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Reactivity of mixed organozinc and mixed organocopper reagents: 14. Phosphine-nickel catalyzed aryl-allyl coupling of (n-butyl)(aryl)zincs. Ligand and substrate control on the group selectivity and regioselectivity

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ABSTRACT

The group selectivity and regioselectivity in the allylation of mixed (n-butyl)(aryl)zinc reagents in THF depends on the nickel catalyst type and also on nature of the allylic substrate. Allylation of (n-butyl)(phenyl)zinc reagent with alkyl substituted primary allylic chlorides and acetates in the presence of $NiCl_2$(dppf) catalysis affords the phenyl coupling product with γ-selectivity. However, allylation with aryl substituted primary allylic substrates results in both phenyl- and alkyl-coupling products with medium α-selectivity in the presence of $NiCl_2$(dppf) catalysis whereas phenyl coupling product is formed with α-selectivity in the presence of $NiCl_2(Ph_3P)_2$ catalysis. This new $NiCl_2$(dppf) catalyzed protocol for γ-selective aryl allylation of (n-butyl)(aryl)zinc reagents with alkyl substituted primary allylic chlorides in THF at room temperature provides an atom economic alternative to allylation of $(aryl)_2Zn$ reagents. A mechanism for the dependence of group selectivity and regioselectivity of Ni catalyzed allylation of (n-butyl)(aryl)zinc reagents on the catalyst ligand and the substrate was proposed.

1. Introduction

Transition metal catalyzed coupling of organozinc reagents with carbon electrophiles are among the most valuable methodologies in organic synthesis [1–3]. Organozinc reagents RZnX and R_2Zn have proved to be intensively useful due to their easy preparation, high reactivity and functional group tolerance. Diorganozincs, R_2Zn are more reactive than monoorganozincs, RZnX. However, the use of R_2Zn reagents are not atom-economic, since only one of the R groups can be transferred to the electrophile. The problem has been solved by developing mixed diorganozincs, R^1R^2Zn type, in which one of the R groups has a lower transfer rate than the other [4–18], and recently R_RR_TZn type, composed of one transferable group, R_T together with the residual group, R_R with almost no transfer [19,20]. R_RR_TZn reagents have been mostly used in 1,2-addition [19–22] and 1,4-addition reactions [23–26], but their C–C coupling reactions are quite limited [27].

Mixed diorganocuprates, R_RR_TCuM (M = Li, MgBr) have been also developed to use instead of homo diorganocuprates [28,29]. For the group selectivity of mixed cuprates, R^1R^2CuLi the widely accepted hypothesis is that the group with a stronger C–Cu bond acts as the group of lower selectivity, i.e. better residual group [28–31]. Theoretical studies on the control of group selectivity have been reported by Nakamura [32,33] and experimental studies on the effects of organyl groups on the reactivity and selectivity of mixed cuprates have been reported by Bertz [34] and Nakamura [35].

Our group carried out a series of synthetic and mechanistic work [36–40] on the reactivity and group selectivity of mixed diorganozincs, R^1R^2Zn [36]; mixed diorganocuprates, R^1R^2CuM (M = MgBr [37], ZnCl [38]) and Cu catalyzed mixed triorganozincates, $R^1(R^2)_2ZnMgBr$ [38] in their C–C [36], C-COR [39], C-COOR [38] and C–N coupling [40] reactions. We showed that the group selectivity of both mixed diorganocuprates and diorganozincs can be controlled by changing reaction parameters, i.e. the solvent and the temperature as well as the transition metal catalyst and the organocatalyst.

Recently, we have studied on the allylation of mixed (n-alkyl)(aryl)zinc reagents with the aim of controlling not only the group selectivity, but also the regioselectivity by changing the reaction

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parameters [36]. Transition metal catalyzed allylic coupling of Grignard, organolithium and organozinc reagents are very useful reactions in organic synthesis [41]. Over the past decade, investigation of their regiochemistry and stereochemistry have attracted much attention [42]. Cu catalysis favors γ-selective allylation of alkylzinc reagents whereas α-selective allylation takes place in the presence of Ni or Pd catalysis [43]. However, regioselectivity of allylation of arylzinc reagents has not been well documented.

Our previous work on the allylic coupling of (n-butyl)(phenyl) zinc reagent with E-crotyl chloride in the presence of Cu, Pd or Ni catalysis at room temperature (Scheme 1) has revealed the following points:

(i) The allylation in THF in the presence of CuI or CuCN gives almost quantitative total yield, but does not give a satisfactory group selectivity, i.e. n-Bu: Ph transfer ratio is about 2:3 and 3:2 with CuI and CuCN catalysis respectively. n-Bu transfer takes place with γ-selectivity.
(ii) The allylation in the presence of CuI in THF:HMPA (4:1 v/v) results in n-Bu transfer: Ph transfer ratio of about 4:1 (and total n-Bu transfer takes place in the presence of CuCN and $MgCl_2$).
(iii) The allylation in the presence of CuI catalyst and n-Bu_3P (5 mol%) in THF takes place with quantitative yield with a n-Bu transfer: Ph transfer ratio of about 1:3. Ph transfer results in moderate α-selectivity (α:γ = 3:1).
(iv) The allylation takes place with complete Ph transfer in the presence of $NiCl_2(Ph_3P)_2$ in THF with a yield of 76% ($NiCl_2$ catalysis yields 45% yield). α:γ ratio is about 3:2.
(v) The allylation in the presence of $Pd(OAc)_2$ in THF results in complete Ph transfer, however with a quite low yield of 24%.

As seen, in the allylation of n-BuPhZn **1ab**, group selectivity can be controlled by transition metal catalysis, i.e. CuI catalysis leads to n-Bu group and Ph group transfer whereas $NiCl_2(Ph_3P)_2$ catalysis leads to Ph group transfer. It is quite interesting that organic catalysis can also change the group selectivity. The use of HMPA or n-Bu_3P in the presence of CuI catalysis results in an important increase or decrease respectively in n-Bu transfer.

As expected, CuI catalyzed n-Bu group transfer gave predominantly γ-product, whereas $NiCl_2(Ph_3P)_2$ catalyzed Ph group transfer did not take place with complete regioselectivity due to our all efforts. So, we were interested in a study to find new Ni catalysts and/or organic catalysts to control both group selectivity and regioselectivity allylation of mixed (n-alkyl)(aryl)zinc reagents.

