

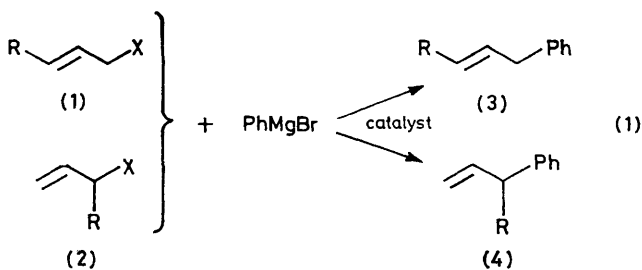
Regioselective Allylation of a Grignard Reagent Catalysed by Phosphine-Nickel and -Palladium Complexes

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Summary Nickel and palladium complexes of the 1,1'-bis(diphenylphosphino)ferrocene ligand effectively catalysed the regioselective cross-coupling of allylic ethers with phenylmagnesium bromide; use of the nickel catalyst leads to carbon-carbon bond formation giving the terminal alkene while the palladium catalyst gives the non-terminal alkene.

THERE has been intense interest in the control of regiochemistry in coupling reactions of allylic systems with organometallics.^{1,2} Here we report a new type of regioselective and high-yielding allylation reaction of a Grignard reagent catalysed by nickel- or palladium-phosphine complexes, where the regiochemistry of the product is dependent entirely on the catalyst; either of the isomeric products (3) or (4) shown in equation (1) can be obtained selectively by the choice of an appropriate catalyst from either of the starting allylic compounds (1) or (2).



a; R = Me, X = OSiEt₃
 b; R = Prⁿ, X = OSiMe₃
 c; R = Me, X = OPh
 d; R = Me, X = OTHP
 e; R = Me, X = Cl
 f; R = Me, X = OH

THP = Tetrahydropyran-2-yl.

Some phosphine-nickel and -palladium complexes were tested for catalytic activity and regioselectivity in the reaction of phenylmagnesium bromide with (*E*)-1-triethyl-

siloxylbut-2-ene (1a) and 3-triethylsiloxylbut-1-ene (2a). The reaction conditions and results are summarized in the Table.

TABLE. Reactions of allyl silyl ethers with phenylmagnesium bromide in the presence of nickel and palladium complexes.^a

Allyl ether	Catalyst ^b	Time/h	Total yield ^c /%	Product ratio ^d (3)(<i>E/Z</i>):(4)
(1a)	i	4	100 (85)	12(11/1):88
	ii	40	44	59(59/0):41
	iii	4	100	67(66/1):33
	iv	4	100 (75)	96(92/4):4
	v	40	3	
	vi	40	68	93(80/13):7
	vii	20	52	90(85/5):10
(2a)	i	4	91	19(10/9):81
	ii	40	81	58(53/5):42
	iii	4	93	55(39/16):45
	iv	4	83	91(75/16):9
	vi	40	60	88(80/8):12
	(1b)	i	20	(92)
iv		20	(91)	93(87/6):7

^a To a mixture of the allyl ether (2 mmol) and catalyst (0.04 mmol) was added the Grignard solution (4 mmol) in ether. The mixture was stirred at room temperature for a given period, hydrolysed, and then analysed by g.l.c. ^b i, NiCl₂(dppf); ii, NiCl₂(dppp); iii, NiCl₂(PPh₃)₂; iv, PdCl₂(dppf); v, PdCl₂(dppe); vi, PdCl₂(dppp); vii, Pd(PPh₃)₄. ^c Determined by g.l.c. using an internal standard. Isolated yields are given in parentheses. ^d Isomeric purity was determined by n.m.r. and g.l.c. analysis.

The reaction of (1a) in the presence of NiCl₂(dppf)³ catalyst [dppf = 1,1'-bis(diphenylphosphino)ferrocene]⁴ gave 3-phenylbut-1-ene (4a) selectively rather than its isomer 1-phenylbut-2-ene (3a). The reaction of (2a) catalysed by NiCl₂(dppf) also gave (4a) as the main product. Thus NiCl₂(dppf) is a unique catalyst in that it can give rise to regioselective carbon-carbon bond formation yielding the terminal alkene starting with either of the regioisomeric allylic ethers (1a) or (2a). Use of the nickel complexes NiCl₂(PPh₃)₂⁵ and NiCl₂(dppp)⁶ [dppp = 1,3-bis(diphenylphosphino)propane] resulted in the formation of both regioisomers (3a) and (4a) in comparable amounts. Felkin

and co-workers have reported⁷ similar results in that $\text{NiCl}_2(\text{PPh}_3)_2$ catalyst lacks regioselectivity in the reaction of PhMgBr with α - and γ -methylallyl alcohols.

