Mechanistic Studies of Iron Catalysis in the Cross Coupling of Alkenyl Halides and Grignard Reagents

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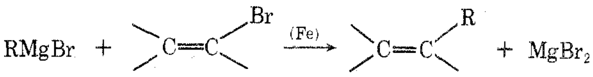
The cross coupling of 1-bromopropene with a variety of primary, secondary, and tertiary alkylmagnesium bromides can be effected with an iron(I) catalyst derived from tris(dibenzoylmethido)iron(III). A detailed study with ethylmagnesium bromide reveals the presence of ethane, ethylene, propylene, propenylmagnesium bromide, and 2,4-hexadiene as side products formed in addition to 2-pentene. The quantities of these products are shown to be in agreement with those expected for a complete material balance and electron balance in the catalytic process. 2-Pentene is formed stereospecifically from either (*Z*)- or (*E*)-1-bromopropene, as is the 2,4-hexadiene side product. Isotopic labeling of the ethyl group shows that ethane, ethylene, and propylene are formed by disproportionation of ethylmagnesium bromide and 1-bromopropene. A mechanism which accommodates all the products as well as the stereochemical and labeling results is proposed, in which the oxidative addition of 1-bromopropene to iron(I) is rate limiting and stereospecific. The propenyliron(III) intermediate subsequently undergoes metathetical exchange with the Grignard reagent and finally reductive elimination of the cross coupled product to regenerate the iron(I) species. Side reactions are considered to proceed from organoiron(III) intermediates by multiple exchanges and reductive disproportionations.

Grignard reagents are cross coupled stereospecifically with alkenyl halides such as 1-bromopropene in the presence of catalytic amounts of iron complexes.[1]


(1)

Iron(III) complexes are employed, but they are rapidly reduced by Grignard reagent in situ to generate a catalytically active reduced iron species, presumably iron(I). Among various iron complexes examined, tris(dibenzoylmethido)iron(III), Fe(DBM)$_3$, was found to be the most effective, particularly with respect to deactivation of the catalyst.[2] The yields of olefins obtainable by this catalytic process vary according to the structure of the alkyl moiety in the Grignard reagent. Thus, high yields of cross coupled products are obtainable with methylmagnesium bromide. Under the same conditions, ethylmagnesium bromide afforded ethane and ethylene as side products in addition to the expected cross coupled product. The difference can be attributed to the availability of β hydrogens in the latter, a factor which is also important in a variety of other organometallic reactions.[3]

In this study we have carried out a thorough analysis of the products formed during the reaction of ethylmagnesium bromide with (*Z*)- and (*E*)-1-bromopropene in the presence of tris(dibenzoylmethido)iron(III). A complete accounting of the material balance as well as the electron balance has been achieved. Together with stereochemical and isotopic labeling studies, they provide substantial mechanistic information about this interesting catalytic process.

Results

Cross Coupling of EtMgBr and 1-Bromopropene with Fe(DBM)$_3$. The iron-catalyzed reaction of ethylmagnesium bromide and 1-bromopropene was examined in detail initially because the yields of cross coupled product were the lowest and significant amounts of side products were generated with this combination. Furthermore, the gaseous hydrocarbon products could be examined directly and quantitatively by gas chromatography without recourse to prior hydrolysis of the reaction mixture.

A. Products and Stoichiometry. 1-Bromopropene was added to a solution of the iron catalyst and ethylmagnesium bromide in tetrahydrofuran (THF). The catalyst was prepared beforehand by adding an aliquot of the Grignard solution to a known amount of tris(dibenzoylmethido)iron(III) in the absence of oxygen. The small amount of ethane and ethylene formed during the preparation of the catalyst solution[4] was determined by gas chromatography using the internal standard method.

The cross coupled product, 2-pentene, is formed in approximately 40–50% yields according to the stoichiometry in eq 2. The remainder of the material balance is made up of ethane and ethylene (in excess of that formed during the catalyst preparation), together with propylene and 2,4-hexadiene as shown in Table I. Only traces (<0.01 mmol) of *n*-butane were observed. Control experiments showed that no reaction occurred in the absence of Fe(DBM)$_3$.

$$\mathrm{CH_3CH_2MgBr + BrCH{=}CHCH_3 \xrightarrow{(Fe)} CH_3CH_2CH{=}CHCH_3 + MgBr_2} \quad (2)$$

Ethane and ethylene formally represent the oxidation of ethylmagnesium bromide according to eq 3. The resultant electron deficit can be balanced by the formation of an equivalent amount of 2,4-hexadiene by the reduction given in eq 4. A comparison of the yields of ethane and hexadiene in Table I is in accord with this expectation.

$$\mathrm{2CH_3CH_2MgBr \xrightarrow{-2e} CH_3CH_3 + CH_2{=}CH_2 + 2MgBr^+} \quad (3)$$

$$\mathrm{2CH_3CH{=}CHBr \xrightarrow{+2e} CH_3CH{=}CHCH{=}CHCH_3 + 2Br^-} \quad (4)$$

Stoichiometrically, the formation of propylene can be offset by an equivalent amount of ethylene according to the iron-catalyzed disproportionation represented in eq 5.

$$\mathrm{CH_3CH{=}CHBr + CH_3CH_2MgBr \xrightarrow{(Fe)} CH_3CH{=}CH_2 + CH_2{=}CH_2 + MgBr} \quad (5)$$

Indeed, the combined yield of propylene and ethane in Table I is close to that of ethylene as given by the sum of eq 3 and 5.

The side reactions represented in eq 3–5 were deduced largely on the basis of material balance and electron balance. Mechanistic information for such processes was obtained by isotopic labeling and stereochemical studies described in the following sections.

Table I
Products and Stoichiometry of the Iron-Catalyzed Reaction of Ethylmagnesium Bromide and 1-Bromopropene[a]

C_2H_5MgBr, mmol	BrC_3H_5,[b] mmol	Products, mmol					Mat. bal,[c] %
		C_2H_4	C_2H_6	Propene	2-Pentene	2,4-Hexadiene	
1.02	2.96[d]	0.23	0.18	0.10	0.41	0.18	92
2.04	1.2	0.30	0.27	0.10	0.35	nd	105[e]
0.96	1.0	0.24	0.14	0.14	0.32	nd	102[f]
0.96	9.4	0.33	0.14	0.15	0.45	nd	105
0.96	25.8	0.34	0.12	0.19	0.53	nd	108

[a] In reactions containing 3.6×10^{-3} mmol of $Fe(DBM)_3$ in 9 ml of THF at 25° for 1 hr. [b] Mixture of 95% (*Z*)- and 5% (*E*)-1-bromopropene. [c] Based on EtMgBr as limiting reagent. [d] 24% *E* and 76% *Z* isomers. Includes [e] 0.28 and [f] 0.31 mmol of EtMgBr unreacted. nd = not determined.