In the Ni catalyzed allylation of diorganozincs, we selected (n-alkyl)(aryl)zincs for the following reasons: (i) To control the group selectivity and the regioselectivity in the allylic coupling of n-alkyl and aryl groups on the same reagent, (ii) To find atom-economic routes for regioselective synthesis of n-alkyl or aryl selective allylic coupling products, and (iii) To present new reagent/catalyst systems for catalyst controled regioselective n-alkyl or aryl coupling of substituted primary allylic substrates.

In this paper, we wish to report our succesful results on the group selective and regioselective Ni catalyzed allylation of (n-alkyl)(aryl)zinc reagents and an atom economic synthetic procedure for γ-selective aryl-allyl coupling with alkyl substituted primary allylic chlorides.

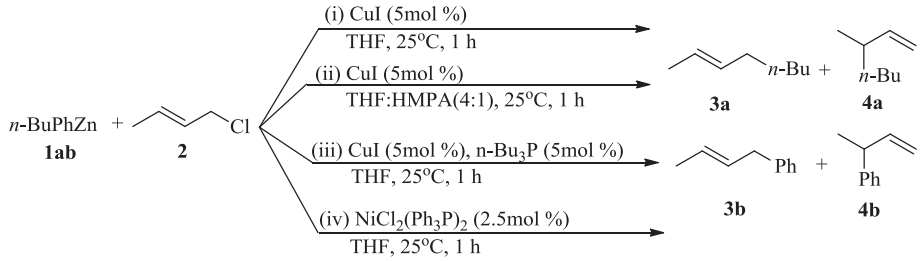
2. Results and discussion

In order to draw conclusions about the effect of Ni catalysis on the group selectivity and regioselectivity of the allylation of (n-alkyl)(aryl)zinc reagents, we planned firstly to investigate the allylation in the presence of Ni catalysts and also in the presence of nickel-copper dual metal catalysis (Scheme 2). Secondly, we were interested in using different γ-mono- and γ,γ-disubstituted allylic substrates in the presence of CuI, $NiCl_2(Ph_3P)_2$ and $NiCl_2$(dppf) to make a comparison for the effects of catalyst, structure of electrophile and leaving group on the group selectivity and regioselectivity.

On the basis of our previous studies [36], allylation of (n-butyl)(phenyl)zinc **1ab** with E-crotyl chloride **2** in THF was chosen as the model reaction. We used magnesium-based organozinc reagents in THF [36]. For the preparation of n-BuPhZn **1ab**, n-butylmagnesium bromide was added to phenylzinc chloride prepared by transmetallation of phenylmagnesium bromide with $ZnCl_2$/THF at −15 °C. Allylation was carried out by adding allylic substrate **2** to the mixed diorganozinc reagent **1ab** in THF in the presence of a transition metal catalyst and if necessary, organic catalyst. Group selectivity of **1ab**, i.e. n-Bu group transfer: Ph group transfer ratio and regioselectivity, i.e. α-coupling: γ-coupling ratio for each group were determined by finding the GC yields of coupled products **3a**, **4a**, **3b** and **4b**.

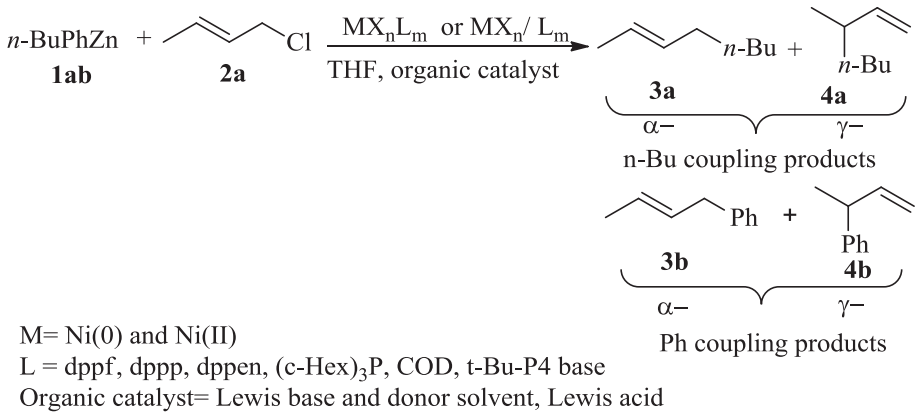
2.1. Nickel catalysis with phosphine ligands

A number of Ni catalysts were screened to find the group selectivity and regioselectivity in the allylation of (n-butyl)(phenyl)zinc **1ab** with E-crotyl chloride **2a**. For ligands in $NiCl_2.L_2$ complexes, we used bidentate phosphine ligands dppp(1,2-bis(diphenylphosphino)



	Coupling yield, %	Group selectivity n-Bu coupling: Ph coupling	Regiochemistry **3a**:**4a**	**3b**:**4b**
(i)	98	42:58	5:95	53:47
(ii)	95	82:18	7:93	63:37
(iii)	100	23:77	5:95	76:24
(iv)	76	0:100	-	59:41

Scheme 1. Group selective and regioselective allylation of (n-butyl)(phenyl)zinc **1ab** with E-crotyl chloride **2** in THF in the presence of transition metal and organic catalysis.

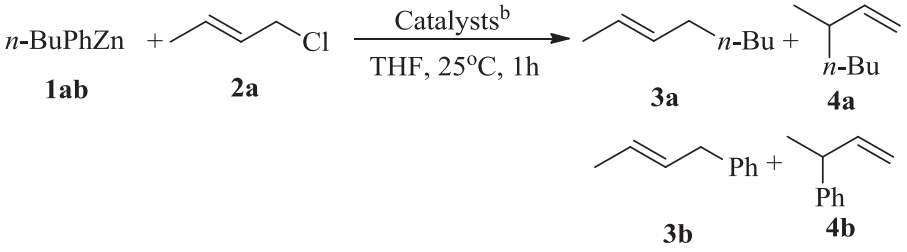


Scheme 2. Group selective and regioselective coupling of (n-butyl)(phenyl)zinc **1ab** with allylic substrates **2** in the presence of transition metal and organic catalyst.

propane), dppen (1,2-bis(diphenylphosphino)pentane), and dppf (1,2-bis(difenilphosphino)ferrocene) and also monodentate phosphine ligand (c-Hex)$_3$P (Table 1). Catalytic reactivity of Ni(COD) and nano NiO were also examined in the presence of Ph_3P and dppf.

