The Reactions of Grignard Reagents with Transition Metal Halides: Coupling, Disproportionation, and Exchange with Olefins

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The reactions of transition metal halides (Mn, Fe, Co, Ni, Pd, Cu, and Ag) with the low-molecular-weight alkyl Grignard reagents in tetrahydrofuran and diethyl ether, especially in the presence of styrene were reinvestigated. An alkyl transition metal species formed *in situ* by metathesis decomposed to a dialkyl (oxidative dimerization) or to an alkene and an alkane (oxidative disproportionation). Silver(I) and copper(II) were particularly effective in oxidative dimerization of primary alkyl groups. Alkyl groups which contain no β-hydrogen were also coupled by iron, cobalt, nickel, palladium, and copper(I) halides with varying degrees of efficiency. Oxidative disproportionation was generally the more common route to decomposition for alkyl groups which have β-hydrogens. It seemed to proceed directly *via* a bimolecular interaction of alkylmetals or indirectly by elimination of a hydrido-metal species. If the latter added to an alkene reversibly, exchange was observed between Grignard reagent and alkene. Styrene was reduced to ethylbenzene during the reaction both in tetrahydrofuran and in diethyl ether in varying yield with transition metal halide and Grignard reagent. In addition to alkyl exchange, dehydrogenation of the ethereal solvent by active (reduced) metal species complicated the stoichiometry of decomposition as measured by the value of the empirical parameter, Q(R). The selection of transition metal in addition to the temperature, solvent and triphenylphosphine was effective variables in promoting the efficiency of the exchange process.

The reactions of various transition metal salts and Grignard reagents in which alkane, alkene and coupling dimer are obtained as products have been studied for some time.[1] In some cases, there is evidence for stable and isolable organometallic compounds.[1] However, the transition metal salt is generally reduced to the metallic state in the presence of excess Grignard reagent, and the stoichoimetry of the reaction is represented

$$n\mathrm{RMgX} + \mathrm{MY}_n \longrightarrow [\mathrm{RH}, \mathrm{R(-H)}, \mathrm{R{-}R}] + n\mathrm{MgXY} + \mathrm{M}^\circ \qquad (1)$$

as follows:

$$Q(R) = \frac{\mathrm{R(-H)} + \mathrm{RH} + 2\mathrm{R{-}R}}{\mathrm{MY}_n} = n \qquad (2)$$

The distribution of products is dependent on the transition metal salt as well as the Grignard reagent, and also varies with the reaction conditions. Most of the studies reported for these reactions are so fragmentary that the differences in reactivity of various transition metal salts cannot be compared directly.[1] We have examined the mechanism of the Kharasch reaction catalyzed by various transition metal salts in which we postulated organometallic compounds as intermediates.[2,3] To provide support for our studies of the mechanism of the Kharasch reaction we felt that it was desirable to learn about the chemical properties of such organometallic compounds under the reaction conditions.

Metathesis of transition metal salts and organometallic compounds such as organolithium species and Grignard reagents is often the simplest method of obtaining σ-bonded transition metal alkyl complexes.[1] In this study we examined the reactions

$$n\mathrm{RMgX} + \mathrm{MY}_n \longrightarrow \mathrm{R}_n\mathrm{M} + n\mathrm{MgXY} \qquad (3)$$

of transition metal halides and Grignard reagents in tetrahydrofuran (THF) and diethyl ether ($\mathrm{Et_2O}$) under comparative conditions. The reactions were also examined in the presence of styrene and other olefins in order to probe for exchange processes.

Results

The Reactions of Transition Metal Halides and Grignard Reagents in Tetrahydrofuran. The reactions of transition metal halides with various Grignard reagents in THF are summarized in Table 1 and Table 2, which show clearly that the distribution of products was greatly dependent on the transition metal halide and the Grignard reagent. The yield of coupling dimer was almost quantitative independently of the Grignard reagent in the cases of argentous and cupric halides. It was also generally larger with the higher oxidation state of a given metal, *i.e.*, cupric chloride$\gg$cuprous chloride and ferric chloride$>$ferrous chloride.

Coupling dimer was also formed in fairly good yield almost independently of the transition metal halide from the reaction with methyl, neopentyl, benzyl, vinyl or phenylmagnesium bromide which has no available β-hydrogens. For a given transition metal salt, the yield of coupling dimer increased generally in the sequence: methyl$>$neopentyl, benzyl.

The yield of ethyl chloride was negligibly small and the formation of n-butane was predominated in the reaction of cupric chloride and ethylmagnesium bromide. This result was quite different from that in the

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[1] F. A. Cotton, *Chem. Rev.*, **55**, 551 (1955); G. W. Parshall and J. J. Mrowca, *Advan. Organometal. Chem.*, **7**, 157 (1968); C. D.M. Beverwijk and G. J. M. Van der Kerk, *Organometal. Chem. Rev.*, **A5**, 215 (1970); G. E. Coates, M. L. H. Green, and K. Wade "Organometallic Compounds" Vol. 2, Third ed., Methuen and Co., Ltd., London (1968).

[2] M. Tamura and J. Kochi to be published.

[3] M. S. Kharasch and O. Reinmuth, "Grignard Reagents of Nonmetallic Substances," Prentice-Hall Co., New York, N. Y. (1954).

TABLE 1. THE REACTIONS OF FERROUS, FERRIC, COBALTOUS, NICKELOUS, AND PALLADOUS HALIDES WITH GRIGNARD REAGENTS IN TETRAHYDROFURAN[a]

Transition Metal Salt MX_n	Grignard Reagents RMgBr	Q(R)	Products %[b] R(-H)	RH	R-R	EtPh[c] mmol
$FeCl_3$	Et	3.7	22.5	59.6	17.9	
$FeCl_2$	Et	2.1	25.9	67.6	6.5	
$FeCl_3$	Me	3.0		32	68[f]	
$FeCl_2$	Me	2.0		70	30[f]	
$FeCl_3$	Neopentyl	3.0		62	38	
$FeCl_2$	Benzyl			n.d.[e]	38	
$FeCl_2$	Ph			n.d.[e]	98	
$CoBr_2$	Et	2.8	17.1	78.7	4.2	
$CoBr_2$[d]	Et	2.7	47.0	49.0	4.0	1.15
$CoBr_2$	Me	2.2		90	10[f]	
$CoBr_2$[d]	Me	2.0		70	30[f]	0.40
$CoBr_2$	Neopentyl	2.0		94	4	
$CoBr_2$	Benzyl			n.d.[e]	0	
$CoBr_2$	Vinyl	2.0		36	64[g]	
$CoBr_2$[d]	Ph			n.d.[e]	92	0.22
$CoBr_2$	Ph			n.d.[e]	91	
$NiCl_2$	Et	2.6	36.4	61.2	2.4	
$NiCl_2$	Me	2.1		94	6[f]	
$NiCl_2$	Neopentyl	2.1		74	26	
$NiCl_2$	Benzyl			n.d.[e]	27	
$NiCl_2$	Vinyl	1.9		20	80[g]	
$NiCl_2$	Ph			n.d.[e]	99	
$PdCl_2$	Et	2.2	48.4	51.6	0	
$PdCl_2$	Me	2.0		49	51[f]	
$PdCl_2$[d]	Me	2.1		37	63[f]	0.23
$PdCl_2$	Neopentyl	2.0		89	11	
$PdCl_2$[d]	Neopentyl	2.0		55	45	0.12
$PdCl_2$	Benzyl			n.d.[e]	59	
$PdCl_2$	Vinyl	2.0		12	88	
$PdCl_2$	Ph			n.d.[e]	93	

a) In 21 ml THF containing 1.0 mmol of transition metal halide and excess Grignard reagents (4.0~9.0 mmol) for 60 minutes at 2.0°C. All reactions were complete under these reaction conditions.
b) Based on Q(R), % of R-R was doubled.
c) After acidic hydrolysis
d) In the presence of 26.1 mmol styrene
e) No determination
f) Varying amount of ethylene (less than 30%) was included in R-R.
g) After hydrolysis

same reaction in Et_2O (see below).

