the maximum interaction of each lithium atom with the π charge density of the stilbene molecule and for this reason is favored over the twisted structure. Intramolecular nonbonded interactions are negligible in the planar trans dianion, so that twisting need not occur, unlike other more sterically crowded systems, such as the tetraphenylethylene dianion, where such interactions are present. Even in the ion pair containing trisolvated lithium cations, the planar dianion is still present. Thus, the planar structure can provide a good model for the ion-paired stilbene dianion in solution.

Features observed in the two crystal structures presented here are helpful in explaining the results Szwarc obtained in his electron transfer induced cis-trans isomerization studies of stilbene.[7] The rate-determining step in the isomerization was found to be conversion of the *cis*-stilbene dianion to the *trans*-stilbene dianion. Because of the presence of excess cation in solution inhibiting dissociation, the dianionic species existed predominantly as contact ion pairs. In the cis dianion, placement of metal cations above and below the stilbene molecule, with each cation associated with both ethylenic carbon atoms, would lead to hindered rotation about the formally reduced carbon-carbon double bond, since the interaction of the metal cation with the π charge density between the ethylenic carbon atoms would have to be decreased before rotation could occur. The trans dianion formed in the isomerization step would then resemble the structures observed here in the solid state.

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Supplementary Material Available: A listing of the observed and calculated factor amplitudes in electrons for stilbene bis(lithium TMEDA) (Table VII) and stilbene bis(lithium PMDTA) (Table XIV) (26 pp). Ordering information is given on any current masthead page.

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Halogen Cleavage Reactions of *threo*-$PhCHDCHDFe(CO)_2(\eta^5\text{-}C_5H_5)$

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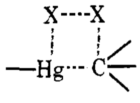
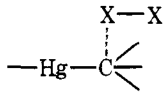
Abstract: Halogen cleavage reactions of the metal-carbon bond of the compound *threo*-$PhCHDCHDFe(CO)_2(\eta^5\text{-}C_5H_5)$ have been studied under a variety of conditions. The major product in most cases is the *threo*-α,β-dideuteriophenethyl halide, although *threo*-α,β-dideuteriophenethyl methyl ether is produced when reactions are carried out in methanol. Analogous cleavage reactions of samples labeled with ^{13}C at the α-carbon atom show that, in most cases, the methylene carbon atoms become equivalent at some point along the reaction pathway. A mechanism is proposed which involves initial oxidation of the metal to give the fluxional intermediate $[\eta^5\text{-}C_5H_5Fe(CO)_2X(CHDCHDPh)]^+$ (rather than direct attack of halogen on the α-carbon atom), followed by reductive elimination of *threo*-phenethyl halide. The intermediate also yields *erythro*-phenethyl halide, not by nucleophilic attack on the intermediate by halide ion, but more probably via nonchain radical processes. It is proposed that halogen cleavage of transition metal alkyl complex containing nonbonding d electrons may generally proceed via initial oxidation of the metal, and that the long-accepted SE2 (cyclic) mechanism for the cleavage of main group metal alkyl compounds is a symmetry-forbidden process.

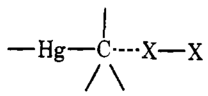
Electrophilic cleavage of transition metal-carbon σ bonds by reagents as diverse as protic acids, halogens, and mercury(II) salts has long been used for synthetic purposes as well as an aid in the identification of organometallic compounds;[1] in the case of halogens, cleavage normally results in the formation of metal halide and alkyl halide, i.e.

$$RML_n + X_2 \rightarrow RX + XML_n \qquad (1)$$

Although numerous examples of such reactions are to be found in the literature, very little is known about mechanisms. Unfortunately, reaction rates are often apparently much too rapid to be studied by normal techniques, and although stereochemical studies have long been at least feasible, again little has been done. Mechanistic conclusions have often been made by analogy to the much more extensively studied electrophilic cleavage reactions of organomercury(II) compounds.[2-4] Besides unimolecular (SE1) and radical processes, halogenations of mercury-carbon bonds have been considered from the point of view of three types of concerted, bimolecular processes, i.e.


SE2 (cyclic)
1


SE2 (open, retention)
2


SE2 (open, inversion)
3

As halogen cleavage reactions of organomercury compounds in polar solvents seem generally to proceed with retention of configuration, cyclic intermediates such as **1** have long been the most favored intermediate, although **2** probably could not be entirely ruled out.[5] Although it has proven tempting on occasion to infer that similar reactions of alkyl transition metal compounds will proceed similarly,[6] in fact alkyl cleavage reactions of several main group metals, tin,[7] lithium,[8,9] and boron,[10] as well as mercury,[3] can proceed with inversion of configuration at carbon. Where studies have been done, halogen cleavage of alkyl transition metal compounds often appears to involve initial attack at the metal rather than at carbon. Thus halogenation of four-coordinate alkylplatinum(II) and -palladium(II) complexes generally proceeds via oxidative addition to give six-coordinated platinum(IV) and palladium(IV) intermediates, followed by reductive elimination of alkyl halide.[1] In the case of palladium(II) enyl complexes, at least, the reductive elimination step takes place with retention of configuration.[11,12] The bromine cleavage of optically active $MeCH(CO_2Et)Mn(CO)_5$, which proceeds with retention of configuration,[13] is believed to involve a similar mechanism.[14]

Halogenation of six-coordinate cobaloxime complexes of the type $RCo(DH)_2L$ (DH = dimethylglyoximate anion, L = neutral ligand) appears to involve initially a one-electron oxidation of the metal to a cobalt(IV) species, followed by nucleophilic attack by halide ion on the α-carbon atom of the alkyl group[15-17] (backside attack), i.e.

