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Nickel-catalyzed cross-coupling of aryl or 2-menaphthyl quaternary ammonium triflates with organoaluminum reagents

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ABSTRACT

The cross-coupling of aryltrimethylammonium triflates with $AlMe_3$ and β-H-containing trialkylaluminums was performed in dioxane at 110 °C under catalysis of $(dppp)NiCl_2$ to afford alkylated arenes. The cross-coupling of 2-menaphthyltrimethylammonium triflate with trialkylaluminums and 1-naphthyltrimethylammonium triflate with triarylaluminums was also carried out respectively under the same conditions.

1. Introduction

The catalytic activation and transformation of C–N bonds of amines have attracted considerable attention in recent years. Amines are widely available from natural resources and industrial products. The amino groups of aromatic amines and benzylamines are important directing groups which direct the introduction of other functional groups onto the aromatic ring.[1,2] Hence, the transformation of amines through catalytic activation of C–N bonds is an attractive topic. However, direct cleavage of the C–N bond in an amine is rare due to the inertness of the C–N bonds.[3] An effective tactic is to transform amines to ammonium salts, aryldiazonium salts or aryltriazenes to weaken the C–N bonds before catalytic cleavage.[4–27] Early in 1988 Wenkert et al. reported nickel-catalyzed Kumada coupling of aryltrimethylammonium iodides with Grignard reagents in low to moderate yields.[4] In 2003 MacMillan et al. performed cross-coupling of aryltrimethylammonium triflates with arylboronic acids using $Ni(cod)_2$/IMes catalyst.[5] More recently, we and other groups developed transition-metal-catalyzed cross-coupling of aryl- or benzyltrimethylammonium salts with various nucleophiles such as Grignard reagents, organozinc reagents, organoboron reagents, and organotin reagents.[7–16] On the other hand, organoaluminum reagents exhibited high chemoselective reactivity and good compatibility of functional groups in C–C bond formation reactions. Al also has low toxicity and is one of the most inexpensive and earth-abundant metals.[28,29] However, compared with other organometallic nucleophiles using in the cross-coupling utility of organoaluminum reagents is limited. Successful reactions are largely restricted to the couplings of aryl- and alkenylaluminum compounds, while those of alkylaluminum compounds are still rare. The electrophilic partners in the cross-couplings using organoaluminum reagents are mainly restricted to organic halides and triflates.[28–38] It is interesting to explore cross-coupling of aryl- and benzyltrimethylammonium salts with organoaluminum reagents, especially trialkylaluminums. Here we report the results.

2. Results and discussion

Reaction of 1-naphthyltrimethylammonium triflate with $AlMe_3$ was chosen as a model reaction to screen catalyst and

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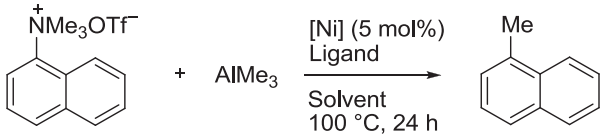
conditions. Nickel was often used in catalyzing the cross-coupling of aryltrimethylammonium salts, while palladium was often employed to catalyze reactions of organoaluminum reagents.[29–34] We chose more earth-abundant nickel to test the catalytic reaction and the results are listed in Table 1. A combination of $Ni(COD)_2$ and IPr was demonstrated to catalyze the reaction and lead to 1-methylnaphthalene in 21% yield (Table 1, entry 1). Better results were achieved when phosphines such as Xantphos and PCy_3 were employed as the ligand (Table 1, entries 2 and 3). Further screening showed that dioxane was better solvent than toluene. The reaction catalyzed by $Ni(COD)_2/PCy_3$ in dioxane led to 93% product yield (Table 1, entry 4). $Ni(PCy_3)_2Cl_2$ gave almost the same catalytic result as the $Ni(COD)_2/PCy_3$ combination (Table 1, entry 5). $Ni(PPh_3)_2Cl_2$ exhibited lower catalytic activity than $Ni(PCy_3)_2Cl_2$, while $Ni(dppp)Cl_2$ revealed almost same activity as $Ni(PCy_3)_2Cl_2$ (Table 1, entries 6 and 7). We also examined solvent effect when $Ni(dppp)Cl_2$ was employed as a catalyst. The results showed that dioxane is more effective than toluene, hexane, DMF, DMAC, THF and Et_2O (Table 1, entries 8–13). Reaction temperature is also an important factor to the reaction. Lower temperature than 100 °C resulted in lower product yields (Table 1, entries 14 and 15). When reaction temperature was raised to 110 °C, the product yield achieved 98% (Table 1, entry 16). Employing 1 equiv. of $AlMe_3$ or 2 mol% $Ni(dppp)Cl_2$ as well as shortening reaction time led to decrease of the product yields (Table 1, entries 17–19).