On the other hand, the yield of coupling dimer was negligibly small and ethane and ethylene were main products in the reactions of ferrous, cobaltous, nickelous, palladous, manganous and cuprous halides with ethylmagnesium bromide which has β-hydrogens. The ratio of ethane to ethylene obtained was almost 1 : 1 with palladous, cupric and cuprous chlorides. Conversely, this ratio was approximately 2—5 with ferric, ferrous, cobaltous, nickelous and manganous halides.[4] When excess of styrene was added to the reaction in order to learn about the heterolytic cleavage of alkyl-transition metal bond and to check the material balance of hydrogen, the ratio of ethane : ethylene approached one. Under these conditions styrene was partially reduced to ethylbenzene. Styrene was also partially reduced to ethylbenzene even in the reactions of cobaltous and palladous halides with methyl, neopentyl, and phenylmagnesium bromides which have no β-hydrogens.

Q(R) given by Eq. 2 was independent of the presence of styrene in all cases. Q(Et) was also somewhat higher than n when ferric, cobaltous and nickelous halides were used. The high value of Q(Et) may be related to the abstraction of hydrogen from solvent.[2]

In those reactions involving argentous, cupric, cuprous and manganous halides, a black precipitate was formed and a colorless supernatant solution appeared after the reaction was completed. On the other hand, ferric, ferrous, cobaltous, nickelous, and palladous halides produced black-brown solutions in addition to varying amounts of black precipitate.[5]

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[4] Sneeden and Zeiss have also observed these phenomena. R. P. A. Sneeden and H. H. Zeiss, *J. Organometal. Chem.*, **22**, 713 (1970).

[5] H. H. Abraham and H. J. Hogarth *ibid.*, **12**, 1 (1968) and references cited therein; G. Costa, G. Mestroni, and G. Boscarato, *Ric. Sci.*, **7**, 315 (1964).

TABLE 2. THE REACTIONS OF MANGANOUS, CUPROUS, CUPRIC, AND ARGENTOUS HALIDES WITH GRIGNARD REAGENTS IN TETRAHYDROFURAN[a]

Transition Metal Salt MX_n	Grignard Reagents RMBr	Temp. (C°)	Period (min)	Q(R)	Products (%)[b]		
					R(–H)	RH	R–R
$MnCl_2$	Et	30	60	2.2	28.2	71.8	0
$MnCl_2$[c]	Et	30	600	2.2	43.6	56.4	0
$MnCl_2$	Me	25	8100[d]			91	9
$MnCl_2$	Benzyl	60	1440		No	decompd	
$MnCl_2$	Vinyl	25	60[e]			30	70[f]
$MnCl_2$	Ph	60	1440		No	decompd	
$CuCl_2$	Et	25	60	2.1	26.1	28.1	45.8[g]
$CuCl_2$	Et	25	60	1.0	50.9	49.1	0
CuCl	Me	25	900	0.9		7	93
CuCl	Neopentyl	25	5760	1.0		47	53
CuCl	Benzyl	25	30			n.d.[h]	88[h]
CuCl	Vinyl	25	180	0.9		19	81
CuCl	Phenyl	60	1440			n.d.[h]	90
AgBr	Et	25	60	1.0	2.1	6.2	91.7
AgBr	Me	2	30	1.0		4	96
AgBr	Neopentyl	2	60	1.0		17	83
AgBr	Benzyl	2	60			n.d.[h]	95[h]
AgBr	Vinyl	2	60	1.0		5	95
AgBr[i]	Ph	65	120			n.d.[h]	97[h]

a) In 21 m*l* THF containing 1.0 mmol of transition metal halide and excess Grignard reagent (3.0—8.0 mmol). All reactions were complete under these reaction conditions unless otherwise mentioned.
b) Based on Q(R). % of R–R was doubled.
c) In the presence of 8.7 mmol styrene, 0.17 mmol of ethylbenzene was obtained after hydrolysis.
d) Partial decomposition; *ca.* 20%
e) Partial decomposition; *ca.* 50%
f) After hydrolysis
g) Included 6% of EtCl in R–R
h) No determination, Calculated from $Q(R)=n$
i) In the presence of 26.1 mmol styrene, none of ethylbenzene was detected after hydrolysis.

The results in Table 1 and Table 2 show that the yield of coupling dimer was generally higher in the presence of styrene, and this effect may be attributed to styrene as a π-ligand. In order to support this point, the reactions of palladous chloride and Grignard reagents were carried out in the presence of triphenylphosphine, since the bis-triphenylphosphine complex with palladous chloride is readily formed.[6] Table 3 shows that the yield of coupling dimer was indeed increased in the presence of triphenylphosphine.

Q(R) was not altered by the presence of triphenylphosphine.

The Reactions of Lithium Chlorocuprate and Grignard Reagents in Tetrahydrofuran. The reaction of cupric chloride and Grignard reagent is obscure because the reaction is occurring mainly on the surface (Table 2).

TABLE 3. THE REACTIONS OF PALLADOUS CHLORIDE WITH ALKYL GRIGNARD REAGENTS IN TETRAHYDROFURAN IN THE PRESENCE OF TRIPHENYLPHOSPHINE[a]

Grignard Reagent RMgBr	$\frac{RMgBr}{PdCl_2}$	Ph_3P (mmol)	Q(R)	Products (mol %)[b]		
				R(–H)	RH	R–R
Et	7.5		2.2	48.4	51.6	0
Et	7.0	4.0	2.0	31.0	47.6	21.4
n-Pr	7.0		2.2	45.1	51.9	3.0
n-Pr	7.0	4.0	2.1	31.0	43.0	26.0
i-Pr	7.0		2.2	47.0	47.4	5.6
i-Pr	7.0	4.0	2.1	33.9	39.3	26.8
t-Bu	6.0		2.1	48.6	48.9	2.5
t-Bu	6.0	4.0	2.1	40.7	46.0	13.3

a) In 21 m*l* THF containing 1.0 mmol $PdCl_2$ at 2.0°C for 60 min. The reaction of $PdCl_2$ with Ph_3P was carried out in THF at room temperature for 2 hrs (yellow precipitate was formed) before Grignard reagent was added.
b) Based on Q(R)

TABLE 4. THE REACTIONS OF LITHIUM CHLOROCUPRATE WITH GRIGNARD REAGENTS IN TETRAHYDROFURAN[a]

Grignard Reagent RMgBr	$\frac{RMgBr^{b)}}{Cu(II)}$	Temp. (°C)	Distribution of Products[c]	
			R-R(%)	R-Cl(%)
Et	0.6	2	50.6	49.4
Et	1.2	2	53.9	46.1
Et	2.5	2	73.7	26.3
Et	1.2	–78	75.7	24.3
Et	1.2	25	61.5	38.5
Me	1.2	2	81.3	18.7
Neopentyl	1.2	2	19.0	81.0
Ph	1.2	2	45.3	54.7

a) In 21 m*l* THF containing 2.5 mmol $CuCl_2$ and 5.8 mmol LiCl for 20 minutes.
b) Molar ratio
c) $\frac{\text{R–R or R–Cl}}{\text{R–R+R–Cl}}\times 100$. Total yield of R–R and R–Cl was more than 80% based on RMgBr or Cu(II) in all runs. R–R and R–Cl did not form from Cu(I) in the case of ethylmagnesium bromide (Table 2).

