Neglecting the voltage drop across the cell, the overall applied electrical potential between the working and counter electrodes necessary to drive this reaction (or any of the others previously discussed) using the (trpy)(bpy)Ru(OH_2)$^{2+}$ catalyst is approximately 1.2 V, which is the potential difference between the H^+/H_2 and Ru(IV)/(III) couples at pH 7. Given the thermodynamics of the combustion of H_2 in air, eq 11 has been carried out in the net sense with a near energy balance.[21] Perhaps more importantly, it follows that, if a reversible, high current density O_2 electrode can be developed and coupled with the catalyzed oxidations reported here, the resulting cells could be made to operate spontaneously, in effect becoming chemical synthesis fuel cells.

Acknowledgment is made to the National Science Foundation for support of this research through Grant CHE77 04961.

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(19) At 50 °C in phosphate buffer solution, *p*-benzoquinone by itself rapidly undergoes decomposition to give hydroquinone (as shown by NMR) plus insoluble products, consistent with observations in the catalysis experiments. Although the ultimate fate of the *p*-benzoquinone that is probably being formed in the catalytic oxidation of cyclohexene is uncertain, previous work[17,18] has demonstrated that quinone compounds are particularly susceptible to attack by nucleophiles, including water. In the case of hydrolysis of benzoquinone, the product may well be further oxidized by benzoquinone, thus giving rise to the hydroquinone.

(20) Instead of the electrochemical method used here to oxidize Ru(II) to Ru(IV), chemical oxidation is possible as in the oxidation of (bpy)$_2$pyRu(OH_2)$^{2+}$ by HNO_3.[9a]

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Substitution and Cleavage in the Reaction of Some Benzyl(carbonyl)metal Complexes with Trifluoroacetic Acid

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Abstract: Several benzyl(carbonyl)metal complexes, including benzyldicarbonylcyclopentadienyliron(II) (**1**), undergo substantial deuteration in the ortho and para postions prior to acidolysis of the carbon-metal bond in [$^2H_1$]trifluoroacetic acid. Comparison of the rates of substitution with that for substitution in anisole shows that the metallomethyl substituents, e.g., $CH_2Fe(CO)_2(C_5H_5)$, have large negative substituent constants indicative of very strong hyperconjugative electron donation in the transition states for substitution reactions. There is no evidence that electrophilic attack on the aromatic ring causes cleavage of the carbon-metal bond. The kinetics of the anaerobic acidolysis of **1** and of its 4-fluoro derivative in trifluoroacetic acid and in [$^2H_1$]trifluoroacetic acid in chlorinated solvents show that the acidolysis is first order with respect to acid and to substrate, is influenced by the nature of the cosolvent, and has a very high kinetic isotope effect, k_H/k_D = 15-25. It is suggested that these results are indicative of an attack on the metal prior to cleavage of the carbon-metal bond.

Studies of the acidolysis of σ-bonded organotransition metal complexes have repeatedly demonstrated that the proton is a relatively poor electrophile for attack at saturated carbon. The study of the cleavage of organochromium(III),[1] organocobalt(III),[2] organomanganese(I)[4,5] and organoiron(II)[5,6] complexes (**1-6**, respectively) in aqueous acidic solution has demonstrated that a wide range of electrophiles, including Hg(II), Tl(III), Hg(I), NO^+, and halogens, are capable of displacing one or more of the above metals from carbon under conditions in which the proton, though present in appreciably higher concentration than the other electrophile, plays no direct part in the reaction. Indeed, the pyridylmanganese complex **3** undergoes acidolysis by an *unimolecular* process, and the pyridyliron complex **6** is unchanged after several months, in 4 mol dm^{-3} aqueous perchloric acid at 65 °C under anaerobic conditions.[7] In the case of some organochromium(III) complexes there is evidence for a pathway that is first order in acid, but this is usually accompanied by a competing unimolecular path that is zero order in acid.[8]

In principle, an electrophile such as the proton may attack

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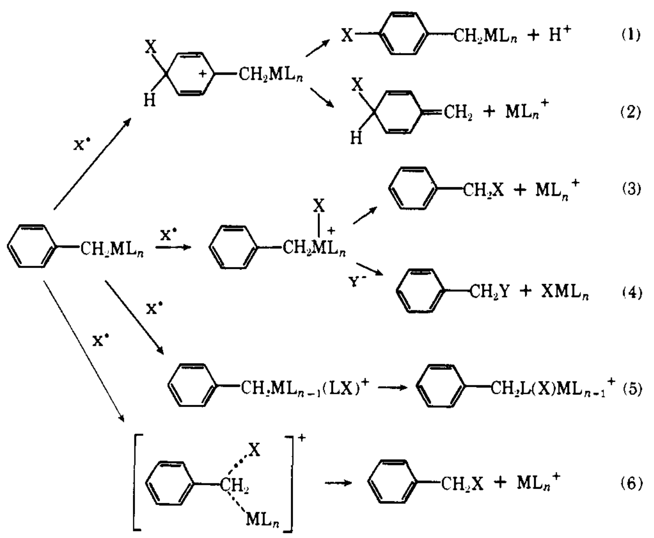
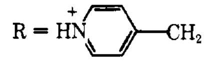
a benzylmetal complex ($PhCH_2ML_n$) at a variety of sites:[9] attack may take place at the benzene ring leading either to substitution (eq 1)[10] and/or to metal-carbon bond cleavage (eq 2);[11] attack may take place at the metal[12] leading to a variety of possible products including those from a reductive elimination process (eq 3) and from *nucleophilic* displacement at the α carbon (eq 4); attack may take place at a ligand L leading to a variety of products including those from an insertion (ligand migration) process;[13] or attack may take place directly at the α carbon (or the carbon-metal bond orbital) (eq 6).[1b,14] Reactions of all five types are known and the path followed is clearly a function of the particular electrophile, its interaction with the HOMO of the complex,[15] and the nature of the reaction medium. In all cases a degree of electron transfer occurs to the electrophile and in some cases, though probably not with the proton, complete electron transfer may be detected.