Although $Ni(PCy_3)_2Cl_2$ exhibited almost same catalytic activity as $Ni(dppp)Cl_2$ based on above evaluation, we chose $Ni(dppp)Cl_2$ as the catalyst for the next substrate extending because (1) dppp is less expensive than PCy_3, and (2) $Ni(dppp)Cl_2$ behaved better than $Ni(PCy_3)_2Cl_2$ in catalyzing the reaction of β-H-containing AlR_3.

Under the optimized conditions, we first examined reaction of $AlMe_3$ with various aryltrimethylammonium triflates. Both 2-naphthyltrimethylammonium triflate and 2-anthryltrimethylammonium triflate exhibited good reactivity. Their reaction with $AlMe_3$ afforded corresponding methylated products in excellent yields (Table 2, entries 1 and 2). However, reaction of 2-(4-methoxynaphthyl)trimethylammonium triflate and 2-(*N*,*N*-dimethylaminonaphthyl)trimethylammonium triflate resulted in relatively low product yields (Table 2, entries 3 and 4). This is ascribed to deactivation of MeO and Me_2N groups and steric hindrance of Me_2N group in 2-(*N*,*N*-dimethylaminonaphthyl)trimethylammonium triflate. Substituted phenyltrimethylammonium triflates exhibited lower reactivity than the naphthyltrimethylammonium triflates (Table 2, entries 5–9). Some of the substrates include reactive functional groups or heterocyclic group (Table 2, entries 6, 7 and 9). However, the existence of side reactions led to relatively low product yields. For example, reaction of 4-(4′–$CF_3C_6H_4$)$C_6H_4NMe_3^+OTf^-$ with $AlMe_3$ gave corresponding product in 64% yield although 4′–$CF_3C_6H_4$ is an activating group in the molecule. Some unidentified side products were observed from TLC of the reaction mixture. The substrates containing carbonyl functional groups such as COOEt and PhC(O) groups were not tolerated. No expected cross-coupling products can be obtained when 4-$EtO_2CC_6H_4NMe_3^+OTf^-$ or 4-PhC(O)$C_6H_4NMe_3^+OTf^-$ were employed as the electrophilic substrates. The catalyst system

Table 1
Screening of reaction conditions.[a]



Entry	[Ni]	Ligand (mol%)	Solvent	Yield (%)[b]
1	$Ni(COD)_2$	IPr·HCl (10)	Toluene	21
2	$Ni(COD)_2$	Xantphos (5)	Toluene	48
3	$Ni(COD)_2$	PCy_3 (10)	Toluene	76
4	$Ni(COD)_2$	PCy_3 (10)	Dioxane	93
5	$Ni(PCy_3)_2Cl_2$		Dioxane	92
6	$Ni(PPh_3)_2Cl_2$		Dioxane	85
7	$Ni(dppp)Cl_2$		Dioxane	92
8	$Ni(dppp)Cl_2$		Toluene	89
9	$Ni(dppp)Cl_2$		Hexane	83
10	$Ni(dppp)Cl_2$		DMF	75
11	$Ni(dppp)Cl_2$		DMAC	87
12[c]	$Ni(dppp)Cl_2$		THF	79
13[d]	$Ni(dppp)Cl_2$		Et_2O	85
14[d]	$Ni(dppp)Cl_2$		Dioxane	80
15[c]	$Ni(dppp)Cl_2$		Dioxane	86
16[e]	$Ni(dppp)Cl_2$		Dioxane	98
17[e,f]	$Ni(dppp)Cl_2$		Dioxane	91
18[e,g]	$Ni(dppp)Cl_2$		Dioxane	87
19[e,h]	$Ni(dppp)Cl_2$		Dioxane	93

[a] Unless otherwise specified, the reactions were carried out using 0.5 mmol of 1-naphthyltrimethylammonium triflate and 1.5 equiv. of $AlMe_3$ in 3 mL of solvent according to the conditions indicated by the above equation.
[b] Isolated yield.
[c] The reaction temperature was 80 °C.
[d] The reaction temperature was 50 °C.
[e] The reaction temperature was 110 °C.
[f] 1.0 equiv. of $AlMe_3$ was employed.
[g] 2 mol% of $Ni(dppp)Cl_2$ was employed.
[h] Reaction time was 12 h.