Table II
Stereochemistry of 2-Pentene and 2,4-Hexadiene Formation during the Reaction of Ethylmagnesium Bromide and (*Z*)- or (*E*)-1-Bromopropene[a]

$1\text{-}BrC_3H_5$, mmol	Convn,[b] %	Products, mmol						Mat. Bal,[d] %
		C_2H_4	C_2H_6	C_3H_6	$2\text{-}C_5H_{10}$	$2,4\text{-}C_6H_{10}$	C_3H_5MgBr[c]	
1.16 *Z*	84	0.33	0.28	0.12	0.35 (*Z*)	0.21[e] (*Z*,*Z*)	0.08	103
1.16 *E*	22	0.16	0.15	0.03	0.06 (*E*)	0.07[d] (*E*,*E*)	0.09	97

[a] In reactions containing 2.04 mmol of EtMgBr and 3.6×10^{-3} mmol of $Fe(DBM)_3$ in 9 ml of THF at 25° for 1 hr. [b] Based on C_2H_6 formed on hydrolysis. [c] Based on extra C_3H_6 formed after hydrolysis. [d] Based on EtMgBr consumed, including 0.08 mmol in the catalyst preparation. [e] <0.01 mmol of other isomers.

B. Examination of the Effect of Various Iron(III) Compounds on the Cross Coupling Reaction. Ferric chloride ($FeCl_3$), ferric pivalate [$Fe(Pv)_3$], and tris(acetylacetonato)iron(III) [$Fe(acac)_3$] were also used to catalyze the reactions of ethylmagnesium bromide and 1-bromopropene in order to investigate the effect of different types of ligands on the cross coupling reaction. The mixture containing ethylmagnesium bromide and the iron(III) complex was cooled to −46°C after formation of the reduced iron intermediate, in order to inhibit deactivation of this intermediate.[2] Upon addition of 1-bromopropene, the reactions were allowed to warm to room temperature for 1 hr. The results for all four iron(III) complexes showed no significant differences among the products formed in the reaction.

C. Concentration of Reactants and Temperature. Ethane, ethylene, and propylene are undesired side products in the cross coupling of ethylmagnesium bromide and 1-bromopropene to 2-pentene. Figure 1 shows that all of these products are formed concurrently, albeit at different rates. An accurate kinetic study of the reaction was not carried out because of the multiplicity of products. However, the rate of production of 2-pentene responded roughly in proportion to the variation in the bromopropene concentration, but it was relatively unaffected by changes in the concentration of ethylmagnesium bromide. This result is in agreement with an earlier more detailed kinetic study of the ferric chloride promoted cross coupling of methylmagnesium bromide and 1-bromopropene, in which side reactions are relatively minor.[1,2]

The amounts of side products are somewhat dependent on the relative concentrations of ethylmagnesium bromide and 1-bromopropene as shown in Table I. Thus, the yield of 2-pentene rises slightly with increasing concentrations of 1-bromopropene; ethylene and propylene change more slowly with variations in concentrations.

The production of propylene can be eliminated by reducing the temperature of the reaction to −40°C, but cross coupling to 2-pentene proceeds much more slowly under these conditions. The production of ethane and ethylene parallels that of 2-pentene and could not be avoided by temperature variations. Interestingly, the addition of catalytic amounts of molecular oxygen into a reaction carried out at −46°C appeared to increase the rates of formation of products. It was also noted that the addition of oxygen caused a change of the blue color[2] to yellow, but no effect on the yields of products was apparent.

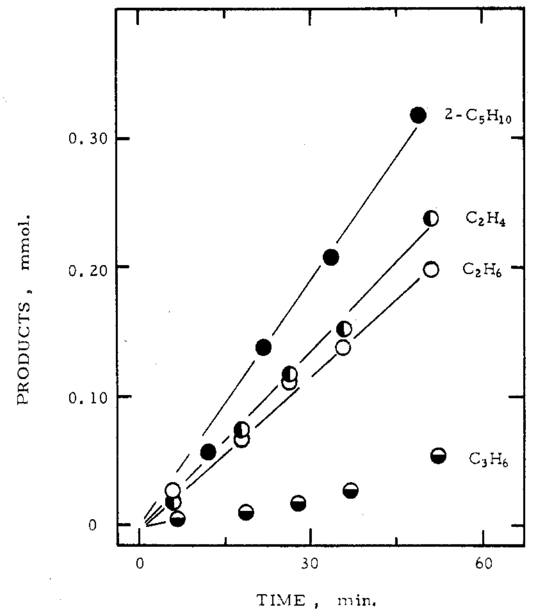


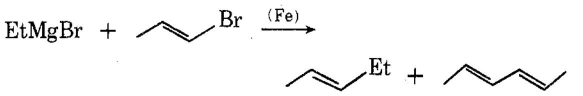
Figure 1. Catalyzed reaction of 0.11 *M* ethylmagnesium bromide and 0.35 *M* 1-bromopropene with 4.2×10^{-4} *M* $Fe(DBM)_3$ in tetrahydrofuran at 5°C (initial portion only).

D. Formation of 2-Pentene and 2,4-Hexadiene. Stereochemistry. The stereochemistry of the coupling reaction in the presence of $Fe(DBM)_3$ was examined using isomerically pure (*Z*)- and (*E*)-1 bromopropenes. The results in Table II show that the cross coupled product, 2-pentene, is formed stereospecifically. Furthermore, the homo coupled side product, 2,4-hexadiene, is also formed stereospecifically since only (*Z*,*Z*)-2,4-hexadiene was found starting with (*Z*)-1-bromopropene. Likewise, only (*E*,*E*)-2,4-hexadiene was formed from (*E*)-1-bromopropene.

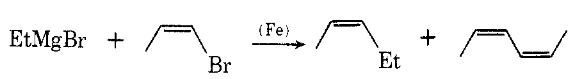
Table III
Iron-Catalyzed Coupling of 1-Propenylmagnesium Bromide and 1-Bromopropene[a]

$1\text{-}C_3H_5MgBr$,[b] mmol	$1\text{-}BrC_3H_5$, mmol	Convn,[c] %	Products, mmol		Mat. bal,[d] %
			$2,4\text{-}C_6H_{10}$	C_3H_6	
0.94 *Z*[f]	1.16 *Z*	26	0.16 (*Z,Z*) 0.075 (*Z,E*) <0.01 (*E,E*)	0.02	107 (*e*)
1.00 *E*[f]	1.16 *E*	30	0.25 (*E,E*) 0.07 (*E,Z*) <0.01 (*Z,Z*)	0.02	108 (105)

[a] In THF solutions at 25° for 1.5 hr. [b] Isomer employed in Grignard preparation. [c] Based on extra propylene liberated on aqueous quench after 1 hr (includes that consumed in catalyst preparation). [d] Material balance based on RMgX (BrC_3H_5). [e] Not determined. [f] Grignard reagent contains 20–25% of the other isomer.