Studies of the ^{19}F NMR spectra of the related fluorobenzyl complexes (**7**-**11**, respectively) and the acid dissociation constants of the pyridinium ions **2**-**6**[18] have shown that the metallomethyl groups $CH_2Co(CN)_5{}^{3-}$, $CH_2Mn(CO)_5$, $CH_2Mo(C_5H_5)(CO)_3$, $CH_2W(C_5H_5)(CO)_3$, and $CH_2Fe(C_5H_5)(CO)_2$ are very strongly electron donating, not only inductively, but also hyperconjugatively, in the ground states of these molecules and ions. Such effects might also be expected in transition states of, for example, electrophilic substitution reactions in the aromatic rings of compounds **12**-**16**; reaction 1 might therefore be greatly enhanced, and reaction 2 might play an important role in the cleavage of the carbon-metal bonds.

In this paper are described studies of the substitution and cleavage reactions of some benzyliron complexes in trifluoroacetic acid in order to determine the relevance of reactions 1 and 2 to the acidolysis process, with some additional observations on the corresponding reactions of other benzylmetal complexes.

complex	R = 	4-$FC_6H_4CH_2$	$PhCH_2$
$RCr(H_2O)_5{}^{2+}$	1		
$RCo(CN)_5{}^{3-}$	2	7	12
$RMn(CO)_5$	3	8	13
$RMo(CO)_3(C_5H_5)$	4	9	14
$RW(CO)_3(C_5H_5)$	5	10	15
$RFe(CO)_2(C_5H_5)$	6	11	16

Results

The benzyliron complex **16** decomposed readily in trifluoroacetic acid, trifluoroacetic acid/methylene chloride, and trifluoroacetic acid/deuteriochloroform mixtures under nitrogen, giving toluene and trifluoroacetatodicarbonylcyclopentadienyliron(II) (eq 7). The reaction was characterized by

$$ArCH_2Fe(CO)_2(C_5H_5) + CF_3COOH \rightarrow ArCH_3 + Fe(CO)_2(C_5H_5)(OCOCF_3) \quad (7)$$

smooth changes in the ^1H NMR spectrum (in $CF_3COOH/CDCl_3$; initial spectrum δ 2.73 CH_2, 4.63 C_5H_5; final spectrum δ 2.37 CH_2, 5.20 C_5H_5) and in the infrared spectrum (in CF_3COOH/CH_2Cl_2; initial 1950 and 2004 cm^{-1}; final 2026 and 2070 cm^{-1}). The reaction is strongly influenced by oxygen: in the NMR studies using concentrated solutions of substrate, oxygen present above the solution reacted with the upper part of that solution, causing ghost spectra characteristic of inhomogeneous solutions, and in the ultraviolet spectroscopic studies using dilute solutions the decomposition was very much faster under aerobic conditions and did not lead to toluene. Instead, the products were a mixture containing benzyl trifluoroacetate, benzaldehyde, benzyl hydroperoxide, and unidentified products.

Table I. Deuterium Content of Unreacted Benzylmetal Complexes ($PhCH_2M$) during Acidolysis in [$^2H_1$]Trifluoroacetic Acid at 25 °C[a]

M	cosolvent	t/min	deuterium content/% d^0	d^1	d^2	d^3
$Fe(CO)_2(C_5H_5)$	CH_2Cl_2	20	43	53	3	
$Fe(CO)_2(C_5H_5)$	CH_2Cl_2	30	23	66	10	
$Fe(CO)_2(C_5H_5)$	CH_2Cl_2	80	13	73	15	
$Fe(CO)_2(C_5H_5)$	CH_2Cl_2	160	10	67	22	1
$Mn(CO)_5$	none	60	8	70	20	2
$Mn(CO)_5$	none	120	5	49	38	8
$Mn(CO)_5$	none	180	3	33	46	18

[a] 3.4 mol dm^{-3} acid.

The acidolyses of the 4-fluorobenzyliron complex **11**, the 4-fluorobenzylmolybdenum complex **9**, and the benzyltungsten complex **15** were also studied using ^1H NMR spectroscopy. (For **11**: initial spectrum in $CH_3COOH/CDCl_3$ δ 2.67 CH_2, 4.60 C_5H_5; final spectrum δ 2.35 CH_3, 5.20 C_5H_5. For **9**: initial spectrum δ 2.91 CH_2, 5.24 C_5H_5; final spectrum δ 2.35 CH_3, 5.76 C_5H_5. For **15**: initial spectrum δ 3.00 CH_2, 5.30 C_5H_5; final spectrum δ 2.37 CH_3, 5.89 C_5H_5.)

The kinetics of anaerobic acidolysis of the iron complexes **11** and **16** were measured in three ways: with concentrated solutions of substrate (ca. 0.2 mol dm^{-3}) by ^1H NMR spectroscopy, and with less concentrated solutions (ca. 0.02 mol dm^{-3}) by ultraviolet and infrared spectroscopy. The latter method was the least accurate but gave further confirmation that the process observed was the same in each case. All the reactions were first order in substrate in the presence of an excess of trifluoroacetic acid. The first-order rate coefficients are shown in Table I together with rate coefficients for the anaerobic acidolysis of **11** and **16** determined in [$^2H_1$]trifluoroacetic acid/$CDCl_3$ and in [$^2H_1$]trifluoroacetic acid/CH_2Cl_2 mixtures.