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6) F. G. Mann and A. F. Wells, *J. Chem. Soc.*, **1938**, 702; J. Chatt and L. M. Venanzi, *ibid.*, **1957**, 2351.

Cupric chloride became soluble by the formation of lithium chlorocuprate[7] (λ max. 444 mμ, ε: *ca.* 10^3) when two or more equivalent lithium chloride was mixed in THF. The reactions of lithium chlorocuprate with Grignard reagents were examined in THF in order to find the differences in the mechanisms of the formations of coupling dimer and alkyl chloride in the reaction of cupric chloride and Grignard reagent. It is obvious from Table 4 that the yield of ethyl chloride was larger at the smaller ratio of ethylmagnesium bromide to lithium chlorocuprate. Temperature also influenced the distribution of products.

Ethane was major product in the reaction with methylmagnesium bromide and neopentyl chloride was favorably formed from neopentylmagnesium bromide.

Evolutions of *n*-butane and ethyl chloride were completed immediately and the resulting solution turned to purple gradually in the case of ethylmagnesium bromide (molar ratio: 2.5). At this stage, none of ethane or ethylene was evolved.

Both total yield and distribution were not altered by the presence of excess styrene.

A following competitive mechanism may be applicable to the explanation of these results.

$$\underset{\text{(I)}}{[\mathrm{Cu^{II}Cl_4}]^{-2}} + \mathrm{RMgBr} \longrightarrow \underset{\text{(II)}}{[\mathrm{RCuCl_3}]^{-2}} + \mathrm{MgBrCl} \qquad (4)$$

$$\text{(II)} \begin{array}{l} \overset{\text{(I)}}{\nearrow} \mathrm{R{-}Cl} + 2[\mathrm{Cu^{I}Cl_2}]^- + 2\mathrm{Cl}^- \\ \underset{\text{(II)}}{\searrow} \mathrm{R{-}R} + 2[\mathrm{Cu^{I}Cl_2}]^- + 2\mathrm{Cl}^- \end{array} \qquad (5)$$

A predominant yield of *n*-butane in the reaction of cupric chloride and excess ethylmagnesium bromide (Table 2) can also be explained by this mechanism.

The Reactions of Transition Metal Halides with a Mixture of Two Grignard Reagents in Tetrahydrofuran. The reactions of transition metal halides with a mixture of Grignard reagents in THF were also examined in order to learn about the mechanism of the disproportionation of alkyl transition metal complex which is assumed to be formed in the Kharasch reaction. The results are summarized in Table 5. In the combination con-

TABLE 5. THE REACTIONS OF TRANSITION METAL SALTS WITH A MIXTURE OF TWO GRIGNARD REAGENTS IN TETRAHYDROFURAN[a]

Transition Metal Salt MX_n	Combination of Grignard Reagent[b]	RMgBr+R'MgBr/ MX_n	Period (min)	Q(R,R')[c]	Products (mol %)[d]							R(−H)/ RH	R'(−H)/ R'H
					R–R	R–R'	R'–R'	R(−H)	RH	R'(−H)	R'H		
$CoBr_2$	A	3.6	30	2.8	0	0	0		47.0	31.2	21.8		1.4
$CoBr_2$[e]	A	3.6	30	2.7	0	0	0		41.1	43.8	15.1		2.9
$PdCl_2$	A	3.6	30	2.0	19.3	0	0		32.7	29.6	18.4		1.6
$PdCl_2$[f]	A	3.6	30	1.9	27.8	0	0		26.8	30.4	15.0		2.0
CuCl[g]	A	1.4	1200	1.0	4.0	34.7	0		26.0	22.7	12.6		1.8
$CuBr_2$[g]	A	3.6	720	2.2	4.4	26.3	30.0		9.2	20.6	10.5		2.0
AgBr	A	3.6	30	1.0	23.5	30.2	40.4		1.7	0.8	3.4		0.3
$FeCl_3$	B	5.3	30	3.3	3.3	4.9	3.2	0.4	37.6	39.7	11.8	0.0	3.4
$CoBr_2$	B	2.3	30	2.0	0	0	0	0.0	48.0	15.3	36.7	0.0	0.4
$CoBr_2$[h]	B	2.3	30	2.2	5.9	2.4	1.2	16.2	22.3	33.5	18.5	0.7	1.8
$NiCl_2$	B	2.3	30	2.0	0	0	0	0.0	41.0	34.9	24.1	0.0	1.4
$PdCl_2$	B	2.3	30	2.1	0	0	0	22.3	25.7	24.1	27.9	0.9	0.9
CuCl	B	0.8	60	0.8	0	0	0	20.6	30.3	31.2	17.9	0.7	1.7
$CuBr_2$	B	4.0	120	2.0	15.6	23.4	12.3	11.5	15.6	14.6	7.1	0.7	2.0
AgBr	B	3.1	60	1.0	46.5	33.7	11.6	1.2	3.5	1.2	2.3	0.3	0.5
$FeCl_3$	C	5.3	30	3.4	2.3	2.8	3.2	2.4	39.7	32.8	16.8	0.1	2.0
$CoBr_2$[i]	C	2.3	30	2.3	8.2	0	0	15.6	23.3	33.8	19.1	0.7	1.8
$PdCl_2$	C	2.3	30	2.0	0	0	0	14.7	39.4	33.2	12.7	0.4	2.6
CuCl	C	1.1	60	1.0	0	0	0	32.7	14.8	18.3	34.2	2.2	0.5
$CuBr_2$	C	4.0	85	2.0	3.9	7.9	19.8	17.8	7.3	18.2	25.1	2.5	0.7
AgBr	C	3.1	60	1.0	40.5	28.1	10.1	1.7	2.2	7.3	10.1	0.7	0.7

a) In 21 m*l* THF containing 1.0 mmol transition metal salt and an equimolar mixture of two Grignard reagents at 2.0°C.

b) A; RMgBr=MeMgBr, R'MgBr=*n*-PrMgBr
B; RMgBr=EtMgBr, R'MgBr=*n*-PrMgBr
C; RMgBr=EtMgBr, R'MgBr=*i*-PrMgBr

c) $\dfrac{2(\mathrm{R{-}R+R{-}R'+R'{-}R'})+\mathrm{R(\text{-}H)+RH+R'(\text{-}H)+R'H}}{\mathrm{MX}_n}$

d) Based on Q(R,R')

e) In the presence of 8.7 mmol styrene, the yield of ethylbenzene was 1.07 mmol after hydrolysis

f) In the presence of 8.7 mmol styrene, the yield of ethylbenzene was 0.38 mmol after hydrolysis

g) 25°C

h) In the presence of 8.7 mmol styrene, the yield of ethylbenzene was 1.10 mmol after hydrolysis.

i) In the presence of 8.7 mmol styene, the yield of ethylbenzene was 1.14 mmol after hydrolysis.

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[7] R. P. Eswain, E. S. Howald, R. A. Howald, and D. P. Keeton, *J. Inorg. Nucl. Chem.*, **29**, 437 (1967).

sisting of methyl and *n*-propylmagnesium bromides, disproportionation afforded methane from the methyl moiety and propylene from the *n*-propyl group. The selectivity was more pronounced when styrene was added to the reaction consisting of cobaltous or palladous halide. Styrene was partially reduced to ethylbenzene. The formation of cross coupling dimer (*n*-butane) was facilitated by cuprous chloride. On the other hand, more random coupling occurred with ferric, argentous, and cupric halides.