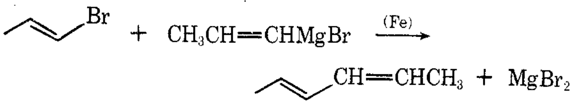
(6a)[5]



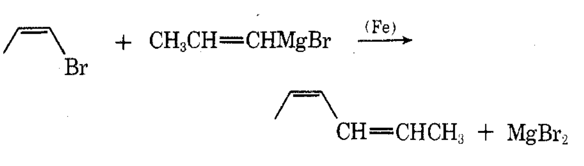
(6b)

The isomeric 2,4-hexadienes were analyzed by gas–liquid chromatography using either 1,2,3-tris(cyanoethoxy)propene, Apiezon L, or β,β-oxydipropionitrile in the liquid phase as previously established.[6] A mixture of all three isomers, (*E,E*)-, (*E,Z*)-, and (*Z,Z*)-2,4-hexadienes, was prepared by thermolysis of the mixture of propenylsilver complexes derived from (*Z*)- and (*E*)-propenylmagnesium bromide and silver(I).[7]

The stereochemistry of hexadiene formation was also examined in the cross coupling reaction of 1-propenylmagnesium bromide and 1-bromopropene in the presence of $Fe(DBM)_3$. Propenylmagnesium bromide prepared from either pure (*Z*)- or (*E*)-1-bromopropene and magnesium consisted of a mixture of *Z* and *E* isomers, as shown by carboxylation followed by GLC analysis of the methyl esters. Reaction of propenylmagnesium bromide [prepared from (*Z*)-1-bromopropene] with (*Z*)-1-bromopropene afforded a mixture of (*Z,Z*)- and (*Z,E*)-2,4-hexadienes, but no *E,E* isomer. Analogously, propenylmagnesium bromide [derived from (*E*)-1-bromopropene] and (*E*)-1-bromopropene produced only (*E,E*)- and (*E,Z*)-hexadienes as listed in Table III. These results strongly suggest that homo coupling of propenyl groups is stereospecific, similar to the cross coupling of alkyl and propenyl groups described in eq 1. Unfortunately, the partial isomerization of the propenyl moiety during the preparation of the Grignard reagent[8] prevented us from establishing this point unequivocally. Moreover, the iron-catalyzed cross coupling of vinylmagnesium bromide and either (*Z*)- or (*E*)-1-bromopropene (designed to eliminate stereochemistry at the vinylic center in the Grignard reagent) was unsuccessful. The latter could not be attributed to inhibition of the cross coupling reaction by 1,3-pentadiene or its destruction under reaction conditions; addition of 1,3-pentadiene had little effect on the iron-catalyzed reaction of ethylmagnesium bromide and 1-bromopropene from which it could be recovered.



(7a)



(7b)

Iron-Catalyzed Exchange and Disproportionation of Ethylmagnesium Bromide and 1-Bromopropene. *Exchange* of halogens between ethylmagnesium bromide and 1-bromopropene would afford propenylmagnesium bromide according to eq 8.

$$CH_3CH_2MgBr + CH_3CH{=}CHBr \xrightarrow{(Fe)} CH_3CH{=}CHMgBr + CH_3CH_2Br \quad (8)$$

The propenyl moiety converted in this manner does not generate propylene during the reaction, but only after subsequent hydrolysis. Indeed, at the end of the reaction the results in Table II (column 8) show that about 7% of the propenyl bromide is converted to an "anionic" form (which affords propylene on hydrolysis). The exchange is most noticeable when ethylmagnesium bromide is present in amounts in excess of that of 1-bromopropene. In order to verify this source of propylene, the iron-catalyzed reaction of EtMgBr (in excess) and 1-bromopropene was run to completion and the volatile components (C_2–C_3 hydrocarbons) removed in vacuo. The addition of D_2O to the mixture afforded propylene-d_1 (>80% isotopic enrichment), determined by comparison of the mass spectral cracking pattern with authentic 1-deuteriopropylene (see Experimental Section). Equivalent results were obtained when the Grignard component was substituted with β,β,β-trideuterioethylmagnesium bromide; and acidolysis with acetic acid afforded propylene-d_0 (<10% isotopic enrichment).

$$C_2H_5MgBr + CH_3CH{=}CHBr \xrightarrow{(Fe)} C_2H_5Br + CH_3CH{=}CHMgBr \xrightarrow{D_2O} CH_3CH{=}CHD \quad (9)$$

If the metathetical exchange in eq 8 were the sole source of propenylmagnesium bromide, an equimolar amount of ethyl bromide should also be produced. However, analysis of the reaction mixtures indicated the presence of less than 0.01 mmol of ethyl bromide. Part of the deficiency arises from its subsequent catalytic reaction with either ethylmagnesium bromide according to eq 10[4]

$$CH_3CH_2Br + CH_3CH_2MgBr \xrightarrow{(Fe)} CH_3CH_3 + CH_2{=}CH_2 + MgBr_2 \quad (10)$$

or propenylmagnesium bromide as described in Table IV. Alternatively, it is possible to obviate ethyl bromide as an intermediate, i.e., halogen exchange as described in eq 8, since its replacement with reaction 11

$$CH_3CH{=}CHBr + 2CH_3CH_2MgBr \xrightarrow{(Fe)} CH_3CH{=}CHMgBr + C_2H_6 + C_2H_4 + MgBr_2 \quad (11)$$

is tantamount to summing eq 8 and eq 10.

Disproportionation of 1-bromopropene with ethylmag-

Table IV
Iron-Catalyzed Reaction of Propenylmagnesium Bromide and Ethyl Bromide[a]

C_2H_5Br, mmol	C_3H_5MgBr,[b] mmol	Time,[c] min	Convn,[c] %	Products, mmol[d] C_2H_6	C_3H_6	2-C_5H_{10}[e]	C_2H_5MgBr[f]	Mat. bal,[c] %
1.34	1.66	90	17	0.08	0.10	0.15	0.01	79
1.34	2.07	500	38	0.19	0.14	0.25	0	74
3.00	0.82	90	60	0.13	0.09	0.22	0	70
3.00	0.97	500	71	0.27	0.14	0.32	0.03	58

[a] In the presence of 3.6×10^{-3} mmol of $Fe(DBM)_3$ in 9 ml of THF at 25°. [b] Mixture of *Z* and *E* isomers. [c] Based on C_3H_6 formed on hydrolysis after time indicated. [d] In addition to traces of ethylene, 2,4-hexadiene, and propyne. [e] Mixture of *Z* and *E* isomers. [f] Determined by extra ethane formed on hydrolysis.

nesium bromide according to eq 12 could account for the propylene which is observed *during* the catalytic reaction.

$$CH_3CH{=}CHBr + CH_3CH_2MgBr \xrightarrow{(Fe)} CH_3CH{=}CH_2 + CH_2{=}CH_2 + MgBr_2 \quad (12)$$

This type of disproportionation would result in the transfer of a β hydrogen of the ethyl group onto the propenyl moiety. Thus, labeled Grignard reagent, D_3CCH_2MgBr, was treated with 1-bromopropene and the resultant mixture of C_2–C_3 hydrocarbons transferred directly from the reaction mixture in vacuo without an aqueous quench. Analysis of the hydrocarbon mixture with the aid of a tandem gas chromatograph–mass spectrometer combination (see Experimental Section) showed that the ethylene fraction consisted exclusively of $C_2H_2D_2$ and the propylene fraction was roughly 90% C_3H_5D.

$$CH_3CH{=}CHBr + D_3CCH_2MgBr \xrightarrow{(Fe)} CH_3CH{=}CHD + D_2C{=}CH_2 + MgBr_2 \quad (13)$$

Moreover, the ethane fraction was enriched with $C_2H_2D_4$ to an extent of 82%, suggesting that ethane is also produced by a disproportionation process such as that in eq 10 or 11.

