{-C}_5\text{H}_5\text{Cr}(\text{NO})_2\text{CH}_3$  with  $\text{HgCl}_2$ .** A THF solution (25 mL) of  $\eta^5\text{-C}_5\text{H}_5\text{Cr}(\text{NO})_2\text{CH}_3$  (0.10 g, 0.52 mmol) and  $\text{HgCl}_2$  (0.20 g, 0.74 mmol) was stirred for 1.5 h at  $25^\circ\text{C}$ , at which time the IR spectrum showed complete conversion of the alkyl complex to  $\eta^5\text{-C}_5\text{H}_5\text{Cr}(\text{NO})_2\text{Cl}$ . Chromatography on a Florisil column, eluting with benzene and then with 3:1 (v/v)  $\text{CH}_2\text{Cl}_2$ /acetone, yielded  $\text{CH}_3\text{HgCl}$  (0.12 g, 92%) and  $\eta^5\text{-C}_5\text{H}_5\text{Cr}(\text{NO})_2\text{Cl}$  (0.10 g, 90%). Some decomposition of the products occurred upon workup.

**Reactions of  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{R}$  with  $\text{HgCl}_2$  in Dilute Solution.** The reactions of selected  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{R}$  with excess  $\text{HgCl}_2$  ( $\sim 0.01$  M) in THF ( $\text{R} = \text{CH}_3, \text{CH}_2\text{Si}(\text{CH}_3)_3, \text{CH}(\text{CH}_3)\text{C}_6\text{H}_5$ , and  $\text{C}(\text{CH}_3)_3$ ) or isopropyl alcohol ( $\text{R} = p\text{-C}_6\text{H}_4\text{OCH}_3$ ) at  $25^\circ\text{C}$  yielded the same products as the corresponding reactions run at higher  $[\text{HgCl}_2]$  (up to 1 M). The only detected iron carbonyl product was

$\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{Cl}$  when  $\text{R} = \text{CH}_3$ ,  $\text{CH}_2\text{Si}(\text{CH}_3)_3$ , and  $p\text{-C}_6\text{H}_4\text{OCH}_3$ , and the only observed iron carbonyl product was  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{HgCl}$  when  $\text{R} = \text{CH}(\text{CH}_3)\text{C}_6\text{H}_5$  and  $\text{C}(\text{CH}_3)_3$ .

**Attempted Reaction of  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{C}(\text{CH}_3)\text{CH}_2\text{C}(\text{CN})_2\text{C}(\text{CN})_2\text{CH}_2$  with  $\text{HgCl}_2$ .** No reaction was observed by IR spectroscopy when a THF solution (10 mL) of the title iron carbonyl (0.45 g, 1.25 mmol) and  $\text{HgCl}_2$  (0.34 g, 1.25 mmol) was stirred for 24 h at 25 °C. The solution was then saturated with  $\text{HgCl}_2$  and stirred for an additional 3 h. Still no reaction was noted.

**Attempted Reaction of  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CH}_3$  with  $\text{CH}_3\text{HgCl}$ .** A THF solution (2 mL) of  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CH}_3$  (0.34 g, 1.8 mmol) and  $\text{CH}_3\text{HgCl}$  (0.41 g, 1.6 mmol) was stored in a stoppered flask for 48 h at 25 °C. No  $(\text{CH}_3)_2\text{Hg}$ ,  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{Cl}$ , or any other products were detected by  $^1\text{H}$  NMR spectroscopy.

**Attempted Reactions of  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{Cl}$  and  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{HgCl}$  with  $\text{HgCl}_2$ .** Neither of the iron carbonyls ( $\sim 1.2$  mmol) was found by IR spectroscopy to react with  $\text{HgCl}_2$  (5 mmol) in THF (25 mL) in 24 h at 25 °C.

**Kinetic Measurements. A. By Infrared Spectroscopy.** Rates of the cleavage reactions were for the most part determined by following the disappearance of the lower frequency CO stretching absorption,  $\nu_{\text{as}}(\text{C}\equiv\text{O})$ , of the  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{R}$  on a Beckman Model IR-9 spectrophotometer using 0.05-mm  $\text{CaF}_2$  solution cells. In some cases, the disappearance of the higher frequency CO stretching band,  $\nu_s(\text{C}\equiv\text{O})$ , of the  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{X}$  product was also monitored for an independent check. Recrystallized  $\text{HgCl}_2$  was found to react with  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CH}_3$  at the same rate as reagent grade  $\text{HgCl}_2$ ; in view of this observation no further purification of any  $\text{HgX}_2$  was carried out. Solutions of  $\text{HgX}_2$  and  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{R}$  were prepared in a drybox, mixed there, and then placed in a thermostated bath ( $\pm 0.1$  °C) where they were magnetically stirred. Samples of these reaction solutions were periodically withdrawn with a syringe and transferred to the  $\text{CaF}_2$  cell for a single measurement of the absorbance of the appropriate  $\nu(\text{C}\equiv\text{O})$ . The faster reactions were followed by syringing freshly prepared solution mixtures directly into the IR cell for periodic measurements. The instrument room was maintained at  $25 \pm 1$  °C and care was exercised not to leave the solution cell in the IR beam between the measurements.

All reactions were run under pseudo-first-order conditions, with the concentration of  $\text{HgX}_2$ , generally 0.02–0.20 M, in at least tenfold excess of that of the iron complex. In the slower reactions, higher  $[\text{HgX}_2]$  was sometimes employed. Most of the cleavage reactions were followed for at least 3 half-lives; however, the slower ones and those yielding  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{HgX}$  could be monitored only for up to 2 half-lives. This is because the increasing concentration of  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{HgX}$  causes its  $\nu_{\text{as}}(\text{C}\equiv\text{O})$  band at ca.  $1960\text{ cm}^{-1}$  eventually to contribute to the intensity of the monitored  $\nu_{\text{as}}(\text{C}\equiv\text{O})$  absorption of the  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{R}$ . When solutions in THF were prepared at 25 °C and then thermostated at a different temperature for kinetic runs, a correction in the concentration of reactants was made by taking into account the density change of the solvent.

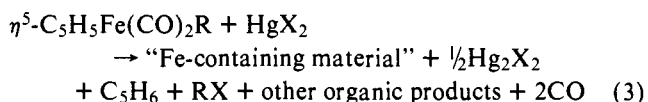
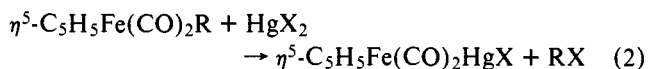
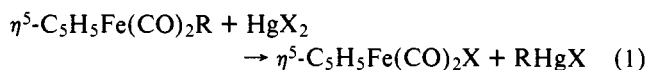
Beer's law was found to hold for the  $\nu_{\text{as}}(\text{C}\equiv\text{O})$  absorption of  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{R}$ , where  $\text{R} = \text{CH}_3$ ,  $\text{C}_2\text{H}_5$ ,  $\text{CH}(\text{CH}_3)_2$ , and  $\text{CH}_2\text{C}(\text{CH}_3)_3$ , in the concentration range  $2 \times 10^{-3}$  to  $5 \times 10^{-2}$  M in THF. It was assumed also to be valid for the other iron-alkyl and -aryl complexes studied. Pseudo-first-order rate constants,  $k_{\text{obsd}}$ , were obtained by plotting  $-\ln(A - A_\infty)$  vs. time, where  $A$  is the absorbance at any time of the reaction and  $A_\infty$  is the absorbance at infinite time. As all of the cleavages were found to proceed to completion,  $A_\infty$  is zero. Rate constants are reproducible to  $\pm 5\%$  except as noted in the tables.