Palladium complexes exhibited the opposite regioselectivity to $\text{NiCl}_2(\text{dppf})$, *i.e.* they preferred the formation of the carbon-carbon bond to give the non-terminal alkene (**3a**) selectively from either (**1a**) or (**2a**).[†] Of the palladium complexes, $\text{PdCl}_2(\text{dppf})$ ⁸ is by far the best catalyst, having both high catalytic activity and high regioselectivity. Similar high regioselectivity was observed in the reaction with $\text{PdCl}_2(\text{dppp})$ [‡] or $\text{Pd}(\text{PPh}_3)_4$,⁹ but they catalysed the reaction only sluggishly. $\text{PdCl}_2(\text{dppe})$ [‡] [$\text{dppe} = 1,2$ -bis(diphenylphosphino)ethane] was almost inactive, as has been found for other Grignard cross-coupling reactions.⁸

The reaction of the other but-2-enyl derivatives (**1c-f**) was also examined in the presence of $\text{NiCl}_2(\text{dppf})$ or $\text{PdCl}_2(\text{dppf})$ catalyst. The phenyl ether (**1c**), tetrahydropyranylether (**1d**), and chloride (**1e**) were all converted into the phenylated products (**3a**) or (**4a**) in > 80% yield (for 20 h at room temperature). The ratios of (**3a**) to (**4a**) obtained in the $\text{NiCl}_2(\text{dppf})$ -catalysed reactions of (**1c**), (**1d**),

and (**1e**) were 14:86, 19:81, and 25:75, respectively, and those obtained in the $\text{PdCl}_2(\text{dppf})$ -catalysed reactions were 90:10, 89:11, and 82:18, respectively. The lower regioselectivity observed with the chloride (**1e**) is ascribed to competing noncatalysed reactions, which give both (**3a**) and (**4a**) in a 2:1 ratio. The alcohol (**1f**) was also phenylated regioselectively with $\text{NiCl}_2(\text{dppf})$ [(**3a**):(**4a**) = 20:80] or $\text{PdCl}_2(\text{dppf})$ catalysts [(**3a**):(**4a**) = 91:9],[§] though the conversion was low (30–50%). Thus, the regioselectivity in the present catalytic allylation is independent of the nature of the leaving group. The nearly identical product distribution from all the starting allylic compounds with each catalyst suggests the formation of a common intermediate, most likely π -allyl(phenyl) ML_2 ($\text{M} = \text{Ni}^7$ or Pd^{10}) species. The nature of the metal and the phosphine ligand must influence the regiochemistry of carbon-carbon bond formation in the reductive elimination from the intermediate.

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[†] Copper salts have been reported to catalyse the Grignard coupling with allylic ethers, sulphides, and sulphones to form carbon-carbon bonds at the less substituted position (A. Commercon, M. Bourgain, M. Delaumeny, J. F. Normant, and J. Villieras, *Tetrahedron Lett.*, 1975, 3837; Y. Gendreau, J. F. Normant, and J. Villieras, *J. Organomet. Chem.*, 1977, 142, 1; M. Julia, A. Righini, and J.-N. Verpeaux, *Tetrahedron Lett.*, 1979, 2393).

[‡] $\text{PdCl}_2(\text{dppe})$ and $\text{PdCl}_2(\text{dppp})$ were prepared by the reaction of dichlorobis(acetonitrile)palladium with a stoichiometric amount of the corresponding diphosphine ligand in benzene. See also W. L. Steffen and G. J. Palenik, *Inorg. Chem.*, 1976, 15, 2432.

[§] The reaction of (**1f**) with 1-phenylethylmagnesium chloride in the presence of $\text{PdCl}_2(\text{dppf})$ gave a mixture of coupling products with lower regioselectivity: T. Hayashi, M. Konishi, and M. Kumada, *J. Organomet. Chem.*, 1980, 186, Cl.

¹ For a review, see R. M. Magid, *Tetrahedron*, 1980, 36, 1901.

² For example, see Y. Yamamoto, S. Yamamoto, H. Yatagai, and K. Maruyama, *J. Am. Chem. Soc.*, 1980, 102, 2318.

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⁴ J. J. Bishop, A. Davison, M. L. Katcher, D. W. Lichtenberg, R. E. Merrill, and J. C. Smart, *J. Organomet. Chem.*, 1971, 27, 241.

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