In the combinations involving ethyl/*n*-propyl and ethyl/isopropyl, ethane was formed mainly from the ethyl group and propylene mainly from the propyl group. Furthermore, in these combinations, the trend became more conspicuous when styrene was added to the reaction. In the reaction of palladous chloride with a mixture of ethylmagnesium bromide and *n*-propyl or isopropylmagnesium bromide, the yield of alkene (ethylene and propylene) and the yield of alkane (ethane and propane) were approximately equal. The further hydrogenation of the initially formed olefin was not significant. In fact, the amount of ethylbenzene was much smaller from the reactions carried out with palladous chloride compared to cobaltous bromide (Table 5).

In the combination of ethyl/*n*-propylmagnesium bromide, the ratio of ethylene: ethane was 0.9 and the ratio of propylene: propane was also 0.9. On the other hand, in the combination of ethyl/isopropylmagnesium bromide, the ratio of ethylene: ethane was 0.4, whereas the ratio of propylene: propane was 2.6. That is, the tendency for alkane to be formed mainly from the ethyl group and alkene from the propyl group was more conspicuous in the latter combination. With cuprous or cupric halide, ethane was formed mainly from the ethyl group and propylene from *n*-propyl group: Conversely, propane was formed mainly from the isopropyl group and ethylene from the ethyl group. This observation has been discussed previously.[2]

The Reactions of Transition Metal Halides with Grignard Reagents in Diethyl Ether. All the reactions discussed above were carried out in THF. In most studies examined heretofore, Et_2O has usually been the medium of choice. For comparison, a number of the same reactions were carried out in Et_2O, especially in the presence of styrene. As seen in Table 6, the yield of ethylene was much higher in the presence of styrene than that in the absence of styrene with all transition metal halides except argentous and cupric bromides. At the same time, styrene was reduced to ethylbenzene in high yield, especially with ferric, ferrous, cobaltous, and nickelous halides. In the reaction of methylmagnesium bromide with nickelous chloride, the amount of ethylbenzene was also small. In the reactions of cupric chloride with methyl and ethylmagnesium bromides, methyl and ethyl chlorides, respectively, were formed in fairly good yields.[2,8] The higher yield of ethyl chloride and the formations of ethane and ethylene from copper(II) complex (based on Q(Et)) were sharp contrast with the results in THF (Table 2). The ratio of ethane to ethylene was closer to one in Et_2O than in THF (Table 1) with most of transition metal halides, in the reaction with ethylmagnesium bromide, in the absence of styrene. The

TABLE 6. THE REACTIONS OF TRANSITION METAL SALTS WITH ETHYLMAGNESIUM BROMIDE IN DIETHYL ETHER IN THE PRESENCE OF STYRENE[a]

Transition Metal Salt MX_n	Styrene (mmol)	Period (min)	Q(Et)	Products(mol%)[d] R(−H)	RH	R–R	PhEt[f] (mmol)
$FeCl_3$		10	3.5	40.4	45.3	14.3	
$FeCl_3$	26.1	60	3.9	62.6	26.0	11.4	1.88[g]
$FeCl_2$		120	2.0	41.4	51.1	7.5	
$FeCl_2$	26.1	120	4.2	78.0	18.6	3.4	2.53
$CoBr_2$		10	2.2	34.1	65.0	0.9	
$CoBr_2$	26.1	30	3.4	56.4	34.9	8.7	1.49
$NiCl_2$		120	2.3	47.6	52.4	0	
$NiCl_2$	26.1	180	5.2	75.6	22.9	1.5	3.02
$NiCl_2$[b]	26.1	90	1.9		57.3	42.7[e]	0.18
$PdCl_2$		30	2.2	49.8	50.2	0	
$PdCl_2$	26.1	30	1.9	53.0	47.0	0	0.17
$MnCl_2$		140	1.9	40.1	59.9	0	
$MnCl_2$	26.1	120	2.0	49.3	50.7	0	0.26
CuCl		180	1.0	52.1	47.9	0	
$CuCl_2$		120	2.1[h]	40.8	37.8	5.8	
$CuCl_2$	26.1	180	2.0[i]	42.1	35.8	5.3	0.07
$CuCl_2$[b,c]		1000	2.0[j]		9.2	73.8	
AgBr		30	1.0	0.7	1.0	98.3	

a) In 21 m*l* of Et_2O solution containing sytrene, 1.0 mmol of transition metal salt and 5.7 mmol of EtMgBr at 2.0°C b) Methylmagnesium bromide c) 25°C d) Based on Q(Et). e) C_2H_4; 36.6% in R–R f) After hydrolysis g) PhEt was 1.05 mmole before hydrolysis. h) Ethyl chloride was 15.6% based on Q(Et). i) Ethyl chloride was 16.8% based on Q(Et) j) Methyl chloride was 17.0% based on Q(Me).

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[8] H. Gilman and J. M. Straley, *Rec. Trav. Chim. Pays-Bas*, **55**, 821 (1936).

TABLE 7. THE EXCHANGE BETWEEN ETHYLMAGNESIUM BROMIDE AND STYRENE BY FERRIC CHLORIDE[a)]

$FeCl_3$ conc. $\times 10^4$ M	Solvent	Temp. (°C)	Period (min)	C_2H_4 (mmol)	C_2H_6 (mmol)	PhEt (mmol)	
						Before hydrolysis	After hydrolysis
24	Et_2O	2.0	90	0.55	0.01	0.18	0.57
12	Et_2O	2.0	90	0.57	0.01	0.17	0.60[f)]
2.4	Et_2O	2.0	90	0.51	0.01	n.d.[e)]	0.50
2.4	Et_2O[c)]	2.0	90	0.40	0.01	n.d.	0.42
2.4	Et_2O	25	90	0.06	0.00	n.d.	0.06
2.4	Et_2O[d)]	2.0	480			0.04	0.04
2.4[b)]	Et_2O	2.0	90	0.34	0.01	0.10	0.37
2.4	THF	2.0	100	0.05	0.00	n.d.	0.03
2.4	THF	25	60	0.61	0.06	n.d.	0.59

a) In 21 m*l* solvent containing 1.24M styrene and 0.18M EtMgBr
b) $CoBr_2$ instead of $FeCl_3$ c) 0.09M EtMgBr
d) Methylmagnesium bromide e) No determination
f) Composition of ethylbenzene after deuterolysis with D_2O (NMR analysis) $\mathrm{Ph}\underset{\mathrm{D}}{\mathrm{C}}\mathrm{HCH_3}$ (71%), $PhCH_2CH_2D$ (5%), $PhCH_2CH_3$ (24%)

rates of decompositions of diethylmanganese and ethylcopper were approximately 6 times faster in Et_2O than in THF.[2)] These solvent dependencies will be discussed later in this paper.

The mixture on completion of reaction was usually a seemingly black-brown solution[5)] (at least partially) except when argentous, cuprous, cupric, and manganous halides were used. The latter gave colorless solutions and black precipitates. These observations were similar to those obtained in THF.

