Tetrahedron. Vol. 30, pp. 2669 to 2675. Pergamon Press 1974. Printed in Great Britain

EVIDENCE FOR THE INTERMEDIACY OF π-ALLYLIC METAL COMPLEXES IN THE REACTION OF ALLYLIC HALIDES WITH GRIGNARD REAGENT IN THE PRESENCE OF TRANSITION METAL HALIDES

Y. OHBE,* M. TAKAGI and T. MATSUDA

Department of Organic Synthesis, Faculty of Engineering, Kyushu University; Hakozaki, Higashi-ku, Fukuoka, Japan

(*Received in Japan* 9 *March* 1974; *Received in the UK for publication* 19 *March* 1974)

Abstract—The reactions of allyl bromide and crotyl chloride with Grignard reagent catalyzed by π-allyl and crotyl metal complexes of nickel, cobalt, and iron, and the stoichiometric reaction of the complexes with the Grignard reagent have been examined. The similarity in catalytic behaviour of the complex and the corresponding metallic halide affords further evidence in support of the previous proposal that the π-allylic metal intermediate plays an important role in the catalytic reaction. The stoichiometric reaction suggests that the dependence of distribution of product in the catalytic process on the type of both allylic halide and metal is attributable to the facility of ligand exchange between the π-allylic complex and Grignard reagent.

INTRODUCTION

In a previous paper,[1] we examined the catalytic behaviour of several transition metal chlorides in the Kharasch type reaction of allyl and crotyl halides with Grignard reagents.

The nature of the products and its dependence on the structure of the alkyl group of the Grignard reagent utilized (presence or absence of β-hydrogen) strongly suggested that the Ni and Co chloride promoted reactions proceeded *via* formation of the corresponding π-allylic metal intermediate as active species. However, the following problems have remained to be solved; (1) the products from allyl halides differ considerably from those from crotyl halides, and (2) the catalytic functions of Fe(III) and Cu(II) chlorides in the reaction differ from those of Ni(II) and Co(II) chlorides.

The present work was undertaken to solve these problems and to collect further information about the role of the active intermediates in the reaction. The reactions of allyl bromide and crotyl chloride with Grignard reagents (Me, i-Pr and n-Bu or n-Pr) in the presence of catalytic amounts of π-allylic metal complexes of Ni, Co and Fe were examined. The stoichiometric reaction of the Ni and Fe complexes with Grignard reagents in the absence of the allylic halides was also investigated.

π-Allylic metal complexes utilized were bis(π-allylnickel bromide),[2] bis(π-crotylnickel),[3] π-allylcobalt tricarbonyl,[4] π-crotylcobalt tricarbonyl,[4] π-allyliron tricarbonyl bromide[5] and π-crotyliron tricarbonyl bromide.[5]

RESULTS AND DISCUSSION

Reaction of allyl bromide under catalytic conditions. Table 1 shows the results of the reactions of allyl bromide with three Grignard reagents in the presence of catalytic amounts of the π-allylic Ni, Co and Fe complexes.

The values in parentheses are data obtained in the presence of the corresponding metal chlorides under the same conditions.

The results with the Ni and Co complexes in Table 1 indicate that product distributions closely resemble those obtained in the presence of Ni(II) and Co(II) chlorides.

The structure of the alkyl moiety of the Grignard reagent has a marked effect on the nature of the products, as was observed previously[1] for the metallic halide catalyzed reactions.

The similarity of the results with the two types of catalyst can be considered to provide strong evidence in support of the previous proposal that π-allyl metal complexes play an important role in the reaction of allyl halide catalyzed by Ni(II) and Co(II) salts. It should also be pointed out that with the Grignard reagents bearing β-hydrogen in their alkyl moiety, the π-allyl metal complexes show a marked tendency to direct the reaction into a hydrogen transfer pathway (formation of R(–H) and propylene).