$$RCo^{III}(DH)_2L + \tfrac{1}{2}X_2 \rightarrow \underset{\mathbf{4}}{[RCo^{IV}(DH)_2L]X} \qquad (2)$$

$$[RCo^{IV}(DH)_2L]^+ + X^- \rightarrow [X^- \cdots RCo^{IV}(DH)_2L] \rightarrow RX + Co^{II}(DH)_2L \qquad (3)$$

$$Co^{II}(DH)_2L + \tfrac{1}{2}X_2 \rightarrow XCo^{III}(DH)_2L \qquad (4)$$

Species of the type **4** have been generated electrochemically and shown to react with nucleophiles as illustrated.[18,19] The mechanism is also consistent with the inversion of configuration at carbon observed in several cases,[15-17] although no kinetic studies have been reported. Interestingly, in the halogenation of alkylpalladium(II) complexes, the presence of excess free halide ion can result in nucleophilic displacement of palladium(II) from the α-carbon atom (with inversion) being competitive with the reductive elimination step described above.[12]

Different mechanisms again may be operative in the bromine cleavages of the complexes $[RCr^{III}(H_2O)_5]^{2+}$ [20] and *erythro*- and *threo*-$(\eta^5\text{-}C_5H_5)_2ZrCl(CHDCHDCMe_3)$.[21] In the former case, rate studies rule out a unimolecular process while the stoichiometry of the reaction

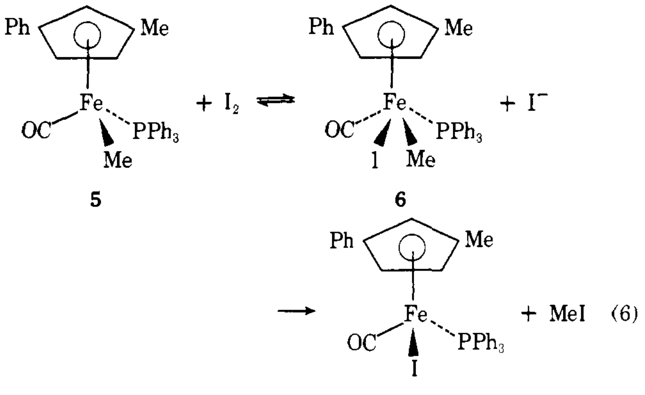
$$[RCr(H_2O)_5]^{2+} + Br_2 \rightarrow [Cr(H_2O)_6]^{3+} + RBr + Br^- \qquad (5)$$

in which the kinetically stable $[CrBr(H_2O_5]^{2+}$ is not formed, appears to rule out a cyclic intermediate such as **1**. An SE2 (open) mechanism was tentatively suggested on the ground that the correlation of rates with R corresponded approximately with those of other SE2 reactions in which inversions are known to occur, an argument which the same authors have later shown to be easily misinterpreted.[22]

The zirconium(IV) compounds (d^0 systems) are perhaps the only known transition metal alkyl compounds which are cleaved by halogens by the same mechanism as that observed for the organomercury systems. Cleavage proceeds with retention of configuration, and it was pointed out[21] that the zirconium(IV) compounds are similar to mercury(II) compounds in that low-lying, vacant orbitals are available to facilitate frontside attack, but dissimilar to the other transition metal systems discussed above in that there are no nonbonding d electrons available to facilitate an oxidative mechanism.

Closely related to the research discussed here is work reported by Whitesides et al.[23,24] who found that *threo*- and *erythro*-$Me_3CCHDCHDFe(CO)_2(\eta^5\text{-}C_5H_5)$ are brominated as in (1) with inversion of configuration in a reaction whose stereochemistry shows no significant dependence on solvent polarity; iodination in carbon disulfide and chlorination in chloroform proceeded similarly, the latter in very low yields. On the other hand, oxidation with bromine, chlorine, oxygen, or cerium(IV) in methanol gave the methyl ester, $Me_3CCHDCHDCO_2Me$, with retention of configuration, while chlorination in chloroform also yielded the acid chloride, $Me_3CCHDCHDCOCl$, again with retention of configuration. The latter reactions, which involve alkyl migration to a coordinated carbonyl group, have previously been observed for similar iron compounds containing a variety of alkyl and aryl groups.[25,26]

Two mechanisms have been considered to explain halogenation with inversion,[24] an SE2 (open, inversion) (as in **3**), and a preliminary two-electron oxidation of the iron followed by backside nucleophilic attack on the α-carbon atom as in (3). Support for the latter mechanism was provided by Attig and Wojcicki,[27] who demonstrated that cleavage of **5** (and its epimer) with a deficiency of iodine (as well as with HI and HgI_2) resulted in partial epimerization at iron of both unreacted **5** and the resulting iodide, **7**.



5
6
7

The observed epimerization was best accommodated by a mechanism involving an intermediate such as **6**. It was argued that such a species might well be fluxional, giving rise to rapid configurational changes at iron. Intermediates such as **6** also explain the products of alkyl migration reactions to coordinated carbon monoxide during oxidation of the compounds η^5-$C_5H_5Fe(CO)_2R$ in polar solvents.[24-26] The reactions occur much more rapidly than do similar ligand-induced migration reactions of the parent iron(II) alkyls[25,26] and thus must take place after the metal atom has been "activated" in some way.

In an attempt to gain further understanding of the stereochemical consequences of a variety of reactions of organometallic compounds, we have been investigating the chemistry of the *threo*-α,β-dideuteriophenethyl ligand, *threo*-PhCHDCHD-. We have earlier demonstrated the utility of this ligand in studying alkyl migration and β-elimination reactions of rhodium(III) and iridium(III),[28] as well as mercuric halide cleavage[29] and sulfur dixide insertion[30] reactions of *threo*-$PhCHDCHDFe(CO)_2(\eta^5$-$C_5H_5)$ (**8**). As expected,[23,24] the mercuric halide cleavage proceeds with retention, the sulfur dioxide insertion with inversion of configuration at carbon. Surprisingly, however, halogen cleavage reactions of **8** proceeded with retention of configuration,[29] in direct contrast with the results of Whitesides et al.[23,24] on a very similar compound. This paper reports further studies on the halogenation reactions of **8**, under a variety of reaction conditions, in an attempt to better understand the apparent dichotomy. We find that the phenethyl group does not always behave as a "typical" primary alkyl ligand, but rather exhibits phenonium ion-like character in some cases.