The rate of conversion of ethylmagnesium bromide with nickelous and ferrous chlorides to ethylene and ethane is shown in Fig. 1, which shows that the yield of ethane rapidly reached a plateau, but the yield of ethylene continued to increase with time, in the presence of styrene. The yield of ethylene shown in Fig. 1 and Table 6 was greater than the stoichiometric amount based on *Q*(Et) and indicated that part of the ethylene was produced from the exchange between ethylmagnesium bromide and styrene (see below). In order to confirm this point, the exchange between ethylmagnesium bromide and styrene was studied in the presence of catalytic amounts of ferric and cobaltous halides. It can be seen in Table 7 that equivalent amounts of ethylene and ethylbenzene were obtained at 2.0°C in Et_2O. The amount of ethane was negligibly small in both cases. At 25°C, the yields of ethylene and ethylbenzene were quite small. Furthermore, the yields of ethylene and ethylbenzene were negligibly small in THF at 2.0°C, but at 25°C they were almost the same as those formed in Et_2O at 2.0°C. Thus, the effect of temperature on the exchange reaction was highly dependent on the solvent. In the case of methylmagnesium bromide, the amount of ethylbenzene was quite small even in Et_2O at 2.0°C.

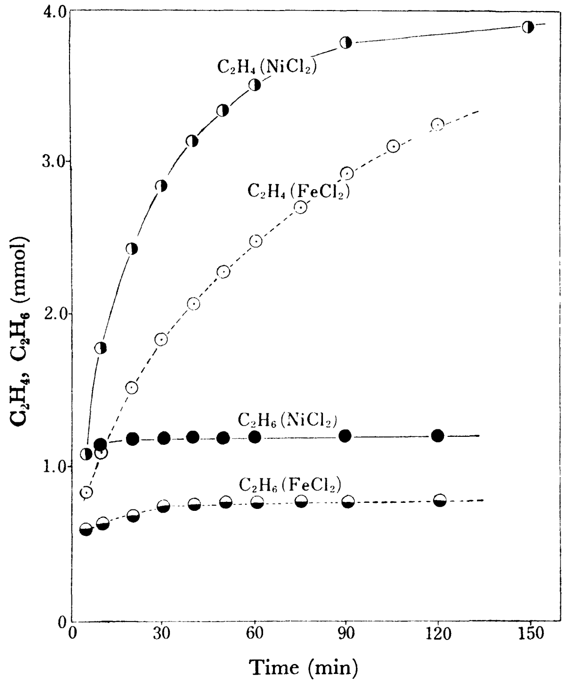


Fig. 1. The rate of formation of ethylene in the reaction of ferrous chloride (0.8 mmol) or nickelous chloride (1.0 mmol) with EtMgBr (5.7 mmol) in Et_2O (18 m*l*) in the presence of 26.1 mmol styrene at 2.0°C

◑ ethylene ($NiCl_2$) ● ethane ($NiCl_2$)
⊙ ethylene ($FeCl_2$) ◒ ethane ($FeCl_2$)

TABLE 8. THE IRON-CATALYZED EXCHANGE BETWEEN GRIGNARD REAGENT AND OLEFIN[a)]

Grignard Reagent RMgBr	Olefin R′(-H)	Solvent	Temp. (°C)	Products (mmol)	
				R(-H)	R′H after hydrolysis
Et	C_3H_6	THF	25	0.03	0.03
Et	C_3H_6	Et_2O	2.0	<0.01	<0.01
n-Pr	C_2H_4	THF	25	0.68	0.70
n-Pr	C_2H_4	Et_2O	2.0	0.45	0.45
i-Pr	C_2H_4	THF	25	1.20	1.33
i-Pr	C_2H_4	Et_2O	2.0	0.31	0.33
t-Bu	C_2H_4	THF	25	0.15	0.16

a) In 21 m*l* solution containing 3.0 mmol Grignard reagent, 2.0 mmol olefin and 0.025 mmol ferric chloride for 60 min. No appreciable amounts of R′H was detected before hydrolysis in all runs.

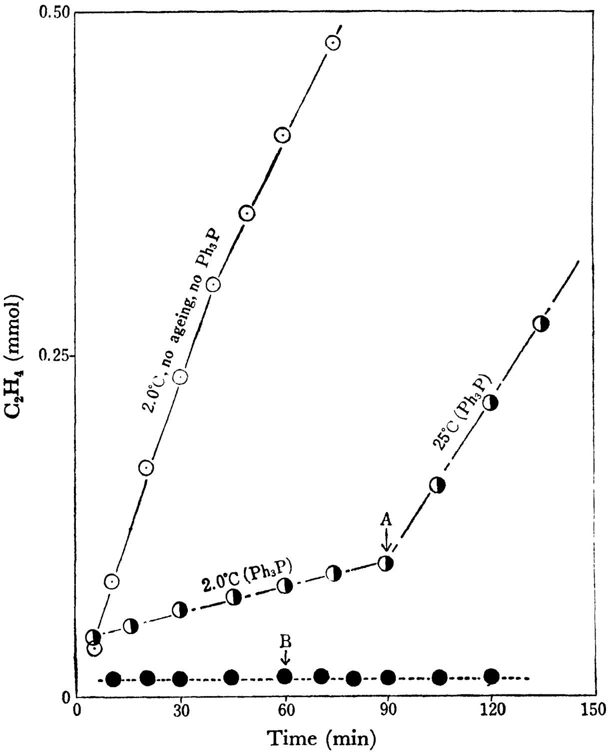
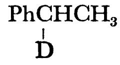


Fig. 2. The iron-catalyzed exchange between EtMgBr and styrene in Et_2O (Et_2O+styrene 21 m*l*, 0.18M EtMgBr, 1.24M styrene, 2.4×10^{-4}M $FeCl_3$) at 2.0°C.
⊙ 2.0°C, no Ph_3P, no ageing, ◐ In the presence of Ph_3P (0.18M), A; Warmed up to 25°C at this point, ● 2.0°C, no Ph_3P, B; Styrene was added at this point (ageing).

Ethylene and propylene were also used in the iron-catalyzed exchange with various Grignard reagents in THF at 25°C and in Et_2O at 2.0°C. The results are summarized in Table 8 which shows that olefins were formed in high yields from *n*-propyl, isopropyl, and *t*-butylmagnesium bromides in THF at 25°C and in Et_2O at 2.0°C when ethylene was present in the reaction. The amount of ethane after acidic hydrolysis was exactly equal to the yield of olefin derived from the Grignard reagent. On the other hand, the yields of ethylene and propane from ethylmagnesium bromide and propylene were low in Et_2O at 2.0°C and in THF at 25°C. Exchange between Grignard reagent and olefin is, thus, dependent on the particular combination chosen. Additional experiments were performed in order to probe the mechanism of this reaction. The rate of formation of ethylene from the iron-catalyzed exchange of ethylmagnesium bromide and styrene is shown in Fig. 2. No ethylene was formed if styrene was added to an aged catalyst solution, that is 60 minutes after ethylmagnesium bromide and ferric chloride were mixed. The rate of formation of ethylene in the presence of a large excess of triphenylphosphine was also very slow at 2.0°C, but was accelerated when the temperature was raised to 25°C. The effect observed with triphenylphosphine is consistent with those obtained by variation of the temperature and the solvent (Table 7). Finally, the composition of ethylbenzene formed after deuterolysis was shown by NMR analysis (Table 7), to consist of the following:

 $\mathrm{Ph\underset{D}{C}HCH_3}$	$PhCH_2CH_2D$	$PhCH_2CH_3$
71%	5%	24%

The deuterium content in the ethylbenzene was much smaller at high concentrations of catalyst (Table 6) than at low concentrations (Table 7).