On the other hand, when the π-allyl Fe complex was used, there was considerably less correspondence in product distribution with the two kinds of catalysts. For example, in the reaction with n-

Table 1. Reaction of allyl bromide with Grignard reagent catalyzed by π-allylic metal complex

	Complex	Bis(π-allylnickel bromide)[b]			π-Allylcobalt tricarbonyl[b]			π-Allyliron tricarbonyl bromide[c]		
	RMgX	MeMgI	n-BuMgBr	i-PrMgBr	MeMgI	n-BuMgBr	i-PrMgBr	MeMgI	n-BuMgBr	i-PrMgBr
reaction products[a]	Propylene	2(1)[d]	56(50)	83(75)	2(1)	70(64)	83(74)	trace (15)	18(15)[4][e]	35(14)
	R(+ H)	3(1)	2(3)	−(−)	2(1)	5(5)	−(−)	2(42)	22(10)[10]	16(5)
	R(− H)	−(−)	67(63)	83(75)	−(−)	75(70)	83(74)	−(−)	45(21)[12]	35(14)
	R-R	16(10)	5(7)	−(−)	19(21)	11(8)	−(−)	14(16)	10(10)[20]	−(−)
	$RCH_2CH{=}CH_2$	20(27)	14(10)	−(−)	44(61)	2(5)	−(−)	65(11)	19(54)[49]	−(14)
	1,5-Hexadiene	56(56)	14(12)	3(2)	30(28)	3(8)	−(−)	20(26)	30(10)[13]	11(14)

[a] Values (%) are based on the theoretical yield (0·1 mol).
[b] Metal complex; 2×10^{-3} mol, Grignard reagent; 0·1 mol.
[c] Metal complex; 5×10^{-3} mol, Grignard reagent; 0·1 mol.
[d] ( ): Results obtained in the presence of metallic chloride; this applies also to the other Tables.
[e] [ ]: The results for $CuCl_2$.

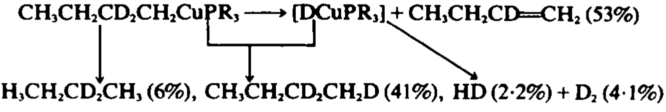
BuMgBr, the complex catalyst gave a greater amount of butene [R(–H)] and a lesser amount of the cross-coupling product than were obtained with Fe(III) chloride catalyst. It is to be noted that the product distribution with Fe(III) chloride catalyst is more like that with Cu(II) chloride (shown in brackets) than that with Fe complex catalyst. In view of the fact that Cu rarely affords an π-allylic complex in the absence of a stabilizing ligand, σ-type organocopper compounds being formed under such conditions,[6] one can reasonably assume that the active catalytic species from Fe(III) chloride principally involved in the reaction is of a σ-type rather than a π-allylic one.

Reaction of crotyl chloride under catalytic conditions. The results of the reactions of crotyl chloride with Grignard reagents catalyzed by the π-crotyl metal complexes of Ni, Co and Fe are tabulated in Table 2.

The correspondence in product distribution in the reactions with the complex and those with the corresponding metallic chloride catalysts was fairly good, and decreased in the order iron > cobalt ≧ nickel for all the Grignard reagents used.

Although the latter trend is somewhat different from that for allyl bromide, the results again indicate a common type of active catalytic species irrespective of the type of catalyst, and π-crotyl metal intermediate can be considered to be one of the important species in the catalytic system, since formation of homo-coupling product, C_8 diene mixture, occurred to a considerable extent.[7] It is also noted that the dependence of the yield of homo-coupling product on the structure of the Grignard reagent is considerably less in the reaction of crotyl chloride, especially in that with π-crotyl nickel complex (Me; 49%, n-Pr; 43%, i-Pr; 42%), than in the allyl bromide reaction with π-allyl nickel complex (Me; 56%, n-Bu; 14%, i-Pr; 3%). Another feature of the crotyl chloride reaction is the formation of hydrogen, which was scarcely observed in the corresponding allyl bromide reaction.

