# Synthesis of Olefins. Cross Coupling of Alkenyl Halides and Grignard Reagents Catalyzed by Iron Complexes

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Grignard reagents are coupled with alkenyl halides such as 1-bromopropene and  $\beta$ -bromostyrene in the presence of catalytic amounts of iron(III) complexes to afford alkenes. This cross-coupling reaction can be employed as a synthetic route for alkenes, in which primary, secondary as well as tertiary alkyl groups like isopropyl, cyclohexyl, and *tert*-butyl Grignard reagents are utilized. The reaction is stereospecific since *trans*-1-bromopropene affords only *trans*-butene-2 with methylmagnesium bromide and iron(III) pivalate. Furthermore, the rearrangement of branched alkyl groups such as *tert*-butyl has not been observed with an iron catalyst. Among various iron(III) complexes examined, tris(dibenzoylmethido)iron(III) is the most effective from the standpoint of rates and deactivation. Product and spectral studies suggest that the active catalyst is a labile iron species derived by reduction of iron(III) *in situ* by the Grignard component. High rates of cross coupling are limited by deactivation of the catalyst due to an aging process attributed to aggregation of the active iron species. Several mechanistic schemes are considered for cross coupling including (a) oxidative addition of alkenyl halide to a low valent alkyliron species followed by reductive elimination of the cross-coupled product and (b) assistance by reduced iron in the concerted displacement of halide at the alkenyl center by the Grignard reagent.

Olefins are produced from the cross-coupling reaction 1 between Grignard reagents and alkenyl halides in the pres-

$$RMgX + C = C \xrightarrow{X} \xrightarrow{(FeCl_3)} C = C \xrightarrow{R} + MgX_2 \quad (1)$$

ence of catalytic amounts of ferric chloride.<sup>1</sup> Thus, *n*-propylmagnesium bromide and vinyl bromide in tetrahydrofuran (THF) afford pentene-1. *cis*- and *trans*-1-propenyl bromide are converted stereospecifically into *cis*- and *trans*-butene-2 in the presence of methylmagnesium bromide and  $10^{-4} M$  ferric chloride.

$$CH_{3}MgBr \xrightarrow{(FeCl_{3})} \underbrace{\xrightarrow{Br}}_{Br} \xrightarrow{CH_{3} + MgBr_{2}}_{CH_{3} + MgBr_{2}} (2a)$$

Catalysis of the cross coupling reaction 1 occurs with a reduced iron species, since it can be shown in separate experiments<sup>2</sup> that iron(II, III) chlorides rapidly oxidize alkylmagnesium halides to afford a soluble form of iron, together with alkane and alkene. This soluble iron species is capable of catalyzing the cross-coupling reaction, but its effectiveness is decreased markedly simply on standing. Deactivation of the iron catalyst has been attributed to aggregation of the reduced iron species. In this report, we wish to examine the use of other iron complexes as more effective catalysts, particularly with respect to aging, and to extend the utility of the cross-coupling reaction to Grignard reagents containing secondary and tertiary alkyl groups.

#### Results

**Examination of Iron(III) Complexes as Catalyst Precursors.** The cross-coupling reaction between 1-bromopropene and methylmagnesium bromide was used as a model for testing the effectiveness of various iron(III) complexes under a standard set of conditions given in Table I. The optimum concentration of the iron(III) complexes for these screening experiments was determined by varying the concentration of ferric chloride from  $2 \times 10^{-5} M$ , where the rate was too slow, to  $4 \times 10^{-3} M$ , at which point aging (to be discussed later) severely restricted the production of butene-2. All of these studies were carried out by adding an excess of neat 1-bromopropene to a standard solution of methylmagnesium bromide and iron(III) complex which had previously been stirred for 5 min.

 Table I

 Iron(III) Complexes as Catalyst Precursors<sup>a</sup>

Run	Iron(III) complex <sup>b</sup>	Conversion, %c
$1^d$	FeCl <sub>3</sub>	25
$2^{e}$	$Fe[O_2CC(CH_3)_3]_3$	73
3 <i>°</i>	Fe(CH <sub>3</sub> COCHCOCH <sub>3</sub> ) <sub>3</sub>	90
$4^{e}$	$FeCl_3(PPh_3)$	27
5 <sup>e</sup>	Fe(CF <sub>3</sub> COCHCOCF <sub>3</sub> ) <sub>3</sub>	25
$6^{f}$	Fe(CH <sub>3</sub> COCHCOCH <sub>3</sub> )Cl <sub>2</sub>	57
7	Fe(CH <sub>3</sub> COCHCOCH <sub>3</sub> ) <sub>2</sub> Cl	> 99
8 <sup>f</sup>	$Fe[(CH_3)_3CCOCHCOC(CH_3)_3]_3$	>99
. 9 <sup>f</sup>	Fe(PhCOCHCOPh) <sub>3</sub>	>99

<sup>a</sup> In THF containing 0.12 *M* CH<sub>3</sub>MgBr, 0.35 *M* bromopropene. <sup>b</sup> 4.11  $\times$  10<sup>-4</sup> *M*. <sup>c</sup> % completion of reaction within 45 min at 25°; 100% implies all CH<sub>3</sub>MgBr consumed. <sup>a</sup> THF, 34 ml. <sup>e</sup> THF, 17 ml. <sup>f</sup> THF, 8.5 ml.

Butene-2 accounted for more than 97% of all the products formed in the reaction, with small amounts (1-2%) of propene as a side product. Traces of isobutylene derived from the 2-bromopropene impurity in the starting material, as well as methane and ethane produced during the generation of the catalyst (vide infra), were the only other products observed.

The data in Table I clearly show that the conversion (rate) into butene-2 is highly dependent of the structure of the iron(III) compound.<sup>3</sup> Fe(III) complexes containing  $\beta$ diketonate ligands in all or most of the coordination sites of iron(III) were the most effective. The color changes occurring during the course of reaction are noteworthy. The iron(III) complexes in THF solution varied from red to orange. Addition of the colorless Grignard reagent caused an immediate change to clear yellow, whereupon the reaction mixture gradually turned darker until at the end of the reaction it became clear gray-black, with a slight tendency toward yellow depending on the iron(III) compound employed. However, with tris(dibenzoylmethido)iron(III) the wine-red solution of iron(III) became lime-green immediately upon addition of the Grignard reagent and then gradually turned more gray as the reaction proceeded. The solutions in all cases are unstable to air and water. They lose color and activity slowly when exposed to air and guite rapidly with water, giving clear homogeneous solutions.

