Cu-catalyzed alkylation and Fe-catalyzed alkenylation of organomanganese reagents

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Abstract: Two new selective C-C bond formation procedures are described; the Cu-catalyzed alkylation of organomanganese chlorides by alkyl halides and the Fe-catalyzed alkenylation of organomanganese chlorides by alkenyl halides. These reactions have a large scope and give high yields under mild conditions (rt, 1 h). They are highly chemoselective and allow the preparation of numerous functionalized molecules. In both cases, the presence of NMP as cosolvent (THF/NMP) is determinant. For preparative organic chemistry, these two reactions compare favorably to the other related procedures since they are very easy to carry out and involve no toxic or expensive product. The Fe-catalyzed reaction is the first general Fe-catalyzed alkenylation procedure of preparative interest since no excess of alkenyl halides is required and even alkenyl chlorides can be used successfully.

INTRODUCTION

The chemistry of organomanganese reagents has been essentially developed by our group since 1974 (G. Cahiez and coll.[1]). From a general point of view, organomanganese reagents are more stable than many organotransition metal compounds and are easily prepared from manganese chloride or bromide, two cheap starting materials. The most part of the reactions reported until now concerns the chemistry of carbonyl compounds: acylation, 1,2-addition, 1,4-addition and enolization[1]. These reactions, which have a very large scope, are of interest for preparative organic synthesis since they can be performed very chemoselectively under mild conditions (ether or THF, 0°C to rt) and give high yields.

Cross-coupling reactions of organometallics with organic halides have been extensively studied these last years. Many of these reactions involved organotransition metal compounds as stoichiometric reagents (*e.g.* cuprates)[2] or as catalytic intermediates (*e.g.* Cu-, Pd- and Ni-catalyzed reactions of RMgX, RZnX...)[2, 3]. In spite of the numerous investigations performed, no general procedure involving organomanganese reagents has been described until now. In recent years, we have decided to take advantage of the interesting characteristics of these reagents for preparative organic chemistry to develop new cross coupling reactions (alkylation, alkenylation, arylation...). Our first results are described below.

Cu-CATALYZED ALKYLATION OF ORGANOMANGANESE REAGENTS[4]

Preliminary results

Organomanganese reagents do not react with alkyl halides or give a mixture of decomposition products (essentially the β-elimination or dimerization products). The alkylation reaction was only observed with reactive organic halides such as allylic halides.
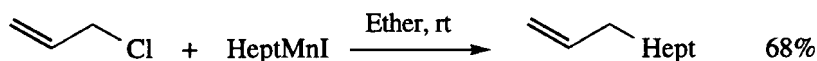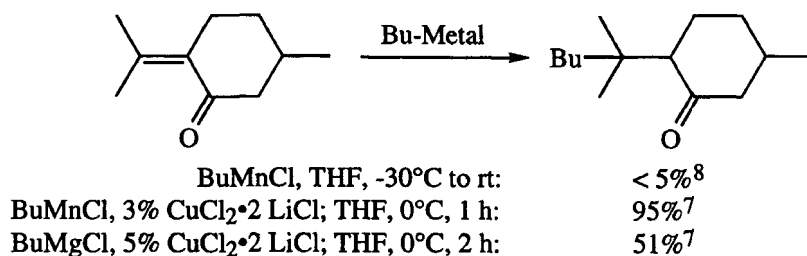

However, the reaction is generally very slow and gives moderate yields. Better results can be obtained with organomanganates which are more reactive. It is worthy of note that γ-substituted allylic halides react regioselectively to afford almost exclusively the S_N2 substitution product.[5]

$$\xrightarrow[\text{then rt}]{\substack{Me_3MnMgCl \\ \text{THF, -30°C, 16h}}}$$
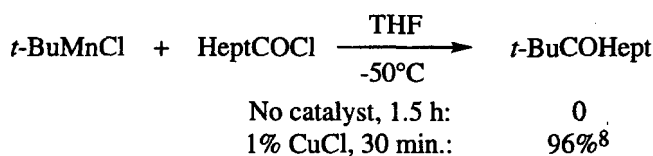
91%
$S_N2 \geq 99.5\%$
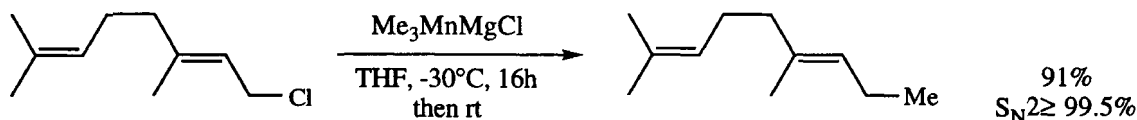
Unfortunately, even with organomanganates the alkyl halides which are less reactive only lead to a mixture of decomposition products.