Hydrogen formation was not observed in the reaction with MeMgI, but occurred with n- and i-propyl–magnesium bromides. The decrease in the amount of hydrogen in the order i-Pr > n-Pr and concomitant decrease of R(–H), propylene, suggest that the hydrogen formation is closely related to the presence of β-hydrogen in the alkyl group of the Grignard reagent. Whitesides[8] discussed formation of hydrogen in the thermal decomposition of n-butyl(tri-n-butyl-phosphine)copper and proposed the following reaction involving the formation of an intermediate copper hydride complex, which yields hydrogen by decomposition.



$$CH_3CH_2CD_2CH_2CuPR_3 \longrightarrow [DCuPR_3] + CH_3CH_2CD{=}CH_2\ (53\%)$$

$$CH_3CH_2CD_2CH_3\ (6\%),\ CH_3CH_2CD_2CH_2D\ (41\%),\ HD\ (2{\cdot}2\%) + D_2\ (4{\cdot}1\%)$$

Thus, it could be deduced that the most probable origin of the hydrogen is an alkyl metal intermediate formed by crotyl-alkyl exchange between π-crotyl metal complex (or intermediate) and Grignard reagent, since other reactions of the π-allylic metal complex can not account for the hydrogen formation.

Although there remains considerable ambiguity in the nature of the exchange at present, the presumable orders of the stability of π-allylic metal complexes in the absence of any stabilizing ligand, π-allyl > π-crotyl and Ni ≧ Co > Fe, do not conflict with the observed dependence of the hydrogen yield on the structure of the π-allyl metal complexes.

As a feasible test for the crotyl-alkyl exchange, diethyl-copper lithium in ether was allowed to react with crotyl bromide.

The formation of C_8 diene mixture (42%), cross-coupling product (15%), and hydrogen (3%) indicated that the exchange also takes place in an organocopper compound of δ-type.

Stoichiometric reaction of the π-allylic metal complexes. The results in the preceding section showed that lignad exchange in the π-allylic metal complex under the reaction conditions seems to be one of the factors governing the outcome of the present catalytic reactions. In order to collect further information about the role of the π-allylic metal complex (or intermediate) in the catalytic process, stoichiometric reaction of the nickel and iron complexes with Grignard reagent was next carried out. The results are shown in Table 3.

In the reaction with bis(π-allylnickel bromide), n-BuMgBr and MeMgI reacted preferentially by hydrogen transfer and cross-coupling, respectively, formation of 1,5-hexadiene being markedly diminished.

This can be considered unambigous proof of the proposition that the Ni and Co chloride promoted reactions proceed *via* an π-allyl metal intermediate.

On ther other hand, a fair amount of 1,5-hexadiene was formed in the reaction of the Fe complex with the Grignard reagents, even under stoichiometric reaction conditions.

The occurrence to a measurable extent of allyl–alkyl exchange to form allyl Grignard reagent would be a principal factor in diene formation and could be attributed to the Ni complex under the conditions used. The reaction of the π-crotyl metal complexes with Grignard reagents afforded interesting information for the behavior of allyl and crotyl halides in the preceding catalytic reactions.

Both the Ni and Fe complexes afforded C_8 diene

Table 2. Reaction of crotyl chloride with Grignard reagent catalyzed by π-crotyl metal complex[a]