Kinetics. Two related types of kinetic behavior are observed in the cross-coupling reaction depending on the



Figure 1. Formation of butene-2 from the cross-coupling reaction with  $3.5 \times 10^{-3}$  mmol of Fe(DPM)<sub>3</sub> using (a) 1.5 mmol of CH<sub>3</sub>MgBr and 0.5 mmol of BrCH=CHCH<sub>3</sub>; additional 0.5 mmol of 1-bromopropene added at arrow; (b) 0.5 mmol of CH<sub>3</sub>MgBr and 1.5 mmol of BrCH=CHCH<sub>3</sub>; additional 0.26 mmol of CH<sub>3</sub>MgBr added at arrow.

iron(III) complex. With the active catalyst derived from tris(dipivaloylmethido)iron(III),  $Fe(DPM)_3$ , the rate of formation of butene-2 is zero order in Grignard reagent after a very short initial period. In the presence of excess 1-bromopropene, this reaction stops abruptly when the methylmagnesium bromide is consumed. The reaction continues unabated when more Grignard reagent is added as shown in Figure 1. The reaction is first order in 1-bromopropene in the presence of excess methylmagnesium bromide, and it can be carried to higher conversions by adding more 1-bromopropene after the first aliquot has been consumed. Fe(DBM)<sub>3</sub> shows similar behavior to  $Fe(DPM)_3$ .

Iron(III) pivalate,  $Fe(Pv)_3$ , is less active than either  $Fe(DBM)_3$  or  $Fe(DPM)_3$ , and the conversion of methylmagnesium bromide is not complete even in the presence of a large excess of 1-bromopropene. Furthermore, the addition of more Grignard reagent to the reaction mixture has no effect. More butene-2 is formed only if additional  $Fe(Pv)_3$  is added.

Aging the Catalyst. We attributed the foregoing difference in the kinetic behavior between Fe(DBM)3 and  $Fe(Pv)_3$  to the irreversible deactivation of the catalytic species during the course of reaction. To test this hypothesis, we varied the time of mixing the iron(III) complex with methylmagnesium bromide before the addition of 1-bromopropene. If the time of mixing was less than 5 min, which was carried out by reversing the order of addition of methylmagnesium bromide and 1-bromopropene (*i.e.*,  $t_{\text{mix}} \simeq 0$ ), we otained more or less the same results as those in Table I. All of the Fe(III) complexes except one showed a diminished conversion into butene-2 when the aging time was extended beyond 15 min as shown in Table II. The single exception to this trend is Fe(DBM)<sub>3</sub>, which we also noted as being anomalous in its color changes during the reaction. Indeed, the aging time with  $Fe(DBM)_3$  could be extended to as long as an hour without serious deleterious effects. Further aging produced a sharp retardation of about 90% which then appeared to remain reasonably constant.

The effects of temperature on aging the catalyst derived

 Table II

 Effect of Aging on the Catalyst Activity<sup>a</sup>

Run	Fe(III) complex <sup>b</sup>	Aging time, min	Con- version, c %	Retarda - tion, <sup>d</sup> %
10 <sup>e</sup>	FeCl <sub>3</sub>	40	2.1	92
$11^{f}$	$Fe(Pv)_3$	15	9.2	87
$12^{f}$	$Fe(acac)_3$	15	40	56
13 <sup>f</sup>	$FeCl_3(PPh_3)$	15	12	56
14 <sup>+</sup>	$Fe(facac)_3$	15	10	60
15 <sup>s</sup>	$Fe(acac)Cl_2$	15	12	79
16 <sup>e</sup>	Fe(acac) <sub>2</sub> Cl	15	6	94
$17^{s}$	$Fe(DPM)_3$	15	4	94
18"	$Fe(DBM)_3$	15	> 99	0

<sup>a</sup> In THF solutions containing 0.12 *M* CH<sub>3</sub>MgBr and 0.35 *M* BrCH=CHCH<sub>3</sub>. <sup>b</sup> 4.11  $\times$  10<sup>-4</sup>, Pv = pivalate, acac = acetylacetonide, facac = hexafluoroacetylacetonide, DPM = dipivaloylmethide, DBM = dibenzoylmethide. <sup>c</sup> % reaction at 45 min. <sup>d</sup> Relative to results in Table I. <sup>e</sup> THF, 34 ml. <sup>f</sup> THF, 17 ml. <sup>g</sup> THF, 8.5 ml.

in situ from  $Fe(acac)_3$  is illustrated in Figure 2. At 25°, the catalytic activity falls off rapidly as the time of mixing is increased. However, the rate of conversion at 1° reaches a maximum at about 25 min. The decreased conversions beyond 30 min are similar to those found at 25°. Thus, a decrease in temperature serves only to displace the curve in Figure 2 to longer times. We interpret the slower rates of reaction observed at short mixing times and low temperatures to the rather slower rate of reduction of  $Fe(acac)_3$  by Grignard reagent at this temperature. Deactivation or aging appears to be a subsequent step which is only slightly affected by cooling.

We attribute the lower conversions obtained from other iron(III) complexes listed in Table I to a similar deactivation of the catalytic species. Aging is largely irreversible, since the addition of more Grignard reagent or bromoalkene is without noticeable effect. Higher conversions to butene-2 under such conditions can only be achieved by the addition of more iron(III) complex.



Figure 2. Effect of aging time on the conversion of 0.35 M 1-bromopropene and 0.12 M methylmagnesium bromide to butene-2 at 25° (•) and 1° (•) using  $4.1 \times 10^{-4} M$  Fe(acac)<sub>3</sub>.



Figure 3. (a) Visible absorption spectrum of  $1 \times 10^{-3} M$  Fe(DBM)<sub>3</sub> in 0.7 ml of THF; (b) after addition of 0.2 *M* isopropylmagnesium bromide in 1.0 ml of THF to a; (c) after addition of 0.3 mmol of BrCH=CHCH<sub>3</sub> to b.

If aging of the catalytic species is due to aggregation, a change in coordination around iron by a free ligand in solution could retard deactivation. Several neutral ligands list-

J. Org. Chem., Vol. 40, No. 5, 1975 601

 Table III

 Effect of Neutral Ligands on Aging<sup>a</sup>

 Fe(III) complex <sup>b</sup>	Ligand <sup>C</sup>	Aging time, min	Conver- sion, %	Retarda- tion, %
Fe(Pv) <sub>3</sub>	PPh <sub>3</sub>	5	35)	46
$Fe(Pv)_3$	$\mathbf{PPh}_3$	15	19∮	10
$Fe(Pv)_3$	DPPE	5	53)	01
$Fe(Pv)_3$	DPPE	15	5∫	91
Fe(acac) <sub>3</sub>	$PPh_3$	5	63)	0.6
Fe(acac) <sub>3</sub>	$PPh_{3}$	45	8∫	80
Fe(acac) <sub>3</sub>	DPPE	5	28)	00
Fe(acac),	DPPE	45	4∮	69

<sup>a</sup> In 18 ml, THF containing 0.11 *M* CH<sub>3</sub>MgBr and 0.33 *M* BrCH=CHCH<sub>3</sub>. <sup>b</sup> 3.9 × 10<sup>-4</sup> *M* Fe(III). <sup>c</sup> 3.9 × 10<sup>-4</sup> *M* free ligand; DPPE = Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>.