Experimental Section

Ir spectra were measured on Beckman IR10 and Perkin Elmer 180 spectrometers, NMR spectra in both continuous wave and Fourier transform modes on a Bruker HX 60 spectrometer.

***erythro*-α,β-Dideuteriophenethyl methyl ether,** *erythro*-PhCHDCHDOMe, was prepared by treating a solution of $RhCl(PPh_3)_3$[31] (0.5 g) in neat *cis*-β-methoxystyrene (Aldrich) (25 g) with deuterium (50 psi) in a Parr catalytic apparatus. Olefin reduction by $RhCl(PPh_3)_3$ is known to take place stereospecifically cis[28,31] and, in the system described here, reaction was very rapid and was essentially complete after a few hours. The product was purified by distillation [57-60 °C (10 mm)] [lit.[32] 72-74 °C (15 mm), 46-47 °C (3-4 mm)].

***erythro*-α,β-Dideuteriophenethanol,** *erythro*-PhCHDCHDOH, was prepared by refluxing the methyl ether with 47% hydriodic acid for 3 days, when the NMR spectrum of the organic phase showed that reaction was essentially complete. The product was extracted with methylene chloride, and the methylene chloride solution was successively washed with 5% aqueous $NaHCO_3$ and $Na_2S_2O_5$ solutions, and dried over anhydrous Na_2SO_4. The product was purified by distillation at 60 °C (1 mm) [lit.[33] 97.2 °C (10 mm)].

***erythro*-α,β-Dideuteriophenethyl tosylate,** *erythro*-PhCHDCHDOTs, was prepared from the alcohol by standard methods[34] and was recrystallized from petroleum ether (bp 40-60 °C) as white crystals, mp 37 °C (lit.[35] 37.5-38.2 °C). Phenethyl tosylate, labeled with ^{13}C to the extent of 5% at the α-carbon atom, was prepared by treating phenylacetic acid (Merck Sharp and Dohme) (labeled with ^{13}C to the extent of 90% at the carboxyl carbon) with lithium aluminum hydride to yield labeled phenethanol.[36] The latter was diluted with unlabeled phenethanol and converted to the tosylate, as above.

Dicarbonyl-η^5-cyclopentadienyl-*threo*-α,β-dideuteriophenethyliron(II), *threo*-$PhCHDCHDFe(CO)_2(\eta^5$-$C_5H_5)$ (**8**), was prepared by adding a THF solution of $Na[\eta^5$-$C_5H_5Fe(CO)_2]$ to the *erythro*-tosylate (1:1 molar ratio) in dry THF under nitrogen in the usual manner.[37] The product was obtained by removing the solvent under reduced pressure, extraction of the residue with petroleum ether (bp 40-60 °C) and passage of the extract through an alumina column (80-200 mesh). Removal of the solvent under reduced pressure gave yellow-brown crystals in about 75% yield, mp 74-75 °C (lit.[38] 73-74 °C). The compound was also identified by its ir and NMR spectra.[38] Although its solutions are somewhat air sensitive, the dry solid may be handled in air.

Unless otherwise specified, halogenation reactions were normally carried out by adding a solution of the halogen to a stirred solution of an equimolar amount of the iron complex under nitrogen at room temperature. The reaction mixtures were generally stirred for 15-30 min, after which the solvent was removed under reduced pressure. The resulting oil was extracted with petroleum ether (bp 40-60 °C) and passed through a short alumina column to remove paramagnetic impurities. On removing the petroleum ether under vacuum, reasonably pure phenethyl halide could be obtained; products were then identified on the basis of the proton NMR spectra in $CDCl_3$. Yields of phenethyl halide, where calculated, were greater than 70%. In cases in which the solvent was relatively high boiling (pyridine, nitrobenzene), little effort was made to obtain very pure product, as the resonances of the solvent in these cases did not overlap the critical resonances of the phenethyl halide (see below).

Table I. ^1H NMR Data for the Compounds PhCHDCHDX (in $CDCl_3$)

X	τ (α-CH)	τ (β-CH)	$^3J_{HH}$ (threo)	$^3J_{HH}$ (erythro)
Cl	6.33	6.97	6.5	8.0
Br	6.50	6.90	6.4	8.4
I	6.68	6.92	6.0	9.4
OH	6.27	7.25		6.6
OMe[a]	6.47	7.20		7.8
OTs[b]	5.85	7.12		7.4
C_5H_5Fe-$(CO)_2$[c]	8.38	7.35	4.8	12.6

[a] OMe, τ 6.73. [b] Me, τ 7.63. [c] C_5H_5, τ 5.30.

NMR data for the series of *threo*- and *erythro*-α,β-dideuteriophenethyl compounds used here are presented in Table I. Vicinal hydrogen-hydrogen coupling constants for the diastereomeric deuterated phenethyl bromide and iodide were obtained by allowing the *erythro*-tosylate to equilibrate with sodium bromide and iodide, respectively. Ample precedents are available for assuming that $^3J_{HH}$(erythro) > $^3J_{HH}$(threo);[39,40] in addition, pure *threo*-PhCHDCHDCl could readily be obtained and identified from the reaction of the *erythro*-tosylate and chloride ion because epimerization by free chloride ion is very slow. Where comparisons with literature values are possible, the agreement is very good.