Previously, we have shown that the reactivity of organomanganese reagents is deeply modified in the presence of copper salts as catalyst. This is well demonstrated by the following reactions:

-the Cu-catalyzed 1,4-addition of organomanganese halides to various α,β-unsaturated aldehydes, esters, ketones... [6,7]
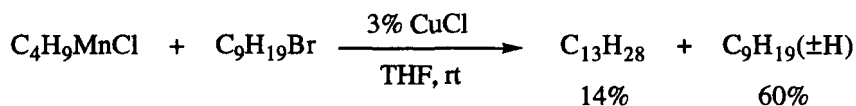

BuMnCl, THF, -30°C to rt:	< 5%[8]
BuMnCl, 3% CuCl$_2$•2 LiCl; THF, 0°C, 1 h:	95%[7]
BuMgCl, 5% CuCl$_2$•2 LiCl; THF, 0°C, 2 h:	51%[7]

- the Cu-catalyzed acylation of *sec-* or *tert*-alkylmanganese halides by carboxylic acid chlorides.[9]

$$t\text{-BuMnCl} \quad + \quad HeptCOCl \quad \xrightarrow[\text{-50°C}]{\text{THF}} \quad t\text{-BuCOHept}$$

|	
No catalyst, 1.5 h:	0
1% CuCl, 30 min.:	96%[8]

As shown above, the influence of the copper salts is determinant in both cases.

It is interesting to note that the scope and the efficiency of the Cu-catalyzed conjugate addition reaction mentioned above is often superior to those of the classical organocuprate, organocopper and Cu-catalyzed Grignard reagent procedures.[7]
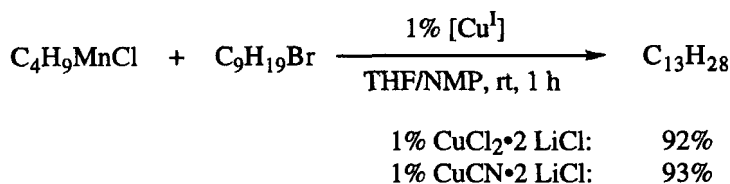
Copper salts are well known to catalyze efficiently the substitution of various organic halides by organometallics.[2] Therefore, we have tried to react organomanganese halides with alkyl halides in the presence of copper chloride.

$$C_4H_9MnCl \quad + \quad C_9H_{19}Br \quad \xrightarrow[\text{THF, rt}]{\text{3% CuCl}} \quad C_{13}H_{28} \quad + \quad C_9H_{19}(\pm H)$$

14%   60%

Unfortunately, under classical conditions, the copper-catalysis only allows one to obtain a fair yield . A general study on the influence of various parameters has shown that the nature of the solvent is crucial. Thus, the addition of some polar cosolvents such as DMF or DMSO (40 ml/50 mmoles) clearly favored the formation of the alkylation product. However, the best cosolvent is indisputably the NMP (N-methyl pyrrolidone) which allows one to obtain excellent results under mild conditions (rt, 1 h).

$$C_4H_9MnCl \quad + \quad C_9H_{19}Br \quad \xrightarrow[\text{THF/NMP, rt}]{\text{3% CuCl}} \quad C_{13}H_{28} \quad 88\%$$
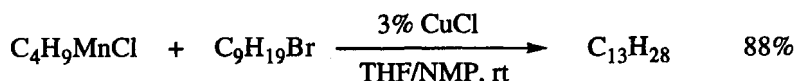
Later, we have found that the best yields are obtained with a soluble catalyst such as CuCl$_2$•2 LiCl (Kochi's catalyst)[10] or CuCN•2 LiCl (Knochel's catalyst).[11] No excess of organomanganese chlorides is required (1.05 equiv.).