 Table IV

 Reduction of Iron(III) by Methylmagnesium Bromide<sup>a</sup>

Iron(III) complex	CH <sub>3</sub> MgBr, (10 <sup>2</sup> mmol)	CH3- MqBr/ Fe(III)	CH <sub>4</sub> , (10 <sup>2</sup> mmol)	C <sub>2</sub> H <sub>6</sub> , (10 <sup>2</sup> mmol)	n <sup>b</sup>
Fe(acac) <sub>8</sub>	20	4	6.15	1.16	1.7
Fe(acac),	30	6	3.41	3.29	2.0
$FeCl_{3}(PPh_{3})$	30	6	4.53	2.48	1.9
Fe(acac) <sub>3</sub>	50	10	1.40	3.54	1.7
Fe(acac) <sub>3</sub>	125	25	1.96	2.66	1.5

 $^{a}$  In THF solutions containing 5  $\times$  10<sup>-2</sup> M iron(III).  $^{b}n$  = (CH<sub>4</sub> + 2C<sub>2</sub>H<sub>6</sub>)/5.

ed in Table III were added to iron(III) complexes to test this hypothesis. The results in Table III indicate that triphenylphosphine does indeed reduce the aging effect on  $Fe(Pv)_3$ , but unfortunately it also reduces the catalytic activity. Bisdiphenylphosphinoethane shows a similar effect on  $Fe(acac)_3$ .

Studies on the Catalytic Iron Species. The foregoing results indicate that the catalytic species produced from the reaction of iron(III) complexes and methylmagnesium bromide is highly labile and strongly discourage attempts at isolation. The formation of methane and ethane suggested the following stoichiometric relationship:

$$Fe(III) + nCH_3MgBr \longrightarrow Fe(III-n) + XCH_4 + YC_2H_6$$
(3)

where n = X + 2Y. The determination of the value for n according to eq 3 could provide information about the oxidation state of the reduced iron species, which is assumed to be the active catalyst. The experimental determination of n in Table IV was carried out by carefully measuring the amounts of methane and ethane evolved during the reaction of Fe(acac)<sub>3</sub> with various amounts of methylmagnesium bromide. We tentatively conclude from the results in Table IV that Fe(acac)<sub>3</sub> is reduced to an Fe(I) species.<sup>4</sup>

We attempted to exploit the color changes during the cross-coupling reaction to observe possibly the formation of metastable reduced iron species. In those catalytic systems in which yellow solutions were visually observed, no relevant information could be gleaned since the visible spectrum of the iron(III) complex merely disappeared and no distinctive bands appeared. On the other hand, the reaction of Fe(DBM)<sub>3</sub> with Grignard reagent is accompanied by the appearance of a new band at approximately 700 nm.

The absorption spectrum of  $Fe(DBM)_3$  in THF solution exhibits two principal bands at 408 nm ( $\epsilon$  7550) and 520 (shoulder) as shown in Figure 3. Addition of isopropylmagnesium bromide to this solution immediately causes a new

Table V	
Absorption Spectra of Reduced Iron Species	fron
Fe(DBM), and Grignard Reagent <sup>a</sup>	

	Absorption spectrum, nm		
Grignard Reagent	Band I (e)	Band II (6)	
CH <sub>3</sub> MgBr	360 (130,000) <sup>b</sup>	703 (4300)	
(CH <sub>3</sub> ) <sub>2</sub> CHMgBr	379	708	
	393		
c-C <sub>6</sub> H <sub>11</sub> MgBr	379	709	
• • • •	394		
$C_{g}H_{s}MgBr$	386	706	

<sup>a</sup> In THF solution. <sup>b</sup> Based on total conversion of Fe(DBM)<sub>3</sub>.

Table VI Reduction of Fe(DBM)<sub>3</sub> and Fe(DBM)<sub>2</sub> by Methylmagnesium Bromide in THF

 Iron complex <sup>a</sup>	Absorption spectrum, $\lambda_{\max}, nm(\epsilon)$
Fe(DBM) <sub>3</sub>	409(7550), 500(sh)
$Fe(DBM)_3 + CH_3MgBr$	360(130,000)
	704(4300), 655(sh)
$Fe(DBM)_2$	514(4200)
$Fe(DBM)_2 + CH_3MgBr$	360 <sup>b</sup>
	702(4800),650(sh)

 $^a$  In solutions approximately 10<sup>-3</sup> M Fe and 0.2 M CH<sub>3</sub>MgBr.  $^b$  Not determined.

band to appear at 708.5 nm with a shoulder at about 650 nm, and the band at shorter wavelength is shifted to 378 and 393 nm as a doublet. The color is rapidly bleached by 1-bromopropene, but the spectrum does not revert to that of Fe(DBM)<sub>3</sub>, showing mainly a band at 355 mm but of roughly the same molar intensity. The color change is not simply due to olefinic  $\pi$  coordination to the iron complex, since pentene-1 in large excess had no effect on the spectrum.

 $Fe(DBM)_3$  reacts similarly with other Grignard reagents listed in Table V. In each case, the band at 700 nm retains the same features shown in Figure 3, and it is largely unaffected by the Grignard reagent used. Moreover, the absorptions in the short wavelength region of the spectrum also show pronounced similarities, with the slight exception of the spectrum resulting from methylmagnesium bromide. The absence of significant differences in the absorption spectra of the reduced iron species,<sup>4</sup> presumably Fe(I) or Fe(0), suggest that R groups from the Grignard reagent may not be tightly coordinated, but more studies are required to establish this point.

The possibility existed that the spectrum was not that of an Fe(I) or Fe(0) species but the spectrum of an Fe(II) species. In order to resolve this problem, we independently prepared a sample of bis(dibenzoylmethido)iron(II) dihydrate. The visible absorption spectrum of Fe(DBM)<sub>2</sub> in THF has a principal band at 514 nm which is clearly at variance with those of either Fe(DBM)<sub>3</sub> or the supposed Fe(I) species. Moreover, addition of methylmagnesium bromide to Fe(DBM)<sub>2</sub> resulted in a species whose absorption spectrum is the same as that derived from Fe(DBM)<sub>3</sub> under similar conditions (Table VI). These spectral results coupled with the stoichiometric value of n in eq 3, are consistent with Fe(I) or Fe(0) species being the catalyst derived from Fe(DBM)<sub>3</sub> or Fe(DBM)<sub>2</sub> and Grignard reagent.