As $NiCl_2(Ph_3P)_2$ catalysis gives Ph transfer with α-selectivity (α:γ = 59:41) (Scheme 1), we expected to observe Ph transfer possibly with a higher α-selectivity in the presence of bidentate phosphine ligands. Surprisingly and gratifyingly, allylation of **1ab** in the presence of $NiCl_2$(dppf) resulted in γ-selective Ph transfer with α:γ ratio of 16:84. We also carried out the allylation using the ligand dppf as an organic catalyst in the presence of $NiCl_2$. It is worth noting that using dppf as an additive (entry 2) did not make a change on the γ-selective Ph transfer outcome of the allylation, except gave somewhat lower yield. The optimized conditions in allylation of **1ab** with $NiCl_2/L_2$ were applied to a series of phosphine ligands (entries 3–6). However, $NiCl_2$ catalyzed allylation did not take place in the presence of dppp (entry 3). $NiCl_2$ catalyzed allylation in the presence of dpppen led to a moderate yield and poor regioselectivity (α:γ = 26:74) for Ph transfer (entry 4) compared to $NiCl_2$ catalyzed allylation in the presence of dppf. Using $NiCl_2$(dppf) with Ph_3P ligand (entry 5) did not lead to a change in the yield and α:γ ratio of Ph transfer compared to dppf catalyzed allylation

Table 1
Screening of ligands with Ni(II) and Ni(0) catalysts and Ni(II) and Cu(I) dual catalysis for the group selectivity and regioselectivity in the allylation of n-butylphenylzinc **1ab** with E-crotyl chloride **2a** in THF.[a]



Entry	Catalysts[b]	Coupling yield[c],%	Group selectivity[d]	Regioselectivity	
			n-Bu coupling: Ph coupling	**3a**: **4a**[e]	**3b**: **4b**[f]
1	$NiCl_2$(dppf)	99	0:100	–	16:84
2	$NiCl_2$/dppf	84	0:100	–	11:89
3	$NiCl_2$/dppp	–	–	–	–
4	$NiCl_2$/dppen	42	0:100	–	26:74
5	$NiCl_2$(dppf)/Ph_3P	94	0:100	–	16:84
6	$NiCl_2$/dppf/Ph_3P	84	0:100	–	14:86
7	$NiCl_2[(c\text{-}Hex)_3P]_2$	59	0:100	–	47:53
8	$NiCl_2$/t-Bu-P4 base	40	0:100	–	60:40
9	Nano NiO	–	–	–	–
10	$Ni(COD)_2$	47	0:100	–	62:38
11	$Ni(COD)_2/Ph_3P$	80	0:100	–	73:27
12	$Ni(COD)_2$/dppf	74	0:100	–	41:59
13	$NiCl_2$/CuI	79	30:70	12:88	64:36
14	$NiCl_2$/CuI/Ph_3P	96	21:79	5:95	72:28

[a] All the data are the average of at least two experiments. The reactions were carried out on a 2 mmol scale according to the conditions indicated by the above equation, unless otherwise specified. Molar ratio of **1ab:2** was optimized to be 1.1:1.
[b] Catalytic amounts of all Ni(II) and Ni(0) catalysts and ligands were optimized to 2.5 mol %. 5 mol % CuI was used.
[c] The sum of GC yields of n-Bu coupling products (**3a** and **4a**) and Ph coupling products (**3b** and **4b**).
[d] The ratio of GC yields of (**3a**+ **4a**) and (**3b**+ **4b**).
[e] The ratio of GC yields of **3a** and **4a**.
[f] The ratio of GC yields of **3b** and **4b**.

possibly due to strong binding of dppf as a ligand to Ni. Also, using $NiCl_2$ with dppf and Ph_3P together (entry 6) just resulted in somewhat lower yield. A drastic decrease in the yield and α:γ ratio (47:53) of Ph transfer was observed when $NiCl_2[(c\text{-}Hex)_3P]_2$ was used as a catalyst (entry 7). Phosphazene base (t-Bu-P4 base) as a ligand to $NiCl_2$ gave low yield and poor regioselectivity (α:γ = 60:40) (entry 8). Allylation in the presence of nano NiO was unsuccessful (entry 9). We also tried $Ni(COD)_2$ and $Ni(COD)_2$/L as a catalyst in the allylation (entries 10–12). $Ni(COD)_2$ afforded a moderate yield of Ph transfer, however with a poor α-selectivity (α:γ = 62:38) (entry 10). $Ni(COD)_2/Ph_3P$ resulted in a high yield, but did not make an appreciable change in the regioselectivity (α:γ = 73:27) (entry 11). Catalysis with $Ni(COD)_2$/dppf resulted in a lower α:γ ratio (41:59) (entry 12). As expected, $Ni(COD)_2$ catalysis in the presence of Ph_3P and dppf increased α-selectivity and γ-selectivity, respectively due to a possible ligand exchange.

The allylation of (n-butyl)(phenyl)zinc **1ab** with **2a** was also carried out in the presence of copper and nickel dual metal catalysis with the aim of finding different chemoselectivity and/or regioselectivity (entries13 and 14). As summarized in Scheme 1 catalysis by CuI and $NiCl_2$ resulted in 98% and 76% total yield, respectively. n-Bu transfer: Ph transfer ratio is 42:58 in the presence of CuI and total Ph transfer takes place in the presence of $NiCl_2$. Using CuI and $NiCl_2$ together led to 79% yield with n-Bu transfer: Ph transfer ratio of 30:70 possibly due to the higher catalyst reactivity of Cu (entry 13). As a result, α:γ ratio for n-Bu and Ph transfer did not change appreciably in the presence of Cu and Ni dual catalysis compared to that in the presence of Cu catalysis. As expected, addition of Ph_3P to CuI and $NiCl_2$ resulted in low n-Bu transfer and high Ph transfer with a higher α:γ ratio of selectivity (entry 14).