Results and Discussion

As shown previously,[28,29] the α,β-dideuteriophenethyl group readily allows the determination of the stereochemical courses of a wide variety of reactions of primary alkyl ligands. Although the differences, $^3J_{HH}$(erythro) − $^3J_{HH}$(threo), are not as large for compounds of the type PhCHDCHDX as for the analogous $Me_3CCHDCHD$- compounds,[24] the compounds *erythro*-PhCHDCHDOTs (reported here) and *threo*-PhCHDCHDCOCl[28] may be prepared much more easily and conveniently than similar *tert*-butyl compounds.[24] Deuteration of *cis*-β-methoxystyrene proceeded much more rapidly than does deuteration of other olefins, such as cinnamic acid;[28] the observed high degree of specificity of the cis addition of deuterium to the olefin provides further evidence of the great utility of $RhCl(PPh_3)_3$ in preparing specifically labeled deuterated hydrocarbons.[28,31] Conversion of *erythro*-PhCHDCHDOTs was unexceptional and requires no comment. Conversion of the tosylate to **8**, with inversion of configuration, was also as expected.[24]

The organic products from the halogenation of **8** under a wide variety of conditions are listed in Table II. Chlorination reactions (no. 1-3), which yield phenethyl chloride or phenethyl methyl ether, proceed very differently from those of a number of other complexes of the type η^5-$C_5H_5Fe(CO)_2R$, which generally yield products resulting from alkyl migration to coordinated carbon monoxide,[24-26] i.e., the acid chloride or ester. In all cases, a very high degree of retention of configuration was observed. Iodination reactions (no. 7-11) yielded phenethyl iodide in most cases and also exhibited a high degree of retention, although not as high as was observed for chlo-

Table II. Products from Halogen Cleavage Reactions (R = PhCHDCHD-)

Experiment number	Halogen (solvent)	Product(s)	% retention (±3%)	Comments
1	Cl_2 (n-C_5H_{12})	RCl	89	
2	Cl_2 (CH_2Cl_2)	RCl	95	
3	Cl_2 (MeOH)	ROMe	$\geq 90^a$	
4	ICl (n-C_5H_{12})	RCl	71	RCl/RI ~4
		RI	80	
5	ICl (CH_2Cl_2)	RCl	87	RCl/RI ~8
		RI	89	
6	ICl (MeCN)	RCl	77	RCl/RI ~3
		RI	80	
7	I_2 (n-C_5H_{12})	RI	81	
8	I_2 ($CHCl_3$)	RI	81	
9	I_2 (CH_2Cl_2)	RI	78	
10	I_2 (MeCN)	RI	79	
11	I_2 (MeOH)	RI	~60	Major product[b]
		ROMe, RCO_2Me	$>90^a$	Minor products
12	Br_2 (n-C_5H_{12})	RBr	68	
13	Br_2 (n-C_5H_{12})	RBr	65	−78 °C
14	Br_2 (n-C_5H_{12})	RBr	69	In air
15	Br_2 (n-C_5H_{12})	RBr	68	Irradiated by Hanovia lamp
16	Br_2 (n-C_5H_{12})	RBr	69	Excess cyclohexene[c]
17	Br_2 (n-C_5H_{12})	Br	63	Excess p-benzoquinone
18	Br_2 (CCl_4)	RBr	70	
19	Br_2 (C_6H_6)	RBr	78	
20	Br_2 (CS_2)	RBr	70	
21	Br_2 ($CHCl_3$)	RBr	80	
22	Br_2 (CH_2Cl_2)	RBr	90	
23	Br_2 (Pyridine)	RBr	61	
24	Br_2 (Me_2CO)	RBr	75	
25	Br_2 (MeOH)	ROMe	$\geq 90^a$	
26	Br_2 ($PhNO_2$)	RBr	65	
27	Br_2 (MeCN)	RBr	75	
28	Br_2 ($MeNO_2$)	RBr	75	
29	Br_2 (CH_2Cl_2)	RBr	92	10× excess of $Ph_4As^+Cl^-$;
		RCl	94	RCl/RBr ~3
30	Br_2 (Me_2CO)	RBr	78	Saturated LiCl solution
		Cl	78	(~5× excess); RCl/RBr ~1
31	Br_2 ($CHCl_3$)	RBr	87	1 molar equiv of $MePh_3P^+Br^-$
32	Br_2 (MeCN)	RBr	78	1 molar equiv of $MePh_3P^+Br^-$
33	Br_2 (MeCN)	RBr	70	1 molar equiv of KF

[a] Erythro isomer not present in sufficiently high quantities to be detected. [b] Low degree of retention may be a result of epimerization of RI by free iodide ion. [c] Since the desired products were observed, the rate of bromination of the cyclohexene must be slower than that of the cleavage reaction.

rination reactions. In addition, the stereospecificity of the iodination reactions appeared to be independent of solvent. Reactions of iodine monochloride (no. 4-6) gave predominantly alkyl chloride rather than iodide. Both the ratio, RCl/RI, and the stereospecificity appeared to be somewhat solvent dependent, being higher for CH_2Cl_2 than for a solvent of either higher or lower dielectric constant (MeCN and n-C_5H_{12}, respectively).

