and bridgehead sites ($H_{1,5,8}$), respectively, upon inspection of the spectra obtained from the 1-deuterio and 9-deuterio derivatives of **1**-OH. The carbon-13 NMR spectrum of **2** similarly displays three absorptions of approximately equal intensity which are assigned as indicated in Table I according to the effects of deuterium substitution.[5]

The methyl substituted ion **5** was similarly generated by reaction of **3**-OH with antimony pentafluoride in sulfuryl chlorofluoride at −80°. The proton NMR spectrum of **5** (R = CD_3) exhibits four absorptions (δ_H 2.00, 2.38, 3.82, and 4.07) in the ratio 2:3:2:1. The signal at δ 3.82 may be assigned to the equivalent bridgehead sites ($H_{1,8}$) since its intensity is reduced to one proton in the deuterated ion. The three-proton peak at δ 2.38 is attributed to the superposition of the two types of cyclopropane sites ($H_{2,3}$ and H_4) rather than the charged sites since the chemical shift is identical with that of the corresponding cyclopropane ring protons in the parent ion. This spectrum shows a reversible temperature dependence upon warming. At ca. 0–5° the bands at δ 2.00 and 2.38 merge into a single peak at δ 2.19 (~4 H), the band at δ 4.07 disappears, and that band at δ 3.82 remains unchanged. This behavior is consistent with a degenerate bridge-flip rearrangement which exchanges $H_{2,3}$ with $H_{6,7}$ and H_4 with H_5. Owing to decomposition, it was not possible to achieve sufficiently rapid exchange of H_4 and H_5 to observe the peak expected at the average position. The free energy of activation at coalescence ($\Delta G^{\ddagger}_{-8°}$ = 13.0 kcal/mol) is remarkably close to that found for the analogous bridge-flip rearrangement of the 7-methylnorbornadienyl ion ($\Delta G^{\ddagger}_{-14°}$ = 12.4 kcal/mol).[7] The carbon-13 NMR spectrum of **5** (R = CH_3) at −80° shows seven peaks which may be assigned as indicated in Table I on the basis of off-resonance decoupling, relative intensities of signals for carbons bearing one proton, the effect of deuterium substitution at C-1, and comparison with chemical shifts of the corresponding carbons in **2.**

The long-lived ion from the 9-phenyl precursor (**4**-OH) was best generated with fluorosulfonic acid. Since the proton NMR spectrum shows only three signals (δ 2.25, 3.40, and 4.60) in the ratio 4:2:2, in addition to the aromatic ring protons, and is unaffected by temperature changes in the range −75 to −25°,[8] the phenyl substituted ion evidently is undergoing a rapid bridge-flip rearrangement on the NMR time scale. This conclusion is supported by the observation of four signals (other than those for the aromatic ring carbons) in the carbon-13 NMR spectrum. Thus, the NMR chemical shifts reported in Table I for positions 2,3,6,7 and 4,5 are time-averaged values.

The relatively high field position of the charged carbons bearing the substituent in the carbon-13 NMR spectra of **5** ($\delta_{C_9^+}$ 69.12) and **6** ($\delta_{C_9^+}$ 87.62) as compared to the charged carbons in the 1-methylcyclopentyl ($\delta_{C_1^+}$ 337) and 1-phenylcyclopentyl ($\delta_{C_1^+}$ ~265) carbonium ions[9] is convincing evidence for the delocalized trishomocyclopropenium structures for both substituted ions. This conclusion is in line with the inability of a *p*-anisyl substituent to "level" homocyclopropylcarbinyl participation (and by inference either a methyl or phenyl substituent since their leveling capabilities are much less than that of the *p*-anisyl group) in the solvolysis of 8-*p*-anisy-*endo,anti*-tricyclo[3.2.1.$0^{2,4}$]oct-8-yl *p*-nitrobenzoate.[10] The high field position of the NMR signals for both the protons and carbons at the charged sites in **2** is consonant with data recently reported by Masamune and coworkers for the parent trishomocyclopropenium ion (δ_{H_1} 1.15; $\delta_{C_1^+}$ 4.7) and its ethano-bridged analog ($\delta_{H_{2,4}}$ 2.10, δ_{H_3} 1.44; $\delta_{C_{2,4}^+}$ 19.58, $\delta_{C_8^+}$ 0.0).[11] The high ^{13}C–H coupling constant at the charged sites ($J_{^{13}C_1-H}$ = 204 Hz) is indicative of a high S-character for these C–H bonds and typical of nonclassical ions.[9]