In the $NiCl_2$(dppf) catalyzed Ph selective allylation of **1ab**, donor solvents and LiCl as a Lewis acid were also used to see if a further improvement could be obtained in the yield and γ-selectivity. However, HMPA, DMF and DMSO as cosolvents all decreased the yield (78, 72 and 83%, respectively) and γ-selectivity (α:γ ratio = 22:78, 54:46 and 32:68, respectively). The use of LiCl also did not give a better result with a yield of 74% and α:γ ratio of 24:76. Carrying out the allylation of **1ab** in THF at 60 °C did not an appreciable change in the chemoselectivity and regioselectivity of the coupling.

As seen, the yield and regioselectivity of Ph transfer in the allylation of (n-butyl)(phenyl)zinc **1ab** with **2a** catalyzed by Ni(II) complexes with mono- and bidentate ligands strongly depends on the ligand.

2.2. Allylic substrate scope in copper and nickel catalyzed allylation

In order to examine the compatibility of the optimized conditions for $NiCl_2$(dppf) catalyzed γ-selective phenyl allylation of (n-butyl)(phenyl)zinc **1ab** with E-crotyl chloride **2a**, we screened a series of γ-mono and γ,γ-disubstituted allylic electrophiles with different leaving groups and observed the dependence of both group selectivity and regioselectivity on the allylic electrophile and also leaving group. The results are given in Table 2. For comparison, allylation of **1ab** were examined not only in the presence of $NiCl_2$(dppf), but also in the presence of CuI, $NiCl_2(Ph_3P)_2$ and $NiCl_2[(c\text{-}Hex)_3P]_2$ catalysis.

As outlined in Scheme 1, CuI catalyzed allylation of **1ab** with E-crotyl chloride **2a** is not group selective. $NiCl_2(Ph_3P)_2$ catalysis leads to Ph selective allylation with an α:γ ratio of about 3:2. In this study, we observed that $NiCl_2$(dppf) afforded Ph transfer with γ-selectivity (entry 1). E-crotyl bromide **2b** showed the same γ-selective Ph transfer in $NiCl_2$(dppf) catalyzed allylation. $NiCl_2(Ph_3P)_2$ catalysis provided Ph selective allylation with an α:γ ratio of about 3:2 (entry 2). CuI catalysis increased α:γ ratio of Ph transfer in the allylation with **2b**. Compared to E-crotyl chloride **2a**, 2-hexenyl acetate **2c** provided somewhat higher and lower yield in $NiCl_2(Ph_3P)_2$ and $NiCl_2$(dppf) catalyzed allylation, respectively. CuI catalyzed allylation was not succesful (entry 3). Diethyl crotyl phosphonate **2d** was not found reactive under the same conditions (entry 4). This screening of leaving groups on γ-alkyl substituted allyl chlorides showed that chloride was the best for their $NiCl_2$(dppf) catalyzed γ-selective arylation using (n-butyl)(aryl) zinc reagents.

Allylation of **1ab** with cinnamyl substrates, **2e** (entry 5) and **2f** (entry 6) in the presence of $NiCl_2(Ph_3P)_2$ catalysis provided mostly α-selective phenyl transfer, as expected. Reactivity of cinnamyl chloride **2e** was found slightly better than that of cinnamyl acetate **2f**. However, in cinnamyl substrates, $NiCl_2$(dppf) catalysis did not lead to Ph selective allylation of **1ab** with γ-selectivity. Yields (and n-Bu transfer: Ph transfer ratios) are 55% (37:63) and 34% (47:53) in the allylation of **2e** and **2f**, respectively. α:γ ratios in Ph transfer with $NiCl_2(Ph_3P)_2$ catalysis were not different than those found with $NiCl_2$(dppf) catalysis.

Among γ,γ-disubstituted allylic substrates tested (entries 7–9), only prenyl chloride (1-chloro-3-methyl-2-butene) **2g** was found reactive in allylation of **1ab** (entry 7). $NiCl_2(Ph_3P)_2$ and $NiCl_2$(dppf) catalysis provided Ph selective allylation with medium and high yields and with low α- and γ-selectivity, respectively. Prenyl acetate **2h** led to very low yields in Cu and Ni catalyzed reactions and geranyl acetate **2ı** did not show reactivity.

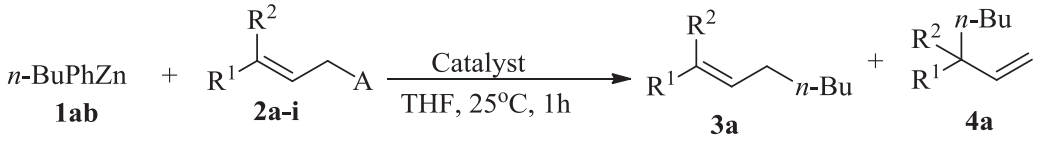
We further investigated Cu and Ni catalyzed allylation of homodiorganozincs, $n\text{-}Bu_2Zn$ **1a₂** and Ph_2Zn **1b₂** with some of the allylic substrates **2a-ı** (Table 3) to find support for group selective and regioselective allylation of mixed n-BuPh. In Ni catalyzed allylation with crotyl substrates **2a** and **2b**, **1a₂** gave quite low yield in the presence of $NiCl_2$(dppf) and showed no reactivity in the presence of $NiCl_2(Ph_3P)_2$, however **1b₂** gave high and quantitative yields (Table 3, entries 1 and 5). These are expected results since Ni catalysis furnished Ph selective allylation of **1ab**. The regioselectivity of Ph transfer in the allylation of **1b₂** also appeared in the Ph transfer in the allylation of **1ab**. It is interesting to observe that γ-selectivity of Ph transfer in $NiCl_2$(dppf) allylation of **1ab** (Table 2, entry 1) was higher than that obtained in the allylation of **1b₂** (Table 3, entry 5).

We also used **1a₂** and **1b₂** in the allylation with cinnamyl substrate **2f** to check the α-selectivity of Ph transfer in the allylation of **1ab** with CuI, $NiCl_2(Ph_3P)_2$ and with $NiCl_2$(dppf) catalysis (Table 2, entry 6). **1a₂** was not reactive in CuI catalyzed allylation with **2f**, however allylation yields in the presence of $NiCl_2(Ph_3P)_2$ and $NiCl_2$(dppf) catalysis were quantitative with α-selectivity (Table 3, entry 3). Allylation of **1b₂** afforded 47%, 66% and 91% yields in the presence of CuI, $NiCl_2(Ph_3P)_2$ and $NiCl_2$(dppf) catalysis. Thus, **1ab** could be readily allylated with **2f** giving a mixture of n-Bu transfer and Ph transfer products in the presence of Ni catalysis. As expected, in allylation of **1ab**, $NiCl_2$(dppf) catalysis led to both n-Bu and Ph transfer, however $NiCl_2(Ph_3P)_2$ catalysis resulted in only Ph transfer (Table 2, entry 6). α-selectivity in both n-Bu transfer and Ph transfer in the allylation of **1a₂** and **1b₂** remained in the allylation of **1ab** with **2f**.