Discussion

I The Distribution of Products from the Reactions of Transition Metal Halides with Grignard Reagents

The Formation of Coupling Dimer. The yield of coupling dimer is strongly dependent on the transition metal halide and the Grignard reagent. The coupling dimer is formed quantitatively from argentous bromide almost independently of the structure of the alkyl of the Grignard reagent except for secondary and tertiary alkyl Grignard reagents.[2] We have proposed a bimolecular mechanism for the silver-catalyzed coupling of a Grignard reagent and an alkyl bromide in order to explain the effects of catalyst concentration, the reaction temperature and the presence of styrene on the yield and stereochemistry of coupling.[2]

$$\mathrm{RAg + R'Ag \longrightarrow R\text{-}R'(R\text{-}R,\ R'\text{-}R') + 2Ag^0}\ . \quad (6)$$

Methyl and ethyl chlorides are formed together with coupling dimers from the reactions of cupric chloride with methyl and ethylmagnesium bromides in Et_2O and that of lithium chlorocuprate with these Grignard reagents in THF. The yield of alkyl chlorides are dependent on the solvent and the molar ratio of Grignard reagent to lithium chlorocuprate and the reaction may also proceed by a bimolecular mechanism expressed by Eq. 5.

Radical mechanism can be neglected for coupling since large excess of styrene does not influence $Q(R)$. Whitesides have also emphasized this point for the decompositions of alkenylcopper and alkenylsilver complexes.[9]

The reaction of ethylmagnesium bromide and ferrous, cobaltous, nickelous, palladous or cuprous halide produces little or no coupling dimer. The coupling dimer is formed, however, in fairly good yields when the Grignard reagent is methyl, neopentyl, phenyl, vinyl, and benzylmagnesium bromides which have no available β-hydrogens.

The yield of coupling dimer is also dependent on the structure of the alkyl group because for a given transition metal salt, the yield of coupling dimer increases generally in the sequence: methyl>neopentyl, benzyl, and ethane and neopentyl chloride are preferably formed in the reactions of lithium chlorocuprate with the corresponding Grignard reagents.

The yield of coupling dimer is enhanced by styrene and triphenylphosphine (Table 3) and it is generally higher in THF than in Et_2O. The salutary effect of these compounds on the yield of coupling dimer may be attributed to the stabilization of the transition metal-carbon bond[10] and or occupation of the coordination

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[9] G. M. Whitesides and C. P. Casey *J. Amer. Chem. Soc.*, **88**, 4541 (1966).

[10] J. Chatt and B. L. Shaw, *J. Chem. Soc.*, **1959**, 4020.

sites necessary for elimination or disproportionation. A similar effect may be applicable to vinyl and phenylmagnesium bromides.[11]

As a conclusion the coupling reaction is thought to proceed by a following bimolecular mechanism.

$$\mathrm{RMX}_{n-x} + \mathrm{RMX}_{n-x} \longrightarrow \mathrm{R\text{-}R} + 2\mathrm{MY}_{n-x} \qquad (7)$$

Thus the stability of transition metal-carbon bond (transition metal, solvent, ligand as well as reaction temperature), the availability of β-hydrogen and bulkiness of alkyl group are effective factors for coupling. The higher yield of coupling dimer with a higher oxidation state of a given metal may be due to the formation of stable MY_{n-x} salt (Cu and Fe). This mechanism is also supported by the facts that the order of the yield of coupling dimer is primary>secondary>tertiary for argentous bromide and three coupling dimers are formed in the reaction of cupric, argentous or ferric halide with a mixture of two Grignard reagents (Table 5).

The Disproportionation. The disproportionation to afford alkene and alkane is also strongly dependent on the transition metal, the availability of β-hydrogens and the presence of styrene. Styrene is reduced to ethylbenzene except when the reactions are carried out with argentous and cuprous halides. For example, the ratio of ethylene to ethane is 1.0 in the presence of styrene when cobaltous bromide reacts with ethylmagnesium bromide in THF. This ratio is approximately 0.2 in the absence of styrene (Table I). The yield of ethylbenzene is also high when Grignard reagents which have β-hydrogens reacts with cobaltous bromide but it is low from methyl, neopentyl and phenylmagnesium bromide. We deduce from the value of Q(Et) and the ratio of ethylene to ethane (Table 1 and Table 7) that the exchange between ethylmagnesium bromide and styrene can be neglected under these reaction conditions. Thus, *both* hydrogens in ethylbenzene could not have been derived only from the ethyl moiety. Furthermore, the formation of ethylbenzene from methyl, neopentyl, and phenyl Grignard reagents indicates that the hydrogen was derived partially from the solvent.[2] Since the yield of ethylbenzene is much higher with those Grignard reagents possessing β-hydrogens, at least *one* of the hydrogens in ethylbenzene is derived from an alkyl group present in an intermediate.

In the reaction of transition metal halides with a mixture of two Grignard reagents, the trend is for the alkane to be formed mainly from one alkyl group and the alkene to be derived from the other alkyl group (Table 5). This selectivity is more conspicuous when one alkyl group has no β-hydrogen. In all of our experiments, Q(R) is not changed by the presence of styrene and indicates that alkyl radicals does not complicate the interpretation of the mechanism.[2]

Two mechanisms are plausible for the formation of alkane and alkene in the reaction of transition metal halides with Grignard reagents:

A. "Hydride Mechanism"[12]

$$\mathrm{RCH_2CH_2M} \longrightarrow \mathrm{RCH{=}CH_2} + \mathrm{HM} \qquad (8)$$

$$\mathrm{RCH_2CH_2M} + \mathrm{HM} \longrightarrow \mathrm{RCH_2CH_3} + 2\mathrm{M} \qquad (9)$$

B. "Direct Hydride Migration (or Bimolecular) Mechanism"

$$\mathrm{RCH_2CH_2M} + \mathrm{RCH_2CH_2M} \longrightarrow \mathrm{RCH{=}CH_2} + \mathrm{RCH_2CH_3} + 2\mathrm{M} \qquad (10)$$

These two mechanisms have been discussed in the light of the decompositions of alkylcopper and alkylmanganese species.[2]

We infer that hydride mechanism is generally more common for Mn, Fe, Co, Ni, and Pd. On the other hand, bimolecular mechanism is more plausible for Cu(I) and Ag (especially for secondary and tertiary alkyls). The former groups possess great hydrogenation activity and the latter groups do not have it for olefins under the comparative condition. However, even in the former groups, participation of bimolecular interaction between alkyl metals for decomposition should also be considered in the case of special alkyl groups. The formation of cross coupling dimer in the reaction of cuprous chloride with a mixture of methyl and *n*-propylmagnesium bromides, the higher stability of neopentylcopper than methylcopper (bulkiness) and the adverse relationship between *n*-propyl and isopropylcoppers[13] (Table 5) may support this mechanism.

Thus bimolecular interaction between alkyl metals is very important for both coupling and disproportionation. Direct hydride mignation may not be easily occurred when THF is used as a solvent because THF has a great coordination affinity for metal[14] (occupation of coordination site). This effect of THF may be similar to that of triphenylphosphine. In fact, THF as a solvent and the addition of triphenylphosphine render the high yield of coupling dimer. The ratio of alkane: alkene also becomes greater than one in these cases. Dehydrogenation of coordinated ligand is known in analogous situation.[15] Organocopper clusters in ethereal solvent has been reported recently.[16] We have also observed the interaction between two copper nuclei during the decomposition of alkylcopper species.[2] Moreover, degradation of catalytic activity by aging in the Kharasch reaction is more pronounced in $\mathrm{Et_2O}$ than in THF. The ratio of alkane to alkene is greatly dependent on the catalyst concentration in the iron-catalyzed Kharasch reaction.[2] Metal-metal interaction (formation of aggregates), therefore, must be considered in these reactions.