	Complex	Bis(π-crotylnickel)			π-Crotylcobalt tricarbonyl			π-Crotyliron tricarbonyl bromide		
	RMgX	MeMgI	n-PrMgBr	i-PrMgBr	MeMgI	n-PrMgBr	i-PrMgBr	MeMgI	n-PrMgBr	i-PrMgBr
reaction products	R(+ H)	7(6)	23(5)	51(10)	25(22)	26(22)	18(9)	23(28)	29(24)	16(6)
	R(− H)	−(−)	82(62)	58(53)	−(−)	73(58)	65(50)	−(−)	53(55)	50(50)
	Butene	3(1)	21(33)	22(43)	12(10)	31(22)	34(50)	5(8)	18(21)	24(47)
	H_2	−(−)	0·6(0·6)	2·4(1·5)	−(−)	1(1)	3(2)	−(−)	4·6(4·3)	6(4·4)
	R–R	36(40)	5(3)	2(2)	44(39)	2(2)	2(3)	29(34)	1(5)	1(3)
	$RCH_2CH{=}CHMe$	27(32)	1(5)	2(4)	15(11)	1(3)	2(3)	27(33)	2(4)	3(6)
	I	7(4)	6(2)	7(5)	10(7)	10(7)	8(5)	8(7)	9(7)	9(8)
	II[b]	20(14)	16(6)	24(12)	27(23)	21(18)	10(7)	27(25)	20(18)	15(13)
	III	22(14)	21(6)	11(8)	33(29)	18(18)	10(7)	23(25)	19(18)	14(13)

[a] Metal complex; 5×10^{-3} mol, Grignard reagent; 0·1 mol.

[b] I: 3,4-Dimethyl-1,5-hexadiene; II: 3-Methyl-1,5-heptadiene; III: 2,6-Octadiene.

Structures of these compounds were established in the previous paper.[1]

Table 3. Stoichiometric reaction of π-allylic metal complex with Grignard reagent

	Complex[a]	Complex I		Complex II		Complex III		Complex IV	
	RMgX	MeMgI	n-BuMgBr	MeMgI	n-PrMgBr	MeMgI	n-BuMgBr	MeMgI	n-PrMgBr
	R(+ H)	10	trace	61	15	10	trace	70	14
reaction products	R(− H)[b]	—	80	—	61	—	51	—	55
	Propylene	11	83	—	61	13	63	—	55
	Butene-2	—	—	71	75	—	—	78	78
	H_2	—	—	—	4	—	—	—	5·6
	R—R	trace	20	trace	4	trace	35	trace	7
	$RCH_2CH{=}CH_2$	79	trace	—	—	73	trace	—	—
	$RCH_2CH{=}CHCH_3$	—	—	4	trace	—	—	1	2
	1,5-Hexadiene	4	3	—	—	21	28	—	—
	C_8 diene[c]	—	—	25	24	—	—	27	14·4

[a] Complex I: Bis(π-allylnickel bromide); Complex II: Bis(π-crotylnickel); Complex III: π-Allyliron tricarbonyl bromide; Complex IV: π-Crotyliron tricarbonyl bromide.

[b] R(− H) stands for olefines (e.g. propylene from n-PrMgBr).

[c] C_8 diene means the total yields of I, II and III in Table 2.

mixture and hydrogen in considerable amounts. The results indicate that not only the Fe complex but also the Ni complex undergo ligand exchange in the reaction with Grignard reagent, and lead us to the conclusion that the increased lability for exchange with the π-crotyl metal complexes, irrespective of the kind of metal, compared to that with π-allyl Ni or Co complexes is the major reason for the different outcome observed in the catalytic reactions of allyl and crotyl halides.

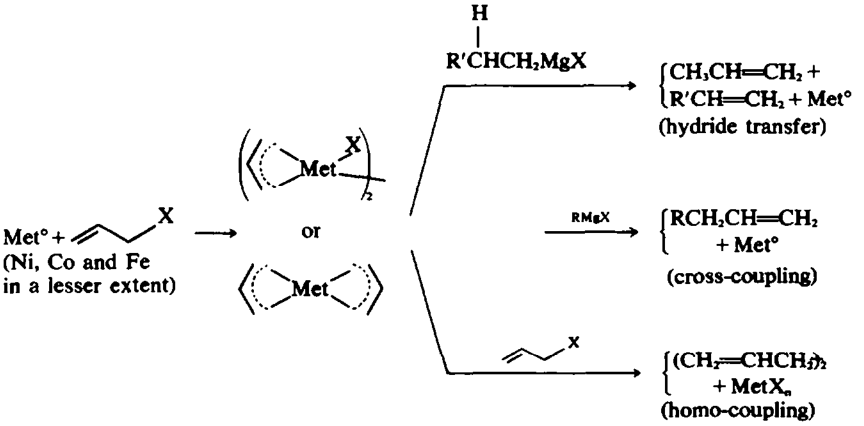
Stoichiometric reaction of Grignard reagents with metallic halide (Ni, Co, Fe and Cu) proceeded similarly with nearly complete decomposition of the Grignard reagent (RMgX) to form R(−H) and R(+ H) under the same condition.