The extent of deuteration of the unreacted benzyliron complexes **11** and **16** and of the unreacted benzylmanganese complex **13** during their respective acidolysis in [$^2H_1$]trifluoroacetic acid/CH_2Cl_2 mixtures was also determined by mass spectrometric analysis of samples recovered at intervals before complete acidolysis (cf. Figure 1 and Table II). Negligible deuteration was observed in the iron complex **11**. The toluene formed in the acidolysis of **16** in [$^2H_1$]trifluoroacetic acid/CH_2Cl_2 mixtures was isolated and its deuterium content was estimated by ^1H NMR spectroscopy and mass spectrometry (Table III). A sample of toluene from **16** and a sample of toluene from the acidolysis of the benzylmolybdenum complex **14** in deuterated acid were separately nitrated with

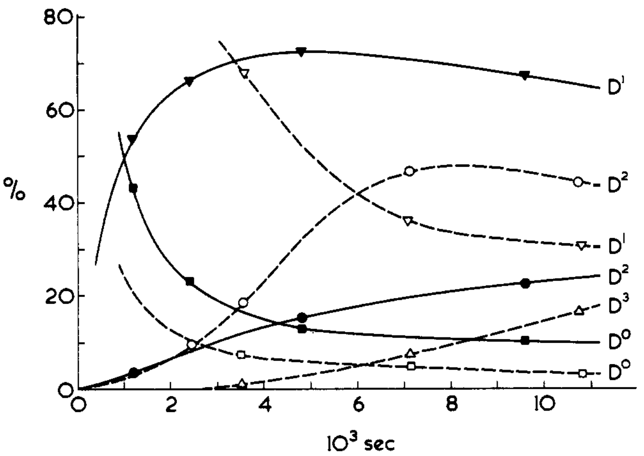


Figure 1. Variation of the proportions of mono-, di-, and trideuterated **16** (—) during acidolysis in 3.4 mol dm^{-3} [$^2H_1$]trifluoroacetic acid in $CDCl_3$, and of **13** (---) during acidolysis in neat [$^2H_1$]trifluoroacetic acid.

Table II. Deuterium Content of Toluene Formed in the Anaerobic Acidolysis of Benzylmetal Complexes ($PhCH_2M$) in [$^2H_1$]-Trifluoroacetic Acid and of Nitrotoluenes Formed by Subsequent Nitration

M	product	deuterium content/% d^0	d^1	d^2	d^3	d^4
$Fe(CO)_2(C_5H_5)$	toluene[a]	12	27	50	13	2
$Fe(CO)_2(C_5H_5)$	toluene[a]	8	27	47	13	2
$Fe(CO)_2(C_5H_5)$	toluene[a,b]	9	36	43	11	1
$Fe(CO)_2(C_5H_5)$	2-nitrotoluene[c]	10	39	41	9	
$Fe(CO)_2(C_5H_5)$	4-nitrotoluene[c]	30	46	19	4	
$Mo(CO)_3(C_5H_5)$	2-nitrotoluene[d]	14	37	40	9	
$Mo(CO)_3(C_5H_5)$	4-nitrotoluene[d]	29	54	14	3	

[a] Results from different experiments with fresh solutions. [b] Source of nitrotoluenes. [c] NMR spectra shown in Figure 2. [d] Toluene not examined.

CF_3COOH/HNO_3 mixtures and the 2- and 4-nitrotoluenes so formed were, in each case, separated and analyzed for deuterium by mass spectrometry and ^1H NMR spectroscopy (cf. Figure 2 and Table III).

Discussion

The changes accompanying the cleavage of benzyl and 4-fluorobenzyliron complexes **11** and **16** in trifluoroacetic acid/chlorinated solvent mixtures are completely in accord with their conversion directly to toluene and and trifluoroacetatodicarbonylcyclopentadienyliron(II) without the formation of observable intermediates. The correspondence of ^1H NMR spectral changes with the smooth changes in the infrared spectra, particularly in the change from two carbonyl bands of substrate to two carbonyl bands of product, shows also that no carbon monoxide is lost during the acidolysis.

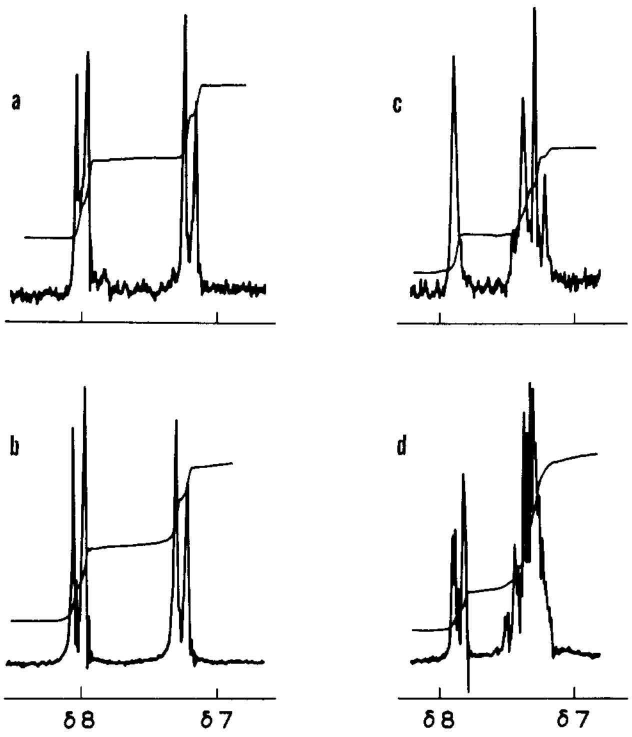


Figure 2. ^1H NMR spectra of (a) a sample of 4-nitrotoluene isolated after nitration of the acidolysis product from **16** in [$^2H_1$]trifluoroacetic acid; (b) pure 4-nitrotoluene; (c) a sample of 2-nitrotoluene isolated as above; (d) pure 2-nitrotoluene.