Using activated γ,γ-disubstituted allylic chloride **2g** in the allylation of **1a₂** was not succesful in the presence of $NiCl_2(Ph_3P)_2$ and $NiCl_2$(dppf) catalysis (entry 4), however **1b₂** reacted with 81% and 100% yields (entry 8), respectively. This result supported the observed Ph transfer in the allylation of **1ab**. However, 1:1 α-to γ-selectivity in Ph transfer in allylation of **1b₂** turned to γ-selectivity in the presence of $NiCl_2$(dppf) catalysis.

At this stage, it is worth noting that the outcome of the allylation of (n-butyl)(phenyl)zinc reagent **1ab** in the presence of Cu and Ni catalysts seemed consistent with those obtained for the allylation

Table 2
Group selectivity and regioselectivity in CuI and $NiCl_2.L_2$ (L = Ph_3P, $(c\text{-}Hex)_3P$, dppf) catalyzed reaction of n-butylphenylzinc **1ab** with allylic substrates **2**.[a]

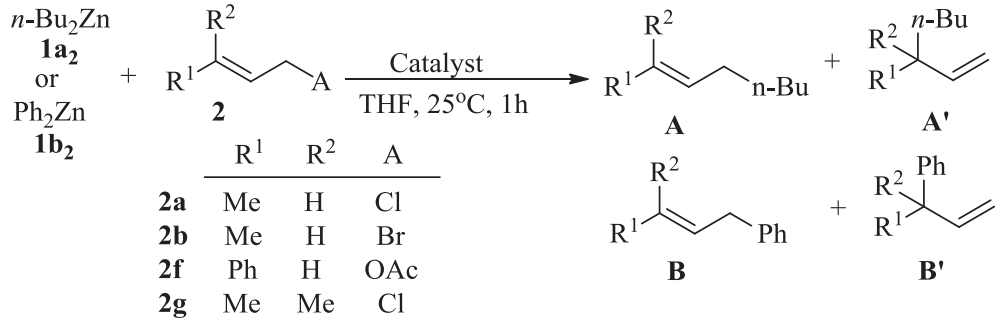


	R^1	R^2	A
2a	Me	H	Cl
2b	Me	H	Br
2c	n-Pr	H	OAc
2d	Me	H	$OPO(OEt)_2$
2e	Ph	H	Cl
2f	Ph	H	OAc
2g	Me	Me	Cl
2h	Me	Me	OAc
2i		Me	OAc

Entry	Allylic substrate	Catalyst[b]	Coupling yield,%[c]	Group selectivity[d]	Regioselectivity	
				n-Bu coupling: Ph coupling	**3a**: **4a**[e]	**3b**: **4b**[f]
1	**2a**	CuI	97[g]	53:47	4:96	43:57
		$NiCl_2(Ph_3P)_2$	76[g]	0:100	–	59:41
		$NiCl_2[(c\text{-}Hex)_3P]_2$	59[h]	0:100	–	47:53
		$NiCl_2$(dppf)	99[h]	0:100	–	16:84
2	**2b**	CuI	99	2:98	0:100	62:38
		$NiCl_2(Ph_3P)_2$	88	0:100	–	65:35
		$NiCl_2$(dppf)	90	0:100	–	18:82
3	**2c**	CuI	16	0:100	–	88:12
		$NiCl_2(Ph_3P)_2$	86	0:100	–	49:51
		$NiCl_2[(c\text{-}Hex)_3P]_2$	33	0:100	–	39:61
		$NiCl_2$(dppf)	70	0:100	–	16:84
4	**2d**	$NiCl_2$(dppf)	No reaction[i]		–	–
5	**2e**	$NiCl_2(Ph_3P)_2$	69[j]	0:100	–	86:14
		$NiCl_2$(dppf)	55	37:63	75:25	62:38
6	**2f**	CuI	20	0:100	–	90:10
		$NiCl_2(Ph_3P)_2$	55[j]	0:100	–	76:24
		$NiCl_2[(c\text{-}Hex)_3P]_2$	28	61:39	0:100	45:55
		$NiCl_2$(dppf)	34[k,l]	47:53	67:33	76:24
7	**2g**	CuI	100	32:68	100:0	78:22
		$NiCl_2(Ph_3P)_2$	54	0:100	–	65:35
		$NiCl_2$(dppf)	99	0:100	–	38:62
8	**2h**	CuI	6	0:100	–	Not determined
		$NiCl_2(Ph_3P)_2$	18	0:100	–	Not determined
		$NiCl_2[(c\text{-}Hex)_3P]_2$	10	0:100	–	Not determined
		$NiCl_2$(dppf)	12	0:100	–	Not determined
9	**2i**	CuI	No reaction			
		$NiCl_2(Ph_3P)_2$	No reaction			
		$NiCl_2$(dppf)	No reaction			

[a] All the data are the average of at least two experiments. The reactions were carried out on a 2 mmol scale according to the conditions indicated by the above equation, unless otherwise specified. Molar ratio of **1ab:2** was optimized to be 1.1:1.
[b] 5 mol % CuI and/or 2.5 mol % Ni catalyst was used.
[c] The sum of GC yields of n-Bu coupling products (**3a** and **4a**) and Ph coupling products (**3b** and **4b**).
[d] The ratio of GC yields of (**3a**+ **4a**) and (**3b**+ **4b**).
[e] The ratio of GC yields of **3a** and **4a**.
[f] The ratio of GC yields of **3b** and **4b**.
[g] Taken from Scheme 1.
[h] Taken from Table 1.
[i] No activity even after 24 h reaction.
[j] Taken from Ref. [46].
[k] In a 2 h reaction, the coupling yield increased to 60%, the group selectivity did not change appreciably (40:60), **3a**:**4a** = 96:4 and **3b**: **4b** = 81:19.
[l] In the presence of 5 mol % of catalyst in a 1 h and 2 h reaction, the coupling yields are 61% and 96%, respectively. Group selectivity is 44:56 in 1 h reaction and 42:58 in 2 h reaction. In 1 h reaction, regioselectivities are **3a**:**4a** = 96:4 and **3b**: **4b** = 74:26. In 2 h reaction, regioselectivities are **3a**:**4a** = 90:10 and **3b**: **4b** = 66:34.