Bromination reactions of **8** were studied in twelve solvents of varying dielectric constant (no. 12, 18-28). With pyridine the only notable exception, the stereospecificity of the reactions yielding RBr was at a maximum in CH_2Cl_2 and decreased as the dielectric constant both increased and decreased (no. 12, 18-28 are arranged in order of increasing solvent dielectric constant). Furthermore, in n-C_5H_{12}, decreasing the reaction temperature to −78 °C (no. 13), carrying out the reaction in the presence of air (no. 14) or radical scavengers (no. 16, 17), and ultraviolet irradiation during the reaction had little effect on the stereospecificity. Bromination in the presence of free chloride ion (no. 29, 30) yielded η^5-$C_5H_5Fe(CO)_2Br$ and both alkyl chloride and bromide, both with essentially the same stereospecificity obtained on bromination (no. 22, 24) and chlorination (no. 2) in the absence of free halide. Similarly, bromination in the presence of free bromide ion under conditions in which epimerization of RBr by bromide ion should be negligible also had little effect on the stereospecificity. One molar equivalent of free fluoride ion in acetonitrile solution during bromination yielded no phenethyl fluoride and had little effect on the stereospecificity of the bromination reaction. Using 0.16 M 18-crown-6, concentrations of KF as high as 3.5 mM were obtained.[41]

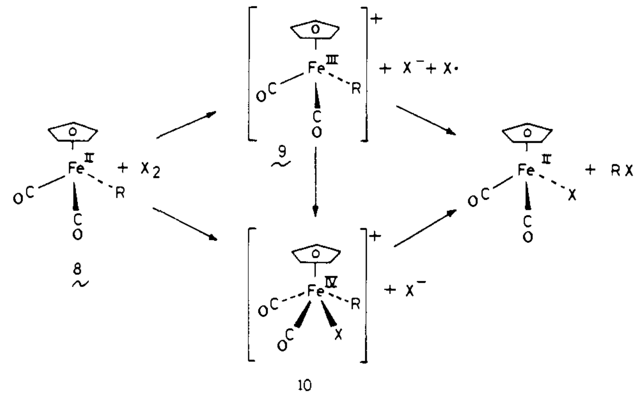
Samples of **8** enriched in ^{13}C at α-carbon atom to the extent of 5% were also prepared and subjected to halogenation reactions under the conditions of experiments 1-3, 8, 9, 12, 22, 23, 26, 29, and 30. As representative ^{13}C chemical shift data for phenethyl compounds do not appear to be generally available in the literature, data for the compounds studied here are listed in Table III. With the sole exception of bromination in pyridine, every experiment resulted in complete label rearrangement (i.e., 50%) such that the α- and β-carbon atoms of the products were completely scrambled, i.e., equally enriched. Similar conclusions were reported while this work was in progress by Flood and DiSanti,[42] who studied cleavage reactions of η^5-$C_5H_5Fe(CO)_2CD_2CH_2Ph$. In the case of bromination in pyridine, the label rearrangement occurred only to the extent of 26%. In addition, bromination reactions in n-pentane and methylene chloride with a deficiency of bromine yielded unreacted **8** in which little or no label rearrangement had occurred, while stop-flow kinetics studies indicate that bromination in benzene is first order in both **8** and bromine.

The data in Table II suggest that bromination reactions which yield RBr proceed by at least three different mechanisms, one which yields RBr with retention of configuration in a variety of solvents, one which yields RBr with either epimerization or stereospecific inversion of configuration in solvents of low dielectric constant, and a third which results in epimerization or inversion in solvents of high dielectric constant. Furthermore, as the ^{13}C labeling experiments show that, with the exception of cleavage in pyridine, *all three* processes involve complete scrambling of methylene carbon atoms, it seems likely that all three involve a *common* intermediate.

On this basis, it is possible to exclude several modes of electrophilic attack which apparently have successfully rationalized mechanistic data in other metal systems. Thus mechanisms which involve direct attack on α-carbon atom, such as SE2 (cyclic), SE2 (open, retention), and SE2 (open, inversion), similar to **1, 2,** and **3** respectively, may be rejected because they cannot explain the observed methylene carbon rearrangements. Similarly, the rather ill-defined radical chain process(es) which have been hypothesized to explain racemization during halogen cleavage reactions of organomercurials in nonpolar solvents[3] may also be rejected, as the stereochemical dependence on the presence of oxygen exhibited by those systems[3] is not observed here. The lack of effect of uv irradiation and radical scavengers (no. 15-17) also mitigates against chain radical reactions.

A reasonable mechanism would involve initial "activation" of the metal via oxidation by one- and/or two-electron transfer steps, as suggested in Scheme I. (The assignment of oxidation states is somewhat arbitrary, but we prefer to follow the convention that **8** is a complex of iron(II). It then follows that **9** and **10** are complexes of iron(III) and iron(IV), respectively.) A one-electron oxidation of **8** has precedent in the work of Treichel et al.,[43] who obtained complexes of the type $[\eta^5\text{-}C_5H_5Fe(diphos)X]^+$ (X = halide, CH_3) by the electrochemical oxidation of the compounds $\eta^5\text{-}C_5H_5Fe(diphos)X$, and in the halogenation reactions of alkylcobaloximes.[15-17] RX could then be formed from **9** by several reactions such as the homolysis of the iron-carbon bond to give a radical, which could react with X· with epimerization, or direct attack on the α-carbon atom of R by X· or X^-, both of which would be expected to proceed with inversion.

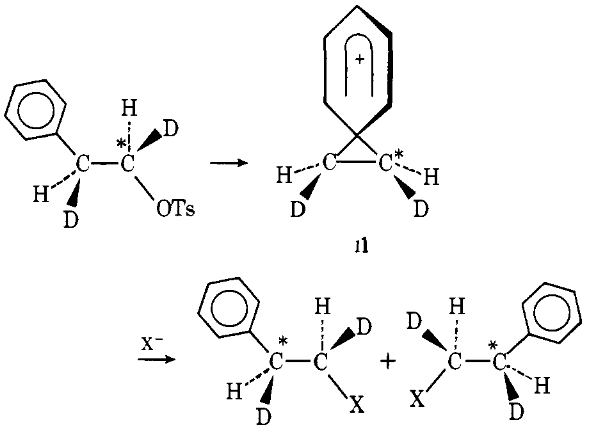
Scheme I



The predominant formation of RX with retention of configuration probably requires an intermediate such as **10**, which has recently been hypothesized by Attig and Wojcicki[27] for cleavage reactions of very similar iron compounds. Reductive elimination from **10** to give PhCHDCHDX and $\eta^5\text{-}C_5H_5Fe(CO)_2X$ might well proceed with retention of configuration,[11,12] although epimerization and inversion processes are also possible. The reverse reaction, oxidative addition of alkyl halides to low-valent metal complexes, occurs by mechanisms which can result in both racemization[44] and inversion,[44,45] and the principle of microscopic reversibility would predict the same for reductive elimination reactions. Experiments 29-32 of Table II, however, appear to rule out backside attack of halide ion on the α-carbon atom as an explanation for the presence of erythro products, as has been suggested for this[42] and similar[21,24] alkyliron systems. If such a reaction were important, the presence of excess halide ion would result in significantly greater amounts of erythro products, which is not the case.