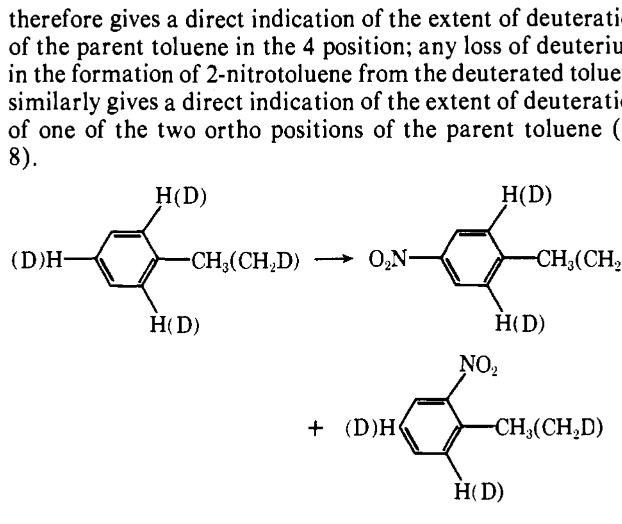
Deuteration of the Aromatic Rings. It is evident from the results in Figure 1 and Table II that substantial deuteration of the benzyliron complex **16** takes place prior to its acidolysis in [$^2H_1$]trifluoroacetic acid. The ^1H NMR spectra measured during acidolysis show that none of this deuteration takes place in the benzylic methylene group or in the cyclopentadienyl ring, but they do not show directly the positions of deuteration in the aromatic ring. We have, however, been able to determine the latter from the extent and position of ring deuteration of the toluene formed during the acidolysis. The extent and position of deuteration of the toluene were determined by a comparison of the mass spectrum of that toluene with those of the two mononitrotoluenes derived from it, and from the ^1H NMR spectra of the same two mononitrotoluenes. Thus, as the ni-

Table III. Kinetics of the Anaerobic Acidolysis of $4\text{-}XC_6H_4CH_2Fe(CO)_2(C_5H_5)$ in Trifluoroacetic Acid/Chlorinated Solvent Mixtures at 33 °C

X	method	cosolvent	[CF_3COOH]	[CF_3COOD]	10^5k_{obsd}	10^5k_{cor}[a]
F	UV	CH_2Cl_2	6.5		190	
F	NMR	$CDCl_3$	4.3		68	
F	UV	CH_2Cl_2	3.4		60	
F	NMR	CH_2Cl_2	3.4		58	
F	NMR	$CDCl_3$	2.15		26	
F	UV	CH_2Cl_2	1.4		17	
F	UV	CH_2Cl_2	0.65		5.9	
F	UV	CH_2Cl_2	0.33		2.6	
F	NMR	$CDCl_3$		4.3	4.8	3.4
F	NMR	$CDCl_3$		3.4	2.8[b]	
F	NMR	$CDCl_3$		2.15	2.0	1.5
F	NMR	$CDCl_3$		1.4	1.1	0.90
H	NMR	$CDCl_3$	3.4		98	
H	NMR	$CDCl_3$	1.7		32	

[a] After allowance for 2% protium in deuterated acid. [b] Exact amount of protium not measured.

tration of toluene is a reaction which does not show a deuterium isotope effect,[19] the replacement of a deuterium atom by a nitro group takes place with the same probability as the replacement of a hydrogen atom by the nitro group. Any loss of deuterium in the formation of 4-nitrotoluene from the deuterated toluene therefore gives a direct indication of the extent of deuteration of the parent toluene in the 4 position; any loss of deuterium in the formation of 2-nitrotoluene from the deuterated toluene similarly gives a direct indication of the extent of deuteration of one of the two ortho positions of the parent toluene (eq 8).



(8)

The ^1H NMR spectrum of the 2-nitrotoluene formed from the deuterated toluene (Figure 2a) shows clearly that substantial amounts of deuterium are present in the 4 position, i.e., the 3-proton resonance is substantially a broad singlet due to deuterium coupling, instead of the complex doublet found in the spectrum of pure 4-nitrotoluene (Figure 2b). The ^1H NMR spectrum of the 4-nitrotoluene formed from the deuterated toluene (Figure 2c) shows that there is little if any deuteration in each of the 3 and 5 positions and only slight (ca. 10%) deuteration in each of the 2 and 6 positions. This is evident from the small diminution in area of the 2- and 6-proton resonances and the slight changes in the character of the 3- and 5-proton resonances compared with those of pure 4-nitrotoluene (Figure 2d). Comparison of the deuterium content of the parent toluene, as determined from its mass spectrum, with those of the two mononitrotoluenes confirms the substantial loss of deuterium accompanying 4-nitration and the much smaller loss of deuterium accompanying the 2-nitration of the toluene. The results, taken together, indicate that the average deuterium content of the parent toluene is approximately: 4 position 70% D, 2 and 6 positions 12% D in each, and the α position 65% CH_2D, assuming zero deuteration in the 3 and 5 positions. The extent of deuteration of the α position was confirmed by comparison of the integrals of the partially deuterated methyl resonance with those of the essentially undeuterated 3 and 5 positions in the ^1H NMR spectrum of the 4-nitrotoluene.

Comparison of the *extent* of deuteration of the final product toluene with that of the substrate **16** during the acidolysis reaction (Table I) indicates that substantially all the deuteration in the aromatic ring takes place *prior to* the acidolysis, and hence that the positions of deuteration in the aromatic ring of the toluene represent essentially those in the unreacted substrate (eq 9). Similar considerations of the toluene and the nitrotoluenes obtained from the benzylmolybdenum complex **14** indicate that deuteration takes place to a similar extent, at a similar rate, and in the same positions, as with the iron complex **16**. The positions of deuteration of the benzylmanganese complex **13** were not investigated, but the extent of deuteration (Figure 1 and Table II) prior to the much slower acidolysis is consistent with predominantly 4- and partially 2- and 6-deuteration. In accord with this is the fact that 3,5-dimethylbenzylpentacarbonylmanganese(I) undergoes extremely rapid deuteration in the 2, 4, and 6 positions, as shown by ^1H NMR spectroscopy to be essentially complete within the time of mixing of the solutions.