Stereospecificity of the Cross-Coupling Reaction Catalyzed by Iron. The coupling of methylmagnesium bromide and 1-bromopropene is stereospecific when induced by ferric chloride.<sup>1</sup> The demonstration of a similar stereospecificity was desirable for the more effective iron-



Figure 4. Correlation of the rates of formation of cis- and transbutene-2 from 0.12 M methylmagnesium bromide and 0.35 M cis/ trans-1-bromopropene using  $4.1 \times 10^{-4}$  M Fe(acac)<sub>3</sub>.

(III) complexes examined in this study. Thus, a sample of pure *trans*-1-bromopropene afforded only *trans*-butene-2 when treated with methylmagnesium bromide in the presence of  $Fe(Pv)_3$ . Similarly, when a mixture of *cis*- and *trans*-1-bromopropene is completely converted into butene-2 with  $Fe(Pv)_3$  it affords the same mixture of *cis* and trans isomers as that contained in the reactant.

The stereospecificity of the reaction and the absence of rearrangement allowed the mixture of *cis*- and *trans*-butene-2 to be used to determine the relative rates of coupling of the isomers. The formations of *cis*- and *trans*-butene-2 are correlated as shown in Figure 4. The competition at low conversions is kinetically pseudo zero order in bromopropene, and the slope is related to the ratio of second-order rate constants  $k_t/k_c$  by eq 4. With several iron(III) com-

$$k_{\rm t}/k_{\rm c} = \text{slope} \left[ \text{cis} \right]_0 / \left[ \text{trans} \right]_0 \tag{4}$$

plexes listed in Table VII, trans-bromopropene is about eight times more reactive than the cis isomer.<sup>5</sup>

Coupling of Alkenyl Halides and Grignard Reagents. We extended the cross coupling of primary alkylmagnesium halides with vinyl and propenyl bromides to include secondary and tertiary alkyl and aryl Grignard reagents as well as  $\beta$ -bromostyrene as reactants. Fe(DBM)<sub>3</sub> was used to promote all of the cross-coupling reactions listed in Table VIII. In at least two examples, the reported yields are based on materials isolated from reactions carried out on a preparatory scale. All other yields were determined by quantitative gas chromatography, but were not necessarily optimized.

Every reaction proceeded through the same or similar color changes, going from the wine red of  $Fe(DBM)_3$  to an opaque blue-green on addition of the Grignard reagent. This solution then cleared instantly and gradually turned deep amber when the bromo olefin was added. The reactions are exothermic, and those carried out on a preparative scale generated sufficient heat to cause THF to reflux if the solutions were not cooled prior to the addition of bromopropene.

Cross-Coupling of Alkenyl Halides and Grignard Reagents

 Table VII

 Relative Reactivities of cis- and trans-Bromopropene<sup>a</sup>

Iron(III) complex	Concn, M	Relative rate $k_t/k_c$	
FeCl <sub>3</sub>	$4 \times 10^{-4}$	7,4	
$Fe(\mathbf{Pv})_{3}$	$4 imes10^{-4}$	6.4	
Fe(acac) <sub>3</sub>	$4  imes 10^{-4}$	7.8	
		(000	

<sup>a</sup> In THF solutions containing 0.35 M bromopropene (69% cis, 31% trans) and 0.12 M CH<sub>3</sub>MgBr at 25°.

 Table VIII

 Synthesis of Olefins by the Cross-Coupling Reaction

 with Fe(DBM)<sub>3</sub><sup>a</sup>

<u>,</u>		Products, % <sup>b</sup>			
Grignard reagent (RMgBr)	Alkenyl bromide (R'Br)	R R'	RH	R(-H)	R R
Ethyl	BrCH-CHCH3 <sup>6</sup>	58	12	29 *	1
Phenyl	BrCH-CHPh	32	d		10
Ethyl	BrCH=CHPh	59	8	6	5
Isopropyl	BrCH=CHCH,	60	9	10	3
Cyclohexyl	BrCH=CHCH <sub>3</sub> <sup>c</sup>	54	d	d	d
-0 0	9	45°			
tert-Butyl	BrCH=CHCH3 <sup>c</sup>	$27^{e}$	d	d	d

<sup>a</sup> In 8.5-ml THF solutions containing 0.12 *M* RMgBr, 0.35 *M* bromo olefin, and  $4 \times 10^{-4}$  *M* Fe(DBM)<sub>8</sub>. <sup>b</sup> Based on RMgBr added. Reaction terminated after 45 min at 25° and products determined be gas chromatography. <sup>c</sup> Mixture of cis and trans isomers. <sup>d</sup> Present but not quantitatively analyzed. <sup>e</sup> Isolated yield.

The cross-coupling reactions listed in Table VIII occurred with no indication of rearrangement of the alkyl group. Thus, isopropylmagnesium bromide and cis/trans 1-bromopropene afforded only 4-methylpentene-2 as cis and trans isomers. Hexene-2, expected from the rearrangement of the isopropyl group to the *n*-propyl group, was not present (<0.5%). Similarly, the coupling of *tert*-butylmagnesium bromide and 1-bromopropene afforded only 4,4dimethylpentene-2, and no isomeric 5-methylhexene-2 resulting from the possible rearrangement of the tert-butyl group to an isobutyl group during the reaction. Isomerization of the bromo olefin was not examined in these studies. We presume from the results of the earlier experiments, however, that the mixture of cis and trans olefins arose directly from the isomeric 1-bromopropenes employed as reactants.

#### Discussion

The cross-coupling reaction of Grignard reagents and alkenyl halides has several interesting features which merit some discussion, including the nature of the catalytic iron species, the specificity, and the stereochemistry of the coupling. Any mechanistic formulation of this process must take each of these factors into consideration.

The unstable character of the catalytic iron species shown by this study unfortunately precludes a detailed description of the mechanism at this juncture. Our studies do show, however, that the added iron(III) complexes are rapidly reduced by the Grignard component to the catalytically active species. The contrary notwithstanding, we tentatively suggest that a monomeric iron(I) species is the active catalyst.<sup>4</sup> Aggregation of the active iron species may be responsible for the deactivation observed on aging the catalyst. In only one case,  $Fe(DBM)_3$ , were we able to obtain independent spectral evidence for a reduced iron species as a discrete entity formed during the reaction with Grignard reagent.