Structural Effects of the Grignard Reagent in the Cross Coupling with 1-Bromopropene. The foregoing studies of the iron-catalyzed reaction between ethylmagnesium bromide and 1-bromopropene indicate that disproportionation of the ethyl moiety occurs by transfer of a β hydrogen, and it is a major side reaction. Various alkylmagnesium bromides, differing in the number and availability of β hydrogens, were treated with 1-bromopropene under a standard set of reaction conditions given in Table V.

Among the primary, secondary, and tertiary alkylmagnesium bromides examined, ethylmagnesium bromide affords the lowest yields of cross coupled product with 1-bromopropene. Otherwise, yields of the cross coupled products in the range of 60–80% were obtainable by GLC analysis. The formation of alkene [R(–H) in Table V] and propylene, which are diagnostic of β-elimination from the Grignard component, is actually less important in secondary alkyl groups such as isopropyl, *sec*-butyl, and 2-pentyl compared to the primary alkyl analogues. We also deduce from the relative yields of *Z* and *E* alkenes formed from reactions containing an excess of (*Z*)- and (*E*)-bromopropenes that primary alkylmagnesium halides react preferentially with (*Z*)-1-bromopropene (Table V). If the same mixture of 1-bromopropenes is used, secondary alkylmagnesium bromides and *tert*-butylmagnesium bromide produce substantially increased yields of *E* alkenes. The same trend, although on a decreased scale, appears to apply to the formation of 2,4-hexadienes.

Discussion

The iron-catalyzed reaction of various alkylmagnesium bromides, RMgX, with 1-bromopropene affords cross coupled products, $RCH{=}CHCH_3$, in relatively good yields with excellent stereospecificity.

$$RMgBr + BrCH{=}CHCH_3 \xrightarrow{(Fe)} RCH{=}CHCH_3 + MgBr_2 \quad (14)$$

Five major types of side products are produced during the catalytic process, in greater or lower yields depending on the relative concentrations of the reactants, the temperature of the reaction, and the structure of the alkylmagnesium bromide. Thus, alkene R(–H) and alkane RH from the Grignard component as well as propylene, propenylmagnesium bromide, and 2,4-hexadiene from 1-bromopropene are always formed. No simple relationship could be found for the formation of these side products in relationship to the predominant cross coupled product. The latter suggests that the side products are intimately connected with the principal reaction, and that both processes involve common reactive intermediates. Alternatively, the side products could arise via concurrent but largely independent reactions from the cross coupling process.[9] The rigorous delineation between these basic mechanistic categories is extremely difficult to make in a catalytic system in which the isolation of intermediates is impractical.

Any mechanistic formulation of the catalytic process must take into account the diversity of side products, as well as the isotopic labeling and stereochemical results. In the following discussion we wish to present a reaction scheme which is consistent with the available data, while at the same time keeping the number of intermediates to a minimum.

The catalyst is best described as an iron(I) species formed by the facile reduction of the iron(III) precursor by the Grignard reagent.[1,2,4,10] It is a metastable species subject to deactivation on standing, probably by aggregation. Formally, iron(I) species consist of a d^7 electron configuration, isoelectronic with manganese(0) and cobalt(II). Only a few complexes of iron(I) have been isolated, but a particularly relevant one is the paramagnetic hydrido complex, $HFe(dppe)_2$, which is stabilized by the bisphosphine ligand, dppe[$Ph_2PCH_2CH_2PPh_2$]. A toluene solution shows a strong ESR signal centered at $\langle g \rangle = 2.085$ with poorly resolved fine structure.[11]

An intense ESR spectrum is also obtained if $Fe(DBM)_3$ is treated with excess ethylmagnesium bromide in THF solutions at −40°C. The ESR spectrum centered at $\langle g \rangle = 2.08$ is broad ($\Delta H \simeq 200G$) and shows no hyperfine structure. A similar broad resonance is observed when $FeCl_3[\langle g \rangle = 2.07]$ or $Fe(acac)_3[\langle g \rangle = 2.08]$ are employed. In addition to the broad absorption, ethylmagnesium bromide and $Fe(DBM)_3$ afford an additional spectrum in Figure 2 showing hyperfine splittings. This spectrum at $\langle g \rangle = 2.00$ retains the same general features when *n*-pentyl- or *sec*-butylmagnesium bromide are employed as reducing agents. It is destroyed immediately by molecular oxygen and has

Table V
Cross Coupling of Primary, Secondary, and Tertiary Alkyl Grignard Reagents with 1-Bromopropene[a]

Registry no.	RMgBr, mmol	Products, mmol						Mat. bal,[d] %
		R(−H)[b]	RH	C_3H_6	C_3H_5R (%)[c]	C_6H_{10}	R_2	
107-26-6	1.02 CH_3CH_2	0.32	0.12	0.19	0.41 Z 0.05 E (49)	nd[e]	Tr[f]	96
927-77-5	1.04 $CH_3CH_2CH_2$	0.45	0.03		0.65 Z 0.02 E (73)	0.02 (Z,Z)	Tr	101
693-25-4	1.13 $CH_3(CH_2)_4$	0.38	nd	0.29	0.64 Z (60)	0.08 (Z,Z)	nd	96
926-62-5	1.09 $(CH_3)_2CHCH_2$	0.12	0.01	0.11	0.79 Z (79)	nd	Tr	97
920-39-8	1.04 $(CH_3)_2CH$	0.07	0.02		0.79 (82)[g]	0.05[h]	0.05	98
922-66-7	1.01 $CH_3CH_2(CH_3)CH$	0.04	0.03	0.02	0.5 Z 0.2 E (77)[i]	0.05[h]	0.01	94[i]
57325-22-1	1.00 $CH_3CH_2CH_2(CH_3)CH$	0.13	nd	0.02	0.5 Z 0.2 E (75)[i]	nd	nd	102[i]
931-50-0	1.01 c-C_6H_{11}	0.04	nd	Tr	0.56 Z 0.15 E (76)	nd	nd	85
2259-30-5	0.95 $(CH_3)_3C$	0.1	nd	0.08	0.37 Z 0.15 E (60)	nd	0	86

[a] In reactions containing 2.96 mmol of 1-bromopropene (95% Z and 5% E) and 3.6 × 10^{-3} mmol of $Fe(DBM)_3$ in 9 ml of THF at 25° for 1 hr. [b] Alkene by loss of β hydrogen. [c] Cross coupled product (Z is cis and E is trans isomer); yields based on RMgX consumed including 0.08 mmol in catalyst preparation. [d] Based on RMgX consumed (determined by hydrolysis). [e] Not determined (nd). [f] Tr, ~0.01 mmol detected. [g] Mixture of E and Z isomers. [h] 0.04 (Z,Z) and 0.01 (Z,E). [i] Value approximate owing to unavailability of authentic product (see Experimental Section).