**B. By  $^1\text{H}$  NMR Spectroscopy.** The reaction between  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CH}_3$  and  $\text{HgCl}_2$  in THF was also followed by  $^1\text{H}$  NMR spectroscopy in order to obtain directly the dependence of the rate on the concentration of  $\text{HgCl}_2$ . A tenfold excess of alkyl complex ( $\sim 1$  M) over  $\text{HgCl}_2$  was employed and the cleavage was monitored in a sealed NMR tube at  $25 \pm 2$  °C for 2–3 half-lives on a Varian Associates A-60A instrument. No decomposition or precipitation was observed in this time. The reactant and product concentrations were obtained from the relative integrated peak areas of the  $\eta^5\text{-C}_5\text{H}_5$  resonances of the alkyl complex ( $\tau$  5.20) and  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{Cl}$  ( $\tau$  4.88). Each peak area was calculated from the average of at least four integrations. The individual integrations were reproducible to better than 5%. The average integrated area of the two peaks combined remained constant ( $\pm 2\%$ ) throughout the reaction. The area of the peak at  $\tau$  5.20 required a correction ( $\sim 4\%$ ) because of overlap with the  $^{13}\text{C}$

satellite of the proton resonance of the  $\alpha\text{-CH}_2$  group of the THF. The concentration of  $\text{HgCl}_2$  remaining at any time was determined by taking the quantity of  $\text{HgCl}_2$  consumed to be equal to the amount of  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{Cl}$  formed.

## Results

**Stoichiometry and Products.** Cleavage reactions of the organoiron complexes  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{R}$  with  $\text{HgX}_2$  ( $\text{X} = \text{Cl}$ ,  $\text{Br}$ , or  $\text{I}$ ) proceed according to the equations



Infrared spectrophotometric titrations of representative iron alkyls ( $\text{R} = \text{CH}_3$ ,  $\text{CH}(\text{CH}_3)_2$ , and  $\text{C}(\text{CH}_3)_3$ ) with  $\text{HgCl}_2$  yielded end points corresponding to the consumption of the reactants in a 1:1 molar ratio. Further evidence for this stoichiometry was provided by the isolation of  $\text{RHgX}$ ,  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{X}$ ,  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{HgX}$ , and  $\text{Hg}_2\text{X}_2$  in yields exceeding 90%. The formation of  $\text{RX}$  in eq 2 and of the organic products in eq 3 was ascertained qualitatively, but not measured to determine the stoichiometry.

Many of the  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{R}$  complexes examined were found to react by more than one path (i.e., eq 1–3), but generally one path predominated ( $>95\%$ ). A trace amount of  $\text{Hg}_2\text{Cl}_2$ , indicative of path 3, was often observed as one of the products in those reactions of  $\text{HgCl}_2$  where the main path was either 1 or 2. The course of reaction between  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{R}$  and  $\text{HgX}_2$  was found to depend markedly on the ligand  $\text{R}$ , but to be essentially invariant to the solvent and the halide  $\text{X}$ . Neither  $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$  nor elemental mercury was observed in any of these reactions.

The methyl and the primary alkyl complexes were found with one exception to react mainly ( $>95\%$ ) according to eq 1. The reaction of  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CH}_2\text{C}(\text{CH}_3)_3$  with  $\text{HgCl}_2$  proceeds via both pathways 1 and 3, with path 1 dominating at higher concentrations of  $\text{HgCl}_2$  ( $\geq 0.5$  M). No reactivity according to eq 2 was observed for any of the primary alkyliron complexes. The benzyl complex,  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CH}_2\text{C}_6\text{H}_5$ , undergoes cleavage to a significant extent by both paths 1 and 2, with path 1 being the principal reaction course for  $[\text{HgCl}_2] < 0.3$  M in isopropyl alcohol and for  $[\text{HgCl}_2] < 1.0$  M in THF.

The secondary and tertiary alkyliron complexes  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CH}(\text{CH}_3)\text{C}_6\text{H}_5$  and  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{C}(\text{CH}_3)_3$ , respectively, react mainly ( $>95\%$ ) by eq 2. There occurs also a slight amount of reaction 3, but no detectable reaction 1. Another tertiary alkyl complex,  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{C}(\text{CH}_3)\text{CH}_2\text{C}(\text{CN})_2\text{C}(\text{CN})_2\text{CH}_2$ , resists cleavage by  $\text{HgCl}_2$  in THF at 25 °C.

The most complex behavior was displayed by the isopropyl complex, which undergoes cleavage by all three pathways. Path 3 dominates at low concentrations of  $\text{HgCl}_2$  and with low molar ratios  $\text{HgCl}_2/\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CH}(\text{CH}_3)_2$ ; paths 1 and 2 gain importance at higher concentrations of  $\text{HgCl}_2$  and higher molar ratios  $\text{HgCl}_2/\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CH}(\text{CH}_3)_2$ , path 2 significantly and path 1 to a lesser extent. Summarized below are the results. All reactions were run in 25 mL of THF at 25 °C (Table I).

The aryliron complexes ( $\text{R} = \text{C}_6\text{H}_5$ ,  $p\text{-C}_6\text{H}_4\text{OCH}_3$ , and  $p\text{-C}_6\text{H}_4\text{Cl}$ ) cleave mainly according to eq 1. Some reactivity ( $<5\%$ ) along path 2 was observed when  $\text{R} = \text{C}_6\text{H}_5$  and  $p\text{-C}_6\text{H}_4\text{OCH}_3$ , with the latter aryl complex also displaying a

Table I

$\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CH}(\text{CH}_3)_2$ , g (mmol)	$\text{HgCl}_2$ , g (mmol)	Reaction time	$\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{HgCl}$ , %	$\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{Cl}$ , %
0.053 (0.24)	0.68 (2.5)	2 weeks	$2 \pm <1$	$<1$
0.28 (1.29)	3.94 (14.5)	24 h	$8 \pm 1$	$3 \pm 1$
0.14 (0.64)	5.53 (20.4)	24 h	$19 \pm 1$	$4 \pm 1$

Table II. Kinetic Data for the Reactions of  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{R}$  with  $\text{HgCl}_2^a$  at 25 °C