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Mechanism of Electrophilic Cleavage of Iron–Carbon σ Bonds by Mercury(II) Chloride

Sir:

The electrophilic cleavage of transition metal–carbon σ bonds by mercury(II) salts is a reaction of considerable importance[1-3] and current mechanistic interest.[4-18] When the cleaving reagent is HgX_2 (X = Cl, Br, or I), this reaction has been reported[11-16] to follow eq 1.

$$L_nMR + HgX_2 \longrightarrow L_nMX + RHgX \quad (1)$$

Our interest in the mechanism of insertion and eliminative cleavage[19] reactions at iron–carbon σ bonds[14,20,21] prompted a study of the electrophilic scission of η^5-$C_5H_5Fe(CO)_2R$ by $HgCl_2$. Here we report a novel finding that this cleavage does not always proceed according to eq 1 but rather affords products which are dependent on the nature of the alkyl fragment R. We also present a mechanism that differs considerably from those proposed previously for mercury(II) cleavage reactions of other complexes.

Reactions of η^5-$C_5H_5Fe(CO)_2R$ (generally 5×10^{-3} to 5×10^{-2} *M*) with ca. tenfold excess of $HgCl_2$ in THF at 25° proceed via three distinct pathways, as shown in eq 2–4.

$$\eta^5\text{-}C_5H_5Fe(CO)_2R + HgCl_2 \longrightarrow \eta^5\text{-}C_5H_5Fe(CO)_2Cl + RHgCl \quad (2)$$

$$\eta^5\text{-}C_5H_5Fe(CO)_2R + HgCl_2 \longrightarrow \eta^5\text{-}C_5H_5Fe(CO)_2HgCl + RCl \quad (3)$$

$$\eta^5\text{-}C_5H_5Fe(CO)_2R + HgCl_2 \longrightarrow \text{"Fe-containing material"} + \tfrac{1}{2}Hg_2Cl_2 + \text{organic products} + CO \quad (4)$$

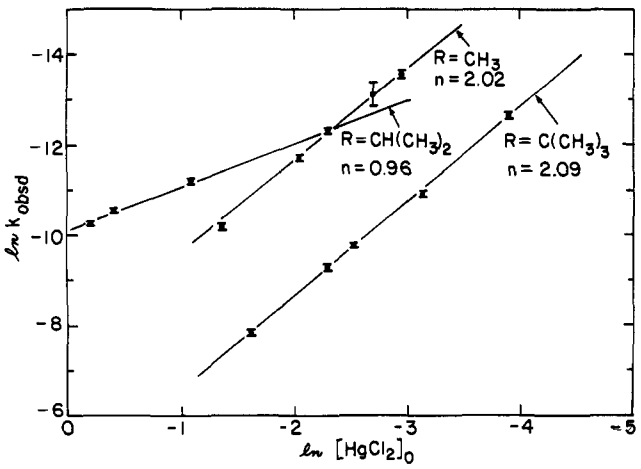

Figure 1. Plots of ln k_{obsd} vs. ln $[HgCl_2]$ for the reactions of η^5-$C_5H_5Fe(CO)_2R$ with ca. tenfold excess of $HgCl_2$ in THF at 25°. n is the slope.