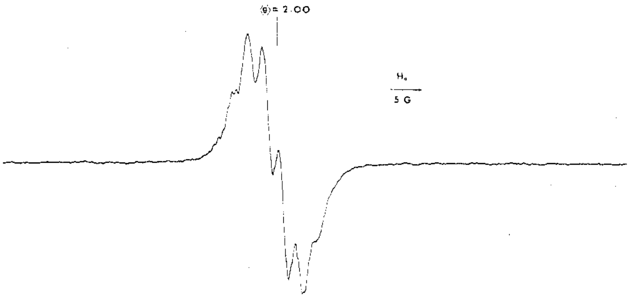
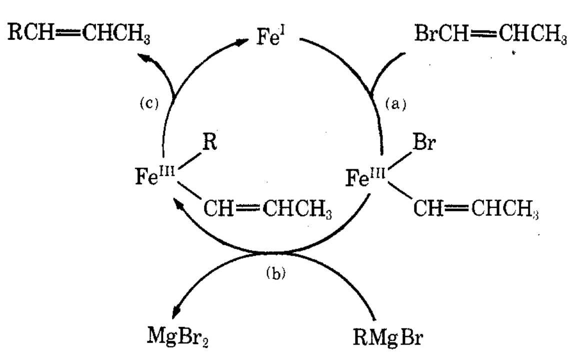


Figure 2. ESR spectrum at ⟨g⟩ = 2.00 obtained from the reaction of $Fe(DBM)_3$ and ethylmagnesium bromide in THF solution.

been assigned to the reduced ligand, dibenzoylmethide dianion radical.[12]

The mechanism of the cross coupling reaction can be accommodated by an oxidative addition of 1-bromopropene to iron(I) followed by exchange with ethylmagnesium bromide and reductive elimination. Scheme I is intended to form a basis for discussion and further study of the catalytic mechanism.[13] In order to maintain the stereospecificity, the oxidative addition of bromopropene in step a should occur with retention. Similar stereochemistry has been observed in oxidative additions of platinum(0) and nickel(0) complexes.[14,15] The methathesis of the iron(III) intermediate in step b is expected to be rapid in analogy with other alkylations.[16] The formation of a new carbon–carbon bond by the reductive elimination of a pair of carbon-centered ligands in step c has been demonstrated to occur with organogold(III), organonickel(II), organoplatinum(IV), and organorhodium(III) complexes.[17]

Scheme I

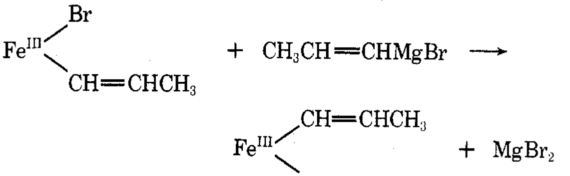


(15)

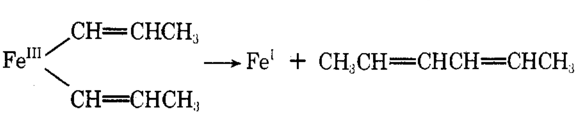
The iron(III) intermediates in Scheme I serve as focal points for the formation of the side products. For example, metathetical exchange of propenyliron(III) with Grignard reagent would afford propenylmagnesium bromide in eq 16.[13,18]

$$Fe^{III}CH{=}CHCH_3 + RMgBr \rightleftharpoons Fe^{III}R + CH_3CH{=}CHMgBr \quad (16)$$

Further exchange in eq 17 would produce bis(1-propenyl)iron(III) species which reductively eliminate to produce the 2,4-hexadienes stereospecifically.[19,20]

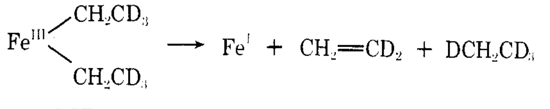


$$Fe^{III}(Br)(CH{=}CHCH_3) + CH_3CH{=}CHMgBr \longrightarrow Fe^{III}(CH{=}CHCH_3)_2 + MgBr_2 \quad (17a)$$

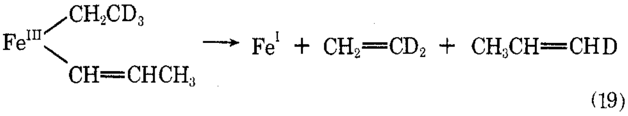


$$Fe^{III}(CH{=}CHCH_3)_2 \longrightarrow Fe^{I} + CH_3CH{=}CHCH{=}CHCH_3 \quad (17b)$$

Disproportionation products are postulated to arise from alkyliron(III) and/or dialkyliron(III) species formed by an analogous metathesis between iron(III) species and alkylmagnesium bromide. Thus, the disproportionation processes previously represented in eq 10 and 12 may proceed as follows.[21,22]



$$Fe^{III}(CH_2CD_3)_2 \longrightarrow Fe^{I} + CH_2{=}CD_2 + DCH_2CD_3 \quad (18)$$



$$Fe^{III}(CH_2CD_3)(CH{=}CHCH_3) \longrightarrow Fe^{I} + CH_2{=}CD_2 + CH_3CH{=}CHD \quad (19)$$

These disproportionations could proceed directly or by a two-step mechanism involving prior transfer of a β hydrogen to iron followed by reductive elimination. Similar disproportionation processes have been described with organocopper(I), organomanganese(II), and organoplatinum(II) complexes.[23]

The mechanism in Scheme I accommodates much of the extant data on the iron-catalyzed cross coupling reaction of Grignard reagents and alkenyl halides. The side products derive naturally from organoiron(III) intermediates by reasonably well-established pathways. However, there are a number of interesting observations which merit further scrutiny in the light of this mechanism. For example, it is commonly held that organometallic compounds such as the alkyl- and propenyliron(III) species in Scheme I undergo elimination of β hydrogens in the order tertiary R > secondary R > primary R. However, the results presented in Table V run counter to this expectation. Furthermore, if the oxidative addition of 1-bromopropene to iron(I) is rate limiting, the reactivities of the *Z* and *E* isomers should be relatively independent of the Grignard reagent. It is found, however, that the (*Z*)-bromopropene is more reactive than the *E* isomer with primary alkylmagnesium bromide, but the converse is true of methyl,[1,2] secondary, and tertiary alkylmagnesium bromides.[24] The degree of association and complex formation[25] of the latter no doubt affect a quantitative evaluation, but even a qualitative rationalization of this result remains obscure. Changes in the concentration of the reactants as well as the temperature of the reaction could affect the rates and equilibria of the various reactions outlined in Scheme I and eq 16–19, in a manner to change the product distribution (cf. Table I). Nonetheless, the apparent anomalies presented above ultimately must be resolved before this mechanistic formulation can be accepted with more confidence.

Finally, the mechanism in Scheme I bears a resemblance to that previously presented for the nickel-catalyzed reaction of methylmagnesium bromide and aryl bromides.[17c] However, there are outstanding differences between iron and nickel in their abilities to effect cross coupling reactions. Iron is a catalyst which is effective at lower concentrations and temperatures than used with nickel. Even more importantly, cross coupling can be effected completely stereospecifically with an iron catalyst and no alkyl isomerization of the Grignard component has been observed, in contrast to the nickel-catalyzed reactions.[15c,26]

Experimental Section

Materials. 1-Bromo-1-propene obtained from Aldrich Chemical Co. (technical grade) was purified by shaking with aqueous sodium carbonate solution, washing with water several times, and drying over anhydrous calcium chloride. Distillation under nitrogen through a 60-cm Teflon-coated spinning band column afforded material boiling at 60–64°C. GLC analysis on a 40-ft column of oxydipropionitrile on Chromosorb P at 55°C indicated a mixture consisting of 76% (*Z*)- and 24% (*E*)-1-bromopropene (retention time relative to *n*-octane: r_Z 2.77, r_E 2.96). Enriched samples of (*Z*)-1-bromopropene (95%) and (*E*)-1-bromopropene (92%) obtained from Chemical Samples Co. were purified further by preparative GLC on a 10 ft × 0.25 in. column of ODPN on Chromosorb P to afford isomerically pure (>99%) samples of each isomer. All samples were stored in Schlenk tubes under an argon atmosphere in the dark.