The kinetic results show that the cross-coupling reaction is largely independent of the concentration of alkylmagnesium halide. The rate is roughly first order in alkenyl halide and iron catalyst. There are essentially two catalytic cycles which can be considered in order to account for our observations and to form the basis for discussion and further study. Schemes I and II basically differ in the nature of the propagation sequence.<sup>6</sup>

## Scheme I

Initiation $Fe(III) + 2RMgX \longrightarrow Fe(I) + R_{ox}$	(5)
$\begin{array}{rcl} \texttt{Propagation} & \texttt{Fe}(I) \ + \ \texttt{RMgX} \  \ \texttt{RFe}(I)^{-} \ + \ \texttt{MgX}^{\star} \end{array}$	(6)
$RFe(I)$ + $R'Br \longrightarrow RR'Fe(III) + Br$	(7)
$RR'Fe(III) \longrightarrow RR' + Fe(I), etc.$	(8)
<b>Fermination</b> $n \operatorname{Fe}(I) \longrightarrow [\operatorname{Fe}(I)]_n$	(9)

 $Fe(I) \xrightarrow{(ox)} Fe(III)$  (10)

The catalytic amounts of iron required for the cross coupling according to the postulate in Scheme I are continually recycled between several oxidation states in a manner demonstrated for the gold-catalyzed coupling of alkyl groups from alkyl halides and Grignard reagents.<sup>7</sup> Analogous mechanisms have been suggested for similar reactions catalyzed by copper, nickel, and rhodium.<sup>7–9</sup>

In Scheme I, the iron(III) complex added as a catalyst precursor is initially reduced in eq 5 by Grignard reagent. Alkene, alkane, and alkyl dimers are the usual products of oxidation  $R_{ox}$  of the Grignard component.<sup>10</sup> The aspects of the ensuing propagation sequence in Scheme I which require further elaboration are (a) the oxidation of the reduced iron species in eq 7 and (b) the reduction of iron in eq 8.

A reaction such as that shown in eq 7 between a reduced metal species and an organic halide is formally represented as an oxidative addition.<sup>11</sup> Since it represents the metal complex essentially as a nucleophilic species, conversion into an anionic complex by coordination with Grignard reagent in eq 6 would facilitate the process.<sup>12,13</sup> Oxidative addition of alkyl halides to reduced iron species were described in previous studies.<sup>10</sup> Moreover, the ability of alkenyl halides to enter into oxidative addition reactions like the related aryl halides has been recently described for nickel(0) and platinum(II) complexes.<sup>14,15</sup>

The completion of the catalytic cycle in Scheme I requires the reduced iron species to be regenerated in a subsequent step. Reductive elimination of the alkyl and alkenyl groups as a cross-coupled product in eq 8 would fulfill this requirement. An analogous reductive elimination from trialkylgold(III) species in eq 11 has recently been demonstrated.<sup>16</sup>

$$RAu^{III}(CH_3)_2PPh_3 \longrightarrow RCH_3 + CH_3Au^IPPh_3$$
 (11)

Scheme I differs significantly from the alternative mechanism in Scheme II in one regard, namely the propagation step. The substitution process in Scheme II requires the reduced iron species to effect substitution by a coordination mechanism. No oxidation or reduction of the iron is re-

## Scheme II

Propagation	$Fe(I) + R'Br \Longrightarrow$	Fe(R'Br)	(6)
Fe(R'Br) +	$RMgX \longrightarrow RR' +$	MgXBr + Fe(I)	, etc.
			(12)

quired for the one-step process in eq 12, in contrast to the stepwise mechanism presented in eq 7 and 8. Such a con-

Table IX
Comparison of Alkyl and Alkenyl Halides in
<b>Iron-Catalyzed Reactions with Methylmagnesium</b>
Bromide <sup>a</sup>

	Products, % <sup>b</sup>					
Organic halides	CH4	C <sub>2</sub> H <sub>6</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>3</sub> H <sub>8</sub>	C <sub>4</sub> H <sub>10</sub>	C <sub>4</sub> H <sub>8</sub> -2
Ethyl bromide	48	6	41	16	8	0
1-Bromopropene <sup>c</sup>	Trace	Trace	0	0	0	100°
Ethyl bromide + 1-Bromopropene	22	7	8	3	0.4	52°

<sup>a</sup> In 8.5-ml THF solution containing 0.12 M CH<sub>3</sub>MgBr, 0.35 M organic halide, and  $4 \times 10^{-4} M$  Fe(DBM)<sub>8</sub>. <sup>b</sup> Based on CH<sub>3</sub>MgBr charged. <sup>c</sup> Mixture of *cis* and *trans* isomers.

certed reaction could readily accommodate the retention of stereochemistry observed in the coupling process.<sup>1,17</sup> It gains important support from the lack of alkyl rearrangement during the coupling reaction of isopropyl and *tert*butylmagnesium bromides. The latter are especially pertinent in view of the extensive rearrangement observed by Kumada, *et al.*, during the related nickel-catalyzed coupling of alkylmagnesium halides with aryl halides.<sup>18</sup> Thus, isopropylmagnesium chloride and various haloarenes with nickel(II) afford not only the expected cumenes, but also significant amounts of the corresponding *n*-propyl isomers are formed depending on the ligand attached to nickel. A stepwise mechanism was postulated in which eq 13 and 14

$$L_2Ni(X)Ar + RMgX \longrightarrow L_2Ni(R)Ar + MgX_2$$
 (13)

$$L_2Ni(R)Ar + ArX \longrightarrow RAr + L_2Ni(X)Ar, etc.$$
 (14)

constitute the propagation cycle. They suggested that isomerization of the isopropyl group occurred by  $\beta$ -elimination-readdition from the diorganonickel(II) intermediate in eq 15.

$$\operatorname{ArL}_{2}\operatorname{NiCH}(\operatorname{CH}_{3})_{2}$$
  $\longrightarrow$   
 $\operatorname{ArL}_{2}\operatorname{NiCH}_{2}\operatorname{CH}_{3}$   $\longrightarrow$   $\operatorname{ArL}_{2}\operatorname{NiCH}_{2}\operatorname{CH}_{2}\operatorname{CH}_{3}$  (15)

Alkyl isomerization and  $\beta$  elimination of other alkyl groups  $\sigma$  bonded to metals have been reported and appear to be rather general properties of transition metal alkyls.<sup>19–21</sup> We would have expected a similar rearrangement and/or elimination during the cross-coupling process if it occurred by Scheme I, especially with the *tert*-butyl moiety which is particularly prone to such an alkyl isomerization and elimination.<sup>20,21</sup>

Further support for a concerted mechanism is obtained by a competition experiment in which the cross-coupling reaction between methylmagnesium bromide and 1-bromopropene is carried out in the presence of ethyl bromide. Alkyl halides such as ethyl bromide have been shown independently to react with Grignard reagents in the presence of iron(III) complexes under conditions similar to the cross coupling reaction.<sup>10</sup> The products such as those given in Table IX for the reaction between ethyl bromide and methylmagnesium bromide are derived from methyl- and ethyliron intermediates which undergo facile reductive elimination by disproportionation and coupling.<sup>10</sup> Such organoiron species cannot be involved in the cross-coupling reaction of 1-bromopropene, since no cross-over product particularly pentene-2 in eq 18 was formed in the competition reaction given in Table IX.