Reaction 2 occurs either exclusively or predominantly when R = CH_3, C_2H_5, $CH_2Si(CH_3)_3$, $CH_2CH_2C(CH_3)_3$, C_6H_5, and p-$C_6H_4OCH_3$; reaction 3 is observed with R = $C(CH_3)_3$ and $CH(CH_3)C_6H_5$; and reaction 4 takes place when R = $CH(CH_3)_2$ and, to a slight extent, when R = C_2H_5, $CH_2CH_2C(CH_3)_3$, $C(CH_3)_3$, and $CH(CH_3)C_6H_5$. When R = $CH(CH_3)_2$, the organic products were analyzed as cyclopentadiene, propene, and 2-chloropropane by VPC–MS; the iron-containing material which shows neither CO nor C_5H_5 was not fully characterized. The isopropyl complex also exhibits some reactivity along paths 2 (trace) and 3, especially at higher concentrations of $HgCl_2$ (>1 M).

The kinetics of the reaction of the R = CH_3 complex with $HgCl_2$ (eq 2) in THF at 25° were followed by ir spectroscopy by monitoring the disappearance of the ν_{CO} band at 1948 cm^{-1} of the iron alkyl. Under pseudo-first-order conditions, with $[HgCl_2] \sim 10[\eta^5\text{-}C_5H_5Fe(CO)_2CH_3]$ = 0.05–0.5 M, the rate of the disappearance of the iron complex follows eq 5, where $k_{obsd} = k[HgCl_2]^n$. A plot of ln

$$-\frac{d[\eta^5\text{-}C_5H_5Fe(CO)_2CH_3]}{dt} = k_{obsd}[\eta^5\text{-}C_5H_5Fe(CO)_2CH_3] \quad (5)$$

k_{obsd} vs. ln $[HgCl_2]$ (Figure 1) yields a straight line with a slope, n, of 2.02. Thus the kinetics obey a third-order rate expression, first-order in η^5-$C_5H_5Fe(CO)_2CH_3$ and second-order in $HgCl_2$ (eq 6; R = CH_3). The third-order rate con-

$$-\frac{d[\eta^5\text{-}C_5H_5Fe(CO)_2R]}{dt} = k[\eta^5\text{-}C_5H_5Fe(CO)_2R][HgCl_2]^2 \quad (6)$$

stant, k, is 4.6×10^{-4} M^{-2} sec^{-1}. The same kinetic expression and a comparable k were obtained when the above reaction was followed by ^1H NMR spectroscopy by monitoring the disappearance of the C_5H_5 resonance (τ 5.20) of the alkyl complex and the appearance of the corresponding resonance of η^5-$C_5H_5Fe(CO)_2Cl$ (τ 4.88). A tenfold excess of η^5-$C_5H_5Fe(CO)_2CH_3$ (~1 M) over $HgCl_2$ was employed.

The kinetics of the reaction of the R = $C(CH_3)_3$ and $CH(CH_3)_2$ complexes with $HgCl_2$ (eq 3 and 4, respectively) were also investigated by ir spectroscopy under conditions similar to those for the R = CH_3 complex. Again a third-order rate expression was obtained when R = $C(CH_3)_3$ (Figure 1), with the cleavage proceeding 20 times faster (k = 9.3×10^{-3} M^{-2} sec^{-1}) than when R = CH_3. However,

Scheme I

$$Fe\text{—}R + HgCl_2 \underset{}{\overset{K_1}{\rightleftharpoons}} Fe(HgCl_2)(R) \xrightarrow{k'} \quad \mathbf{1}$$

$$\tfrac{1}{2}Hg_2Cl_2 + [Fe\text{—}R]Cl \longrightarrow \text{decomp}$$

$$Fe(HgCl_2)(R) + HgCl_2 \overset{K_2}{\rightleftharpoons} [Fe(HgCl)(R)]HgCl_3 \quad \mathbf{2}$$

$$[Fe(HgCl)(R)]HgCl_3 \xrightarrow{k''} Fe\text{—}Cl + RHgCl + HgCl_2$$

or

$$\xrightarrow{k''} Fe\text{—}HgCl + RCl + HgCl_2$$

$$Fe \equiv \eta^5\text{-}C_5H_5Fe(CO)_2$$

when R = $CH(CH_3)_2$, second-order kinetics, first-order in each reactant (eq 7), are obeyed (Figure 1), with k = 4.3 ×

$$-\frac{d[\eta^5\text{-}C_5H_5Fe(CO)_2CH(CH_3)_2]}{dt} = k[\eta^5\text{-}C_5H_5Fe(CO)_2CH(CH_3)_2][HgCl_2] \quad (7)$$