Alkyl bromides were commercial samples repurified by washing and then redistilled through a spinning band column under nitrogen.[27]

2-Pentene was obtained as a mixture of *Z* and *E* isomers (Baker Chemical Co.). **2-Hexene,** 4-methyl-2-pentene, 5-methyl-2-hexene, and 4,4-dimethylpentene-2 (Chemical Samples Co.) and **2-octene** (Phillips Petroleum Co.) were also obtained as mixtures of *Z* and *E* isomers. Propenylcyclohexane was prepared previously.[2] 2,4-Hexadiene as a mixture of *Z,Z* (7%), *E,E* (20%), and *E,Z* (73%) isomers (Aldrich Chemical Co.) was analyzed by GLC on a 3-m 15% TCEP column on Chromosorb W at 45° (retention time relative to the *Z,Z* isomer: $r_{E,E}$ 0.76, $r_{Z,E}$ 0.91). 2,5-Dimethylhexane, 2,3-dimethylbutane (Aldrich Chemical Co.), 3,4-dimethylhexane (Chemical Samples Co.), and cyclohexene (Mallinckrodt) were used without further purification.

Magnesium (triply sublimed) in the form of small boules was kindly supplied by the Dow Chemical Co. and used in this form without further preparation. **Tetrahydrofuran** (THF) generously supplied by E. I. du Pont de Nemours and Co. was further purified by vacuum transfer from a dark blue (purple) solution of potassium benzophenone ketyl (with excess potassium) to a dry flask. It was then partially retransferred to a Schlenk tube in vacuo to remove traces of benzophenone, and the flask filled with argon.

Ethyl-*2,2,2-d*$_3$ bromide was prepared from ethyl-*2,2,2-d*$_3$ alcohol,[28] the deuterium content of which was determined earlier to be >98.5%.[29] The deuterium content of ethyl-*2,2,2-d*$_3$ bromide (bp 38–40°) was checked by its mass spectrum showing important peaks at *m/e* 113 (63%) and 111 (67%).

Iron(II) tris complexes of dibenzoylmethido, acetylacetonato, pivalato, and chloro described earlier were redried in a vacuum oven and used without further purification.[2]

Grignard reagents were prepared under an argon atmosphere by slowly adding a THF solution (~1 *M*) of the alkyl halide to excess magnesium with stirring. The colorless mixture was heated to reflux for 30–60 min to assure complete reaction. An aliquot was quenched with acetic acid and the solution analyzed for any unreacted alkyl halide by GLC (40-ft column of ODPN/Chromosorb P at 55°). The liberated alkane was also determined quantitatively by GLC using the internal standard method. Finally, the solution was analyzed by quenching in water and titrating with standard acid (yields 80–95%). The more reactive bromides, *sec*-butyl (50%), 2-pentyl, and cyclohexyl derivatives (40–80%) yield) were treated at 0°, then stirred at room temperature for an additional period. The low yield (30–40%) of *tert*-butylmagnesium bromide necessitated large corrections for isobutane and isobutylene and may have contributed to some uncertainty in the yields.

General Considerations. All glassware was cleaned in chromic acid–sulfuric acid solutions, rinsed thoroughly, and soaked in concentrated nitric acid for 30 min. It was thoroughly rewashed and dried in an oven at 110°. The flask was then flame dried on a vacuum line, cooled, and filled with argon. Reagents were introduced with a hypodermic syringe via a silicon rubber septum held by a screw-on top. Reagents were stored in Schlenk tubes under an argon atmosphere and dispensed by drawing them into hypodermic syringes with argon pressure. A standard solution (3.6×10^{-3} *M*) of Fe(DBM)$_3$ in THF was stored under argon and used as needed. Retention times reported hereafter as *r* are relative to the internal standard.

Ethylmagnesium Bromide and 1-Bromopropene. Standard Procedure. A solution of ethylmagnesium bromide was added to a solution of Fe(DBM)$_3$ at room temperature, whereupon the solution immediately turned dark blue. Methane was added as internal standard, and the amount of ethane and ethylene measured by GLC (2 ft Porapak Q, $r_{C_2H_6}$ 12.8, $r_{C_2H_4}$ 8.5) immediately. Bromopropene was added after 15 min and the reaction allowed to go to completion for 1 hr, the color of the reaction mixture changing to green and finally yellow. Ethanes and ethylene (Porapak Q) and propylene (*n*-butane internal standard, 15 ft Dowtherm on Chromosorb P, $r_{C_3H_6}$ 0.35) were reanalyzed by GLC. The reaction was quenched with acetic acid and the 2-pentene (*n*-hexane internal standard, 10 ft 15% Carbowax 20M–Chromosorb P at 25°, $r_{(Z)\text{-}2\text{-}C_5H_{10}}$ 0.74, $r_{(E)\text{-}2\text{-}C_5H_{10}}$ 0.59) and 2,4-hexadienes (either *n*-octane internal standard, 40 ft ODPN–Chromosorb P at 55°, $r_{E,E}$ 1.96, or tetramethylbutane internal standard, 15 ft 15% Apiezon L–Chromosorb P at 75°, $r_{Z,Z}$ 0.64, $r_{E,Z}$ 0.59, $r_{E,E}$ 0.56) analyzed, together with additional ethane (to determine conversion) and propylene formed in the acidolysis.

***n*-Propylmagnesium bromide and 1-bromopropene** were examined in an analogous manner. Propene and propane were analyzed on a 20-ft column consisting of 3 *N* silver nitrate–benzyl cyanide on Chromosorb P with ethane as internal standard ($r_{C_3H_6}$ 5.6, $r_{C_3H_8}$ 3.0). 2-Hexene and hexane were analyzed on a 40-ft ODPN column at 60° with *n*-pentane as internal standard ($r_{(Z)\text{-}C_6H_{12}}$ 4.3, $r_{(E)\text{-}C_6H_{12}}$ 3.6, $r_{C_6H_{14}}$ 1.4).

Isopropylmagnesium bromide and 1-bromopropene reacted as above to produce propane and propylene, which were analyzed in a similar manner. 4-Methyl-2-pentene and 2,3-dimethylbutane were analyzed on the 40-ft ODPN column at 60° with *n*-pentane as internal standard ($r_{(Z)\text{-}C_6H_{12}}$ 3.30, $r_{(E)\text{-}C_6H_{12}}$ 3.13, $r_{C_6H_{14}}$ 2.15).

***sec*-Butylmagnesium bromide and 1-bromopropene** produced *n*-butane, 1-butene, (*Z*)- and (*E*)-2-butene, and propylene, which were analyzed on the 15-ft Dowtherm column at 25° with isobutane as internal standard ($r_{1\text{-}C_4H_8}$ 2.00, $r_{C_4H_{10}}$ 1.82, $r_{(Z)\text{-}C_4H_8}$ 3.18, $r_{(E)\text{-}C_4H_8}$ 2.64, $r_{C_3H_6}$ 0.64). The 4-methyl-2-hexenes were analyzed on the 40-ft ODPN column at 60° by comparing the areas of the peaks with (*Z*)-2-hexene as internal standard ($r_{(Z)\text{-}C_7H_{14}}$ 1.33, $r_{(E)\text{-}C_7H_{14}}$ 1.45), assuming the same calibration factor. The methylhexenes were not otherwise identified. 3,4-Dimethylhexane was analyzed on the 40-ft ODPN column at 60° with *n*-octane as internal standard ($r_{C_8H_{18}}$ 0.94).