The competition experiments (no. 3-6, 11, 25, 29, 30), in which more than one product is formed or is possible, are rather difficult to rationalize satisfactorily. The presence of RCl in the products of experiment no. 29 and 30 and ROMe in no. 2, 11, and 29 suggest that substitution of halide ion within the inner coordination sphere by either another halide or by solvent occurs competitively with the elimination. Although the alkyl chloride appears to be eliminated more readily than the alkyl iodide (no. 4-6), iodide ion appears to be less readily displaced by methanol from the soft iron ion than does chloride ion (no. 3, 11). Thus the product distributions appear to be determined by both the relative stability constants of the species in solution and by the relative ease of the reductive elimination steps.

The observed scrambling of methylene carbon atoms is reminiscent of the phenonium ion intermediates (**11**) involved to explain substitution and solvolysis reactions of many β-arylalkyl systems,[46] i.e.



(7)

Attack of a nucleophile on a stabilized carbonium ion such as **11** could occur with equal probability at either methylene carbon atom. In addition, as the bridging phenyl group would effectively shield the carbonium ion from backside attack by X^-, nucleophilic attack should occur with retention of configuration. In the system under consideration here, it is possible (and has been suggested[42]) that a phenethyliron intermediate such as **10** would dissociate to yield $\eta^5\text{-}C_5H_5Fe(CO)_2X$ and a phenonium ion, **11.** Such a mechanism would not only be consistent with the observed retention of configuration in the case of the phenethyliron system, but also with the observed inversion of configuration of the *tert*-butyl analogue, where a phenonium-like intermediate would be impossible and where backside attack by halide ion would be favored. The phenonium ion argument is also favored by the fact that the neutral $\eta^5\text{-}C_5H_5Fe(CO)_2X$ should be a very good leaving group, and may offer an explanation for the observations that halogenation of **8** in methanol gives little or no ester, contrary to what has been reported for a number of other alkyliron systems.[24-26] Phenonium ion elimination could occur faster than phenethyl migration to a coordinated carbonyl group.

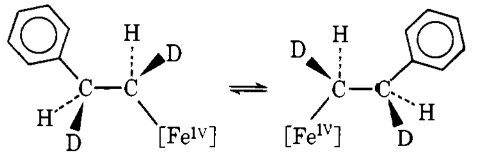
Undermining the phenonium ion idea, however, is the observation that no phenethyl fluoride is obtained from bromination in the presence of free fluoride ion (no. 33 in Table II).

Table III. ^{13}C Chemical Shifts of the Compounds $PhCH_2CH_2X$ (ppm from Me_4Si, in $CDCl_3$)

			Ph			
X	α-CH_2	β-CH_2	C-1	C-2,3	C-4	Other
Cl	39.2	44.9	138.0	128.6, 128.8	126.9	
Br	32.7	39.5	138.9	128.6	126.9	
I	5.3	40.4	140.2	128.3, 128.6	126.8	
OMe	73.7	36.3	138.8	128.4, 128.8	126.2	OMe, 58.4
OTs	70.5	35.3	136.1	128.5, 128.8	126.8	C_6H_4Me:Me, 21.6; C-1, 144.5; C-2,3 127.7, 129.9; C-4, 132.9
CO_2Me	31.0	35.7	140.6	128.3, 128.5	126.3	OMe, 51.4; CO, 173.4
$C_5H_5Fe(CO)_2$	5.5	44.1	146.4	127.9, 128.3	125.4	C_5H_5, 85.3; CO, 216.3

Liotta et al.[41] have shown that 18-crown-6 is a very effective solubilization agent for potassium fluoride in organic solvents. Under the rigorously anhydrous conditions employed, which were essentially the same as those employed by Liotta,[41] fluoride ion is as powerful a nucleophile toward carbon-centered electrophiles as is bromide ion. Thus if a *free* carbonium ion were to be generated under the conditions of experiment no. 33, i.e., in the presence of equimolar concentrations of fluoride and bromide, it is highly unlikely that only phenethyl bromide would be formed. On the other hand, it would not be surprising if fluoride did not displace bromide from the soft iron ion.

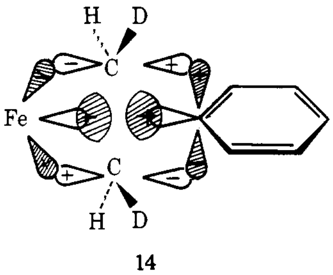
It follows then that the methylene carbon atoms must become equivalent while the phenethyl group is still coordinated to the iron rather than after dissociation, although the effects of differing degrees of possible ion pairing in the different solvents are difficult to assess. We suggest that **10** may exist as a fluxional intermediate containing a dynamic pair of rapidly equilibrating σ bonded phenethyl groups, **12** and **13.**



(8)

12 **13**

A similar proposal has been made earlier in the organic literature[46] as an alternative to the phenonium hypothesis; although subsequently rejected,[46] it remains an interesting possibility in the system under consideration here. A possible intermediate between **12** and **13** would be a π complex, **14**



14

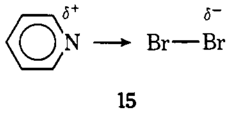
(here, and in subsequent diagrams, filled orbitals are denoted by hatching).