$$C_4H_9MnCl \quad + \quad C_9H_{19}Br \quad \xrightarrow[\text{THF/NMP, rt, 1 h}]{\text{1\% [Cu}^I\text{]}} \quad C_{13}H_{28}$$

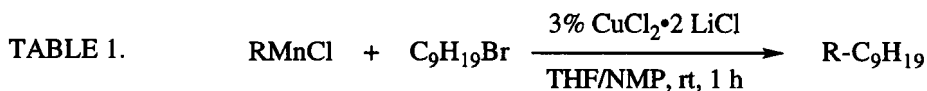|	
1% CuCl$_2$•2 LiCl:	92%
1% CuCN•2 LiCl:	93%

Scope and limitations of the reaction

Under the conditions described above, alkyl bromides, iodides or sulphonates were easily substituted. On the other hand, alkyl chlorides reacted sluggishly and gave poor results.

$$C_4H_9MnCl \ + \ C_{12}H_{25}X \ \xrightarrow[\text{THF/NMP, rt}]{\text{3\% CuCl}_2\text{•2 LiCl}} \ C_{16}H_{34}$$

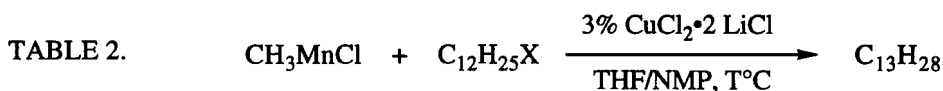X= I: 90%; X= Br: 91%; X= OSO$_2$Ph: 76%; X= Cl: 7%
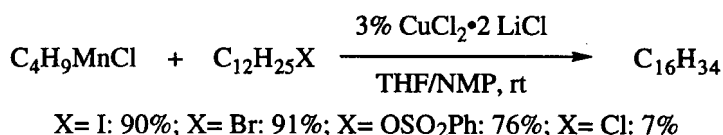
Organomanganese chlorides prepared from the corresponding organomagnesium or organolithium compounds have been used successfully (Entries 1 and 2). Interestingly, *n-*, *sec-*, and *tert*-alkylmanganese chlorides afforded the substitution product in excellent yields (Entries 2 to 4).

TABLE 1. $\quad$ RMnCl $\ + \ $ C$_9$H$_{19}$Br $\ \xrightarrow[\text{THF/NMP, rt, 1 h}]{\text{3\% CuCl}_2\text{•2 LiCl}} \ $ R-C$_9$H$_{19}$

| Entry	1	2	3	4
R	Bu[a]	Bu[b]	*i*-Pr	*t*-Bu
Yield (%)	90	93	79	86

[a] Prepared from BuLi. [b] Prepared from BuMgCl.

Methyl manganese chloride is less reactive than its higher homologues. This difference is not important in the case of alkyl iodides which are readily methylated at room temperature (Entry 5). However, with alkyl bromides, it is necessary to carry out the reaction at 60°C (Entries 6 to 8).

TABLE 2. $\quad$ CH$_3$MnCl $\ + \ $ C$_{12}$H$_{25}$X $\ \xrightarrow[\text{THF/NMP, T°C}]{\text{3\% CuCl}_2\text{•2 LiCl}} \ $ C$_{13}$H$_{28}$

Entry	5	6	7	8
X	I	Br	Br	Br
Temperature	20°C	20°C	40°C	60°C
Yield (%)	91	57	72	80

With aryl manganese chlorides which are also less reactive than their alkyl counterparts, the reaction is slow and led to low yields even at 60°C. Unexpectedly, after various attempts we have found that, in this case, the NMP has a detrimental influence. Thus, satisfactory results were obtained by working in THF alone.