Isobutylmagnesium bromide and 1-bromopropene afforded propylene, isobutane, and isobutylene, which were analyzed on the 15-ft Downtherm column with (*Z*)-2-butene as internal standard ($r_{C_4H_{10}}$ 0.31, $r_{C_4H_8}$ 0.74, $r_{C_3H_6}$ 0.20). 5-Methyl-2-hexene was analyzed on the 10-ft 15% Carbowax column at 25° with *n*-hexane as internal standard ($r_{(Z)\text{-}C_7H_{16}}$ 2.23, $r_{(E)\text{-}C_7H_{16}}$ 1.82) and 2,5-dimethylhexane analyzed on the 15-ft Apiezon L column at 75° with tetramethylbutane as internal standard ($r_{C_7H_{16}}$ 0.94).

***n*-Pentylmagnesium Bromide and 1-Bromopropene.** Before the addition of bromopropene a small aliquot of the reaction mixture was quenched with acetic acid. Accurate analysis of the C_5 hydrocarbons was complicated by their relatively high boiling points. *n*-Pentane, 1-pentene, and 2-pentene were analyzed on the 40-ft ODPN column at 60° with *n*-heptane as internal standard ($r_{C_5H_{12}}$ 0.25, $r_{1\text{-}C_5H_{10}}$ 0.46, $r_{(Z)\text{-}C_5H_{10}}$ 0.60, $r_{(E)\text{-}C_5H_{10}}$ 0.52). 2-Octenes were analyzed on the same column with *n*-octane was internal standard ($r_{(Z)\text{-}C_8H_{16}}$ 2.03, $r_{(E)\text{-}C_8H_{16}}$ 1.76).

2-Pentylmagnesium bromide and bromopropene gave *n*-pentane, 1-pentene, and *Z* and *E* pentenes which were analyzed as described above. 4-Methyl-2-heptene was analyzed on the 40-ft ODPN column at 60° using (*Z*)-2-octene as internal standard ($r_{(Z)\text{-}C_8H_{16}}$ 0.550, $r_{(E)\text{-}C_8H_{16}}$ 0.597).

***tert*-Butylmagnesium bromide and 1-bromopropene** afforded propene, isobutylene, and isobutane, which were analyzed in the manner described above. Relatively large amounts of C_4 hydrocarbons produced during the preparation of the Grignard reagent necessitated sizable corrections of the amounts of these gases produced in the reaction and limit their reliability. 4,4-Dimethyl-2-pentene and tetramethylbutane were analyzed on the 40-ft ODPN column at 60° with *n*-octane as an internal standard ($r_{(Z)\text{-}C_7H_{14}}$ 0.43, $r_{(E)\text{-}C_7H_{14}}$ 0.65, $r_{C_8H_{18}}$ 0.78). No 5-methyl-2-hexenes were found.

Cyclohexylmagnesium bromide and 1-bromopropene produced cyclohexene and cyclohexane, which were analyzed on the 40-ft ODPN column at 60° with *n*-octane as internal standard ($r_{C_6H_{12}}$ 0.67, $r_{C_6H_{10}}$ 1.64). Propenylcyclohexane was analyzed on the 15-ft Apiezon L column at 150° with styrene as an internal standard ($r_{(Z)\text{-}C_9H_{16}}$ 1.10, $r_{(E)\text{-}C_9H_{16}}$ 1.18).

1-Propenylmagnesium Bromide and Bromoethane. 1-Propenylmagnesium bromide was prepared from a mixture of 76% (*Z*)- and 24% (*E*)-1-bromopropenes. Approximately 2–3% of 2,4-hexadienes are formed during the preparation of the Grignard reagent. The analyses were carried out in the same manner as described above. In addition, propyne was analyzed on the 40-ft ODPN column.

Propenylmagnesium bromide was also treated with 1-bromopropene by the standard procedure, and the 2,4-hexadienes analyzed by GLC as decribed above.

Reactions Utilizing $FeCl_3$, $Fe(Pv)_3$, and $Fe(acac)_3$ as Catalysts. THF solutions of known molarity of the iron compounds were prepared [$FeCl_3$, 6.17×10^{-3} *M*; $Fe(Pv)_3$, 3.6×10^{-3} *M*; $Fe(acac)_3$, 3.6×10^{-3} *M*]. One milliliter of iron solution was added to ethylmagnesium bromide in approximately 7 ml of THF and a −46°C cold bath (liquid nitrogen–acetonitrile) was placed under the reaction flask. 1-Bromo-1-propene was added after 15 min while the reaction mixture was at −46°C. In a like manner $Fe(DBM)_3$ and ethylmagnesium bromide solutions remained active for at least 3 hr at −46°C (1-bromo-1-propene was added at this point). The analytical procedures were the same as used for the ethylmagnesium bromide reaction (vide supra).

Rate studies were carried out on reactions prepared using the standard procedure by removing small samples of the head gas to analyze the volatile components. A 0.1-ml aliquot of the reaction mixture was also removed periodically with a hypodermic syringe and quenched with acetic acid. Internal standard (methane, ethane, and *n*-hexane) was added before the commencement of the reaction.

ESR experiments were carried out with 0.1 ml of 3.6×10^{-3} $Fe(DBM)_3$ solution and 1 ml of THF in an ESR tube flushed with argon and capped with a rubber septum. The Grignard reagent (ethyl, *sec*-butyl, or *n*-pentyl) was added (0.1 ml of 1 *M*) at various temperatures and the spectrum measured immediately on a Varian E4 spectrometer, using a solution of sodium [1,2,5]thiadiazolo[3,4-*c*][1,2,5]thiadizole anion radical in THF solution as an external standard [$\langle g \rangle = 2.00648$].

Mass spectral analysis was carried out on a Varian CH7 spectrometer interfaced with a specially designed gas chromatograph which was adapted with a H_2/Pd splitter operated at 260° and a 3-m 0.04 in. column packed with graphitized carbon black. We are indebted to Professor J. M. Hayes for the use of this facility. The chromatography using hydrogen as carrier gas was capable of separating ethane (4.20 min, −46°), ethylene (2.7 min, −46°), propylene (20 min, −40°; 5.9 min, 0°), and *n*-butane (45 min, 0°). The details of the mass spectral analysis are described elsewhere.[30]

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Registry No.—(*E*)-1-Bromopropene, 590-15-8; (*Z*)-1-bromopropene, 590-13-6; (*E*)-1-propenylmagnesium bromide, 13154-15-9; (*Z*)-1-propenylmagnesium bromide, 13154-14-8; bromoethane, 74-96-4.

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(13) (a) Coordination around iron will be largely unspecified hereafter, unless required for the discussion. (b) Oxidation numbers are included only as a device for electron accounting and are not necessarily intended to denote actual changes in oxidation states.