R	Solvent	Reaction path <sup>b</sup>	Taft $\sigma^*$ <sup>c</sup>	$\sigma^+$ <sup>d</sup>	$k_2$ , $\text{M}^{-1} \text{s}^{-1}$	$k_3$ , $\text{M}^{-2} \text{s}^{-1}$	Rel $k_3$	$\nu(\text{C}\equiv\text{O})$ , $\text{cm}^{-1}$ <sup>e</sup>
$\text{C}(\text{CH}_3)_3$	THF	2	-0.30			$9.3 \times 10^{-3}$	5500	1996, 1938
$\text{CH}_2\text{Si}(\text{CH}_3)_3$	THF	1	-0.26			$1.6 \times 10^{-3}$	940	2004, 1948
$\text{CH}(\text{CH}_3)\text{C}_6\text{H}_5$	THF	2	0.11 <sup>f</sup>			$1.2 \times 10^{-3}$	710	2001, 1945
$\text{CH}_3$	THF	1	0.00			$4.6 \times 10^{-4}$	270	2005, 1948
$\text{CH}_2\text{C}(\text{CH}_3)_3$	THF	1, 3	-0.16		$1.0 \times 10^{-4} g$	$1.1 \times 10^{-4} g$	65	1999, 1940.5
$\text{C}_2\text{H}_5$	THF	1	-0.10			$7.1 \times 10^{-5}$	42	2000, 1942
$\text{CH}_2\text{CH}_2\text{C}(\text{CH}_3)_3$	THF	1				$5.9 \times 10^{-5}$	35	2000, 1942.5
$\text{CH}_2\text{CH}_2\text{C}_6\text{H}_5$	THF	1	0.08			$7.4 \times 10^{-5}$ ( $3.7 \times 10^{-5}$ ) <sup>h</sup>	44 (22) <sup>h</sup>	2002, 1944
$\text{CH}(\text{CH}_3)_2$	THF	3, 2	-0.19		$4.3 \times 10^{-5}$	$1 \times 10^{-5} i$	6	1998, 1940
<i>p</i> - $\text{C}_6\text{H}_4\text{OCH}_3$	THF	1		-0.78		$1.1 \times 10^{-5}$ ( $5.5 \times 10^{-6}$ ) <sup>h</sup>	6 (3) <sup>h</sup>	2014, 1958
$\text{CH}_2\text{C}_6\text{H}_5$	THF	1, 2	0.22			$3.4 \times 10^{-6} j$ ( $1.7 \times 10^{-6}$ ) <sup>h</sup>	2 (1) <sup>h</sup>	2004, 1949
<i>p</i> - $\text{C}_6\text{H}_4\text{OCH}_3$	<i>i</i> - $\text{C}_3\text{H}_7\text{OH}$	1		-0.78		$4.9 \times 10^{-3}$	2900	2018, 1966
$\text{CH}_2\text{C}_6\text{H}_5$	<i>i</i> - $\text{C}_3\text{H}_7\text{OH}$	1, 2	0.22			$3.2 \times 10^{-3}$	1900	2010, 1956
$\text{C}_6\text{H}_5$	<i>i</i> - $\text{C}_3\text{H}_7\text{OH}$	1	0.60	0.00		$6.7 \times 10^{-4} k$	390	2019, 1967
<i>p</i> - $\text{C}_6\text{H}_4\text{Cl}$	<i>i</i> - $\text{C}_3\text{H}_7\text{OH}$	1		0.11		$3.8 \times 10^{-4} l$	220	2022.5, 1970

<sup>a</sup> 0.02–0.20 M unless noted otherwise. <sup>b</sup> Minor reaction paths are excluded; see text. <sup>c</sup> From J. Hine, "Physical Organic Chemistry", 2nd ed, McGraw-Hill, New York, N.Y., 1962, p 97, except as noted. <sup>d</sup> From H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **80**, 4979 (1958). <sup>e</sup> Measured in the solvent indicated. <sup>f</sup> From R. W. Taft, Jr., "Steric Effects in Organic Chemistry", M. S. Newman, Ed., Wiley, New York, N.Y., 1956, Chapter 13. <sup>g</sup>  $\pm 0.2 \times 10^{-4}$ . <sup>h</sup> Adjusted rate constant to compensate for the high (0.67 M) concentration of  $\text{HgCl}_2$ ; see text. <sup>i</sup>  $\pm 0.5 \times 10^{-5}$ . <sup>j</sup>  $\pm 0.8 \times 10^{-6}$ . <sup>k</sup>  $\pm 0.4 \times 10^{-4}$ . <sup>l</sup>  $\pm 0.3 \times 10^{-4}$ .

trace of reaction 3. No evidence of either reaction 2 or 3 was found when  $\text{R} = p\text{-C}_6\text{H}_4\text{Cl}$ .

The chromium complex  $\eta^5\text{-C}_5\text{H}_5\text{Cr}(\text{NO})_2\text{CH}_3$  appears to demethylate exclusively as its iron analogue in eq 1.

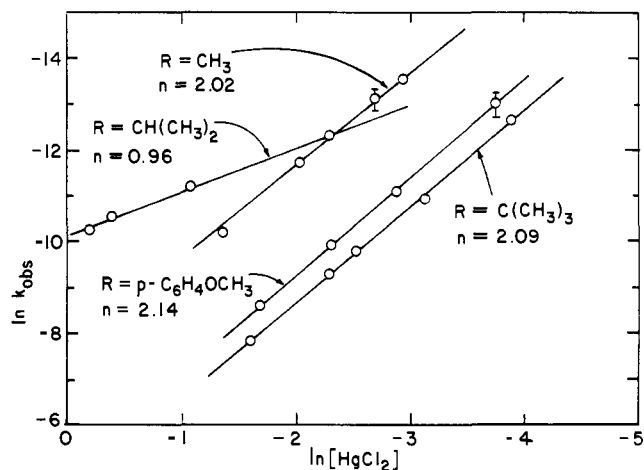
**Kinetic Determinations.** The rate constants for the cleavage reactions of  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{R}$  with  $\text{HgCl}_2$  at 25 °C are presented in Table II, with the principal reaction path(s) for each complex also given. All reactions were found to obey the rate expression

$$-\frac{d[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{R}]}{dt} = k_{\text{obsd}}[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{R}] \quad (4)$$

where  $k_{\text{obsd}} = k[\text{HgCl}_2]^n$ , giving good linear plots of  $-\ln A$  vs. time. No induction period was observed for any of the reactions. Plots of  $\ln k_{\text{obsd}}$  vs.  $\ln [\text{HgCl}_2]$  for the cleavage according to paths 1 and 2 of representative complexes in THF ( $\text{R} = \text{CH}_3$  and  $\text{C}(\text{CH}_3)_3$ ) and in isopropyl alcohol ( $\text{R} = p\text{-C}_6\text{H}_4\text{OCH}_3$ ) afforded straight lines with the slope (2.02, 2.09, and 2.14, respectively) equal to the order of the reaction in  $\text{HgCl}_2$ ,  $n$ . These plots are given in Figure 1. The cleavage of the  $\text{R} = \text{CH}_3$  and  $\text{C}(\text{CH}_3)_3$  complexes by  $\text{HgBr}_2$  and  $\text{HgI}_2$  showed the same second-order dependence on  $\text{HgX}_2$ , as did several other less thoroughly studied reactions of  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{R}$  with  $\text{HgCl}_2$ . Thus the kinetics of both reactions 1 and 2 are consistent with the rate expression

$$-\frac{d[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{R}]}{dt} = k_3[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{R}][\text{HgX}_2]^2 \quad (5)$$

The dependence of  $k_3$  on temperature was determined for the reactions of  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CH}_3$  with  $\text{HgCl}_2$  at 15.0–40.0 °C and  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{C}(\text{CH}_3)_3$  with  $\text{HgCl}_2$  at 10.0–40.0 °C, both in THF. The activation parameters are



**Figure 1.** Plots of  $\ln k_{\text{obsd}}$  vs.  $\ln [\text{HgCl}_2]$  for the reactions of  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{R}$  with ca. tenfold excess of  $\text{HgCl}_2$  in THF ( $\text{R} = \text{CH}_3$ ,  $\text{CH}(\text{CH}_3)_2$ , and  $\text{C}(\text{CH}_3)_3$ ) or isopropyl alcohol ( $\text{R} = p\text{-C}_6\text{H}_4\text{OCH}_3$ ) at 25 °C.  $n$  is the slope.