THF/NMP, 40°C: $\quad$ 40%
THF, 20°C: $\quad$ 86%
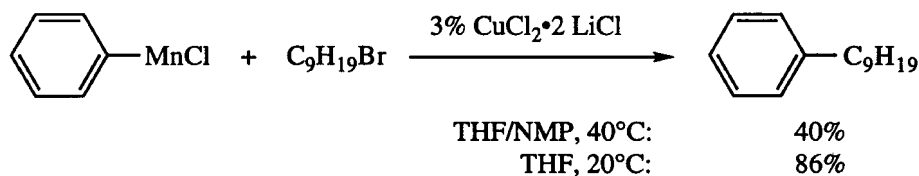
Alkenyl manganese chlorides reacted under classical conditions (THF/NMP, rt). However, the yields are very dependent on the nature of the alkenyl group.
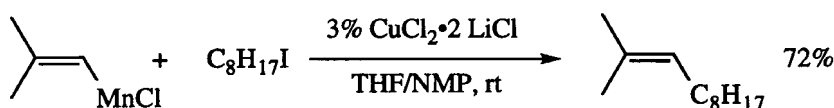
With functionalized alkyl bromides, the chemoselectivity of the reaction is, as expected, excellent. Thus, the substitution of the bromine atom selectively occurred in the presence of another less reactive leaving group (*e.g.* chlorine, entry 9) even when the difference of reactivity is low (*e.g.* sulphonate, entry 10).

After metallation (2 equiv. of RMnCl were used), the hydroxy or carboxylic acid groups do not interfere with the alkylation reaction (entries 11 and 12).

TABLE 3.

$$RMnCl + R'Br \xrightarrow[\text{THF/NMP, rt, 1 h}]{3\% \ CuCl_2 \cdot 2 \ LiCl} R-R'$$

Entry	R	R'	Yield (%)	Entry	R	R'	Yield (%)
9	Hept	-(CH$_2$)$_3$Cl	94	13	Me[a]	-(CH$_2$)$_{10}$COOEt	93
10	Bu	-(CH$_2$)$_6$OSO$_2$Ph	74	14	Bu	-(CH$_2$)$_3$COOEt	92
11	Me[a, b]	-(CH$_2$)$_{10}$COOH	97	15	"	-(CH$_2$)$_2$COOEt	78
12	Me[a, b]	-(CH$_2$)$_{10}$OH	94	16	"	-(CH$_2$)$_{10}$COEt	86

[a] Performed at 60°C. [b] 2 equivalents of MeMnCl were used.

Esters and even keto groups (entries 13 to 16) are also tolerated. Then, the reaction of organomanganese halides with ω-halogenoketones can selectively lead to the 1,2-addition product[12] or to the alkylation product, by choosing the appropriate reaction conditions.

With ω-bromo aldehydes the reaction led to a mixture of the starting aldehyde with the alkylated product as their cyclic trimers.

Interesting results have been obtained with alkyl bromides bearing a leaving group in the β-position. Indeed, it is well known that these compounds are very difficult to alkylate since the competitive β-elimination is generally the main reaction.[13] With our procedure the presence of an acyloxy group in the β-position of the bromine atom is well tolerated and the substitution reaction gave excellent yields (Entries 17 to 19). On the other hand, the 2-bromo chloroethane only led to moderate yields (Entry 20). Nevertheless, it should be noted that with a Grignard reagent in the presence of copper salts as catalyst, only the elimination reaction occurs.[13]

TABLE 4.

$$RMnCl + ZCH_2CH_2Br \xrightarrow[\text{THF/NMP, rt, 1 h}]{3\% \ CuCl_2 \cdot 2 \ LiCl} ZCH_2CH_2R$$

Entry	R	ZCH$_2$CH$_2$Br	Yield (%)	Entry	R	ZCH$_2$CH$_2$Br	Yield (%)
17	Hept	MeCOO(CH$_2$)$_2$Br	71	19	Bu	EtOCOO(CH$_2$)$_2$Br	87
18	Bu	BuCOOCH$_2$)$_2$Br	90	20	Oct	Cl(CH$_2$)$_2$Br	38

The Cu-catalyzed alkylation of organomanganese chlorides can also be selectively performed in the presence of an enone. No trace of 1,4-addition product was detected.

[a] C$_4$H$_9$MnCl was added to the mixture RBr + enone. [b] 98% of enone was recovered.

