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Palladium-catalyzed cross-methylation of aryl triflates by intramolecularly stabilized dialkyl-aluminum, -gallium and -indium reagents

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Abstract

Several phenyl and naphthyl triflates undergo catalytic cross-methylation with the monomeric and dimeric dimethyl-aluminum, -gallium and -indium complexes **1a**, **1b**, **1c**, **3a**, **3b** and **3c** in the presence of either $PdCl_2(PPh_3)_2$, $Pd(PPh_3)_4$ or $Pd(binap)(OAc)_2$. 4-Bromophenyl triflate reacts selectively via the triflate function. Structural features of the substrate and the methylating agent, as well as the nature and quality of the palladium catalyst have a considerable influence on the cross-coupling process. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Aryl triflates; Cross-coupling; Aluminum; Gallium; Indium; Palladium catalysts

1. Introduction

Cross-coupling of vinyl and aryl halides is widely applied to C–C bond formation in organic synthesis [1]. Among the best known cross-coupling processes are the Stille [2,3], Suzuki [4], Negishi [5] and Grignard reactions [6] that have received much attention in academic research, although, their involvement in industrial processes is still limited. Recently, we reported the cross-alkylation of aryl iodides, bromides [7] and chlorides [8] by intramolecularly-stabilized dialkylaluminum reagents. Aryl triflates that were frequently employed in the above named reactions [9] have so far been used successfully only once in our aluminum-mediated cross-coupling [10]. Therefore, we found it imperative to continue to investigate the potential utility of these phenol derivatives in cross-alkylation. In this study, we show that the trifluoromethanesulfonyl moiety in aromatic triflates can be activated selectively in the presence of halogen, carbonyl and some other vulnerable functions (Eq. (1)) and that the activity of the triflate group varies along with variations in the structural features

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of the substrate, the alkylating agent and the palladium catalyst.

$$\mathrm{ArOSO_2CF_3} \xrightarrow[\text{(3) aq HCl}]{\text{(1)[Pd], (2)}\mathrm{R_2ML}\text{, 80–90}^{\circ}\text{C}} \mathrm{ArR + M(OH)_3 + X} \tag{1}$$

where M: Al, Ga, In; L: chelating ligand; R: Me; X: ligand and sulfonyl group residues after hydrolysis.

2. Experimental

2.1. General

^{1}H and ^{13}C NMR spectra were recorded on Bruker AMX-200 and AMX-400 instruments. MS measurements were performed on a Hewlett-Packard model 4989A mass spectrometer equipped with an HP gas chromatograph model 5890 series II. Gas chromatographic separation and analyses were carried out with the aid of a Hewlett-Packard GC Model 417. IR spectra were recorded on a Bruker Model Vector 22 FTIR instrument. All manipulations with the aluminum, gallium and indium compounds were performed either in a glove box or in Schlenk tubes under nitrogen or argon. The triflates were prepared by the general procedure reported by Stang et al. from trifluoromethanesulfonic anhydride and the corresponding phenols [11] and their physical data compared with those reported in the literature [12–18]. [3-(Dimethylamino)propyl-*C*,*N*] dimethylaluminum (**1a**) [19], [3-(dimethylamino)propyl-*C*,*N*]dimethylgallium (**1b**) [20], [3-(dimethylamino)propyl-*C*,*N*]dimethylindium (**1c**) [20], [2-[(dimethylamino)methyl] phenyl-*C*,*N*]dimethylaluminum (**2**) [21], bis[μ-[2-(dimethylamino)ethanolato-*N*,*O*:*O*]tetramethyl]dialuminum (**3a**) [22], bis[μ-[2-(dimethylamino)ethanolato-*N*,*O*:*O*]tetramethyl]digallium (**3b**) [23], bis[μ-[2-(dimethylamino)ethanolato-*N*,*O*:*O*]tetramethyl]diindium

Table 1
Comparison between the cross-methylation of 1- and 2-naphthyl triflate by some stabilized dimethyl-aluminum, -gallium and -indium complexes under comparable conditions[a]