The bonding in such an intermediate could be rationalized in terms of a donor interaction between the filled π orbital of an essentially planar ethylenic moiety and both the iron(II) and a $C_6H_5^+$ moiety. Bonding with the metal would be unexceptional, involving donation of the filled π bond of the "olefin" with a suitable vacant σ orbital on the metal and back-donation from a filled d orbital on the metal into the vacant π^* orbital of the "olefin". Bonding with the aryl group would involve donation from the same π-bonding orbital to the vacant σ orbital of the aryl carbon atom, accompanied by π donation from the filled π-bonding orbitals of the aryl group to the empty π^* orbital of the "olefin". A similar π intermediate has been considered in the solvolysis reactions of phenethylmercury(II)[47,48], i.e.

$$PhCH_2CH_2Hg^+ClO_4^- \xrightarrow{HOAc} PhCH_2CH_2OAc + Hg^0 + H^+ + ClO_4^- \quad (9)$$

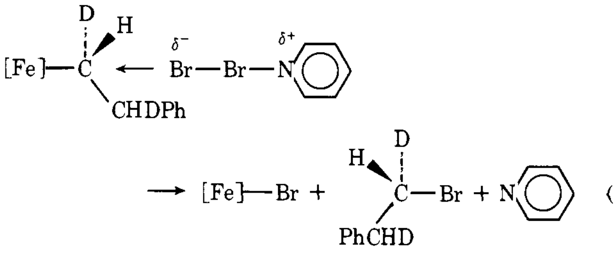
Reaction 9 would be formally analogous to that of the phenethyliron system in that the leaving group is a metal in a reduced oxidation state. Although it may be argued that the assignment of formal oxidation states to these highly covalently bonded complexes is of dubious significance, the proposed formulation of **14** is consistent with the observations that the halogenation cleavage reactions appear to exhibit some phenonium-like character. The apparent internal redox step involved on going from **12** to **14** to **13** may also provide a reason for the stability of **8** with respect to methylene rearrangement. If localization of positive charge on the phenethyl group, such that it effectively changes from a coordinated carbanion to a coordinated carbonium ion, must occur during rearrangement, then such a step for **8** would involve formation of a 20-electron intermediate, an unfavored process.[49] The **12** → **14** step, on the other hand, only involves a change from a 16- to an 18-electron system.

Finally, it would seem that bromination of **8** in pyridine (experiment no. 23 in Table II) must follow to a significant degree a path which does not result in phenyl rearrangement; relatively little scrambling of methylene carbon atoms was observed in this case, which was also the least stereospecific. The major electrophilic reagent in pyridine is the linear charge transfer complex, **15**.[50]



15

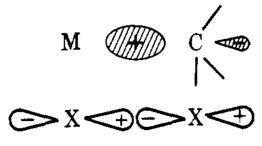
Rather than by initial oxidation of the iron of **8, 15** and **8** probably interact by backside attack of the terminal bromine atom on the α-carbon atom, i.e.



(10)

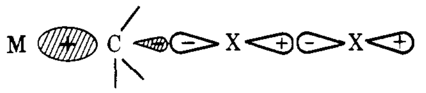
This hypothesis is consistent with both the observed lack of rearrangement of labeled methylene groups and also the observed greater degree of inversion.

Finally, we suggest that a better understanding of electrophilic substitution reactions of organometallic compounds may be achieved if the different postulated mechanisms were to be considered from the point of view of correlation of the interacting molecular orbitals of the metal complex and the electrophile, both with respect to symmetry requirements and relative energies. Following the views of Pearson[51] a necessary condition for reaction is a flow of electron density from the highest occupied molecular orbital (HOMO) of one reactant to the lowest unoccupied molecular orbital (LUMO) of the other. Net positive overlap of the orbitals concerned must occur, and electrons will move from the HOMO of a bond to be broken and in the direction of the more electronegative atoms. The relevant molecular orbitals for halogen–halogen and metal–carbon bonds are shown in Figure 1. Thus, in any concerted process, the halogen $\sigma_u{}^*$ orbital (b) must overlap positively with the metal–carbon σ orbital (c). On this basis, it would seem that two mechanisms discussed above, SE2 (cyclic) (**1**) and SE2 (open, inversion) (**3**), substantially lose their validity as possible modes of electrophilic substitution. The former involves side-on interaction of the halogen $\sigma_u{}^*$ orbital with the metal–carbon σ orbital, as in **16**.

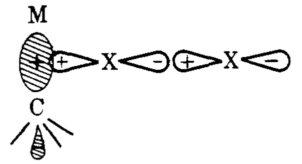


16

As no positive overlap can occur, the type of four-centered intermediate required by the SE2 (cyclic) mechanism is forbidden by orbital symmetry. Similarly it can be seen that the SE2 (open, inversion) mechanism is predicted to be partly forbidden by symmetry, as overlap of the halogen $\sigma_u{}^*$ orbital with the metal–carbon σ^* orbital is large, but with the metal–carbon σ orbital (**17**) is small. An entirely satisfactory mechanism involves end-on interaction of the halogen $\sigma_u{}^*$ orbital with the metal–carbon σ orbital, as in **18**.



17



18

This mechanism is very similar to the SE2 (open, retention) (**2**) process mentioned above, with attack being on a bonding orbital rather than on the carbon atom, and may well account for many reactions which proceed with retention of configuration and which have previously been rationalized in terms of an SE2 (cyclic) mechanism. Although an interaction such as **18** would seem to be "more allowed" than **17**, the latter apparently does occur, as for instance in the bromination of optically active (S)-(+)-*sec*-BuSn(neopentyl)$_3$; this reaction proceeds with inversion of configuration[7] to give (R)-(−)-*sec*-BuBr. The authors suggest[7] (as do others[21]) that the difference between the behavior of the tin compounds studied and that of many mercury compounds[2-4] lies in the fact that the former do not contain readily accessible empty low-lying orbitals to facilitate attack by electrophile on the metal atom. The suggestion apparently presupposes the importance of an interaction between filled, nonbonding orbitals on the halogen with empty, nonbonding orbitals on the metal, a process which would be nonproductive if a positive HOMO–LUMO interaction is accepted as being necessary. As an alternative explanation, we note that the particular tin compounds studied contain very bulky ligands and that an interaction such as **18** may well be hindered for steric reasons, thus allowing the normally electronically less favored **17** to become competitive.