CH<sub>3</sub>MgBr +

$$(CH_3CH=CHBr)_{Fe(DBM)_2} \rightarrow CH_3CH=CHCH$$

(16)

Organoiron species capable of undergoing reductive elimination, however, are present during the cross-coupling process. Thus, the yields of alkane, alkene, and alkyl dimers, as products of oxidation of the Grignard component in Table VIII, are too high to be derived solely by the reduction of the catalytic amounts of iron(III) in the initial phases of the process. They undoubtedly arise from an organoiron species in a higher oxidation state than those presented in eq 6. For example, it is possible that the organoiron species in eq 7 and 8 in Scheme I may be involved by a competing exchange followed by reductive elimination (eq 19). Alternatively, similar organoiron species may be de-

$$RR'Fe(III) + RMgX \Longrightarrow$$

$$R'MgX + R_2Fe(III) \longrightarrow Fe(I) + R_{ox}$$
 (19)

rived by an entirely independent pathway. In either case, the information on hand is insufficient to use such side reactions to distinguish the two mechanistic schemes.

The lines of evidence used above are not sufficient to distinguish Scheme I from Scheme II rigorously, since exceptions to each are known. However, we hope that further studies in progress will help to resolve some of these points.

## **Experimental Section**

Materials. Magnesium was kindly provided by Dow Chemical Co. as triply sublimed metal. Tetrahydrofuran (THF) was supplied in generous quantity by E. I. du Pont and purified by first treating it with potassium benzophenone ketyl, freeze-pump-thaw degassing this solution, and vacuum transferring the purified THF prior to use. 1-Bromopropene (Aldrich Chemical Co.) was purified by shaking with a saturated NaHCO<sub>3</sub> solution, drying with calcium hydride, and distilling the remaining mixture of cis and trans isomers from the 2-bromopropene impurity on a Teflon annular spinning band column. Pure trans-1-bromopropene was supplied by Chemical Samples Co. All other commercially available reagents were purified by published methods before use unless otherwise noted.<sup>22</sup>

**Grignard Reagents.** All Grignard reagents were prepared in the usual manner by adding a solution of alkyl halide in THF to an excess of magnesium shavings and allowing the reaction to go to completion under reflux. The molarity of the Grignard reagents was determined by one of two methods. If the hydrolysis product of the Grignard reagent was a gas, a known volume of the Grignard reagent was hydrolyzed with a 10% sulfuric acid solution, and the alkane liberated as a gas was determined by quantitative gas chromatography. If the hydrolysis product of the Grignard reagent was not a gas, a known volume of Grignard reagent was added to a known excess amount of standard sulfuric acid. The unconsumed acid was then back-titrated with standard sodium hydroxide solution.

**Iron(III) Complexes. Ferric chloride** was commercially available (Fisher Scientific) and dehydrated by azeotropic distillation with benzene prior to use.

**Ferric pivalate** was generously provided by E. I. du Pont Co. and used without further purification.

Ferric acetylacetonate was commercially available material (Shepard Chemical) and purified by recrystallization from absolute ethanol; visible spectrum:  $\lambda_{max}$  354, 436 nm.

Ferric chloride-triphenylphosphine [FeCl(PPh<sub>3</sub>)] was prepared by the method of Singh and Rivest as follows.<sup>23</sup> Iron enneacarbonyl Fe<sub>2</sub>(CO)<sub>9</sub> (1.8 g, 4.8 mmol) was placed in a 200-ml twonecked round-bottom flask in a dry bag filled with nitrogen. Under a flow of nitrogen, 3.0 g (11.4 mmol) of triphenylphosphine in CHCl<sub>3</sub> (100 ml) was added to the flask, which was fitted with a reflux condenser and a fritted disk filter tube with receiver. The mixture was refluxed for 15 hr. After cooling and filtering, the filtrate was concentrated to about 25-ml total volume on a rotary evaporator. The concentrated filtrate was shaken with n-hexane and a dark yellow viscous mass separated. After decanting the supernatant liquid, the residue was treated with absolute ethanol whereupon a yellow solid formed. Recrystallization from absolute ethanol yielded a stable yellow powder (13% yield), mp 156-158°. Although the experimental melting point is approximately 40° higher than that reported, the compound was identified by its infrared spectrum: Ph<sub>3</sub>-P, 1107; Fe-Cl, 372; Fe-P, 522 cm<sup>-1</sup> (Perkin-Elmer 621 using silver chloride and polyethylene windows).

Ferric hexafluoroacetylactonate  $[Fe(HFA)_3]$  was prepared by the method of Juvet and Durbin in the following manner.<sup>24</sup> Hexafluoroacetylacetone (HFA, Eastman Kodak) was shaken several times with concentrated sulfuric acid to dehydrate it prior to use. After removal of the acid the HFA was added directly to 1.06 g (2.26 mmol) of finely divided ferric nitrate in a small flask fitted with a drying tube. The mixture was heated gently to 60° for about 5 min. On cooling, the product was extracted into carbon tetrachloride, removed by rotary evaporation, and subsequently recrystallized from carbon tetrachloride. Fe(facac)<sub>3</sub> was obtained as red needles in 48% yield: mp 48–50° (reported 49°);<sup>25</sup> infrared spectrum 1615 (C=O), 1645 (C=C); 1438, 1113 (C-H); 1255, 1220 (C-F<sub>3</sub>); 663 cm<sup>-1</sup> (C-CF<sub>3</sub>);<sup>25</sup> visible spectrum  $\lambda_{max}$  367 nm.

Fe(acac)Cl<sub>2</sub> was prepared by the method of Puri and Methrotra as follows.<sup>26</sup> To a solution of ferric chloride in benzene (50 ml) was added an equivalent amount of acetylacetone, at which point the solution became red. The solution was allowed to reflux for 24 hr in a 130° oil bath. After cooling, the solid product was collected by filtration of the reaction mixture and recrystallized as a red powder by adding hot hexane to a hot solution of the product in benzene: mp 165–170° dec; visible spectrum  $\lambda_{max}$  328 nm; Cl (as AgCl) calcd 31.4; found 33.2.

Fe(acac)<sub>2</sub>Cl was prepared in the following manner.<sup>26</sup> To a solution of ferric chloride in benzene was added a greater than 2:1 excess of acetylacetone, at which point the mixture became red. The mixture was refluxed for 40 hr and the solid collected on cooling; the filtrate was saved. The collected solid was determined by chloride analysis to be Fe(acac)Cl<sub>2</sub>. After removal of the benzene from the dark red mother liquor by rotary evaporation, the remaining oil was recrystallized by adding hot hexane to a hot benzene solution of the product. The product was obtained as dark red needles: 34% yield; mp 191–196°; visible spectrum  $\lambda_{max}$  350 nm, 442; Cl (as AgCl) calcd 12.2, found 11.4.

 $Fe(DPM)_3$  was prepared by the method of Hammond and coworkers as follows.<sup>27</sup> To an aqueous solution containing an excess of ferric sulfate and an excess of sodium acetate was added an ethanolic solution (20 ml) of dipivaloylmethane (1.82 g, 9.90 mmol). Reaction was immediate and an orange-red powder formed in solution, which was subsequently collected by filtration. Additional product could be precipitated from the mother liquor by adding large amounts of water. Sublimation at 130–140° yielded an orange powder, mp 163.5–164°, yield 33%.