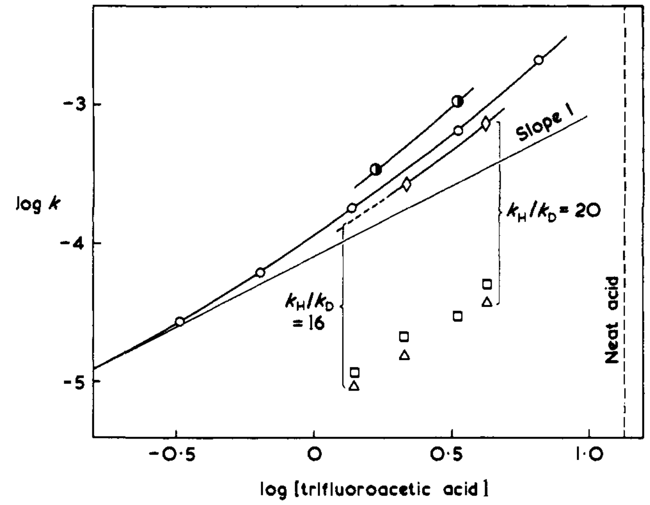
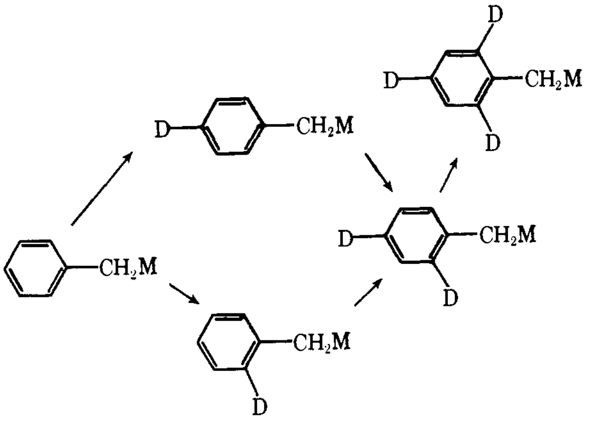


Figure 3. Rate constant vs. concentration profile for reactions in trifluoroacetic acid, [$^2H_1$]trifluoroacetic acid, methylene chloride, and deuteriochloroform mixtures. 4-Fluorobenzyl complex **11**, ◇ with CF_3COOH in $CDCl_3$, □ with [$^2H_1$]CF_3COOH in $CDCl_3$ uncorrected, △ with [$^2H_1$]CF_3COOH in $CDCl_3$ corrected, ○ with CF_3COOH in CH_2Cl_2; benzyliron complex **16**, ◑ with CF_3COOH in $CDCl_3$.

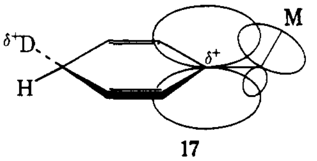


(9)

This ortho and para deuteration of the benzene ring of the benzylmetal complexes **13**, **14**, and **16** takes place appreciably faster than the corresponding ortho and para deuteration of the majority of other aromatic compounds. Indeed, the approximate first-order rate coefficient for monodeuteration of **16**, estimated from the data in Table II, is 2×10^{-4} dm^3 mol^{-1} s^{-1}, which is some 20 times faster than that for the monodeuteration of anisole under the same conditions. The modified Hammett ρ value (eq 10) for deuteration of aromatic rings in

$$\log k/k_0 = \rho\sigma_p^+ \qquad (10)$$

trifluoroacetic acid[20] is ca. −8, and applying this value to the trifluoroacetic acid/chlorinated solvent mixtures gives an electrophilic substituent constant σ_p^+ for the substituent $CH_2Fe(CO)_2(C_5H_5)$ of ca. −1.0, which is intermediate between that for the conjugatively electron-donating methoxyl group ($\sigma_p^+ = -0.78$) and the conjugatively highly electron-donating amino group ($\sigma_p^+ = -1.3$).[21] The very marked hyperconjugatively electron-donating character of the substituent $CH_2Fe(CO)_2(C_5H_5)$ noted earlier in ground-state properties[17,18] is clearly effective in the transition state (**17**) of elec-



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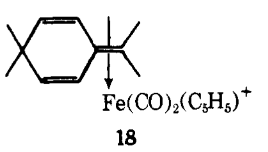


18

trophilic aromatic substitution reactions. A similar high negative value of σ_p^+ must also be appropriate for the substituents $CH_2Mn(CO)_5$ and $CH_2Mo(CO)_3(C_5H_5)$, also in accord with earlier work.

Cleavage of the Carbon–Metal Bond. A. Relevance of Reaction 2. Two factors indicate that the acidolysis of **11** and of **16** does not take place as a result of the attack of a proton on the aromatic ring (i.e., eq 2) followed by isomerization of the exocyclic methylene derivative to the toluene. First, the rate of acidolysis of the benzyl complex **16** is only about twice as fast as that of its 4-fluoro derivative **11**, yet it is known that a 4-fluorine substituent retards the rate of attack of an electrophile on the aromatic ring by several orders of magnitude.[22] This retardation is borne out by the negligible incorporation of deuterium in **11** during its acidolysis in deuterated acid. Secondly, the observed isotope effect in the acidolysis of **11** (k_H/k_D = 8–25, after adjustment for protium present in the deuterated acid) is much higher than those isotope effects normally associated with aromatic substitution reactions.[23]

It is surprising, therefore, that, despite the very frequent occurrence of attack of protons on the ring, this does not lead to the formation and decomposition of a cationic π-methylenecyclohexadienyl complex **18**.