The reaction pathways. Plausible pathways for the present catalytic reactions of allyl and crotyl halides with Grignard reagent can be depicted as follows.

Reduction of metallic halides with RMgX

$$RMgX + MetX_n \rightarrow R_nMet \begin{cases} \nearrow R(+H) + R(-H) + Met^\circ & (1) \\ \searrow R(-H) + H_2 + Met^\circ & (2) \end{cases}$$

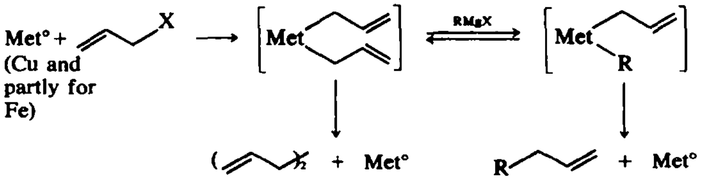
Reaction of allyl halides



(3)

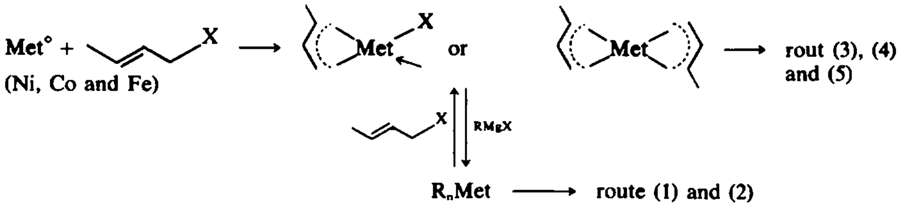
(4)

(5)



(6)

Reaction of crotyl halides



(7)

Eqs 1 and 2 represent the formation of low valent metals (probably of zero valency) in the initial step and in the regeneration step *via* an intermediate, R$_n$Met, which decomposes mainly by disproportionation (Eq 1) but also partly by a secondary route to form hydrogen (Eq 2), depending on the availability of β-hydrogen in R.

The resulting zero-valent Ni or Co undergoes oxidative addition to give π-allylic metal intermediate in the presence of a large amount of allylic halide.

The reactions of the π-allyl metal intermediate with Grignard reagent or allyl halide by three pathways (Eqs 3–5) have been discussed in the previous paper.[1]

Metathesis to form σ-allyl metal species can be considered to be the principal route for Cu(II) halide.

Participation of the σ-type intermediate in the Cu(II) chloride catalyzed reaction does not conflict with the formation of a considerable amount of homo-coupling product, 1,5-hexadiene or C_8 diene mixture, along with the cross-coupling product, and can explain the observed fact that changes of Grignard reagent and allylic halide exerted only a small effect on the reaction pathways. Fe(III) chloride must behave intermediately between the two extremes.

Although similar argument can be applied to the reaction of crotyl halide, the reactivities of the π-crotyl metal intermediates with Ni, Co and Fe differ to some extent from those of the corresponding π-allyl metal intermediates.

The crotyl metal intermediate shows an increased tendency to direct the reaction into the homo-coupling route (Eq 5), and it can enter into ligand exchange with Grignard reagent (Eq 7). The lesser dependency of the yield of C_8 diene mixture on the structure of the Grignard reagent in the crotyl chloride reaction must be a manifestation of the former property.

Presence of the latter process is clearly evidenced by the reaction of π-crotyl metal complexes under stoichiometric conditions.

This process also affords the most probable explanation for hydrogen formation in the crotyl chloride reactions.