10^{-5} M^{-1} sec^{-1}. The rate of this latter reaction is insensitive to added hydroquinone or galvinoxyl. All three reactions exhibit a positive salt effect (up to 85% increase in rate) with added NH_4PF_6 in concentrations equal to those of η^5-$C_5H_5Fe(CO)_2R$ (≤0.01 M). Preliminary experiments show that the rate of the cleavage of the R = CH_3 complex depends markedly on the solvent, viz., THF < isopropyl alcohol < nitrobenzene.

A reasonable mechanism for these reactions is presented in Scheme I.[22] When **1** is stable with respect to decomposition according to the k' path, the rate expression follows eq 8. If $K_1K_2[HgCl_2]^2 \ll 1$, then it reduces to eq 9 and gives

$$-\frac{d[Fe\text{—}R]}{dt} = \frac{k''K_1K_2[Fe\text{—}R][HgCl_2]^2}{1 + K_1K_2[HgCl_2]^2} \quad (8)$$

$$-\frac{d[Fe\text{—}R]}{dt} = k''K_1K_2[Fe\text{—}R][HgCl_2]^2 \quad (9)$$

the observed kinetics for the R = CH_3 and $C(CH_3)_3$ complexes. In contrast, when the concentration of $HgCl_2$ is low and/or $k' > k''K_2$, second-order kinetics result,[23] as noted for R = $CH(CH_3)_2$.

The choice of pathway and the nature of final products of these reactions are dictated strongly by the ligand R. Thus primary alkyl and aryl groups appear to promote reductive elimination of RHgCl from the cation of **2**. The entry of chloride would then account for the observed final products. In contrast, bulky secondary and tertiary alkyl groups such as $CH(CH_3)C_6H_5$ and $C(CH_3)_3$ may dissociate from **2** as carbonium ions, probably with assistance from the solvent or chloride. This latter course of the cleavage is, to our knowledge, completely unprecedented, and its large rate constant when R = $C(CH_3)_3$ is rather unexpected.[24] The observed decomposition reaction when R = $CH(CH_3)_2$ is not fully understood, but it likely results from relative inability of **2** to eliminate R and low stability of **1** toward an internal redox process.

The mechanism in Scheme I differs markedly from those of an SE2 (retention or inversion) type that have been com-

monly invoked for mercury(II) cleavage reactions.[5,7-11,15] Significantly, however, this pathway is entirely consistent with the reported stereochemical outcome of such scission at the pseudotetrahedral, chiral iron center in (η^5-1-CH_3-3-$C_6H_5C_5H_3$)Fe(CO)[$P(C_6H_5)_3$]CH_3.[14] Moreover, a similar mechanism was proposed by McDonald and Basolo[25] for reactions of $Mo(CO)_4$(L-L) (L-L = bipy and phen) with HgX_2 (X = Cl or Br). We believe that such a pathway for eliminative cleavage reactions merits very serious consideration whenever the metal is susceptible to attack by Lewis acids.[26]

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$$2HgCl_2 \rightleftharpoons HgCl^+HgCl_3^-$$

and subsequent reaction of it with η^5-$C_5H_5Fe(CO)_2R$ likewise yields third-order kinetics. We find by osmometry that $HgCl_2$ is monomeric and shows no evidence of association at higher concentrations in THF in the range of 0.027–0.13 *M*. It is also a nonelectrolyte at 0.1–0.002 *M* concentrations. Thus $HgCl^+HgCl_3^-$, if formed at all, exists in very low concentrations and would be required to exhibit a much higher reactivity than $HgCl_2$ toward η^5-$C_5H_5Fe(CO)_2R$ for this mechanism to be credible. Studies *in aqueous media* on the cleavage of η^5-$C_5H_5Fe(CO)_2CH_2C_5H_4NH^+$ by $HgCl_n^m$ indicate that $HgCl^+$ is 7000 times as reactive as $HgCl_2$ (ref 11c); however, no data are available for THF solutions.
(23) By considering the k' path only, one obtains