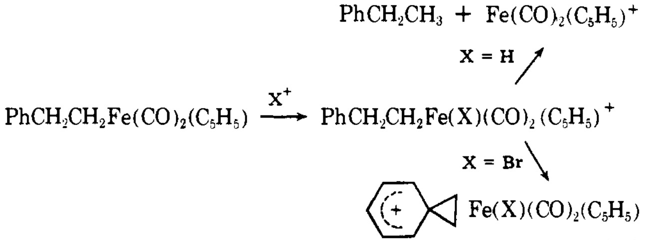
B. Kinetic Order and Isotope Effects. The hydrogen-deuterium exchange of the unsubstituted benzyl complexes was such that they were unsuitable for the study of kinetic isotope effects in the acidolysis. In the more concentrated solutions of substrate used for the NMR studies, the liberation of protium into the deuterated solvent led to a significant increase in the acidolysis rate, especially in the early stages of the reaction. This release of protium, coupled with the very high isotope effect, accounts for the very high (ca 35%) proportion of deuterated toluene product which has an *un*deuterated methyl group. The majority of kinetic studies were therefore carried out on the 4-fluorobenzyl complexes, with which such problems do not arise.

However, the low rate of reaction of **11**, its sensitivity to oxygen under acidic conditions, and the high isotope effect[24] meant that rather high concentrations of trifluoroacetic acid (0.1–7 mol dm^{-3}) and of substrate (10^{-1}–10^{-2} mol dm^{-3}) were necessary. Under these conditions the rate of acidolysis was influenced not only by the concentration and character of the acid, but also by changes in the composition of the solvent. Thus, the isotope effect[24] rises from ca. 15 in 1 mol dm^{-3} acid to ca. 20 in 4 mol dm^{-3} acid when $CDCl_3$ is cosolvent. The extrapolated isotope effect for pure trifluoroacetic acid is 25–30. Similarly, the order of reaction with respect to trifluoroacetic acid rises from ca. unity in the lower concentration range to ca. 1.5 in 7 mol dm^{-3} acid, when CH_2Cl_2 is cosolvent. We ascribe this behavior to a reaction which is predominantly first order with respect to acid, but which is also influenced by the changes in solvent composition. First-order behavior for the acidolysis of several alkyl- and aryliron complexes in solutions corresponding to the lower end of our concentration range has also been observed by Wojcicki, though, with more reactive substrates in less concentrated acid, the order with respect to acid changed to two.

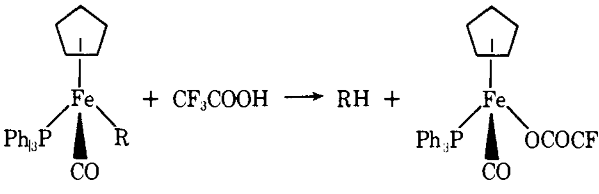
The system is clearly sufficiently ill defined that it may prove difficult to give a detailed picture of the transition state even with an exact knowledge of the state[26] of trifluoroacetic acid in the range of solutions used and with a more detailed knowledge of the variation in reaction order. Some further indication of the type of process involved may, however, be gained from consideration of the very high isotope effects and the sensitivity to oxygen in acidic solution.

There are no known kinetic isotope effects for electrophilic attack on saturated carbon, but the observed high isotope effects are not completely inconsistent with an attack on carbon, being in the high end of the range found for rate-determining proton transfer *from* saturated carbon acids (R_3CH) to external bases (frequently k_H/k_D is 10 and in rare cases, especially at low temperatures where tunnelling effects are more evident, it may be as high at 24).[27] The isotope effects are, however, more consistent with an attack on the metal followed by a reductive elimination of toluene (eq 13, path a). A similar very high isotope effect (k_H/k_D = 27) has also been estimated in the reaction of trifluoroacetic acid with a π-bonded organoiron complex and has been ascribed to an attack of the acid on iron,[28] though a fully satisfactory explanation of the size of the isotope effect has not so far been put forward, and it is likely that some tunnelling occurs. Attack on iron is further supported by the observation that 2-fluorobenzyldicarbonylcyclopentadienyliron(II), present as a distinguishable impurity (^{1}H NMR δ 2.58 (doublet) CH_2, 4.68 C_5H_5) in some of our samples of **11**, reacts at the same rate as the 4-fluorobenzyl complex **11** under all conditions of acidolysis.

Electrophilic attack on the metal has also been postulated in several recent studies of organoiron complexes related to **11** and **16**. Thus, the mercuration of alkyliron complexes in tetrahydrofuran gives some products which are indicative of a prior attack of mercury(II) on the metal,[12a] and the halogenation of the 2-phenylethyliron complex in several solvents gives products indicative of the formation of a phenonium ion by attack of halogen on iron[12b,c] (eq 11). In the acidolysis of the same 2-phenylethyl complex there is no evidence for phenonium ion formation, but it is possible that the lifetime of the cationic intermediate formed on protonation of iron is so short that cyclization to the phenonium ion is unable to occur. The reaction of trifluoroacetic acid with the chiral ion complex **19** gives alkane and substantial proportions of chiral **20**, despite significant racemization of unreacted substrate, and has also been ascribed to the attack of acid on the iron prior to a reductive elimination of alkane.[29,30]



(11)



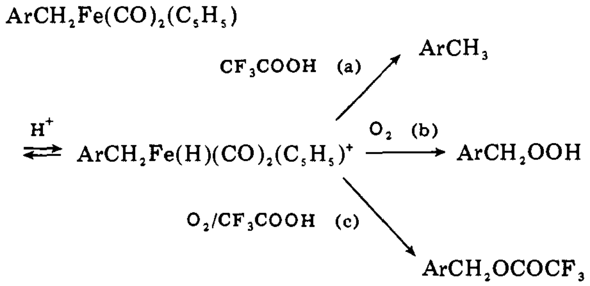
(12)

19 **20**

The greatly enhanced rate of reaction of **11** and of **16** in the presence of both trifluoroacetic acid and oxygen, and the products of that reaction, may also be the result of the presence of an intermediate hydridometal complex present either on or adjacent to the acidolysis path. The formation of benzyl trifluoroacetate in that reaction is indicative of an oxidatively induced nucleophilic displacement[31] and the formation of benzyl hydroperoxide may be via a reductive elimination process, both resulting from attack of oxygen on the hydridometal species (eq 13, paths a and b) which proceeds much faster than the alternative acidolysis (path a).