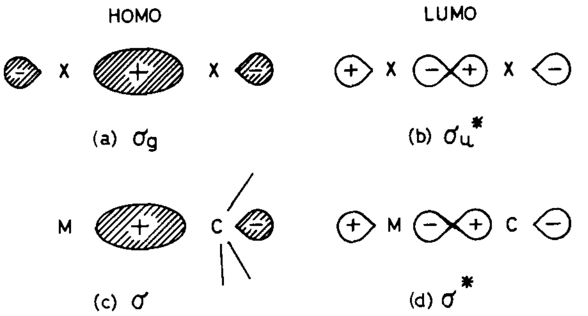


Figure 1. Highest occupied and lowest unoccupied molecular orbitals for halogen–halogen (a and b) and metal–carbon (c and d) bonds.

In the case of many alkyl transition metal compounds, as noted above, halogen cleavage reactions do not normally involve concerted mechanisms. In many cases in which the alkyl metal compound contains filled nonbonding d orbitals, the initial step involves oxidation of the metal atom rather than attack at orbitals of the carbon atom. Although too few systems are sufficiently well understood to permit broad generalizations, it may be suggested that electron flow to the halogen $\sigma_u{}^*$ orbital should always occur from the highest occupied metal orbital, whether bonding or nonbonding. Molecular orbital treatments of transition metal complexes of high symmetry, at least, predict that nonbonding d orbitals lie at higher energy than do the filled, bonding orbitals.[52] Thus it may be predicted that halogen cleavage reactions of d^1–d^9 transition metal alkyl compounds will normally involve initial oxidation of the metal rather than a concerted attack on the metal–carbon bond. With respect to the complex studied here, we note that two very recent photoelectron spectroscopic investigations of the compound η^5-$C_5H_5Fe(CO)_2CH_3$, while differing in details, suggest that the iron–methyl σ-bonding orbital is stabler than the nonbonding metal-centered d orbitals by at least 0.6 eV.[53,54]

The prediction is quite consistent with the observed cleavages with retention of *threo*-Bu^{t}CHDCHDZrCl(η^5-C_5H_5)$_2$,[21] which is a d^0 system, and of alkylmercury(II) compounds, which are $5d^{10}$ systems utilizing 6s and 6p orbitals for bond formation; both cases are thus susceptible to attack via an intermediate such as **18**. Even the compound $Ph_3SnMn(CO)_5$, which reacts with halogens with cleavage of the tin–carbon rather than the tin–manganese bond,[55] may not be an exception. Photoelectron spectra of triphenyltin compounds exhibit intense bands at about 9.1 eV, attributed to ionization from the π orbitals of the phenyl rings.[56] These are of approximately the same energy as ionizations arising from the nonbonding, essentially d orbitals of $CH_3Mn(CO)_5$,[54,57] and thus, although the photoelectron spectrum of $Ph_3SnMn(CO)_5$ has not been reported, it seems highly likely that the phenyl π orbitals may be as susceptible to electrophilic attack, perhaps a charge-transfer interaction,[50] as the manganese nonbonding d orbitals to direct oxidative attack. Interestingly the methyl analogue, $Me_3SnMn(CO)_5$, reacts with iodine *only* at the tin–manganese bond.[58]

Our hypothesis is also consistent with the postulated mode of attack on **8** by the bromine–pyridine charge-transfer complex (**15**). The bonding in the charge-transfer complex presumably involves electron donation from the pyridine to the $\sigma_u{}^*$ orbital of the bromine. The latter is then filled and can interact directly with the metal–carbon σ^* orbital.

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The Isomerization of Bicyclo[2.1.0]pent-2-enes

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Abstract: The isomerization of 1- and 2-methylbicyclo[2.1.0]pent-2-enes has been studied in the gas phase and in solution. The rates of decomposition, product ratios, and rates of product interconversion have been measured. The results are well explained by a mechanism in which central bond cleavage produces a chemically activated cyclopentadiene, which then undergoes competitive hydrogen shifts and collisional deactivation. This model is supported by RRKM calculations.

The isomerization of bicyclo[2.1.0]pent-2-enes to cyclopentadienes is a mechanistic problem that has been under investigation for several years. The bicyclo[2.1.0]pent-2-enes are the lowest homologues of the fused ring cyclobutene series, but geometric constraints in this system prevent a symmetry-allowed $\sigma_a^2 + \pi_s^2$ electrocyclic ring opening analogous to that observed for cyclobutenes.[1] Therefore, the valence bond isomerization is forced to proceed via an alternative mechanism, and several possible ones have been tested and excluded using deuterium or methyl-substituted bicyclopentenes.[2] Arguments for two of the remaining candidates, a $\sigma_s^2 + \sigma_a^2$ symmetry-allowed concerted process involving the 1,5 and 3,4 or 1,2 and 4,5 bonds in the starting bicyclopentene, or central (1,4) bond cleavage by some nonallowed pathway, have been presented.[3,4] These arguments are based on experiments that determine the relative amounts of 1- and 2-methylcyclopentadienes (**3** and **4**) produced by the decomposition of either 1- or 2-methylbicyclo[2.1.0]pent-2-ene (**1** and **2**); see Scheme I.

We have investigated the isomerization of the methylbicy-