 $Fe(DBM)_3$  was prepared in the following manner.<sup>28</sup> To an aqueous solution of 0.6 g of ferric chloride was added an ethanolic solution of dibenzoylmethane (1.85 g, 2.76 mmol). An immediate reaction afforded a red solid which was completely precipitated by the addition of 50% aqueous ammonia. The solid was filtered, washed with water, and dried. Recrystallization by addition of hot hexane to a hot benzene solution of product gave a 70% yield of red needles: mp 240° dec; visible spectrum  $\lambda_{max}$  408 nm, 500 (sh).

Fe(DBM)2.2H2O was prepared by analogy to the work of Emmert as follows.<sup>29</sup> To a degassed aqueous solution of excess ferrous sulfate was added 2.24 g (3.34 mmol) of dibenzoylmethane in ethanol. At this point the green solution immediately turned pink. On addition of 20 ml of 5% sodium hydroxide, the product precipitated as a bluish purple solid which readily oxidized in solution and more slowly in air. The solid was collected by filtration under a blanket of nitrogen and dried at 40° in vacuo for 15 hr. The product was recrystallized by adding hot, degassed hexane to a hot solution of product in degassed benzene, visible spectrum  $\lambda_{max}$  513 nm. Although Fe(DBM)<sub>2</sub>·2H<sub>2</sub>O was not characterized directly by additional physical methods, comparing it to reports by other workers on analogous compounds leaves little doubt as to its identity.<sup>30,31</sup> Visible spectra were taken on a Cary 14 instrument using Pyrex air-tight 1-cm or 1-mm cells specially made in the Indiana University glass shop.

**Procedure for Studying Activity of Fe(III) Catalysts.** A 200-ml two-neck flask was equipped with a stirring bar and a rubber septum and dried in the oven. It was taken hot from the oven and placed on a vacuum line where it was evacuated until cool. After filling the flask with nitrogen, butane was added as an internal standard. Aliquots of methylmagnesium bromide and iron(III) complex in THF were added and allowed to mix for 5 min. An excess of neat 1-bromopropene was then added and the head gases analyzed for products 45 min from this point; *cis*- and *trans*-2-butene were identified by gas chromatography using commercial pure samples.

For reactions requiring no aging, into a nitrogen-filled, dry, two-

necked, 200-ml, round-bottom flask was placed a solution of Fe(III) in THF and neat 1-bromopropene. To this was then added methylmagnesium bromide in THF. The butene products were analyzed 45 min from this point by gas chromatography using butane as an internal standard.

Procedure for Experimental Determination of n in Equation 3. A three-necked, 100-ml, round-bottom flask was fitted with a stirring bar, a stopper, a septum, and a sealed angular piece of glass tubing containing 0.05 mmol of the solid Fe(III) compound. The vessel was then carefully evacuated and filled with nitrogen so that none of the Fe(III) compound fell into the flask. After filling, a portion of head gas was removed and 25 ml of dry THF and 20 ml of propane standard were added. Methylmagnesium bromide (2 ml) was added and allowed to equilibrate, and the head gas sampled. The flask was turned so the Fe(III) compound dropped into solution and again was allowed to equilibrate and the head gas sampled for methane and ethane.

Fe(DBM)<sub>3</sub> Catalyzed Reaction of Methylmagnesium Bromide with 1-Bromopropene and Ethyl Bromide. To a nitrogenfilled, dry, two-necked, 200-ml, round-bottom flask containing 5 ml (1 mmol) of methylmagnesium bromide in THF was added 3.5 ml ( $3.5 \times 10^{-3}$  mmol) of Fe(DBM)<sub>3</sub> in THF and the two were allowed to mix for 5 min. Ethyl bromide (0.25 ml, 3 mmol) was added, followed by 0.25 ml (3 mmol) of 1-bromopropene. Products were determined 45 min from this point by gas chromatography after quenching with 5 ml of 0.2 N sulfuric acid. Reversing the order of addition of ethyl bromide and 1-bromopropene had no effect on the product distribution.

Fe(DBM)<sub>3</sub> Catalyzed Reaction of Methylmagnesium Bromide and Ethyl Bromide. To a nitrogen-filled, dry, two-necked, 200-ml, round-bottom flask containing 5 ml (1 mmol) of methylmagnesium bromide in THF was added 3.5 ml ( $3.5 \times 10^{-3}$  mmol) of Fe(DBM)<sub>3</sub> in THF and the mixture stirred for 5 min. Ethyl bromide (0.25 ml, 3 mmol) was added and the products were analyzed by gas chromatography 45 min from this point, following the quench with 5 ml of 0.2 N sulfuric acid.

Metathesis of Methylmagnesium Bromide and Ethyl Bromide. In a dry nitrogen-filled, two-necked, round-bottom flask 5 ml (1 mmol) of methylmagnesium bromide in THF and 0.25 ml (3 mmol) of ethyl bromide were allowed to mix for 45 min. The head gases were analyzed by gas chromatography following the quenching with 5 ml of 0.2 N sulfuric acid. No ethane was observed and 98% of the materials could be accounted for.

Procedure for Studying the Effect of Free Ligand on Fe(III) Catalysts. Into a nitrogen-filled, dry, two-necked, 200-ml, round-bottom flask was placed 7 ml  $(7 \times 10^{-3} \text{ mmol})$  of the Fe(III) complex in THF and 1 ml  $(7 \times 10^{-3} \text{ mmol})$  of free ligand in THF. After these components were mixed for 5 min, 10 ml (2 mmol) of methylmagnesium bromide in THF was added and stirred for the desired time of aging. Then 0.5 ml (6 mmol) of 1-bromopropene was added, and after 45 min the head gases were analyzed for 2-butenes by gas chromatography using a butane standard.

Procedure and Conditions for Various Cross-Coupling Reactions. In a nitrogen-filled, dry, 200-ml, round-bottom flask was placed 5 ml (1 mmol) of Grignard reagent in THF. To this mixture was added  $3.5 \text{ ml} (3.5 \times 10^{-3} \text{ mmol})$  of Fe(DBM)<sub>3</sub> in THF and the two were mixed for 5 min. Alkyl bromide (3 mmol) was added, and products were analyzed 45 min from this point as below.

Ethylmagnesium Bromide and 1-Bromopropene. The 2-pentene cross-coupled product was identified quantitatively by gas chromatography (6 ft, 15% dibutyl tetrachlorophthalate column) using a pure commercial sample (Chemical Samples Co.) and propane as internal standard.