Let us recall that the conjugate addition of organomanganese reagents to enones readily occurs in THF.[6,7] In fact, organomanganese chlorides selectively give either the 1,4-addition product or the alkylation product according to the nature of the solvent.
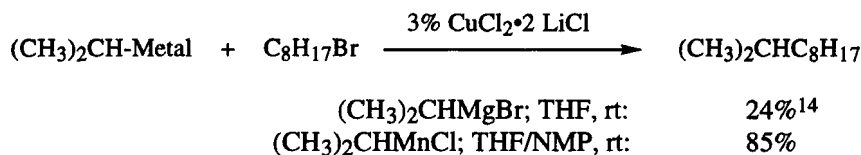
C_4H_9MnCl
3% $CuCl_2\cdot 2$ LiCl
$\xrightarrow{\text{THF/NMP, rt, 1 h}}$ $C_{13}H_{28}$ 93%
(98% of enone was recovered)

C_4H_9MnCl
3% $CuCl_2\cdot 2$ LiCl
$\xrightarrow{\text{THF, rt, 1.5 h}}$ 95%
(98% of $C_9H_{19}Br$ was recovered)

Comparison with the cuprate and the Cu-catalyzed Grignard reagent procedures.

The copper-catalyzed alkylation of organomanganese chlorides is very interesting for preparative organic chemistry. Indeed, it combines the main advantages of the other alkylation procedures previously described.

   - It is less expensive and easier to perform than the cuprate procedures : catalytic amount of copper (manganese is less expensive than copper and easier to eliminate during the final work-up), no excess of organometallic (1.05 equiv.), no low temperature, no expensive or toxic additives such as PR_3, HMPA... .

   - It compares also favorably with the Cu-catalyzed Grignard reagent procedure since it is also easy to carry out but it generally gives higher yields, especially to introduce *sec-* or *tert*-alkyl groups.
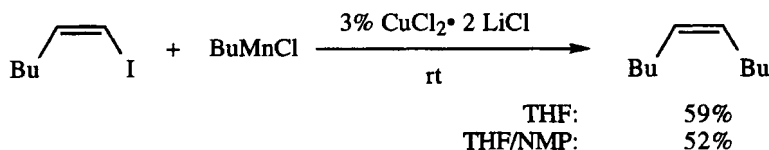
$(CH_3)_2CH\text{-Metal} + C_8H_{17}Br \xrightarrow{3\% \; CuCl_2\cdot 2 \; LiCl} (CH_3)_2CHC_8H_{17}$

$(CH_3)_2CHMgBr$; THF, rt: 24%[14]
$(CH_3)_2CHMnCl$; THF/NMP, rt: 85%

   - Moreover it is more chemoselective.

$\text{Bu-Metal} + Br(CH_2)_5COBu \xrightarrow{3\% \; CuCl_2\cdot 2 \; LiCl} Bu(CH_2)_5COBu$

BuMgCl; THF, rt: 40-45%
BuMnCl; THF/NMP, rt: 90%
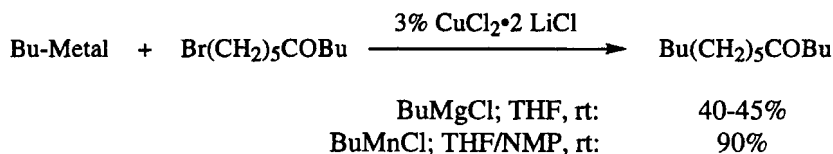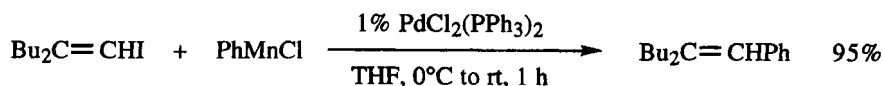
Fe-CATALYZED ALKENYLATION OF ORGANOMANGANESE REAGENTS

Preliminary results

Organomanganese chlorides react with alkenyl iodides in the presence of copper salts to give the substituted olefins in moderate yields. In this case, the addition of cosolvent such as NMP has no influence.

