Available online at www.sciencedirect.com
SCIENCE DIRECT®
Tetrahedron 62 (2006) 1410–1415
Tetrahedron

Cobalt- and rhodium-catalyzed cross-coupling reaction of allylic ethers and halides with organometallic reagents

Hiroto Yasui, Keiya Mizutani, Hideki Yorimitsu* and Koichiro Oshima*

Department of Material Chemistry, Graduate School of Engineering, Kyoto University, Kyoto-daigaku Katsura, Nishikyo-ku, Kyoto 615-8510, Japan

Received 7 October 2005; revised 14 November 2005; accepted 15 November 2005

Abstract—Reactions of 2-alkenyl methyl ether with phenyl, trimethylsilylmethyl, and allyl Grignard reagents in the presence of cobalt(II) complexes are discussed. The success of the reactions heavily depends on the combination of the substrate, ligand, and Grignard reagent. In the reaction of cinnamyl methyl ether, the formation of the linear coupling products predominates over that of the relevant branched products. In the cobalt-catalyzed allylation of allylic ethers, addition of a diphosphine ligand can change the regioselectivity, mainly providing the corresponding branched products. Rhodium complexes catalyze the reactions of allylic ethers and halides with allylmagnesium chloride and allylzinc bromide, respectively, in which the branched coupling product is the major product.

1. Introduction

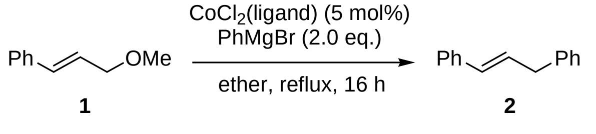
Palladium-, nickel-, and copper-catalyzed cross-coupling reactions of allylic substrates with organometallic reagents are recognized as one of the most useful reactions catalyzed by transition metals.[1] On the other hand, cobalt-catalyzed cross-coupling reactions of allylic substrates are quite rare.[2] We have been interested in cobalt-catalyzed cross-coupling reactions.[3] Here we report the reactions of allylic ethers with phenyl, trimethylsilylmethyl, and allyl Grignard reagents in the presence of cobalt complexes.[4] Rhodium-catalyzed coupling reactions are also disclosed herein.[5]

2. Results and discussions

2.1. Cobalt-catalyzed phenylation reaction of allylic ethers

The coupling reaction of cinnamyl methyl ether (**1**) with phenylmagnesium bromide was first performed (Table 1). A number of ligands were screened, and 1,5-bis(diphenylphosphino)pentane (DPPPEN) proved to be most effective for the phenylation reaction. 3,3-Diphenyl-1-propene was not detected at all. A small amount of β-methylstyrene was the only byproduct in each experiment, along with untouched **1**. The reaction of branched ether **3** with phenylmagnesium reagent under $CoCl_2$(dpppen) catalysis provided linear **2** selectively in good yield (Eq. 1). The regioselectivity of the phenylations suggests that the reactions proceed via a π-allylcobalt intermediate. The phenylation reaction of **1** at 25 °C decreased the yield of **2**. The choice of the solvent was essential to obtain **2** in satisfactory yield. A similar reaction in THF resulted in very low conversion of **1**.

Table 1. Cobalt-catalyzed reaction of cinnamyl methyl ether (**1**) with phenylmagnesium bromide



Entry	Ligand	Yield (%)
1	None	29
2	PPh_3 (10 mol%)	30
3	DPPM	24
4	DPPE	15
5	DPPP	27
6	DPPB	50
7	DPPPEN	72
8	DPPH	58

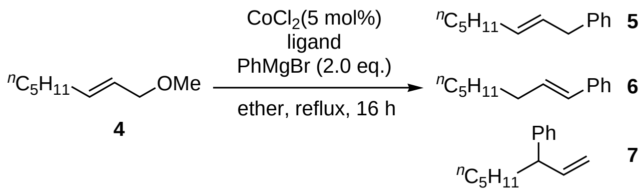
Ligands DPPM–DPPH represent $Ph_2P(CH_2)_nPPh_2$, $n=1$: DPPM; $n=2$: DPPE; $n=3$: DPPP; $n=4$: DPPB; $n=5$: DPPPEN; $n=6$: DPPH.

Keywords: Cross-coupling reaction; Cobalt; Grignard reagent; Rhodium; Allylzinc reagent.

* Corresponding authors. Tel.: +81 75 383 2441; fax: +81 75 383 2438; e-mail addresses: yori@orgrxn.mbox.media.kyoto-u.ac.jp; oshima@orgrxn.mbox.media.kyoto-u.ac.jp

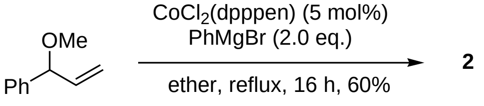
doi:10.1016/j.tet.2005.11.032

Table 2. Cobalt-catalyzed phenylation reaction of *trans*-2-octenyl methyl ether (**4**)