Table 3
Regioselectivity in the reaction of n-Bu_2Zn **$1a_2$** and Ph_2Zn **$1b_2$** with allylic substrates **2** in the presence of CuI and $NiCl_2$.L (L = Ph_3P, dppf).[a]



	R^1	R^2	A
2a	Me	H	Cl
2b	Me	H	Br
2f	Ph	H	OAc
2g	Me	Me	Cl

Entry	R_2Zn	Allylic substrate	Catalyst[b]	Coupling yield,%[c]	Regioselectivity	
					A: **A′**[d]	**B**: **B′**[e]
1	**$1a_2$**	**2a**	CuI	82[f]	7:93	
			$NiCl_2(Ph_3P)_2$	-[f]		
			$NiCl_2$(dppf)	26	6:94	
2		**2b**	CuI	76	16:84	
			$NiCl_2(Ph_3P)_2$	4	Not determined	
			$NiCl_2$(dppf)	28	15:85	
3		**2f**	CuI	–		
			$NiCl_2(Ph_3P)_2$	100	95:5	
			$NiCl_2$(dppf)	96	99:1	
4		**2g**	CuI	63	100:0	
			$NiCl_2(Ph_3P)_2$	–		
			$NiCl_2$(dppf)	–		
5	**$1b_2$**	**2a**	CuI	100[f]		60:40
			$NiCl_2(Ph_3P)_2$	100[f]		56:44
			$NiCl_2$(dppf)	100		37:63
6		**2b**	CuI	98		56:44
			$NiCl_2(Ph_3P)_2$	99		65:35
			$NiCl_2$(dppf)	88		32:68
7		**2f**	CuI	47		81:19
			$NiCl_2(Ph_3P)_2$	66		73:27
			$NiCl_2$(dppf)	91		70:30
8		**2g**	CuI	100		80:20
			$NiCl_2(Ph_3P)_2$	81		77:23
			$NiCl_2$(dppf)	100		53:47

[a] Molar ratio of **$1a_2$:2** and **$1b_2$:2** was optimized to be 1.1:1.
[b] 5 mol % CuI and/or 2.5 mol % Ni catalyst was used.
[c] The sum of GC yields of n-Bu coupling products (**A** and **A′**) or Ph coupling products (**B** and **B′**).
[d] The ratio of GC yields of **A** and **A′**.
[e] The ratio of GC yields of **B** and **B′**.
[f] Taken from Ref. [46].

of the homo diorganozinc reagents, di n-butylzinc **$1a_2$** and diphenylzinc **$1b_2$**.

2.3. γ-Selective aryl-allyl coupling of (n-butyl)(aryl)zinc reagents. A synthetic procedure

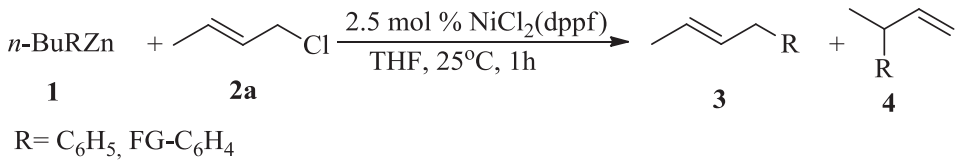
This study showed that $NiCl_2$(dppf) catalyzed allylation of (n-butyl)(aryl)zinc reagents with γ-alkyl and γ,γ-dialkyl substituted allylic chlorides and acetates yields γ-selective aryl-allyl coupling products. Thus, we have been interested in developing a new atom economic method for γ-selective aryl allylation using mixed (n-butyl)(aryl)zinc reagents. The reaction was performed with various (n-butyl)(substituted phenyl)zinc reagents and E-crotyl chloride in the presence of $NiCl_2$(dppf) catalysis (Table 4). The data are averages of at least two independent experiments. Best γ-selective aryl coupling yields were obtained in the allylation of methyl, tert-butyl and methoxy substituted phenyl and biphenyl containing mixed reagents. Yield and regioselectivity decreased in the allylation of bromo substituted phenyl containing zinc reagents. However, $NiCl_2$(dppf) catalyzed coupling of (n-butyl)(aryl)zinc reagents with alkyl substituted allylic chlorides provides a new protocol for the γ-selective aryl transfer. This protocol seems complementary to α-selective aryl transfer using $NiCl_2(Ph_3P)_2$ catalyzed coupling of (n-butyl)(aryl)zinc reagents [36].

2.4. Mechanism

With these results in hand, group selectivity and regioselectivity of Ni catalyzed allylation of (alkyl)(aryl)zinc reagents proved to be a function of catalyst ligand and the nature of allylic substrate as well as solvent. The dependence of allylic regioselectivity on the steric and electronic effects of allylic substrate [44–46] and catalyst [44–47] was already reported in detail for Pd [45] and Ni catalyzed [44,46,47] allylation of Grignard reagents.

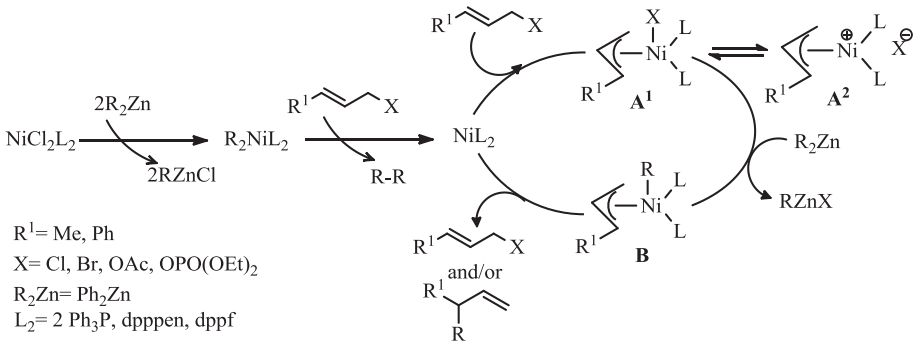
We proposed the catalytic cycle shown in Scheme 3 for Ni catalyzed allylic coupling of (n-butyl)(phenyl)zinc reagent. This mechanism is analogous to that proposed for Ni catalyzed allylic coupling of Grignard reagents [44,47]. For the sake of clarity, the catalytic cycle was drawn for allylation of diphenylzinc **$1b_2$** with allylic reagent, $R^1CH = CH_2CH_2X$ in the presence of a Ni catalyst