$\text{Bu}\diagdown\diagup I + \text{BuMnCl} \xrightarrow[\text{rt}]{3\% \; CuCl_2\cdot 2 \; LiCl} \text{Bu}\diagdown\diagup\text{Bu}$
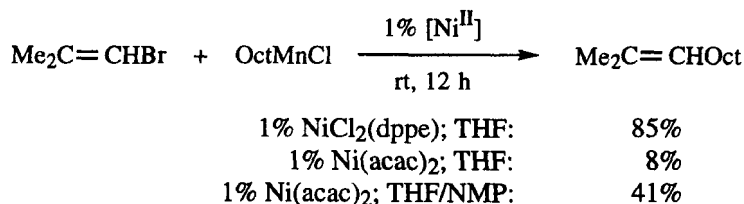
THF: 59%
THF/NMP: 52%

From a preparative point of view, these results are not very interesting. Therefore, we have tried to catalyze the reaction with another transition metal. Our first attempts were performed with palladium[15] and nickel[16] salts.

For instance, good yields of cross coupling products were obtained with the complex $PdCl_2(PPh_3)_2$.[15]

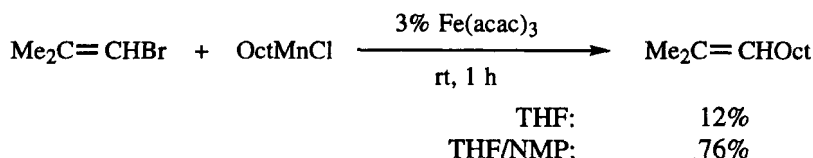$$Bu_2C{=}CHI \quad + \quad PhMnCl \quad \xrightarrow[\text{THF, 0°C to rt, 1 h}]{1\% \ PdCl_2(PPh_3)_2} \quad Bu_2C{=}CHPh \quad 95\%$$

The complex $NiCl_2 \cdot dppe$ has also been used successfully. On the other hand, nickel acetylacetonate gave poor results even in the presence of NMP.[16]

$$Me_2C{=}CHBr \quad + \quad OctMnCl \quad \xrightarrow[\text{rt, 12 h}]{1\% \ [Ni^{II}]} \quad Me_2C{=}CHOct$$

$$1\% \ NiCl_2(dppe); \ THF: \qquad 85\%$$
$$1\% \ Ni(acac)_2; \ THF: \qquad 8\%$$
$$1\% \ Ni(acac)_2; \ THF/NMP: \qquad 41\%$$

These results which will be reported elsewhere are not surprising since numerous examples of Ni- and Pd-catalyzed cross coupling reactions of alkenyl halides with various organometallics have already been described.[3]

Several other transition metal salts have been tested. Interestingly, we have discovered that good yields of substituted olefin could be obtained with iron acetylacetonate as catalyst. It should be emphasized that the presence of NMP as cosolvent has a dramatic influence.

$$Me_2C{=}CHBr \quad + \quad OctMnCl \quad \xrightarrow[\text{rt, 1 h}]{3\% \ Fe(acac)_3} \quad Me_2C{=}CHOct$$

$$THF: \qquad 12\%$$
$$THF/NMP: \qquad 76\%$$

Fe-catalyzed alkenylation of Grignard reagents has been previously reported by Kochi [17] who has performed a very interesting mechanistic study. For large scale applications the replacement of palladium and nickel salts by iron salts is extremely attractive (Fe is less expensive than Pd and less toxic than Ni). However, this reaction is practically unused in preparative organic chemistry since the alkenyl halide must be generally employed in large excess (3 to 5 equiv.).

On the contrary, our first experiments have indicated that the Fe-catalyzed organomanganese procedure does not require an excess of reagents. This substantial advantage prompts us to study this reaction.

Study of the reaction: scope and limitations

At first, we have studied the influence of various parameters to increase the yield of the reaction. As in the case of the Cu-catalyzed alkylation of organomanganese reagents described above, the presence of NMP as cosolvent has a dramatic influence since the yield jumped from 12% to 76%.

$$Me_2C{=}CHBr \quad + \quad OctMnCl \quad \xrightarrow[\text{rt, 1 h}]{3\% \ Fe(acac)_3} \quad Me_2C{=}CHOct$$