EXPERIMENTAL

Materials. Commercial MeI, n-BuBr, n-PrBr, and iso-PrBr were purified by distillation. Bis(π-allylnickel bromide) was prepared from allyl bromide and nickel carbonyl according to Fisher's method;[2] m.p. 92–95°C (dec) (lit. m.p. 93–95°C dec). Bis(π-crotylnickel) was prepared from crotylmagnesium chloride and nickel chloride according to Wilke's method.[3] π-Allylcobalt tricarbonyl was prepared from allyl bromide and sodium cobalt tetracarbonyl[9] according to Heck's method.[4] π-Crotylcobalt tricarbonyl was prepared from crotyl bromide and sodium cobalt tetracarbonyl according to Heck's method;[4] b.p 34–35°/6 mmHg (lit. b.p. 36°/4–5 mmHg). π-Allyliron tricarbonyl bromide was prepared from allyl chloride and iron nonacarbonyl according to Murdoch's method.[5]

π-Crotyliron tricarbonyl bromide was prepared from crotyl bromide and iron nonacarbonyl according to Murdoch's method;[5] m.p. 33–34° (lit. m.p. 34·5°).

Catalytic reaction. Grignard reagent (0·1 mol) in ether (30 ml) was added (− 50°) to a suspension of a catalytic amount (0·1 × 1/200 mol) of π-allylic metal complex in anhydrous ether under N_2. The mixture was stirred until the evolution of gas ceased (reaction A). To the resultant soln, an equiv amount of allylic halide (0·1 mol) in ether was added at − 50° with vigorous stirring, then the soln was heated under reflux until the evolution of gas stopped (reaction B).

The mixture was hydrolyzed in the usual manner.

The liquid product was obtained by distillation of the dried etheral extract. For crotyl halides, the product was analyzed by gas chromatography using 2 m column packed with Silicon 703 (20%)-Celite 545; while for allyl bromide, the ethereal solution containing an internal standard (cyclohexene) was directly injected onto a Golay column HB 2000, 45 m.

The composition of gaseous products obtained in reactions A and B was determined using a silica gel column (2 m) for methane and ethane, and a benzyl ether column (40%, 6 m) for other gaseous hydrocarbons. The amount of hydrogen was determined using a correction factor for the area ratio of the GLC obtained with a mixture of equal volumes of propylene and hydrogen.

Stoichiometric reaction. To the π-allylic metal complex (0·1 mol) suspended in ether (20 ml), an equimolar amount of Grignard reagent was added under N_2 at 0°.

The resultant soln was refluxed until the evolution of gas ceased.

After hydrolysis, gaseous and liquid products were analyzed by GLC in a similar manner as described above.

REFERENCES

[1] Y. Ohbe and T. Matsuda, *Tetrahedron* **29**, 2989 (1973)

[2] E. O. Fischer and G. Burger, *Z. Naturforsch* **16b**, 77 (1961)

[3] G. Wilke, B. Bogdanovic, P. Hardt, P. Heimbach, W. Keim, M. Kroner, W. Oberkirch, K. Tanaka, E. Steinrucke, D. Walter and H. Zimmerman, *Angew. Chem.* Intern. Ed. Engl. **5**, 151 (1966)

[4] R. F. Heck and D. S. Breslow, *J. Am. Chem. Soc.* **83**, 1097 (1961)

[5] H. D. Murdoch and E. Weiss, *Helv Chim. Acta* 1927 (1962)

[6] M. Tamura dnd J. Kochi, *J. Am. Chem. Soc.* **93**, 1483 (1971)

[7] E. J. Corey and M. F. Semmelhack, *Ibid.* **89**, 2755 (1967)

[8] G. M. Whitesides, E. R. Stedronsky, C. P. Casey and J. S. Filippo, *Ibid.* **92**, 1426 (1970)

[9] W. Hieber, O. Vohler and G. Braun, *Z. Naturforsch.* **13b**, 192 (1958)