II The Exchange between Grignard Reagent and Olefin by Iron Catalyst

Exchange reactions between Grignard reagents and

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[11] M. Tsutsui, *The New York Acad. Sci.*, **1961** 135.

[12] G. M. Whitesides, E. R. Stedronsky, C. P. Casey, and J. San Fillipo Jr., *J. Amer. Chem. Soc.*, **92**, 1426, (1970).

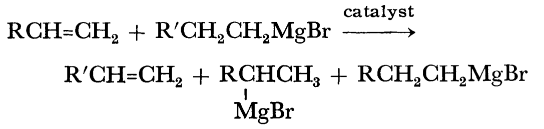
[13] The α,β-elimination of metal hydrides from various main group and transition metal alkyls generally follow the trend tertiary>secondary≫primary [G. E. Coates, M. L. H. Green, and K. Wade, "Organometallic compounds," Vol. I, Methuen and Co., Ltd., London (1967), p. 298], H. H. Zeiss (private communication).

[14] E. C. Ashby, *Quart. Revs.*, **21**, 259 (1967); F. W. Walker and E. C. Ashby, *J. Amer. Chem. Soc.*, **91**, 3845 (1969).

[15] W. H. Knoth and R. A. Schumn, *ibid.*, **91**, 2400 (1969) and references cited therein.

[16] A. Cairncross and W. A. Sheppard, *ibid.*, **93**, 247 (1971).

olefins catalyzed by transition metals including titanium,[17] nickel and cobalt[18] salts have been reported. The mechanism of this reaction has remained unclear, but transition metal hydrides have been postulated as catalysts.



$$RCH{=}CH_2 + R'CH_2CH_2MgBr \xrightarrow{\text{catalyst}} R'CH{=}CH_2 + \underset{\displaystyle MgBr}{\underset{|}{RCHCH_3}} + RCH_2CH_2MgBr \qquad (11)$$

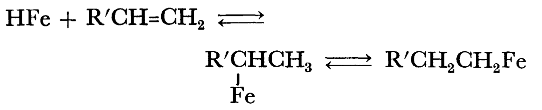
Table 7 and 8 show that the exchange between Grignard reagent and olefin is induced by catalytic amounts of ferric chloride. Thus, the amount of olefin produced from the Grignard reagent is equal to the alkane formed from the olefin. The combination of *n*-propyl or isopropylmagnesium bromide and ethylene affords propylene and ethylmagnesium bromide. On the other hand, the combination of ethylmagnesium bromide and propylene produces no significant exchange (Table 8).

$$CH_3CH_2CH_2MgBr + CH_2{=}CH_2 \xrightleftharpoons{\text{Fe catalyst}} CH_3CH{=}CH_2 + CH_3CH_2MgBr \qquad (12)$$

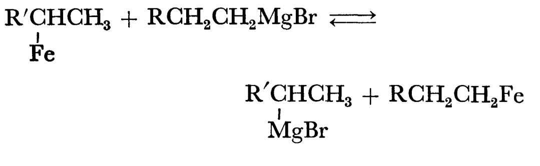
As shown in Fig. 2 and Table 7, no appreciable exchange is detected when styrene is added after the catalyst is aged for 60 minutes at 2.0°C in Et_2O. The catalytic activity is also poor at 25°C even without ageing or at 2.0°C in the presence of excess triphenylphosphine. The effects of ageing and temperature have also been observed in the exchange between Grignard reagent and olefin by nickelous chloride.[18]

We postulate that an iron hydride, *e.g.*, HFe,[19] is the catalytically active species in the exchange reaction, and the following mechanism is proposed:

$$FeCl_3 + RCH_2CH_2MgBr \xrightarrow{\text{solvent}} RCH{=}CH_2 + RCH_2CH_3 + HFe + MgBrCl \qquad (13)^{20)}$$



$$HFe + R'CH{=}CH_2 \rightleftharpoons \underset{\displaystyle Fe}{\underset{|}{R'CHCH_3}} \rightleftharpoons R'CH_2CH_2Fe \qquad (14)$$



$$\underset{\displaystyle Fe}{\underset{|}{R'CHCH_3}} + RCH_2CH_2MgBr \rightleftharpoons \underset{\displaystyle MgBr}{\underset{|}{R'CHCH_3}} + RCH_2CH_2Fe \qquad (15)$$

We relate the effect of ageing the catalyst and the temperature dependence of the exchange to the deactivation of the catalytic species, *e.g.*

$$2HFe \longrightarrow H_2 + Fe_2 \qquad (16)$$

The adverse effect of triphenylphosphine and the temperature requirements for exchange in Et_2O and in THF can be related to coordination of the active metal species by these ligands in competition with the olefin. The addition of metal hydride to alkenes has been observed in a variety of situations.[21] The decomposition of alkylmanganese to alkenes has been shown to proceed *via* a facile α,β-elimination of a hydridomanganese species.[2] The latter process, however, is not readily reversible under these reaction conditions. In order to obtain catalytic activity in the exchange of alkylmagnesium halides and alkenes, both addition as well as elimination must be facile. Iron, cobalt, and nickel species apparently fulfill both requirements.

Experimental

Materials. Triply sublimed magnesium was supplied from Dow Chemical Co., (analysis; Cu, <0.001; Fe, <0.003; Mn, <0.001; Ni, <0.0005; Pb, <0.003; Co, <0.005; Cr <0.005; Ag, <0.001; Rh, <0.005; Pd, <0.001; Mo, < 0.005; Ti, <0.005%). Anhydrous nickelous chloride was prepared from the reaction of its hexahydrate and thionyl chloride.[22] Anhydrous ferrous chloride was prepared from metallic iron and anhydrous ferric chloride in THF.[23] Commercial anhydrous manganous chloride was dried *in vacuo* at 130°C for 50 hrs. Anhydrous cobaltous bromide, palladous chloride, ferric chloride, cupric chloride, cuprous chloride, argentous bromide, and lithium chloride were commercial grade substances and used without further purification. Styrene and all organic halides were purified by distillation before use. Triphenylphosphine was commercial grade and used without further purification. Neopentyl bromide was prepared from neopentyl alcohol and tri-*n*-butylphosphine dibromide.[24]

Solvents. THF was refluxed over lithium aluninum hydride under nitrogen over 2 days, fractionated under a nitrogen atmosphere and stored under helium. Et_2O was refluxed over metallic sodium under nitrogen for 24 hrs, distilled under a nitrogen atmosphere and stored over metallic sodium under helium.

Preparation of Grignard Reagent. All Grignard reagents were prepared using excess of magnesium metal ($1.5\sim2.0$ times excess of the theoretical amount) in order to minimize the amount of unreacted organic halide. Reaction temperature was varied from 5 to 35°C according to the reactivity of organic halide. All solutions of Grignard reagent were filtered under a nitrogen atmosphere and were almost colorless. The exception, vinylmagnesium bromide, had a red brown color. The concentrations of all Grignard reagents were determined by titration and by quantitative analysis of the hydrocarbon produced on acidic hydrolysis (0.5—1.8M).

Product Analysis. All products were analyzed by gas chromatography using the internal standard method.

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[17] G. D. Cooper and H. I. Finkbeiner, *J. Org. Chem.*, **27**, 1439, 3395 (1962).

[18] F. Ungváry, B. Babos, and L. Marko, *J. Organometal. Chem.*, **8**, 329 (1967); L. Farady, L. Bencze and L. Marko *ibid.*, **10**, 505 (1967), **17**, 107 (1969).