Table 4
$NiCl_2$(dppf) catalyzed coupling of (n-butyl)(aryl)zinc reagents with E-crotyl chloride **2a** in THF[a]



Entry.	R	Coupling yield, %[b]	Regoselectivity **3**: **4**[c]
1	Ph	99	16:84
2	4-$MeOC_6H_4$	79	37:63
3	3-$MeOC_6H_4$	77	19:81
4	4-MeC_6H_4	96	22:78
5	3-MeC_6H_4	100	21:79
6	4-BrC_6H_4	54	50:50
7	3-BrC_6H_4	26	65:35
8	4-t-BuC_6H_4	100	16:84
9	C_6H_5–C_6H_5	92	17:83

[a] Reactions were run with 2:1 molar ratio of **1**:**2a**. General reaction conditions: n-BuArZn reagent (2.2 mmol) in THF, E-crotyl chloride (2 mmol), $NiCl_2$(dppf) (0.05 mol) at room temperature for 1 h. For a representative coupling procedure see Experimental Section.
[b] Yields of product mixture of **3** and **4** were determined by GC.
[c] The α:γ ratio was determined by GC.



Scheme 3. Proposed catalytic cycle for $NiCl_2L_2$ catalyzed allylation of diorganozinc reagents.

with two monodentate phosphine ligands or a bidentate diphosphine ligand, i.e. $NiCl_2L_2$ (L_2 = $2Ph_3P$ and dppf, respectively). In the catalytic process, after the generation and coordination of stable $NiCl_2L_2$ complex to the alkene, oxidative addition takes place to give (π-allyl)NiL_2 complex, $\mathbf{A^1}$ and/or $\mathbf{A^2}$ (Scheme 3). It was reported that in the presence of phosphine ligands, an equilibrium between neutral $\mathbf{A^1}$ and cationic $\mathbf{A^2}$ complexes appears and cationic complexes are favored using diphosphine ligands [48]. Diphenylzinc reagent $\mathbf{1b_2}$ attacks the Ni atom in $\mathbf{A^1}$ or $\mathbf{A^2}$ to form the intermediate (π-allyl)$NiRL_2$ **B**. In reductive elimination, regioisomers of allylic coupling product are released with the regeneration of catalyst $NiCl_2$.

Depending on this mechanism, we tried to explain the results on the outcome of the allylation of (n-butyl)(phenyl)zinc **1ab** and diphenylzinc $\mathbf{1b_2}$ with E-crotyl chloride **2a** in the presence of $NiCl_2L_2$ catalysts and also the results on the outcome of the Ni catalyzed allylation of **1ab** and $\mathbf{1b_2}$ with γ-alkyl or γ-phenyl substituted allylic substrates.

(i) Effect of catalyst on the yield and regioselectivity in the coupling of **1ab** and $\mathbf{1b_2}$ with **2a**:

For the C–C coupling of a variety organometallic reagents (Mg, Zn, B, Sn), MCl_2(dppf) (M = Pd, Ni) was already reported to be the most active and selective catalysts among the Pd and Ni catalysts with mono- and diphosphine ligands, MCl_2L_2 (L_2 = $2Ph_3P$, dppe, dppp, dppp, dppb, dpppen (diphenylphosphinoethane, -propane,-butane and –pentane) and metallo-ligand dppf) [44,49–51]. The activity and selectivity of the complexes with bidentate phosphines are known to be strongly dependent upon the P-M-P angle (bite angle) in the complex ML_2Cl_2 [49–51]. In other words, the smaller angle of Cl-M-Cl is important and must be favorable for the easier coupling of π-allyl and R groups in the intermediate (π-allyl)MRL_2 **B** in the reductive elimination step. Our findings on the higher allylation yields of (n-butyl)(phenyl)zinc **1ab** with $NiCl_2$(dppf) or $NiCl_2$/dppf compared to $NiCl_2$/dpppen or $NiCl_2$/dppp (no coupling) (Table 1, entries 1–4) are in accordance with the P–Ni–P bite angle. In the case of monophosphine ligand, Ph_3P, two molecules are free arround the M atom and they may have smaller P-M-P angle than that of dppf ligand [51]. In addition, just a few of the conformations of the free ligands contain the P atoms with the correct orientation to allow bidentate coordination to M. This lower stability of Ph_3P as a ligand compared to dppf can lead to somewhat lower yield allylation of **1ab** with **2a** and also can ensure the turning of regioselectivity from γ-to α-in the $NiCl_2(Ph_3P)_2$ catalysis compared to $NiCl_2$(dppf) catalysis.

It is known that reductive elimination step is favored with coupling partners carrying opposite electronic properties [52]. However, electronic and steric effects are opposing in this step [51,52]. In the catalysis with $NiCl_2$(dppf), due to the stability of

bidentate coordination with a larger P–Ni–P angle, electronic effect may be the main factor. Thus, +I, +M effect of γ-Me group in E-crotyl chloride **2a** is expected to lead the transfer of Ph group (−I, +M effect) of diorganozinc reagents **1ab** and **1b$_2$** to γ-C in allylation (Table 2 entry 1, Table 3 entry 5). In the catalysis with $NiCl_2(Ph_3P)_2$, possibly, occupation of more space by two molecules of ligand compared to $NiCl_2$(dppf) in the coordination sphere of Ni in the intermediate **B** will cause the transfer of R = Ph group to α-C much more than to γ-C due to the steric effects (Table 2 entry 1, Table 3 entry 5).

It was reported that in the Ni catalyzed allylation of phenylmagnesium bromide with crotyl ethers the coupling takes place with higher yield and regioselectivity in the presence of $NiCl_2$(dppf) catalysis compared to $NiCl_2(Ph_3P)_2$ catalysis [44]. The use of $NiCl_2$(dppf) was found to give rise to coupling at γ-C whereas the use of $NiCl_2(Ph_3P)_2$ resulted in mostly at α-C. These results are accordance with our findings.