$\Delta H^\ddagger = 16.6 \pm 1.1$  kcal/mol and  $\Delta S^\ddagger = -18 \pm 4$  eu for the former and  $\Delta H^\ddagger = 15.7 \pm 1.0$  kcal/mol and  $\Delta S^\ddagger = -15 \pm 3$  eu for the latter.

A general phenomenon observed for reactions 1 and 2 is a gradual small increase in the rate constant with increasing concentration of either  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{R}$  or  $\text{HgX}_2$  above ca. 0.20–0.25 M. The extent of this increase appears to be independent of the nature of the organoiron complex; e.g., the values of  $k_3$  for the cleavage of the  $\text{R} = \text{CH}_3$ ,  $\text{C}_2\text{H}_5$ , and  $\text{CH}_2\text{CH}_2\text{C}(\text{CH}_3)_3$  complexes in THF increase identically as the concentration of  $\text{HgCl}_2$  (>0.20 M) increases. However,

the increase is dependent on the reaction path. Path 2 reactions are affected somewhat more than path 1 reactions. When  $[\text{HgCl}_2] = 0.67 \text{ M}$ , the calculated  $k_3$  for each of these path 1 reactions was twice that when  $[\text{HgCl}_2] \leq 0.20 \text{ M}$ . For the reaction of  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CH}_3$  ( $\sim 1 \text{ M}$ ) with  $\text{HgCl}_2$  ( $\sim 0.1 \text{ M}$ ) followed by  $^1\text{H}$  NMR spectroscopy both an excellent second-order dependence on  $\text{HgCl}_2$  and a similar rate enhancement to that found for high  $[\text{HgCl}_2]$  were noted (vide infra). For the above reasons and because of the failure of  $\text{HgCl}_2$  to show any measurable aggregation at concentrations up to  $0.15 \text{ M}$  (vide supra), we believe that this increase in the rate constant results from a change in the nature of the medium owing to the high concentration of reactants.<sup>52</sup> For kinetic runs carried out with  $0.67 \text{ M}$   $\text{HgCl}_2$ , the rate constants obtained from eq 5 are reported as such, and rate constants adjusted by half are given in parentheses in Table II. They are thought to provide a more meaningful comparison with the data obtained at the lower concentrations of  $\text{HgCl}_2$  than do the unadjusted rate constants.

In contrast to the reactions that proceed mainly by eq 1 or 2, the cleavage of  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CH}(\text{CH}_3)_2$  by  $\text{HgCl}_2$  in THF (eq 3) gives a  $\ln k_{\text{obsd}}$  vs.  $\ln [\text{HgCl}_2]$  plot whose slope equals 0.96 (Figure 1), indicative of the rate expression

$$\frac{d[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CH}(\text{CH}_3)_2]}{dt} = k_2[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CH}(\text{CH}_3)_2][\text{HgCl}_2] \quad (6)$$

The stoichiometry of the cleavage of  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{C}-\text{O})_2\text{CH}(\text{CH}_3)_2$  by  $\text{HgCl}_2$  is complicated by the occurrence of two major competing reaction paths. To circumvent this difficulty, the kinetic runs were made using  $[\text{HgCl}_2] < 0.20 \text{ M}$ . Under these conditions path 3 completely dominates and good overall second-order kinetics were observed. The third-order rate constant,  $k_3$ , for the competing reaction 2 was computed by making use of the experimentally determined yield of  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{HgCl}$  and the previously obtained rate constant  $k_2$  for the dominant reaction 3, and by assuming that reaction 2 is third-order overall as found for the cleavage of  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{R}$ , where  $\text{R} = \text{C}(\text{CH}_3)_3$  and  $\text{CH}(\text{CH}_3)\text{C}_6\text{H}_5$ . The rate constants  $k_2$  and  $k_3$  for the main reaction paths of  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CH}_2\text{C}(\text{CH}_3)_3$  with  $\text{HgCl}_2$  were calculated in a similar manner.

For  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CH}_2\text{C}_6\text{H}_5$  the separate rate constants for the two competing pathways 1 and 2 could not be obtained. The  $k_3$  given in Table II is a measure of the cleavage of this complex by both pathways combined.

The  $\eta^5$ -indenyl complex  $\eta^5\text{-C}_9\text{H}_7\text{Fe}(\text{CO})_2\text{CH}_2\text{C}_6\text{H}_5$  reacts with  $\text{HgCl}_2$  in THF some 20 times faster than does  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CH}_2\text{C}_6\text{H}_5$ . The reaction yields  $\eta^5\text{-C}_9\text{H}_7\text{Fe}(\text{CO})_2\text{Cl}$  and is first order in  $\eta^5\text{-C}_9\text{H}_7\text{Fe}(\text{C}-\text{O})_2\text{CH}_2\text{C}_6\text{H}_5$ , with  $k_{\text{obsd}} = 3.2 \times 10^{-5} \text{ s}^{-1}$  when  $[\text{HgCl}_2] = 0.67 \text{ M}$ .

The cleavage of  $\eta^5\text{-C}_5\text{H}_5\text{Cr}(\text{NO})_2\text{CH}_3$  by  $\text{HgCl}_2$  in THF at  $25^\circ\text{C}$  proceeds too rapidly to be measured by the techniques employed here.

The reaction of excess  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CH}_3$  with  $\text{HgCl}_2$  in THF monitored by  $^1\text{H}$  NMR spectroscopy gave linear plots of  $1/[\text{HgCl}_2]$ , vs. time, revealing a clear second-order dependence on  $\text{HgCl}_2$  in accord with the rate law

$$-\frac{d[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CH}_3]}{dt} = k'_{\text{obsd}}[\text{HgCl}_2]^2 \quad (7)$$

where  $k'_{\text{obsd}} = k_3[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CH}_3]$ . A third-order rate constant,  $k_3$ , of  $(1.0 \pm 0.1) \times 10^{-3} \text{ M}^{-2} \text{ s}^{-1}$  was obtained at  $25^\circ\text{C}$ . No formation of  $(\text{CH}_3)_2\text{Hg}$  or of any intermediate was observed.