Entry	Triflate	Alkylating agent	Catalyst	Reaction time (h)	Yield of methylnaphthalene (%)[b]
1	2-Naphthyl	**1a**	$\mathrm{PdCl_2(PPh_3)_2}$	20	81
2	1-Naphthyl	**1a**	$\mathrm{PdCl_2(PPh_3)_2}$[c]	1	98
3	2-Naphthyl	**1a**	$\mathrm{PdCl_2(PPh_3)_2}$[c]	1	86
4	2-Naphthyl	**1b**	$\mathrm{PdCl_2(PPh_3)_2}$	20	15
5	1-Naphthyl	**1b**	$\mathrm{Pd(PPh_3)_4}$	20	46
6	2-Naphthyl	**1b**	$\mathrm{Pd(PPh_3)_4}$	20	31
7	1-Naphthyl	**1b**	$\mathrm{Pd(binap)(OAc)_2}$	20	58
8	2-Naphthyl	**1b**	$\mathrm{Pd(binap)(OAc)_2}$	20	43
9	1-Naphthyl	**1c**	$\mathrm{PdCl_2(PPh_3)_2}$	3	62
10	2-Naphthyl	**1c**	$\mathrm{PdCl_2(PPh_3)_2}$	20	50
11	1-Naphthyl	**1c**	$\mathrm{Pd(PPh_3)_4}$	4	68
12	2-Naphthyl	**1c**	$\mathrm{Pd(PPh_3)_4}$	20	74
13	1-Naphthyl	**1c**	$\mathrm{Pd(binap)(OAc)_2}$	3	88
14	2-Naphthyl	**1c**	$\mathrm{Pd(binap)(OAc)_2}$	3	97
15	1-Naphthyl	**3a**	$\mathrm{PdCl_2(PPh_3)_2}$[c]	1	11
16	2-Naphthyl	**3a**	$\mathrm{PdCl_2(PPh_3)_2}$[c]	1	44
17	1-Naphthyl	**3a**	$\mathrm{Pd(PPh_3)_4}$	20	20
18	2-Naphthyl	**3a**	$\mathrm{Pd(PPh_3)_4}$	3	54
19	1-Naphthyl	**3a**	$\mathrm{Pd(binap)(OAc)_2}$	20	43
20	2-Naphthyl	**3a**	$\mathrm{Pd(binap)(OAc)_2}$	20	91
21	1-Naphthyl	**3c**	$\mathrm{Pd(PPh_3)_4}$	20	40
22	2-Naphthyl	**2**	$\mathrm{Pd(PPh_3)_4}$	20	5
23	2-Naphthyl	**4**	$\mathrm{PdCl_2(PPh_3)_2}$	20	63

[a] Reactions conditions as specified in Section 2.

[b] The yields given are average of at least two experiments with similar results. The missing percentage reflects the unreacted triflate.

[c] Freshly prepared and recrystallized catalyst.

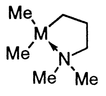
(**3c**) [24], bis[μ-[2-(methylethanolato-O^1:O^1,O^2]tetramethyl]dialuminum (**4**) [25], bis[μ-[2-(methylphenolato-O^1:O^1,O^2]tetramethyl]dialuminum (**5**) [26] and dichlorobis(triphenylphosphine)palladium [27] were prepared as described previously. (±)-Diaceto-[2,2′-bis(diphenylphosphino)-1,1′-dinaphthalene]palladium [Pd(binap)(OAc)$_2$] was formed in situ by interacting of the free ligand (purchased from Stream Chemicals, Inc.) and an equimolar quantity of palladium(II) acetate [10]. Tetrakis(triphenylphosphine)-palladium was purchased from Aldrich Chemical Co.