(ii) Effect of allylic substrate (γ-C substitution of primary allylic chloride and leaving group) on the yield and regioselectivity of Ph transfer in (n-butyl)(phenyl)zinc **1ab** and diphenylzinc **1b$_2$** and group selectivity of **1ab**:

Changing the substituent on γ-C of allylic chloride from Me to Ph, i.e. using cinnamyl chloride **2e** instead of E-crotyl chloride **2a**, and using cinnamyl acetate **2f** instead of 2-hexenyl acetate **2c** led to change in the regioselectivity of Ph transfer in **1ab** and **1b$_2$** and also group selectivity of **1ab** in $NiCl_2$(dppf) catalyzed allylation. According to our suggestions for the regioselectivity of **1ab** and **1b$_2$** in $NiCl_2(Ph_3P)_2$ and $NiCl_2$(dppf) catalyzed allylation with E-crotyl chloride **2a**, we find it reasonable to think that −I, +M effect of γ-Ph group may prevent transfer of Ph group to γ-C in allylation with cinnamyl chloride **2e** and with cinnamyl acetate **2f**. Thus, electronic effect will be an important factor as well as steric factor resulting in mainly α-selectivity in $NiCl_2(Ph_3P)_2$ catalyzed allylations (Table 2 entries 1 and 5; entries 3 and 6). Similarly, in $NiCl_2$(dppf) catalyzed allylations, electronic effect seems to be a dominant factor and mainly γ-selectivity is observed (Table 2 entries 1 and 5; entries 3 and 6). In addition, coupling yield was observed to decrease in the allylation of **1ab** with cinnamyl chloride **2e** compared to crotyl chloride **2a** and also with cinnamyl acetate **2f** compared to 2-hexenyl acetate **2c**. Substitution of Ph group instead of Me group at γ-C also resulted in n-Bu transfer to α-C in $NiCl_2$(dppf) catalyzed allylations as expected (Table 2 entries 3 and 6).

Changing the leaving group from −Cl or −Br to −OAc in crotyl substrate, i.e. allylation with **2b** and **2c** instead of **2a** and also changing the leaving group from −Cl to −OAc in cinnamyl substrate, i.e. allylation with **2f** instead of **2e** did not lead to important changes in the regioselectivity of Ph transfer of **1ab**. Just, the yield of Ph transfer somewhat decreased in allylation with cinnamyl acetate **2f** instead of cinnamyl chloride **2e** (Table 2 entries 5 and 6). However, allylation with crotyl phosphonate **2d** was not succesful.

3. Conclusions

In conclusion, we have demonstrated that (n-butyl)(aryl)zinc reagents react with γ-alkyl substituted primary allylic chlorides in THF in the presence of $NiCl_2$(dppf) catalysis to afford linear alkene with high γ-regioselectivity. This new protocol provides an atom economic alternative to allylation using $(aryl)_2Zn$ reagents in the case of cost-sensitive aryl group. In comparison, allylation of (n-butyl)(phenyl)zinc reagent with cinnamyl chloride gives Ph transfer with α-selectivity in the presence of $NiCl_2(Ph_3P)_2$ catalysis whereas allylation takes place with a n-butyl transfer: phenyl transfer ratio of 37:63 and α: γ ratio of about 3:2 in the presence of $NiCl_2$(dppf) catalysis. Remarkable points of this study are the possibility of obtaining Ni catalyst and allylic substrate controlled regioselectivity and also group selectivity in the allylation of (n-butyl)(aryl)zinc reagents. A mechanism was also proposed for the dependence of group selectivity and regioselectivity of Ni catalyzed allylation of (n-butyl)(aryl)zinc reagents on the catalyst ligand and the substrate.

4. Experimental

4.1. General

All reactions were carried out in oven-dried glassware under a positive pressure of nitrogen using standard syringe-septum cap techniques [53]. GC analyses were performed on a Thermo Finnigan gas chromatograph equipped with a ZB-5 capillary column packed with phenylpolysiloxane using the internal standard technique. THF was distilled from sodium benzophenonedianion; alkyl bromides and bromobenzene were obtained commercially and purified using literature procedures. Mg turnings for Grignard reagents was used without further purification. $ZnCl_2$ (Aldrich) was dried under reduced pressure at 100 °C for 2 h and used as a THF solution. CuI was purified according to the literature procedure, dried under reduced pressure at 60–90 °C for at least 1 h and kept under nitrogen [54]. Ni catalysts and phosphine ligands were used without further purification.

Grignard reagents, RMgBr (R = *n*-Bu, C_6H_5, FG-C_6H_4 (FG = 3-MeO-, 4-MeO-, 3-Me-, 4-Me-, 3-Br-, 4-Br-, 4-t-Bu-, C_6H_5-)) were prepared in THF by standard methods and their concentrations were found by titration before use [55]. For the preparation of (*n*-Bu)(aryl)zinc reagents, (n-Bu)(Ar)Zn (Ar = C_6H_5, FG-C_6H_4, arylzinc chlorides, ArZnCl were reacted with *n*-BuMgBr. ArZnCl were prepared by addition of arylmagnesium bromide (1 mol equiv.) to $ZnCl_2$ (1 mol equiv.) in THF (1.1 ml) at −20 °C and stirring at that temperature for 15 min. To freshly prepared ArZnCl reagent (1 mol equiv.), *n*-BuMgBr (1 mol equiv.) in THF was added dropwise and the mixture was stirred at that temperature for another 15 min.

4.2. Typical procedure for $NiCl_2$(dppf) catalyzed γ-aryl-allyl coupling of (n-butyl)(aryl)zincs with alkyl substituted linear allylic chlorides in THF

To the prepared (n-Bu)(Ar)Zn reagent (2.2 mmol), $NiCl_2$(dppf) (0.05 mmol, 0.0341 g) was added at −20 °C and stirred at that temperature for 15 min. Allylic chloride (2 mmol) was added dropwise at −20 °C. The mixture was stirred at room temperature for 1 h. After addition of internal standard (nonane), the mixture was hydrolyzed with saturated NH_4Cl solution. The aqueous phase was extracted with ether and aliquots were analyzed with GC to determine the coupling yield and α-product: γ-product ratio of aryl coupling product.

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