The rate constants  $k_3$  for the reaction of  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{C}-\text{O})_2\text{C}(\text{CH}_3)_3$  and  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CH}_3$  with  $\text{HgX}_2$  ( $\text{X} = \text{Cl}$ ,

**Table III.** Rate Data for the Reactions of  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{R}$  with  $\text{HgX}_2$  in THF at  $25^\circ\text{C}$

R	X	Reaction path <sup>a</sup>	$k_3, \text{M}^{-2} \text{s}^{-1}$	Rel $k_3^b$
$\text{C}(\text{CH}_3)_3$	Cl	2	$9.3 \times 10^{-3}$	1.0
	Br	2	$3.2 \times 10^{-2}$	3.4
	I	2	$1.4 \times 10^{-2c}$	1.5
$\text{CH}_3$	Cl	1	$4.6 \times 10^{-4}$	27
	Br	1	$3.6 \times 10^{-4d}$	21 <sup>e</sup>
	I	1	$1.7 \times 10^{-5e}$	1

<sup>a</sup> Minor reaction paths are excluded; see text. <sup>b</sup> Different reference  $k_3$  for each alkyliron complex. <sup>c</sup>  $\pm 0.5 \times 10^{-2}$ . <sup>d</sup>  $\pm 0.3 \times 10^{-4}$ . <sup>e</sup>  $\pm 0.3 \times 10^{-5}$ .

Br, or I) in THF at  $25^\circ\text{C}$  are furnished in Table III. Little variation of  $k_3$  with X was found for the cleavage of the *tert*-butyl complex, the reactivity order being  $\text{X} = \text{Br} > \text{I} > \text{Cl}$ . For the methyl complex the reaction with  $\text{HgI}_2$  was markedly slower than that with either  $\text{HgBr}_2$  or  $\text{HgCl}_2$ , the dependence on X being  $\text{Cl} > \text{Br} \gg \text{I}$ . The less extensively studied reactions of  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CH}_2\text{CH}_2\text{C}_6\text{H}_5$  with  $\text{HgX}_2$  showed the same variation of the rate constant with X as those of its methyl analogue, i.e.,  $\text{X} = \text{Cl} > \text{Br} \gg \text{I}$ .

The rate data for the cleavage of the  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{R}$  ( $\text{R} = \text{C}(\text{CH}_3)_3$ ,  $\text{CH}(\text{CH}_3)_2$ , and  $\text{CH}_3$ ) by  $\text{HgCl}_2$  in THF at  $25^\circ\text{C}$  in the presence of added salt are summarized in Table IV. Whereas all three reactions showed a positive salt effect with added  $\text{NH}_4\text{PF}_6$ , only the reaction of  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{C}-\text{O})_2\text{C}(\text{CH}_3)_3$  showed an increase in rate with added LiCl.

Within experimental error, equal rate constants were obtained for the cleavage of  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CH}_3$  and  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CD}_3$  of comparable concentrations by  $0.5 \text{ M}$   $\text{HgCl}_2$  in THF solution at  $25^\circ\text{C}$ .

Addition of equimolar amounts of 2,2-diphenyl-1-picrylhydrazyl, hydroquinone, or galvinoxyl to THF solutions of  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CH}(\text{CH}_3)_2$  and  $\text{HgCl}_2$  (excess) at  $25^\circ\text{C}$  does not affect the rate of the cleavage and causes no induction period.

**Stereochemistry.** The cleavage of the Fe-C  $\sigma$  bond of  $(+)\text{546-}\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2^*\text{CH}(\text{CH}_3)\text{C}_6\text{H}_5$  by a slight excess of  $\text{HgCl}_2$  in acetone at  $25^\circ\text{C}$  proceeds according to eq 2 with complete racemization at the secondary,  $\alpha$ -carbon atom. The organic product,  $\alpha$ -methylbenzyl chloride, is known<sup>53</sup> to be configurationally stable when present alone in acetone at  $25^\circ\text{C}$ , but to undergo racemization in the presence of  $\text{HgCl}_2$ . However, the rate of this  $\text{HgCl}_2$ -promoted racemization of  $\text{C}_6\text{H}_5(\text{CH}_3)\text{CHCl}$  is much too slow to account for the lack of optical activity of the sample isolated from the reaction of the organoiron complex with  $\text{HgCl}_2$ . For comparison, when the concentrations of  $\text{C}_6\text{H}_5(\text{CH}_3)\text{CHCl}$  and  $\text{HgCl}_2$  are  $0.05$  and  $0.393 \text{ M}$ , respectively, Satchell<sup>53</sup> finds a  $k_{\text{obsd}}$  of  $1.26 \times 10^{-4} \text{ s}^{-1}$  ( $t_{1/2} \sim 1.6 \text{ h}$ ) for the racemization of the organic chloride at  $25^\circ\text{C}$ . In our cleavage experiment, where  $k_{\text{obsd}} = 1 \times 10^{-2} \text{ s}^{-1}$ , the initial concentration of the reacting  $\text{HgCl}_2$  was ca.  $0.12 \text{ M}$ , and the reaction was run for ca.  $1 \text{ h}$  at  $25^\circ\text{C}$ . Thus the isolated  $\text{C}_6\text{H}_5(\text{CH}_3)\text{CHCl}$  would have been substantially optically active if the scission of the Fe-C  $\sigma$  bond were reasonably stereospecific.

The observed lack of stereospecificity of the cleavage of  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2^*\text{CH}(\text{CH}_3)\text{C}_6\text{H}_5$  contrasts with the retention of configuration at the  $\alpha$  carbon in the reactions of  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CHDCHDC}(\text{CH}_3)_3^6$  and  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{C}-\text{O})_2\text{CHDCHDC}_6\text{H}_5^7$  with  $\text{HgCl}_2$ , which proceed according to eq 1.

## Discussion

Inspection of the data in Table II reveals that the rate constants for the cleavage generally decrease as the Taft polar



substituent constant,  $\sigma^*$ , of the group R becomes more positive. This points to the electrophilic nature of the cleavage process. Further support for an electrophilic interaction of  $\text{HgX}_2$  with  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{R}$  is found in the decrease of the rate constant for the cleavage of the aryl complexes as a function of increasing  $\sigma^+$  of the group R. A plot of  $\log(k_3/k_{3_0})$  vs.  $\sigma^+$ , shown in Figure 2, gives a linear correlation ( $r = 0.995$ ) and reveals very low sensitivity of the reaction to substituent effects, with  $\rho$  being  $-1.19$ . This may be compared with a  $\rho$  of  $-4.3$  for the  $\text{SO}_2$  insertion reaction of these iron-aryl complexes,<sup>17</sup> and a  $\rho$  of  $-6.3$  for the reactions of  $p\text{-XC}_6\text{H}_4\text{Co}(\text{dmgH})_2(\text{H}_2\text{O})$  ( $\text{dmgH}$  = dimethylglyoximate) with mercury(II) ion in  $\text{H}_2\text{O}$  to yield  $p\text{-XC}_6\text{H}_4\text{Hg}^+$  and  $\text{Co}(\text{dmgH})_2(\text{H}_2\text{O})_2$ .<sup>25</sup> The correlation with  $\sigma$  is not as good ( $r = 0.966$ ).