2.2. 3-Ethylphenyl trifluoromethanesulfonate

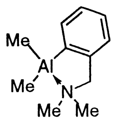
To a solution of 1.01 g (10 mmol) of 3-ethylphenol in 10 ml of CH_2Cl_2 was added under N_2 1.22 g (10 mmol) of dry NEt_3 and 2.82 g (10 mmol) of trifluoromethanesulfonic anhydride in 5 ml of the same solvent. The mixture was stirred for 3 h at room temperature, diluted with 20 ml of pentane and washed twice with cold water, cold 10% aqueous HCl and again with ice water. The organic layer was concentrated, chromatographed on silica gel using hexane as eluent to give 2.20 g (87%) of a colorless oil. The 300 MHz ^{1}H NMR ($CDCl_3$): 1.25 (t = 3, $J = 7.6$ Hz), 2.69 (q = 2, $J = 7.6$ Hz), 7.07 (dd = 2, $J(1) = 7$ Hz, $J(2) = 2$ Hz), 7.08 (s = 1), 7.23 (d = 1, $J = 7$ Hz), 7.35 (td = 1, $J(t) = 7$ Hz, $J(d) = 1$ Hz); ^{13}C (^{1}H) (^{19}F). 75 MHz NMR ($CDCl_3$): 14.88, 28.38, 118.23, 118.65, 120.45, 127.78, 129.81, 147.10, 149.59. Analysis: Found, C = 42.43, H = 3.58. $C_9H_9F_3O_3S$ requires: C = 42.52, H = 3.57.

2.3. General procedure for cross-methylation of aryl triflates

Typically, a pressure tube was charged under exclusion of air with 1.0 mmol of the aryl triflate, the alkylating agent containing 1 meq of metal and 0.02 mmol of $PdCl_2(PPh_3)_2$ in 7 ml of dry benzene. The reaction mixture was heated at 80°C for the desired length of time, cooled to room temperature and quenched with excessive cold 5% aqueous HCl. Products were obtained by phase separation followed by the usual workup, including column chromatography and analyzed by ^{1}H NMR and GC. Some representative results are summarized in Tables 1 and 2.



1a : M = Al
1b : M = Ga
1c : M = In



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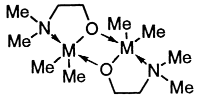
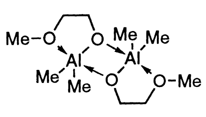


3a : M = Al
3b : M = Ga
3c : M = In



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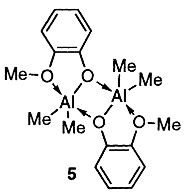

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3. Results and discussion

Although, aryl bromides and triflates are of similar utility for the Stille, Suzuki and Negishi reactions, the triflates were found to be more sensitive than the bromides to the nature of the substrate, the alkylating reagent and the catalyst in cross-methylation by stabilized dimethylaluminum complexes. When 1 mmol of 2-naphthyl triflate and an equimolar quantity of [3-(dimethylamino)propyl]dimethylaluminum (**1a**) are interacted in the presence of 0.02 mmol of our regular stock of $PdCl_2(PPh_3)_2$ (vide infra) under the conditions described in Section 2, 81% of 2-methylnaphthalene is formed as the sole product after 20 h (Table 1, entry 1). Dimeric bis[μ-[2-(dimethylamino)ethanolato]tetramethyldialuminum (**3a**) and bis[1-(2-methoxyethanolato)] tetramethyldialuminum (**4**) react somewhat slower than **1a** (yields 44 and 63% after 20 h, entries 16 and 23, respectively) and the phenylated reagents **2** and **5** do not react at all in the presence of $PdCl_2(PPh_3)_2$. The gallium and indium analogs of **1a**, complexes **1b** and **1c**, form under the same conditions 15 and 50% of the methylated product (entries 4 and 10).