$$-\frac{d[Fe\text{–}R]}{dt} = \frac{k'K_1[Fe\text{–}R][HgCl_2]}{1 + K_1[HgCl_2]}$$

which simplifies to

$$-\frac{d[Fe\text{–}R]}{dt} = k'K_1[Fe\text{–}R][HgCl_2]$$

when $K_1[HgCl_2] \ll 1$. Other mechanisms may be proposed which are also consistent with this observed rate expression.
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cis-Sativenediol, a Plant Growth Promotor, Produced by Fungi

Sir:

In our search for a biologically active substance among fungal metabolites, we have found that two pathogenic fungi, i.e., *Cochliobolus setariae* IFO 6635 and *Helminthosporium sativum*,[1] produced a new compound active for promoting elongation of rice seedlings. The active compound designated as *cis*-sativenediol was isolated from both fungal mycelia and culture filtrates with several related metabolites including its trans isomer. This communication describes the structure elucidation of *cis*- and *trans*-sativenediol (**1** and **2**) and the biological activity of all metabolites isolated from these fungi, emphasizing that the cis diol (**1**) is a new plant growth promotor with gibberellin-like activity. It is interesting that pathogenic fungi containing growth inhibitory substances for host plants produce also a plant growth-promoting substance as well.

The both fungi were cultured by shaking on malt-dextrose medium. The fraction containing *cis*- and *trans*-sativenediol was easily isolated by a column chromatography (silicic acid; elution with 3% ethyl acetate in *n*-hexane) of ethyl acetate extracts of the culture broth. Owing to difficulty of the clear separation of these diols from each other, this mixture was treated with 2,2-dimethoxypropane and *p*-TsOH. Pure *trans*-sativenediol and an acetonide of the cis diol were isolated from the reaction mixture, and the latter compound was subsequently hydrolyzed liberating *cis*-sativenediol in pure form (yields: **1**, 20 and 19 mg, and **2**, 6 and 11 mg, respectively, from 10 l. of the culture broth of *C. setariae* and *H. sativum*).

cis-Sativenediol (**1**) [oil; $C_{15}H_{24}O_2$; *m/e* 236 (M^+); $[\alpha]^{25}D$ −119° (*c* 0.94, $CHCl_3$)] has the following partial structures: an isopropyl [NMR ($CDCl_3$) two 3 H doublets at δ 0.89 and 0.95, J = 7 Hz], a tertiary methyl (3 H singlet at δ 1.08), an exocyclic methylene (two 1 H doublets at δ 4.66 and 4.98), and two vicinal hydroxyl groups [ir (CCl_4) 3670 and 3360 cm^{-1}; NMR two 1 H doublets at δ 3.68 and 4.08, J = 6 Hz], which were decoupled to each other in double resonance experiments and shifted downfield (δ 4.72 and 5.05, respectively) upon acetylation (Ac_2O and pyridine) into the diacetate [*m/e* 320 (M^+); two CH_3COO at δ 2.05]. These data are indicative of **1** being a dihydroxy derivative of sativene,[2] a tricyclic sesquiterpene produced by *H. sativum*, although sativene itself was not isolated from our strain of this fungus. This assumption was unequivocally confirmed by subjecting **1** to oxidation ($NaIO_4$ in MeOH–H_2O) followed by acetal formation (EtOH and *p*-TsOH). The product (**4**) ($[\alpha]^{25}D$ −60° (*c* 0.32, $CHCl_3$)) showed the NMR spectrum completely in agreement with that of the diethyl acetal of prehelminthosporal (**3**) reported by de Mayo.[3] The negative optical rotation of **4**, almost the same as the −68° reported,[3] established that **1** has the same