$$THF: \qquad 12\%$$
$$THF/NMP: \qquad 76\%$$
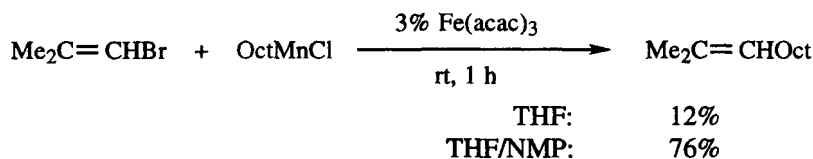
The role of NMP seems very specific since various attempts with some other polar cosolvents (AcOEt, MeCN, sulfolane...) did not allow to get such an improvement.
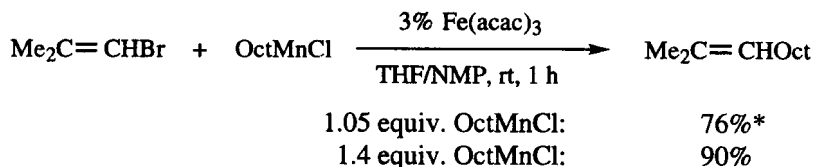
As shown above, the nature of the iron salt used as catalyst is not determinant provided that it is soluble.

$$Me_2C{=}CHBr \quad + \quad OctMnCl \quad \xrightarrow[\text{THF/NMP, rt, 1 h}]{3\% \ [Fe^{III}]} \quad Me_2C{=}CHOct$$
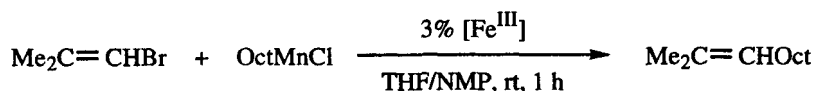
$$Fe(acac)_3: \ 76\%; \quad FeCl_3: 67\%; \quad Fe(dibenzoylmethido)_3: \ 70\%$$

This is surprising since the choice of the iron salts is very important with the corresponding Grignard reagent procedure.[17b]

Finally, we have found that a slight excess of organomanganese chloride (1.4 equiv.) has to be used to consume all the starting alkenyl bromide. Excellent yields were then obtained under mild conditions (rt, 1 h).

$$Me_2C=CHBr \; + \; OctMnCl \xrightarrow[\text{THF/NMP, rt, 1 h}]{3\% \; Fe(acac)_3} Me_2C=CHOct$$

1.05 equiv. OctMnCl:	76%*
1.4 equiv. OctMnCl:	90%

* 15% of Me₂C=CHBr unreacted.

Interestingly, alkenyl iodides, bromides as well as chlorides can be used. This is worthy of note since chlorides are seldom employed owing to their low reactivity.
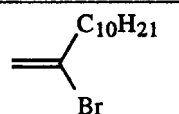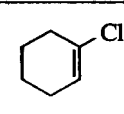

X= I: 90%, X= Br: 89%, X=Cl: 88%
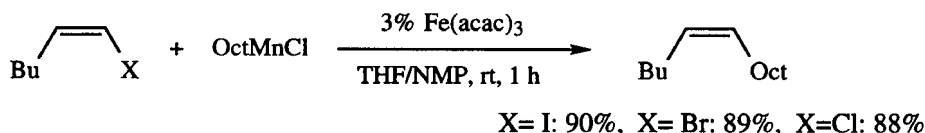
In addition, the substituted olefins were obtained with an excellent stereoselectivity.


90%, E≥ 98%

90%, Z ≥ 98%
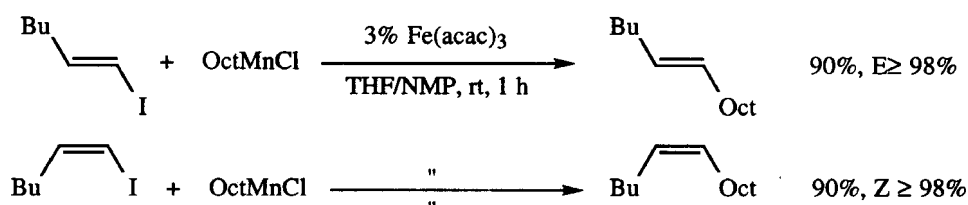
The reaction has a large scope, thus aryl and *n*- or *sec*-alkylmanganese chlorides gave excellent yields (Entries 21, 22 and 24). On the other hand, with *tert*-alkylmanganese chlorides the formation of decomposition products was mainly observed (Entry 23). The vinyl-vinyl cross coupling is more difficult and the yields are very dependant on the structure of the alkenyl group accruing from the organometallic (Entry 26). This point is currently investigated.