Experimental Section

Materials. Trifluoroacetic acid (BDH), [$^2H_1$]trifluoroacetic acid ($\geq$99% $^2H_1$, Merck Sharp and Dohme), [$^2H_1$]chloroform ($\geq$99.5% $^2H_1$, Merck Sharp and Dohme), and methylene chloride (Koch-Light)



(13)

were commercial materials. Benzyl- and fluorobenzyldicarbonylcyclopentadienyliron(II), benzyl- and fluorobenzyltricarbonylcyclopentadienylmolybdenum(II), benzylpentacarbonylmanganese(I), benzyltricarbonylcyclopentadienyltungsten(II), and 3,5-dimethylbenzylpentacarbonylmanganese(I) were prepared as described previously.[17]

Determination of Deuterium Content of Benzylmetal Complexes. The benzylmetal complex (ca. 60 mg) was dissolved in [$^2H_1$]trifluoroacetic acid (1 cm^3) or the equivalent amount of [$^2H_1$]trifluoroacetic acid/methylene chloride mixture, the methylene chloride having previously been washed with [$^2H_2$]water and dried (Na_2SO_4). Aliquots were withdrawn at intervals and shaken with methylene chloride/aqueous sodium hydrogen carbonate mixtures. The methylene chloride layer was separated, dried (Na_2SO_4), and chromatographed on deactivated alumina (5% water). The benzylmetal complex was eluted with hexane and examined directly using an EMI MS12 mass spectrometer. In the case of the benzylmanganese complex **13**, the proportions of molecules containing deuterium were determined from a comparison of the appropriate peaks (*m/e* 286, 287, 288, and 289; 258, 259, 260, and 261; 230, 231, 232, and 233) corresponding to the M, M − CO, and M − 2CO ions. In the case of the benzyliron complex **16**, the deuterium content was determined by consideration of the M − CO peaks at *m/e* 240, 241, and 242, with appropriate corrections for isotopic composition. With the benzylmolybdenum complex **14**, the isotopic composition was sufficiently complicated that accurate estimation of deuterium content was impracticable. However, it was clear that substantial deuteration had been occurring in this molecule during the acidolysis reaction at a similar rate to that with the benzyliron complex **16**. The deuterium content of 3,5-dimethylbenzylpentacarbonylmanganese(I) was determined using ^1H NMR spectroscopy from the relative areas of the three aromatic proton resonances and the methylene proton resonance before and after adding [$^2H_1$]trifluoroacetic acid to a solution of the complex in $CDCl_3$.

Determination of the Deuterium Content of Product Toluene. The acidolysis of **14** and **16** (ca. 60 mg) was carried out in neat [$^2H_1$]trifluoroacetic acid (2 cm^3) and the product mixture was poured onto a large excess of powdered calcium carbonate. After 1 h the toluene was pumped off and its mass spectrum was measured using low (≤ 12 eV) ionizing voltages such that the dominant peaks in the spectrum were *m/e* 92, 93, 94, 95, and 96, corresponding to toluene and its mono-, di-, tri-, and tetradeuterated derivatives. The product composition was calculated after due allowance for isotopic composition. Each sample of toluene was also nitrated with nitric acid/trifluoroacetic acid (1:1) for 1 h at room temperature. The mixture was poured into water and extracted with methylene chloride, and the extract was washed with aqueous sodium hydrogen carbonate, dried (Na_2SO_4), and separated by preparative GLC. The mass spectra and ^1H NMR spectra of the two mononitrotoluene products were recorded, and the deuterium content was estimated by consideration of the peaks at *m/e* 137–141, representing the parent species M to M + 4D, after due allowance for isotopic composition. The acidolysis of **11** and **16** was also carried out in [$^2H_1$]trifluoroacetic acid/methylene chloride mixtures. In these cases, the reaction mixture was poured into water and the methylene chloride fraction was washed with sodium hydrogen carbonate and with water, dried (Na_2SO_4), and carefully fractionated. Traces of methylene chloride in the remaining toluene sample did not unduly influence the critical regions of the mass spectrum.

Kinetic Studies. A. Using ^{1}H NMR. In a typical experiment, the benzyl- or 4-fluorobenzylmetal complex (15–50 mg) was dissolved in the appropriate mixture of trifluoroacetic acid or [$^2H_1$]trifluoroacetic acid and $CDCl_3$ (0.5–1 cm^3) in an NMR tube which was sealed and shaken for at least 1 min. The acidolysis was followed by observation of the changes in the areas of reagent and product cyclopentadienyl resonances in the region 4–6 ppm, and checked by observation of the changes in the reagent methylene and product (deuterated) methyl resonances in the region 2–3 ppm, using a Varian HA100 spectrometer at 28 °C or a T60 spectrometer at 34 °C. Rate constants (Table III) were calculated by standard methods for first-order reactions except in the case of the reactions of **16** in [$^2H_1$]trifluoroacetic acid, for which apparent rate "constants" were calculated directly from the half-life of the substrate. The amount of protium in the [$^2H_1$]trifluoroacetic acid was calculated from the relative areas of the low-field acid proton resonance and those of the substrate of known concentration. Measurements on the benzyl complex **16** confirmed the substantial liberation of protium into the medium during the early stages of the acidolysis. Rate constants for reactions in [$^2H_1$]trifluoroacetic acid were corrected appropriately for the protium in the medium.[24]

B. Using Ultraviolet Spectroscopy. The substrates were so sensitive to the presence of oxygen in acidic solution that no kinetics could be successfully measured using very dilute solutions of substrate and its principal absorption band. However, when the substrate (2–10 mg) was placed in a thermostated spectrophotometer cell (1-mm path length) and degassed trifluoroacetic acid/methylene chloride mixtures were added, reproducible kinetic results were obtained for the faster reactions by monitoring the weak product absorption at ca. 480 nm. In these cases first-order kinetics were observed which corresponded well with those measured by ^1H NMR (Table III). The method was unsuitable for the slower reactions in [$^2H_1$]trifluoroacetic acid because of the instability of the product spectrum over longer periods.