**PhenyImagnesium Bromide and**  $\beta$ -Bromostyrene. The *trans*-stilbene cross-coupled product was identified by gas chromatography (5 ft, 5% SE-30 column) using a pure commercial sample and adamantane as the internal standard.

Ethylmagnesium Bromide and  $\beta$ -Bromostyrene. Butenylbenzene as the cross-coupled product was identified and quantitatively analyzed by gas chromatography (10 ft, 15% Apiezon column) using a pure sample prepared by the base-catalyzed isomerization of 1-phenylbutene-2 (Phillips Petroleum Co.) and purified by distillation. Octane was used as internal standard.

**Isopropylmagnesium Bromide and 1-Bromopropene.** The 4-methyl-2-pentene cross-coupled product was identified and analyzed quantitatively by gas chromatography (10 ft, 15% Carbowax column) using a pure commercial sample (Chemical Samples Co.) and heptane as internal standard. *cis-* and *trans-*hexene-2 (Aldrich Chemical Co.) are well-separated from 4-methyl-2-pentene on a 6

ft. 15% dibutyl tetrachlorophthalate column, and no evidence could be found for their presence in the reaction mixture. Since authentic alkenes were available, quantitative ga chromatography was effected by the internal standard method after careful calibration under conditions which reproduced the reaction as closely as possible.

General Preparative Procedures. To approximately 45 mmol of Grignard reagent in THF was added 0.15 mmol of Fe(DBM)<sub>3</sub> in THF. After mixing for 5 min 10 ml (12 mmol) of 1-bromopropene was added and the solution cooled in an ice bath to prevent the THF from refluxing. After 60 min, the mixture was filtered to give a dark liquid and a white solid. The solid was dissolved in hydrochloric acid and the liquid, which had been concentrated by a factor of 2 by distillation, was extracted with large amounts of 5% hydrochloric acid and an organic solvent. The organic solvent was then removed and the product collected by fractional distillation.

Cyclohexylmagnesium Bromide and 1-Bromopropene. A preliminary determination of the product was made by gas chromatography (10 ft, 15% Carbowax column) which indicated a 60-65% yield of propenylcyclohexane, 54% of which was recovered from a pentane extract: bp 80-90° (90 mm); mass spectrum m/e124 (M<sup>+</sup>); nmr methyl protons (doublet)  $\delta$  1.30 (J = 7 Hz), ring protons (multiplet) 5.48; integration olefinic/alkyl 1:6.8. Anal. Calcd for C<sub>9</sub>H<sub>20</sub>: C, 87.01; H, 12.99. Found: C, 86.91; H. 12.87.

tert-Butylmagnesium Bromide and 1-Bromopropene. A preliminary examination by gas chromatography (6 ft, 15% dibutyl tetrachlorophthalate) identified the 4.4-dimethyl-2-pentene crosscoupled product using a pure sample as the basis for the identification (Chemical Samples Co.). Gas chromatographic analysis indicated a yield of about 55%, of which 27% was isolated from an octane extract: mass spectrum m/e 98 (M<sup>+</sup>); nmr  $\delta$  tert-butyl protons (singlet) 1.00, methyl protons (doublet) 1.60 (J = 4.5 Hz), olefinic protons (multiplet) 5.38; integration tert-butyl/methyl/olefinic 8.6:2.9:1. The reaction mixture was examined by gas chromatography for the presence of the isomeric 5-methylhexene-2 which is readily separated from 4,4-dimethylpentene-2 on a 10 ft, 15% Carbowax 5M column. Authentic 5-methylhexene-2 was prepared from the cross coupling of isobutylmagnesium bromide and 1-bromopropene with Fe(DBM)<sub>3</sub>.

Note Added in Proof. A radical-chain mechanism has recently been proposed for the coupling reaction between  $\pi$ -allylnickel bromide and organic halides [L. S. Hegedus and L. L. Miller, J. Amer. Chem. Soc., 97, 459 (1975)]. Alkyl radicals were postulated as principal chain-carrying species to account for the loss of stereochemistry during the coupling of (S)-2-iodooctane. A different chain mechanism is apparently operative with  $\beta$ -bromostyrene since coupling proceeds with retention of stereochemistry. The latter is similar to the stereochemical observations in the iron-catalyzed couplings reported here. The strongly reducing environment, however, strongly discourages the use of similar tests for inhibition [I. H. Elson, D. Morrel, and J. K. Kochi, J. Organometal. Chem., 84, C7 (1975)] in our system.

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Registry No.—FeCl<sub>3</sub>, 7705-08-0; Fe[O<sub>2</sub>CC(CH<sub>3</sub>)<sub>3</sub>]<sub>3</sub>, 53418-62-5; Fe(CH<sub>3</sub>COCHCOCH<sub>3</sub>)<sub>3</sub>, 14024-18-1; FeCl<sub>3</sub>(PPh<sub>3</sub>), 21144-09-2; Fe(CF<sub>3</sub>COCHCOCF<sub>3</sub>)<sub>3</sub>, 17786-67-3; Fe(CH<sub>3</sub>COCHCOCH<sub>3</sub>)<sub>2</sub>(L, 14689-46-4; Fe[(CH<sub>3</sub>COCHCOCH<sub>3</sub>)<sub>2</sub>C-COCHCOC(CH<sub>3</sub>)<sub>3</sub>]<sub>3</sub>, 14876-47-2; Fe(PhCOCHCOPh)<sub>3</sub>, 14405-49-3;

methylmagnesium bromide, 75-16-1; cis-1-bromopropene, 590-13-6; trans-1-bromopropene, 590-15-8; ethyl bromide, 74-96-4; ethylmagnesium bromide, 925-90-6; phenylmagnesium bromide, 100-58-3: B-bromostyrene, 103-64-0; isopropylmagnesium bromide, 920-39-8; cyclohexylmagnesium bromide, 931-50-0; tert-butylmagnesium bromide, 2259-30-5.

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- (a) The available results at this juncture do not allow a rigorous distinction between Fe(I) and Fe(O) as the catalytic species. For purposes of discussion we have adopted Fe(I) species, but the subsequent discussion is not basically altered if Fe(O) is the actual catalyst. We hope that studies in progress will resolve this ambiguity. (b) For reduction of iron (4)complexes by organometals see also Y. Kubo, A. Yamamoto, and S. Ikeda, *J. Organometal. Chem.*, **46**, C50 (1972); E. O. Fischer and J. Muller, *Ibid.*, **2**, 464 (1964), *Z. Naturforsch.*, *B*, **17**, 776 (1962), **18**, 418 (1963).
- These results are somewhat at variance with the earlier study in ref 1.
- Coordination around iron hereinafter will be largely unspecified unless required for the discussion. Oxidation numbers are only included as a bookkeeping device [J. Halpern, Accounts Chem. Res., 3, 386 (1970)] and are not necessarily intended to denote actual changes in oxidation and are not necessarily interface to denote actual changes in Oxidation states,"
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