TABLE 5.
$$R^1R^2C=CR^3X \; + \; RMnCl \xrightarrow[\text{THF/NMP, rt, 1 h}]{3\% \; Fe(acac)_3} R^1R^2C=CR^3R$$
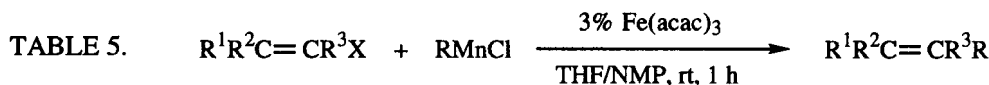
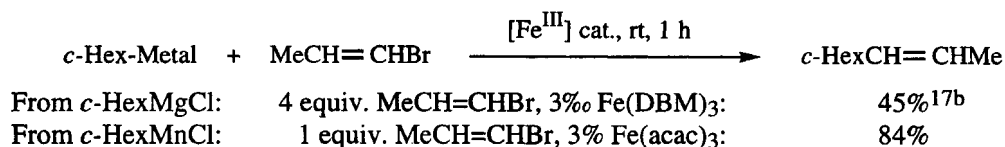| Entry	R	$R^1R^2C=CR^3X$	Yield (%)	Entry	R	$R^1R^2C=CR^3X$	Yield (%)
21	Oct	Me₂C=CHBr	90	26	Me₂C=CH	PhCH=CHBr	25
22	*c*-Hex	MeCH=CHBr	84	27	Oct	(*E*)-MeCH=CHBr	80
23	*t*-Bu	PhCH=CHBr	30	28	Oct	(*Z*)-BuCH=CHCl	88
24	Ph	MeCH=CHBr	71	29	Bu	PhCH=CHBr	87
25	Oct		89	30	Bu		80

No limitation has been found concerning the nature of the alkenyl halide. Thus, the double bond can bear one or many substituents in the α- or β-positions (Entries 25 to 30).

It should be pointed out that this procedure is highly chemoselective. This is well demonstrated by the following example.

75%
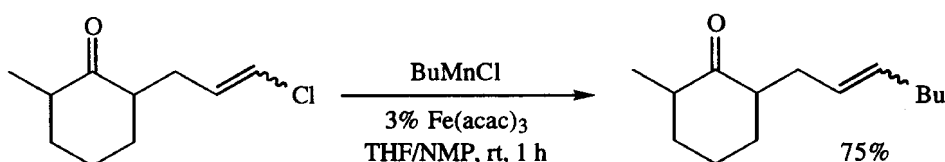
Comparison with the Fe-catalyzed Grignard reagents procedure

Our procedure compares very favorably to the Fe-catalyzed alkenylation of Grignard reagents[17] since it gives higher yields and does not require an excess of alkenyl halides. Moreover, the starting organometallic can be an organomagnesium or an organolithium compound.

$$c\text{-Hex-Metal} \quad + \quad MeCH{=}CHBr \quad \xrightarrow{[Fe^{III}] \text{ cat., rt, 1 h}} \quad c\text{-HexCH}{=}CHMe$$

From c-HexMgCl:	4 equiv. MeCH=CHBr, 3‰ Fe(DBM)$_3$:	45%[17b]
From c-HexMnCl:	1 equiv. MeCH=CHBr, 3% Fe(acac)$_3$:	84%

Interestingly, alkenyl chlorides which are more stable and cheaper than the corresponding bromides and iodides can be used successfully (e.g. Table 5, entries 28 and 30). It is worthy of note since they are seldom used because of their low reactivity.

As shown above, the Fe-catalyzed alkenylation of organomanganese reagents is also very interesting for its excellent chemoselectivity.

Finally, it is important to note that the procedure described above is the first general Fe-catalyzed alkenylation of organometallics of real interest for preparative organic chemistry.

CONCLUSION

The two procedures described above show the interest of the transition metal-catalyzed cross coupling of organomanganese reagents with organic halides for the selective formation of C-C bonds. They combine many advantages; mild reaction conditions, no excess of reagents, no toxic or expensive additive, high yields and excellent selectivity. Therefore, they compare often favorably to the other related organometallic procedures especially for large scale applications. Some other cross coupling reactions involving organomanganese reagents have been developed and will be reported soon.

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