A relationship seems to exist between  $k_3$  and  $\nu(\text{C}\equiv\text{O})$  for the primary alkyl complexes that cleave via path 1, although the numbers compared span narrow ranges. The observed order of the rate constants,  $\text{R} = \text{CH}_2\text{Si}(\text{CH}_3)_3 > \text{CH}_2\text{C}(\text{CH}_3)_3 > \text{C}_2\text{H}_5 > \text{CH}_2\text{CH}_2\text{C}(\text{CH}_3)_3 > \text{CH}_2\text{CH}_2\text{C}_6\text{H}_5 \gg \text{CH}_2\text{C}_6\text{H}_5$ , parallels, with the exception of  $\text{R} = \text{CH}_2\text{Si}(\text{CH}_3)_3$ , the decrease in the carbonyl stretching frequencies of these complexes. The change in the frequencies is in the same direction as the progressively more negative values of  $\sigma^*$ . These trends indicate that the relative amount of electron density at the iron atom seems to influence the rate of the reactions proceeding by path 1.

In line with the above finding is the observed very fast cleavage of  $\eta^5\text{-C}_5\text{H}_5\text{Cr}(\text{NO})_2\text{CH}_3$  compared to that of the isoelectronic  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CH}_3$ . This may result from the lower formal oxidation state of chromium(0) than of iron(II) and is entirely consistent with the electrophilic nature of the reaction.

Steric effects appear to be less important than electronic effects in reactions proceeding by path 1, although the small size of the  $\text{CH}_3$  group may well account for its relatively rapid cleavage. Among the primary alkyl complexes, the two that react fastest are those with the bulkiest R groups,  $\text{CH}_2\text{Si}(\text{CH}_3)_3$  and  $\text{CH}_2\text{C}(\text{CH}_3)_3$ . This may be contrasted with the  $\text{SO}_2$  insertion, where the iron alkyls with large R groups generally react at reduced rates.<sup>17</sup>

The rate constants for reaction 1 are influenced by the nature of X in  $\text{HgX}_2$ . The general order of reactivity toward a given alkyl complex,  $\text{X} = \text{Cl} > \text{Br} \gg \text{I}$ , reflects the relative electrophilicities of these mercury(II) halides.

The cleavage according to path 2 is rather unexpected and, to our knowledge, completely unprecedented.<sup>53a</sup> Organoiron complexes with good electron releasing groups,  $\text{R} = \text{C}(\text{CH}_3)_3$  ( $\sigma^* = -0.30$ ) and  $\text{CH}(\text{CH}_3)_2$  ( $\sigma^* = -0.19$ ), as well as those with poor electron releasing groups,  $\text{R} = \text{CH}(\text{CH}_3)\text{C}_6\text{H}_5$  ( $\sigma^* = 0.11$ ) and  $\text{CH}_2\text{CH}=\text{CHCH}_3$ <sup>54</sup> ( $\sigma^* = 0.13$ ), react at varying but generally rapid rates via eq 2. The relative rate of the cleavage of  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{C}(\text{CH}_3)_3$  by  $\text{HgX}_2$  differs strikingly from that of its insertion of  $\text{SO}_2$ . When compared with the corresponding reactions of other  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{R}$  alkyls, the former is the fastest (cf. Table II) and the latter is one of the slowest.<sup>17</sup> It may seem surprising that  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{C}(\text{CH}_3)_3$  with its bulky *tert*-butyl group blocking both frontside and particularly backside attack at the Fe-C bond should be cleaved so readily. However, it is also to be noted that the size of the dissociating R alone cannot be a major rate enhancing factor as evidenced by the lack of observable reaction between  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{C}(\text{O})_2\text{C}(\text{CH}_3)\text{CH}_2\text{C}(\text{CN})_2\text{C}(\text{CN})_2\text{CH}_2$  and  $\text{HgCl}_2$ . This unreactivity may be a result of the poor electron releasing ability of the substituted cyclopentyl group, which is suggested by the high  $\nu(\text{C}\equiv\text{O})$  ( $2012$  and  $1958\text{ cm}^{-1}$  in THF solution) of its complex. An important feature of the complexes reacting by path 2 appears to be the presence of the ligand R that can dissociate off to generate a relatively stable carbonium ion,  $\text{R}^+$ .

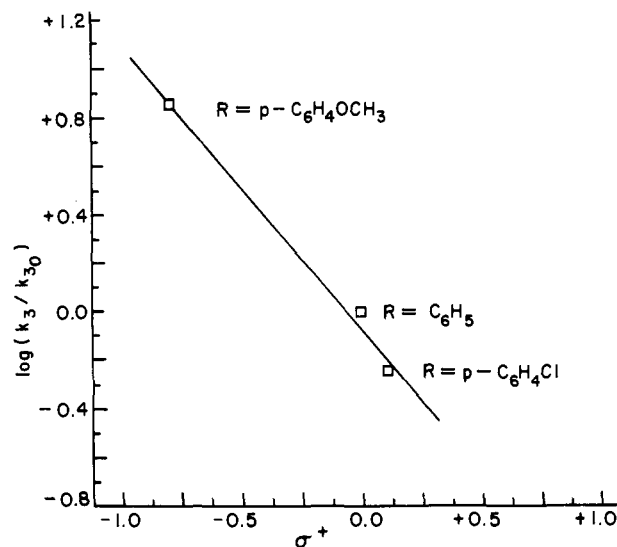


Figure 2. Plot of  $\log(k_3/k_{3_0})$  vs.  $\sigma^+$  for the reactions of some aryl complexes  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{R}$  with  $\text{HgCl}_2$  in THF at  $25^\circ\text{C}$ .

Thus, for example, the complex with  $\text{R} = \text{CH}(\text{CH}_3)\text{C}_6\text{H}_5$  is over 100 times as reactive toward  $\text{HgCl}_2$  as that with  $\text{R} = \text{CH}(\text{CH}_3)_2$ , even though the alkyl group in the latter is a better electron donor. Furthermore, the benzyl complex reacts in part by path 2, as do, to a much lesser extent, the aryl complexes with  $\text{R} = p\text{-C}_6\text{H}_4\text{OCH}_3$  and  $\text{C}_6\text{H}_5$ , but not that with  $\text{R} = p\text{-C}_6\text{H}_4\text{Cl}$ . None of the primary alkyl complexes investigated cleave by this route.

Reaction 3 appears to be a redox process which affords  $\text{Hg}_2\text{Cl}_2$  and products derived from decomposition of the oxidized  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{R}$ . Such behavior is not completely unexpected, since iron complexes of this formula are known to undergo oxidation.<sup>55</sup> The redox reaction 3 is quite common, usually occurring to a slight extent along with the cleavages by paths 1 and 2, and seems to be promoted by good electron releasing groups R. Thus, for example, the complexes with  $\text{R} = \text{CH}_2\text{C}(\text{CH}_3)_3$  and  $\text{CH}(\text{CH}_3)_2$  react with  $\text{HgCl}_2$  to a major extent via eq 3. The absence of an induction period, the failure of radical inhibitors to slow the rate or to trap any reaction species, and the lack of evidence for the formation of  $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$  all argue against a radical chain mechanism for this path.

A reasonable mechanism of these cleavage reactions is presented in Scheme I. The initial step in all three pathways is thought to be electrophilic attack of mercury at the electron-rich iron atom, leading to the formation of **1**, which is in equilibrium with the reactants. As no intermediates have been observed by either infrared or  $^1\text{H}$  NMR spectroscopy, the equilibrium constant  $K_1$  must be small. The formation of **1** would be favored by good electron-releasing groups R; also, as attack is at the iron atom rather than the Fe-C bond, steric inhibition by bulky ligands R will be of secondary importance and the low value of  $\rho$  is not unexpected.