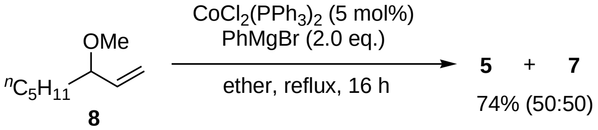
Entry	Ligand (amount)	Combined yield (%)	**5/6/7**
1	DPPPEN (5 mol%)	12	Not determined
2	None	47	58:10:32
3	DPPE (5 mol%)	32	10:53:37
4	PPh_3 (10 mol%)	78	36:7:57
5	$P(2\text{-}MeC_6H_4)_3$ (10 mol%)	39	66:<1:33
6	$P(4\text{-}MeC_6H_4)_3$ (10 mol%)	49	42:6:52
7	$P[3,5\text{-}(CF_3)_2C_6H_3]_3$ (10 mol%)	Trace	Not determined
8	$P(4\text{-}MeOC_6H_4)_3$ (10 mol%)	41	31:16:53

It is worth noting that treatment of cinnamyl bromide under similar conditions furnished a mixture of dimeric compounds such as 1,6-diphenyl-1,5-hexadiene and 3,4-diphenyl-1,5-hexadiene, in addition to a trace of **2**. The formation of the dimeric products implies that single electron transfer from a cobalt complex would yield cinnamyl radical that is destined to dimerize.[2a,c,d]



3 (1)

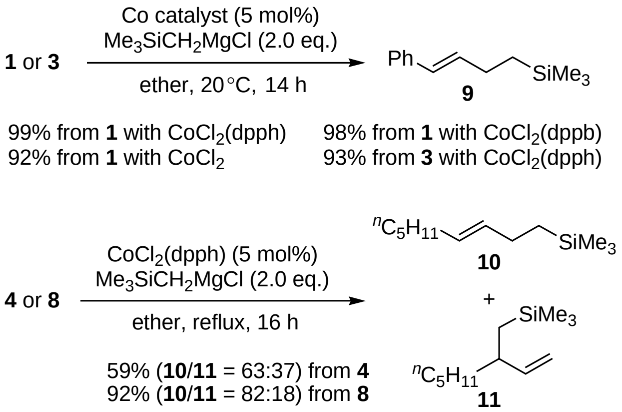
The cobalt-catalyzed phenylation reaction of *trans*-2-octenyl methyl ether (**4**) required triphenylphosphine as a ligand (Table 2, entry 4). A mixture of the corresponding coupling products **5**, **6**, and **7** was obtained. Under the reaction conditions, a part of **5** was transformed into **6**. In contrast to the reaction of **1**, the use of $CoCl_2$(dpppen) led to very poor conversion (entry 1). Without any phosphine ligand, coupling products were obtained in moderate combined yield (entry 2). Other monodentate phosphine ligands were inferior to triphenylphosphine (entries 5–8). Under $CoCl_2(PPh_3)_2$ catalysis, branched ether **8** was also converted into **5** and **7** (Eq. 2), in which no isomerization from **5** to **6** was observed.



8 (2)

2.2. Cobalt-catalyzed trimethylsilylmethylation reaction of allylic ethers

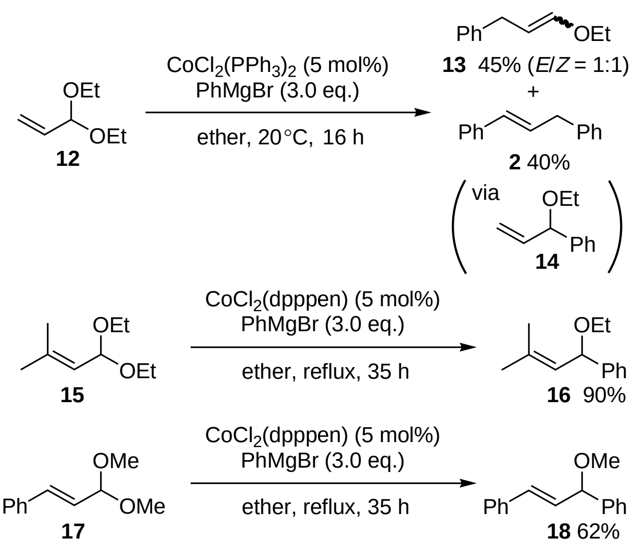
Cross-coupling reaction with Me_3SiCH_2MgCl proceeded much more smoothly than that with PhMgBr (Scheme 1). Treatment of **1** with Me_3SiCH_2MgCl in the presence of $CoCl_2$(dpph) for 14 h at 20 °C afforded the corresponding linear product **9** in 99% yield. Whereas the choice of the ligand was crucial to establish the phenylation, ligandless $CoCl_2$ and $CoCl_2$(dppb) also effected the allylation to afford **9** in 92 and 98% yields, respectively. Reactions of branched **3** with Me_3SiCH_2MgCl afforded **9** in excellent yield. On the other hand, alkyl-substituted allylic ethers **4** and **8** were converted into mixtures of regioisomers **10** and **11**. The reaction required a higher temperature to complete the reaction within a satisfactory reaction time. Trimethylsilylmethylation of branched ether **8** afforded a higher yield of **10** and **11** than that of **4**.



Scheme 1.

2.3. Cobalt-catalyzed reaction of α,β-unsaturated aldehyde dialkyl acetal

Treatment of acrolein diethyl acetal (**12**) with phenylmagnesium bromide in the presence of $CoCl_2(PPh_3)_2$ afforded a mixture of **2** and vinyl ether **13** (Scheme 2) Formation of doubly phenylated **2** would indicate a reaction path via the intermediate **14**. Monophenylation of acetals **15** and **17** having substituents at the terminal olefinic positions was successful under $CoCl_2$(dpppen) catalysis. The dimethyl and phenyl groups of **16** and **18** would interfere with further phenylation.



Scheme 2.