Identification of the Inorganic Reaction Product. The inorganic product of acidolysis was identified as trifluoroacetatodicarbonylcyclopentadienyliron(II) by comparison with authentic material synthesized in situ from iododicarbonylcyclopentadienyliron(II) and silver trifluoroacetate.

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Lewis Acid Mediated Reactions of Organocopper Reagents. A Remarkably Enhanced Regioselective γ-Attack of Allylic Halides and Direct Alkylation of Allylic Alcohols via $RCu{\cdot}BF_3$ System[1]

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Abstract: Chemical reactivities and selectivities of a new class of organocopper reagent, RCu-Lewis acid, are described. Regioselective γ-attack of allylic halides is realized irrespective of the degree of substitution at the two ends of the allylic systems, and of the structural factors (cyclic or acyclic) involved. Among the Lewis acids examined, $BF_3{\cdot}OEt_2$ is the most effective with respect to the selectivity and total yield. Propargyl chloride and acetate are converted into 1,2-heptadiene by *n*-$BuCu{\cdot}BF_3$. Allylic alcohols react with 3 equiv of $RCu{\cdot}BF_3$ to produce the corresponding alkylation products in high yield. The stereochemistry of the reactions of $RCu{\cdot}BF_3$ is examined by using Goering's system, that is, 5-methyl-2-cyclohexenyl chloride, acetate, and alcohol. The substitution proceeds through a formal anti S_N2' in the case of *cis*-5-methyl-2-cyclohexenyl acetate and through a formal syn S_N2' in *trans*-5-methyl-2-cyclohexen-1-ol. On the other hand, the stereochemical integrity disappears in the reaction of *cis*-5-methyl-2-cyclohexen-1-ol and the chloride (**1**). It is proposed that the "ate" complex between RCu and BF_3 is involved as a reactive intermediate.

An important and yet frequently elusive goal of synthetic chemistry is the selective synthesis of a desired stereo- or regioisomer. Examples illustrating the importance of regioselective syntheses are manifold, control of the regiochemistry in the reaction of allylic carbanions with electrophiles being one example[2] while regiochemical control of the reaction of allylic substrates with nucleophiles is another.[3] In general, substitution reactions of allylic substrates without (or with) complete allylic rearrangement via organometallics are still unpredictable processes.[4,5] Among such reactions, several promising results to direct nucleophiles to the α position are obtained. Regioselective α-attack is achieved by using allylic substrates containing oxygen in the leaving group (OAc, OTos, etc.),[6-11] although isomerization, rearrangement, and formation of side products in many cases are reported.[8,10,11] On the other hand, in the case of the reaction of allylic halides[7] with organolithium and magnesium compounds, there are difficulties on the points of allylic transposition, geometrical isomerization, and cyclization.[12-16] Several literature sources refer to prenyl halides, cyclic allylic halides, or branched allylic compounds in which cases the problem of partial rearrangement either does not exist or is overshadowed by attendant factors.[4,17-19] Recently it was reported that acyclic allylic halides undergo cross coupling at the α position via dialkylcuprate-Me_2S system.[20]

The efforts to direct nucleophiles to the γ position are relatively scarce. Although γ-unsubstituted allylic substrates undergo a facile γ-alkylation,[10,21-23] the substitution appears to be controlled by steric factors.[19g-i] Recently exclusive syn γ-attack on the allylic system of 5-phenyl-2-cyclohexenylcarbamates was reported.[24] Consequently, the regiochemistry is highly system dependent[25] and the influencing factors are the nature of the leaving group, the degree of substitution of the two ends of the allylic system, the steric factors, the solvent system, and the nature of the nucleophile.

Previously we reported preliminary results dealing with regioselective γ-attack toward allylic halides by $RCu{\cdot}BF_3$ and direct alkylation of allylic alcohols.[1] We now report the full details of that work as well as the stereochemical aspects via $RCu{\cdot}BF_3$. The results reported here indicate that (1) regioselective γ-attack is realized irrespective of the nature of the leaving group, the degree of substitution at the two ends of the acyclic allylic systems,[26] and the structural factors (cyclic or acyclic), (2) direct displacement of the OH group of allylic alcohols is achieved via $RCu{\cdot}BF_3$, (3) the substitution proceeds through a formal anti S_N2' pathway in the case of *cis*-5-methyl-2-cyclohexenyl acetate and syn S_N2' in *trans*-5-methyl-2-cyclohexenol, and (4) the stereochemical integrity disappears in the reaction of *cis*- and *trans*-5-methyl-2-cyclohexenyl chloride and *cis*-5-methyl-2-cyclohexen-1-ol (eq 1).

Results and Discussion

Regiochemistry of the Reaction of Allylic Halides with Organocopper Reagents in the Presence of Lewis Acids. As we previously reported, certain observations suggest that the regiochemistry in the substitution reaction of allylic substrates with organocopper reagents must be influenced by the presence of organoboranes.[1a,27] Therefore, systematic investigation on the regiochemistry of the reaction of cinnamyl halides with organocopper reagents in the presence of various Lewis acids was carried out (Table I). As evident, an ehanced γ regiose-

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