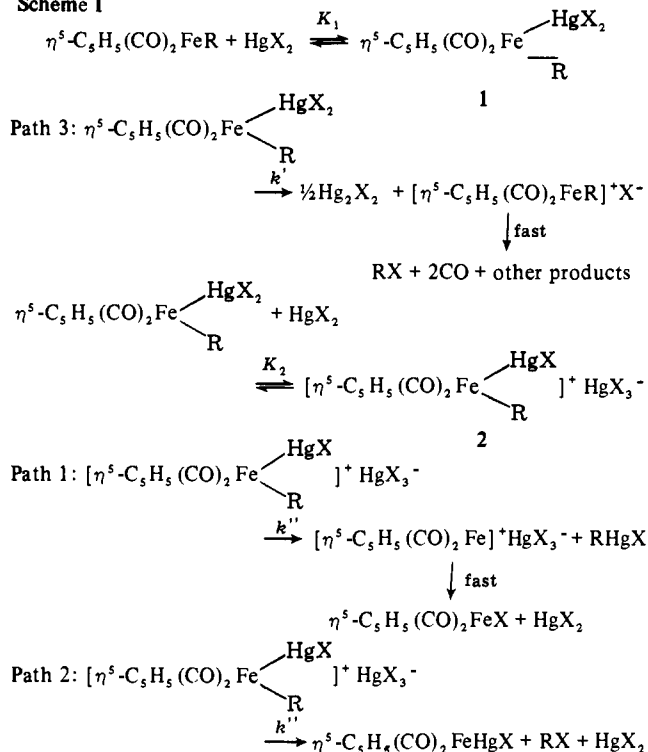
Evidence for 1:1 adducts between iron-alkyl complexes and  $\text{HgX}_2$  in equilibrium with the reactants is provided by a recent stereochemical study.<sup>15</sup> It was demonstrated that the diastereomers of  $(\eta^5\text{-1-CH}_3\text{-3-C}_6\text{H}_5\text{C}_5\text{H}_3)\text{Fe}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]\text{CH}_3$  undergo partial epimerization at iron in the course of their cleavage by a deficiency of  $\text{HgI}_2$ . The observed epimerization was ascribed to the formation of 1:1 adducts analogous to **1** or **2**, which undergo an intramolecular ligand scrambling before dissociation into reactants.

The intermediate **1** can revert to reactants or undergo one of two further processes. It can decompose by an internal redox reaction (path 3) with the formation of  $\text{Hg}_2\text{X}_2$  ( $k'$  sequence) or it can interact with another molecule of  $\text{HgX}_2$  to yield **2**. In

**Table IV.** Rate Data for the Reactions of  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{R}$  with  $\text{HgCl}_2$  in the Presence of Added Salt in THF at 25 °C<sup>a</sup>

R	Salt	Reaction path <sup>b</sup>	$k_{\text{obsd}}, \text{s}^{-1}$	% $\Delta k_{\text{obsd}}^c$
C(CH <sub>3</sub> ) <sub>3</sub>	NH <sub>4</sub> PF <sub>6</sub>	2	$9.3 \times 10^{-5}$	
	LiCl	2	$1.7 \times 10^{-4}$	85
CH(CH <sub>3</sub> ) <sub>2</sub>	NH <sub>4</sub> PF <sub>6</sub>	3	$4.3 \times 10^{-6}$	
	LiCl	3	$6.9 \times 10^{-6}$	60
CH <sub>3</sub>	NH <sub>4</sub> PF <sub>6</sub>	1	$4.6 \times 10^{-6}$	
	LiCl	1	$7.2 \times 10^{-6}$	56
			$4.1 \times 10^{-6}$	-11

<sup>a</sup> 0.1 M  $\text{HgCl}_2$ , 0.01 M  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{R}$ , and 0.01 M salt.  
<sup>b</sup> Minor reaction paths are excluded; see text. <sup>c</sup> Relative to reaction without added salt.

**Scheme I**

the  $k'$  sequence, cleavage of the Fe–R bond may result from nucleophilic attack by  $\text{X}^-$  on the  $\alpha$ -carbon atom of R in  $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{R}]^+$ .<sup>55</sup> When R = CH(CH<sub>3</sub>)<sub>2</sub> this process probably competes with  $\beta$ -hydride elimination to account for the formation of CH<sub>2</sub>=CHCH<sub>3</sub>.

The interaction of **1** with a second molecule of  $\text{HgX}_2$  is thought to occur with abstraction of  $\text{X}^-$  from the coordinated  $\text{HgX}_2$  to afford **2**, which can react further via path 1 or 2. When **2** contains an R group that forms a relatively stable carbonium ion, e.g., C(CH<sub>3</sub>)<sub>3</sub>, CH(CH<sub>3</sub>)C<sub>6</sub>H<sub>5</sub>, or allyl, dissociation of R<sup>+</sup> affords the observed  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{HgX}$  and RX. This mechanism is supported by the isolation of racemic C<sub>6</sub>H<sub>5</sub>(CH<sub>3</sub>)CHCl from the reaction of optically active  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CH}(\text{CH}_3)\text{C}_6\text{H}_5$  with  $\text{HgCl}_2$ . By contrast, if the R group does not give a stable carbonium ion, e.g., CH<sub>3</sub> or C<sub>2</sub>H<sub>5</sub>, reductive elimination of RHgX from **2** occurs instead to yield  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{X}$ . Such reductive elimination of RHgX should lead to retention of configuration at the  $\alpha$ -carbon atom of R, as indeed observed by Whitesides<sup>6</sup> and by Baird.<sup>7</sup> The proposed mechanism for the cleavage via path 1 is also consistent with the absence of any detectable isotope effect for  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CH}_3$  vs.  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CD}_3$ .

The mechanism depicted in Scheme I for the reactions according to paths 1 and 2 accommodates the observed increase in rate either upon changing the solvent from THF to isopropyl alcohol or acetone to nitrobenzene, or upon addition of NH<sub>4</sub>PF<sub>6</sub>. Introduction of LiCl inhibits the rate of reaction 1 probably by reducing the concentration of  $\text{HgCl}_2$  and thus shifting the equilibria  $K_1$  and  $K_2$  to the left. By contrast, the rate of reaction 2 is enhanced by added LiCl. Here a factor of major importance may be the effect of the medium on the dissociation of R<sup>+</sup> from **2**.

