

Preliminary communication

CROSS-COUPLING REACTION OF SECONDARY ALKYL GRIGNARD REAGENTS WITH ALLYLIC ALCOHOLS CATALYZED BY DICHLORO[1,1'-BIS(DIPHENYLPHOSPHINO)-FERROCENE]PALLADIUM(II)

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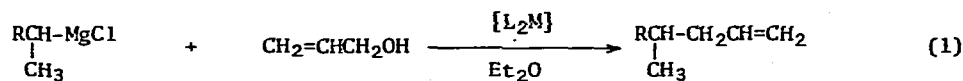
Summary

Dichloro[1,1'-bis(diphenylphosphino)ferrocene]palladium(II) was found to catalyze the reaction of allylic alcohols with 2-octylmagnesium chloride and 1-phenylethylmagnesium chloride to give the corresponding cross-coupling products in high yields.

Felkin and coworkers [1] have reported that phosphine-nickel complexes catalyze the cross-coupling reaction of allylic alcohols with Grignard reagents. Although phenyl, benzyl, and methyl Grignard reagents have been successfully used for this nickel-catalyzed cross-coupling, alkyl Grignard reagents containing β -hydrogens have not given satisfactory results due to the reduction of allylic alcohols as a side-reaction, and no instances of the coupling of secondary alkyl Grignard reagents have been reported [2]. We report here that the cross-coupling reaction of secondary alkyl Grignard reagents with allylic alcohols could be attained for the first time by the use of a palladium complex containing a bidentate phosphine, especially 1,1'-bis(diphenylphosphino)ferrocene (dppf), as a catalyst.

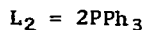
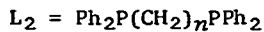
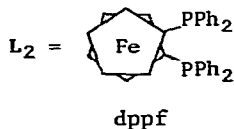
Catalytic activity of some palladium and nickel complexes were examined in the reaction of 2-octylmagnesium chloride (1a) and 1-phenylethylmagnesium chloride (1b) with allyl alcohol (eq. 1). The reaction conditions and results are summarized in Table 1.

C2

1a: R = *n*-C₆H₁₃

2a,b

1b: R = Ph

*n* = 2: dppe*n* = 3: dppp*n* = 4: dppb

As shown in Table 1, PdCl₂(dppf) [3] is the best catalyst, giving rise to the coupling products, 4-methyl-1-decene (2a) and 4-phenyl-1-pentene (2b), in over 90% yields. Of the other palladium complexes, PdCl₂(dppb) showed considerably high activity, while the palladium complexes of triphenylphosphine, dppe, or dppp were much less active. The phosphine-nickel complexes, which have been used for the reaction of phenyl, methyl, and propyl Grignard reagents with allylic alcohols [1], were almost inactive in the present reactions. It is interesting that the catalytic activity of the palladium complexes with bidentate phosphine ligands is strongly dependent upon the molecular framework lying

TABLE 1

CROSS-COUPLING OF SECONDARY ALKYL GRIGNARD REAGENTS WITH ALLYL ALCOHOL IN THE PRESENCE OF PALLADIUM AND NICKEL COMPLEXES^a

Catalyst	Yield (%) ^{b,c} of <i>n</i> -C ₆ H ₁₃ CHMeCH ₂ CH=CH ₂ (2a)	Yield (%) ^{b,d} of PhCHMeCH ₂ CH=CH ₂ (2b)
PdCl ₂ (dppf)	95	91
Pd(PPh ₃) ₄	5	38
PdCl ₂ (dppe)	7	26
PdCl ₂ (dppp)	25	52
PdCl ₂ (dppb)	89	85
NiCl ₂ (dppp)	2	15
NiCl ₂ (PPh ₃) ₂	5	5

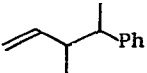
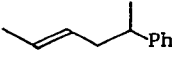
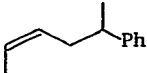

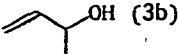
^a To a mixture of allyl alcohol (1 mmol) and a catalyst (0.05 mmol) was added a Grignard solution (1) (4 mmol) in ether. The mixture was refluxed for 5 h, hydrolyzed, and then analyzed by GLC. ^b Determined by GLC using an internal standard. ^c Reaction with 2-octylmagnesium chloride (1a). ^d Reaction with 1-phenylethylmagnesium chloride (1b).

between the two diphenylphosphino groups in the ligand. The order of activity is $dppf > dppb > dppp > dppe$ for the reaction of both 1a and 1b. The superiority of $PdCl_2(dppf)$ over others has also been observed in the coupling reaction of secondary alkyl Grignard reagents with aryl and vinyl halides [3]. It should be noted that the present coupling reaction was not accompanied by alkyl group isomerization from secondary to primary, often observed in the palladium or nickel catalyzed coupling reaction of secondary alkyl Grignard reagents [2], regardless of the structure of the catalyst employed.

The catalyst $PdCl_2(dppf)$ was also effective for other allylic alcohols. Thus, 2-methyl-4-phenyl-1-pentene was obtained in 80% yield in the reaction of 2-methyl-2-propen-1-ol with the 1-phenylethyl Grignard reagent (1b) in the presence of $PdCl_2(dppf)$. The reaction of 1b with (*E*)-2-buten-1-ol (3a) or 3-buten-2-ol (3b) gave a mixture of coupling products (see Table 2). The formation of an S_N1 -type product together with an S_N2 -type product might suggest that the coupling reaction proceeds via π -allylpalladium intermediates [4].

Further work on the mechanism of this reaction is in progress.

TABLE 2
CROSS-COUPLING OF 1-PHENYLETHYLMAGNESIUM CHLORIDE (1b) WITH ALLYLIC ALCOHOLS (3) IN THE PRESENCE OF $PdCl_2(dppf)$ ^a

Allylic alcohol	Yield (%) ^b of the products		
			
 (3a)	23	44	0
 (3b)	37	20	7

^a 3/1b/ $PdCl_2(dppf)$ = 1/4/0.05, refluxed in ether for 9 h. ^b Determined by GLC using an internal standard.

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References

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- 2 For a pertinent review concerning transition metal catalyzed coupling reactions, see K. Tamao and M. Kumada, in "Organometallic Reactions and Syntheses", E.I. Becker and M. Tsutsui, Eds., Plenum, New York, in press.
- 3 T. Hayashi, M. Konishi and M. Kumada, *Tetrahedron Lett.*, (1979) 1871.
- 4 Felkin and coworkers have proposed the mechanism including π -allyl-nickel intermediates for the nickel catalyzed coupling reactions (ref. 1).