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(18) Propenylmagnesium bromide formed in this manner should retain the stereochemistry of the reactant bromopropene in contrast to that formed with magnesium metal. Cf. H. M. Walborsky and M. S. Aronoff, *J. Organomet. Chem.*, **51**, 31 (1973); H. L. Goering and F. H. McCarron, *J. Am. Chem. Soc.*, **80**, 2287 (1958); R. J. Rogers, H. L. Mitchell, Y. Fujiwara, and G. M. Whitesides, *J. Org. Chem.*, **39**, 857 (1974); cf. also ref 8.

(19) Retention of stereochemistry in the reductive elimination of the propenyl moiety is inferred from studies of oxidative addition and cross coupling reactions, but it remains to be proven.

(20) Cf. G. M. Whitesides, C. P. Casey, and J. K. Krieger, *J. Am. Chem. Soc.*, **93**, 1379 (1971).

(21) (a) There are numerous examples of exchanges between Grignard reagents and alkyl halides catalyzed by transition metal species and leading to disproportionation and coupling. For leading references see M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances", Prentice-Hall, Englewood Cliffs, N.J., 1954; L. H. Slaugh, *J. Am. Chem. Soc.*, **83**, 2734 (1961). (b) The presence or absence of alkyl bromide resulting from exchange in this system is uncertain, but it is not crucial to the discussion as presented earlier in eq 8, 10, and 11. (c) Cf. G. Vavon and P. Mottez, *Bull. Soc. Chim. Fr.*, [53] 11 (1944).

(22) Disproportionation of organic ligands as presented in eq 18 and 19 may also proceed between two iron nuclei and is not required by the data to be intramolecular.

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(24) The absence of crossover products reported earlier[1,2] when a pair of different organic bromides are employed also poses some difficult questions for the mechanism in Scheme I.

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A Study of the Chemistry of Lithiotriphenylphosphineacetylmethylene[1]

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Treatment of triphenylphosphineacetylmethylene (**3**) with 1.2 equiv of *n*-butyllithium in THF–hexane at −78° resulted in abstraction of a methyl proton to form the ylide anion, lithiotriphenylphosphineacetylmethylene (**4**, M = Li). Reactions of **4** with several alkyl halides, aldehydes, saturated and α,β-unsaturated ketones, and benzoate esters occurred at the terminal carbanion site to afford β-ketophosphonium ylides **9**, δ-hydroxy-β-keto ylides **14**, and the β,δ-diketo ylide **17**, respectively. Sequential treatment of **4** with *n*-butyl iodide and benzaldehyde or with allyl bromide and 3,4-dichlorobenzaldehyde gave 1-phenyl-1-octen-3-one (**13a**) and 1-(3,4-dichlorophenyl)-1,6-heptadien-3-one (**13b**), respectively. Reaction of **4** with *o*-phthaldehyde afforded 4,5-benzotropone (**16**). Triphenylphosphine(3-phenylpropanoyl)methylene (**9a**) was converted into ylide anion **10** by means of *n*-butyllithium as shown by alkylation with benzyl chloride and allyl bromide to give triphenylphosphine(2-benzyl-3-phenylpropanoyl)methylene (**11a**) and triphenylphosphine(2-allyl-3-phenylpropanoyl)methylene (**11b**). Attempted formation of **4** (M = K) by means of potassium amide in liquid ammonia lead to cleavage of **3** with formation of diphenylacetonylphosphine oxide (**5**) and diphenylphosphinic amide (**6**).

The synthetic utility of 1,3-dicarbanions[2] of type **1** where A may be a ketone,[3a–c] aldehyde,[4a–c] or ester[5a–f] group, and A′ is a ketone function, was discovered and exploited by

$$\underset{\mathbf{1}}{\mathrm{A{-}\bar{C}H{-}A'{-}\bar{C}H_2}} \xrightarrow{\text{electrophiles}} \underset{\mathbf{2}}{\mathrm{A{-}CH_2{-}A'{-}CH_2R}}$$

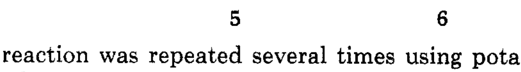
Hauser and his co-workers.[2,6] The major preparative value of these intermediates lies in the fact that they undergo regiospecific reactions with electrophilic reagents at the more nucleophilic carbanion site to form compounds of type **2**, where R corresponds to the moiety furnished by the electrophile. When we began the present study, dianions of type **1** had been used primarily to elaborate the structure of their precursors, e.g., in the synthesis of new β-diketones from various β-diketone dianions.[3–c] It occurred to us that the synthetic utility of intermediates of type **1** might be expanded in an interesting new direction if activating group A could be easily removed or altered in several ways after introduction of appropriate R groups adjacent to A′. Thus, A would act as a control element[7] and its subsequent replacement could give rise to compounds differing significantly from the original dianion precursor.[8]

The ability of the triphenylphosphonium function to stabilize an adjacent carbanion center, its propensity toward cleavage[9] and participation in carbonyl olefination reactions,[9,10] and the fact that no compounds possessing a phosphorus containing activating function had been converted to 1,3-dianions, prompted us to test the above hypothesis with triphenylphosphineacetylmethylene[11] (**3**) as the precursor to ylide anion **4**. The present paper represents an expanded account of our preliminary findings[12] concerning the chemistry of lithiotriphenylphosphineacetylmethylene (**4**, M = Li). Following our communication, Cooke[13] reported on the alkylation of **4** and hydrolysis of the resulting β-keto phosphonium ylides to afford methyl ketones in good yields. Cooke and Goswami[14] also used an ylide dianion related to **4** in the synthesis of an eight-membered-ring diketo ylide. Grieco and Pogonowski have recently made elegant use of dianions containing an expendable activating-control unit in cases involving 1,3-dianions of β-keto phosphonates[15a–b] and β-keto sulfoxides.[16a–b] Kuwajima and Iwasawa[17] have also investigated the chemistry of dianions derived from β-keto sulfoxides.

$$\underset{\mathbf{3}}{(C_6H_5)_3\overset{+-}{P}\overset{}{C}HCOCH_3} \longrightarrow \underset{\mathbf{4}}{[(C_6H_5)_3\overset{+-}{P}CH}COC\overset{-}{H_2}]M^+}$$

Results and Discussion

Initially, formation of ylide anion **4** (M = K) from **3** was attempted using potassium amide in liquid ammonia. However, we were unable to obtain evidence for the desired proton abstraction. Instead, reaction of **3** with 2 equiv of potassium amide in liquid ammonia followed by benzyl chloride afforded a 57% yield of acetonyldiphenylphosphine oxide (**5**) and none of the expected benzyl derivative **9a**.



$$\mathbf{3} \xrightarrow{\mathrm{KNH_2}} \underset{\mathbf{5}}{(C_6H_5)_2\overset{O}{\overset{\|}{P}}CH_2COCH_3} + \underset{\mathbf{6}}{(C_6H_5)_2\overset{O}{\overset{\|}{P}}NH_2}$$

This reaction was repeated several times using potassium amide, but no benzyl chloride. In each case **5** was again produced, along with varying amounts of diphenylphosphinic amide (**6**). Apparently amide ion preferentially attacks the electrophilic phosphorus of **3** to form a pentavalent intermediate such as **7**, which then decomposes with loss of benzene to form iminophosphorane anion **8**. This series of