When **1** is stable with respect to decomposition via path 3 and the step  $k''$  is rate determining, the rate law in eq 8 follows. However, when **1** decomposes by the rate determining step  $k'$  according to path 3, the rate expression in eq 9 is derived

$$-\frac{d[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{R}]}{dt} = \frac{k''K_1K_2[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{R}][\text{HgX}_2]^2}{1 + K_1K_2[\text{HgX}_2]^2} \quad (8)$$

$$-\frac{d[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{R}]}{dt} = \frac{k'K_1[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{R}][\text{HgX}_2]}{1 + K_1[\text{HgX}_2]} \quad (9)$$

The latter reaction is promoted by  $k' > k''K_2$  and/or by low concentrations of  $\text{HgX}_2$ , as was observed for the  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{R}$ , where R = CH(CH<sub>3</sub>)<sub>2</sub> and CH<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub>. If  $K_1K_2[\text{HgX}_2]^2 \ll 1$  and  $K_1[\text{HgX}_2] \ll 1$ , eq 8 and 9 reduce to

$$-\frac{d[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{R}]}{dt} = k''K_1K_2[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{R}][\text{HgX}_2]^2 \quad (10)$$

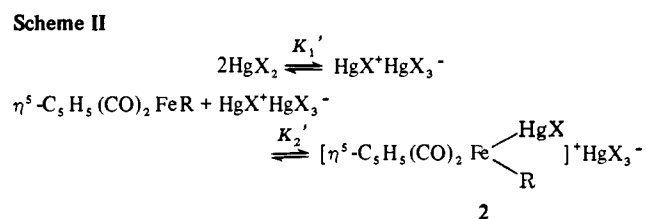
where  $k''K_1K_2 = k_3$ , and

$$-\frac{d[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{R}]}{dt} = k'K_1[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{R}][\text{HgX}_2] \quad (11)$$

where  $k'K_1 = k_2$ , respectively, and the observed kinetics are obtained.

Additional mechanisms may be proposed which are consistent with the observed kinetics; however, they do not fit all the data as well as does the mechanism in Scheme I. For example, the oxidation of the organoiron complexes by reaction 3 need not proceed via an Fe–Hg intermediate such as **1**; it may be occurring by an electron transfer process through ligand or solvent which is independent of paths 1 and 2. However, in such a case reaction 3 might be expected to occur exclusively of reactions 1 or 2 for some complexes. This was not observed. Furthermore, the extent of occurrence of reaction 3 as compared to reactions 1 and 2 is not affected by the use of more polar solvents; nor does reaction 3 exhibit a substantially different salt effect (Table IV).<sup>56</sup>

The second-order dependence on  $\text{HgX}_2$  for paths 1 and 2, the rate variations with ligand R, and the stereochemical results may all be accounted for alternatively by assuming the formation of the ion pair  $\text{HgX}^+\text{HgX}_3^-$  and its subsequent reaction with  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{R}$  to form **2** as depicted in Scheme II. Although molecular weight and conductivity





studies on solutions of  $\text{HgCl}_2$  in THF provide no evidence for the presence of  $\text{HgCl}^+\text{HgCl}_3^-$ , such a species may occur in low concentration and exhibit very high reactivity.<sup>57</sup> Notwithstanding these possibilities, we favor the mechanism in Scheme I, since it provides a more unified explanation of the first- and second-order dependence of these reactions on  $\text{HgX}_2$ . It is also in agreement with the report<sup>58</sup> of stepwise interaction of  $\text{HgX}_2$  with metal carbonyl complexes.

In conclusion we wish to point out that electrophilic addition of  $\text{HgX}_2$  to transition metals in low oxidation states is a well documented process.<sup>59-61</sup> The proposed interaction of  $\text{HgX}_2$  with the iron atom in  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{R}$  may be regarded as representing the same type of reaction. We would expect it to occur in those alkyl or aryl complexes where the metal possesses filled valence orbitals available for bonding and is open to attack by the sterically demanding  $\text{HgX}_2$ . Such complexes may include  $\text{M}(\text{CO})_5\text{R}$ <sup>62</sup> and various  $\text{M}(\text{CO})_{5-x}\text{L}_x\text{R}$  ( $\text{M} = \text{Mn}$  or  $\text{Re}$ ),  $\eta^5\text{-C}_5\text{H}_5\text{Ni}(\text{PR}'_3)\text{R}$ , and possibly  $\eta^5\text{-C}_5\text{H}_5\text{M}(\text{CO})_3\text{R}$  ( $\text{M} = \text{Mo}$  or  $\text{W}$ ), to mention a few. However, in alkylcobalamins and alkylcobaloximes, where the ligands protect the metal from external attack, electrophilic interaction of mercury(II) with the  $\alpha$ -carbon atom of R appears to occur instead.<sup>22</sup> A similar point of attack by mercury(II) has been proposed<sup>29</sup> for the dealkylation of  $\text{Cr}(\text{H}_2\text{O})_5\text{R}^{2+}$ , where interaction between the two metals would be impeded by the charge on the alkyl complex and the electronic configuration of chromium(III).

Very recently Slack and Baird<sup>8</sup> have applied orbital symmetry and energy considerations to reactions of  $d^1\text{-}d^9$  transition metal-alkyl complexes, including  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CH}_3$ . Taking the nonbonding d orbitals in these compounds to lie at higher energy than the filled bonding orbitals,<sup>63</sup> they predict that electrophilic metal-carbon bond scission reactions will normally involve initial oxidation of the metal. Our proposal of electrophilic attack of  $\text{HgX}_2$  at the iron in  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{R}$  is in complete accord with their prediction.

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- It may be noted in Table II that on changing solvent from THF to isopropyl alcohol reaction rates increase by  $\geq 10^3$ , with the reaction of  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CH}_2\text{C}_6\text{H}_5$  by paths 1 and 2 being enhanced more than the reaction of  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{C}_6\text{H}_4\text{OCH}_3$  by path 1. A similar rate enhancement over THF is found for acetone, and an increase on the order of  $10^5$  is observed for nitrobenzene solvent. These numbers underscore marked sensitivity of the rate of the cleavage to the nature of the reaction medium.
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- Note Added in Proof.** An apparent exception is the reaction between  $\eta^5\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{CH}_2\text{SCH}_3$  and  $\text{HgCl}_2$  which affords  $\eta^5\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{HgCl}$  and an unreported organic product; see R. B. King and M. B. Bisnette, *Inorg. Chem.*, **4**, 486 (1965).
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- See, for example, S. N. Anderson, C. W. Fong, and M. D. Johnson, *J. Chem. Soc., Chem. Commun.*, 163 (1973).
- In addition we note that a plot of  $1/k_{\text{obsd}}$  vs.  $1/[\text{HgCl}_2]$  for the reaction of  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CH}(\text{CH}_3)_2$  with  $\text{HgCl}_2$  in THF at  $25^\circ\text{C}$  shows a small positive *y* intercept on interpolation to  $1/[\text{HgCl}_2] = 0$ , consistent with the rate expression in eq 9, since

$$k_{\text{obsd}} = \frac{k'K_1[\text{HgX}_2]}{1 + K_1[\text{HgX}_2]}$$

and therefore

$$\frac{1}{k_{\text{obsd}}} = \frac{1}{k'K_1[\text{HgX}_2]} + \frac{1}{k'}$$

If no preequilibrium were involved in this cleavage, then the intercept would have been zero.

- Studies in aqueous media on the cleavage of  $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CH}_2\text{C}_6\text{H}_4\text{NH}^+$  by  $\text{HgCl}_2$  indicate that  $\text{HgCl}^+$  is 7000 times as reactive as  $\text{HgCl}_2$  (ref 23); however, no data are available for THF solutions.
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