[19] Coordination by ligand around iron is assumed, but not specifically included. The oxidation state of iron may be monovalent despite of the lack of clear evidence.

[20] Equation not balanced. Part of hydrogen no doubt comes from the solvent (Table 1).

[21] H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York (1962); K. Ziegler, *Angew. Chem.*, **64**, 323 (1952); J. Chatt and B. L. Shaw, *J. Chem. Soc.*, **1962**, 5075; R. Cramer, *J. Amer. Chem. Soc.*, **86**, 217 (1964), **87**, 4717 (1965), **88**, 2272 (1966); R. Cramer and R. V. Lindsey. Jr., *ibid.*, **88**, 3534 (1966).

[22] G. Brauer, "Handbuch der Präparative Anorganischen Chemie," Ferdinard Enke Verlag, Stuttgart (1954) p. 1154.

[23] G. Wilkinson, "Organic Synthesis," Coll. Vol. IV, p. 473, (1963).

[24] G. A. Wiley, R. L. Hershkowitz, B. M. Rein, and B. C. Chung, *J. Amer. Chem. Soc.*, **86**, 964 (1964).

Compound	Column	Temperature °C	Internal Standard
Methane	2F′-PorapakQ	Room Temp.	Ethylene or Ethane
Ethylene	2F′-PorapakQ	Room Temp.	Methane
Ethane	2F′-PorapakQ	Room Temp.	Methane
Propylene	15F′-Dowtherm	Room Temp.	Isobutane
Propane	15F′-Dowtherm	Room Temp.	Isobutane
Isobutane	15F′-Dowtherm	Room Temp.	*n*-Butane
Isobutylene	15F′-Dowtherm	Room Temp.	*n*-Butane
n-Butane	15F′-Dowtherm	Room Temp.	Isobutane
Neopentane	15F′-Dowtherm	Room Temp.	Isobutane
Butadiene	15F′-Dowtherm	Room Temp.	*n*-Butane
Isopentane	15F′-FFAP	65	*n*-Heptane
n-Pentane	15F′-FFAP	65	*n*-Heptane
n-Hexane	15F′-FFAP	65	*n*-Heptane
1-Hexene	15F′-FFAP	65	*n*-Heptane
1,5-Hexadiene	15F′-FFAP	65	*n*-Octane
2,2,3,3-Tetramethylbutane	15F′-FFAP	65	*n*-Octane
2,3,5,5-Tetramethylhexane	15F′-FFAP	100	*n*-Decane
2,3-Dimethylbutane	15F′-SF96	90	*n*-Hexane
Benzene	15F′-FFAP	120	Toluene
Toluene	15F′-FFAP	120	Benzene
Ethylbenzene	15F′-FFAP	150	Toluene
Biphenyl	4F′-XF1150	180	Bibenzyl
Bibenzyl	4F′-XF1150	180	Biphenyl
Methyl chloride	15F′-Dowtherm	Room Temp.	Isobutane
Ethyl chloride	15F′-SF96	Room Temp.	Isobutane
Neopentyl chloride	15F′-FFAP	70	*n*-Heptane
Chlorobenzene	15F′-FFAP	160	Isopropylbenzene

Reaction of Cobaltous Bromide with Ethylmagnesium Bromide in Tetrahydrofuran in the Presence of Styrene (A Representative Example). A 250 m*l* round-bottom flask was equipped with a magnetic stirrer bar and a rubber septum. The flask was flushed with nitrogen and 0.224 g (1.0 mmol) cobaltous bromide was added. After the apparatus was tightly sealed, the atmosphere within the flask was swept with helium for 30 min. To this flask, 14.25 m*l* of THF, 1.0 m*l* of standard solution of toluene in THF (1.0M, 1.0 mmol) and 3.0 m*l* of styrene (26.1 mmol) were added with hypodermic syringes. The flask was then immersed in a dry-ice acetone bath and 25 m*l* of methane and 25 m*l* of isobutane were added with syringes. The flask was transferred to an ice-water bath, and after 5 minutes agitation 2.75 m*l* of ethylmagnesium bromide solution (4.0 mmol) was added to the mixture with a syringe. The color of solution changed from sky blue to dark brown immediately. The evolutions of ethane and ethylene was complete within 5 min after the addition of ethylmagnesium bromide. After 30 min agitation at the same temperature (2.0°C), a small sample of gas was taken out and analyzed by gas chromatography (ethylene; 1.26 mmol, ethane; 1.32 mmol, *n*-butane; 0.05 mmol). An aliquot of the reaction mixture was removed with a microsyringe purged with nitrogen. The amount of ethylbenzene (before hydrolysis)[25] was measured immediately by gas chromatography (1.15 mmol). After hydrolysis with 1.0 m*l* of dilute sulfuric acid solution, the amount of ethylbenzene (after hydrolysis) was again analyzed by gas chromatography (1.16 mmol).

Exchange between Ethylmagnesium Bromide and Styrene in Diethyl Ether with Catalytic Amounts of Ferric Chloride. In a similar experiment, 14.0 m*l* of Et_2O, 3.0 m*l* of styrene, 2.0 m*l* of a solution of EtMgBr in Et_2O (3.8 mmol), 1.0 m*l* of a solution of toluene in Et_2O (1.0 mmol) and 25 m*l* of methane were added to the reaction vessel. After the flask was immersed in an ice-water bath and the mixture agitated for 10 min, 1.0 m*l* of a solution of ferric chloride in Et_2O (0.025 mmol) was added. The color of the solution changed from colorless to pale brown immediately. The rate of evolution of ethylene was determined by periodically removing a small aliquot of gas followed by gas chromatographic analysis. After 90 min the amount of ethylene was 0.57 mmol and the amount of ethylbenzene after hydrolysis was 0.60 mmol (Table 7). Isolation of deuterated ethylbenzene from the reaction mixture was made by the following method. To the reaction mixture obtained in the exchange between ethylmagnesium bromide and styrene (see above), 1.0 m*l* of deuterium oxide was added and the mixture was agitated for 30 min at the same temperature. The resulting mixture was extracted with Et_2O and the ethereal layer was dried over anhydrous sodium sulfate. After filtration, Et_2O was removed *in vacuo*. Ethylbenzene was separated from the residue by preparative gas chromatography (10F′–FFAP, 150°C). The distribution of isomers in deuterated and undeuterated ethylbenzene was determined by NMR. (see Table 7).

Exchange between n*-Propylmagnesium Bromide and Ethylene in Tetrahydrofuran with Ferric Chloride Catalyst* THF (18.5 m*l*) and 2.5 m*l* of *n*-propylmagnesium bromide (3.0 mmol), 25 m*l* of methane, 50 m*l* of ethylene and 25 m*l* of isobutane were added to the flask in dry-ice acetone bath. The flask was immersed in a temperature controlled water bath (25°C) and the mixture agitated for 10 min. 1.0 m*l* of solution of ferric chloride in THF (0.025 mmol) was added to the mixture

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[25] Part of ethylbenzene may be formed from the thermal decomposition of phenethylmagnesium bromide in gaschromatography. M. Lefrançois and Y. Gault, *J. Organometal. Chem.*, **16**, 7 (1969).

under agitation. The color of the solution changed to pale brown immediately. The rates of formations of propylene and propane were followed by gas chromatography. The evolution of propylene was almost complete within 10 min after the addition of ferric chloride solution. After 60 min the amount of propylene was 0.68 mmol and the amount of propane was 0.06 mmol. None of ethane was detected before hydrolysis whereas 0.70 mmol of ethane was recovered after acidic hydrolysis.

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