Considerable rate enhancement was observed when our standard $PdCl_2(PPh_3)_2$ catalyst had been replaced by a complex which was freshly prepared and recrystallized before the cross-coupling experiments (compare, e.g. entries 1 and 3). The reason for the differences in activity between the samples of the palladium complexes is not quite clear, as no detectable differences could be observed in their spectra (IR, ^{1}H and ^{31}P NMR) as well as in their mps. It

Table 2
Cross-methylation of phenyl triflate derivatives by some stabilized dimethyl-aluminum, -gallium and -indium reagents under comparable conditions[a]

Entry	Substrate	Alkylating agent	Catalyst	Product	Yield (%)[b]
1	C_6H_5Otf	**1a**	$PdCl_2(PPh_3)_2$[c]	C_6H_5Me	19[d]
2	C_6H_5Otf	**1b**	$Pd(PPh_3)_4$	C_6H_5Me	<1
3	C_6H_5Otf	**1c**	$Pd(PPh_3)_4$	C_6H_5Me	64[e,f]
4	4-MeC_6H_4OTf	**1c**	$Pd(PPh_3)_4$	1,4-$C_6H_4Me_2$	18[e,f]
5	3-EtC_6H_4OTf	**3a**	$PdCl_2(PPh_3)_2$	3-EtC_6H_4Me	70
6	2-ClC_6H_4OTf	**3a**	$PdCl_2(PPh_3)_2$	2-ClC_6H_4Me	25
7	3-ClC_6H_4OTf	**3a**	$PdCl_2(PPh_3)_2$	3-ClC_6H_4Me	<1
8	4-ClC_6H_4OTf	**3a**	$PdCl_2(PPh_3)_2$	4-ClC_6H_4Me	48[f]
9	4-ClC_6H_4OTf	**3a**	$Pd(PPh_3)_4$	4-ClC_6H_4Me	17
10	4-BrC_6H_4OTf	**1b**	$PdCl_2(PPh_3)_2$	4-BrC_6H_4Me	22
11	4-BrC_6H_4OTf	**1c**	$Pd(PPh_3)_4$	4-BrC_6H_4Me	19[e]
12	4-BrC_6H_4OTf	**3a**	$PdCl_2(PPh_3)_2$	4-BrC_6H_4Me	79
13	4-BrC_6H_4OTf	**3a**	$Pd(PPh_3)_4$	4-BrC_6H_4Me	36
14	4-BrC_6H_4OTf	**3a**	$Pd(binap)(OAc)_2$	4-BrC_6H_4Me	52
15	4-$NO_2C_6H_4OTf$	**1b**	$PdCl_2(PPh_3)_2$	4-$NO_2C_6H_4Me$	53
16	4-$NO_2C_6H_4OTf$	**1c**	$Pd(PPh_3)_4$	4-$NO_2C_6H_4Me$	46
17	4-$NO_2C_6H_4OTf$	**3a**	$PdCl_2(PPh_3)_2$	4-$NO_2C_6H_4Me$	84
18	4-(CN)C_6H_4OTf	**1b**	$Pd(binap)(OAc)_2$	4-(CN)C_6H_4Me	21
19	4-(CN)C_6H_4OTf	**3a**	$PdCl_2(PPh_3)_2$	4-(CN)C_6H_4Me	82
20	4-(CHO)C_6H_4OTf	**1b**	$PdCl_2(PPh_3)_2$	4-(CHO)C_6H_4Me	30[g]
21	4-(CHO)C_6H_4OTf	**1c**	$Pd(PPh_3)_4$	4-(CHO)C_6H_4Me	11[g]
22	4-(CHO)C_6H_4OTf	**3a**	$PdCl_2(PPh_3)_2$	4-(CHO)C_6H_4Me	30[g]
23	4-$MeCOC_6H_4OTf$	**1a**	$PdCl_2(PPh_3)_2$	4-$MeCOC_6H_4Me$	12[h]
24	4-$MeCOC_6H_4OTf$	**1a**	$Pd(PPh_3)_4$	4-$MeCOC_6H_4Me$	12[h]
25	4-$MeCOC_6H_4OTf$	**1b**	$PdCl_2(PPh_3)_2$	4-$MeCOC_6H_4Me$	62
26	4-$MeCOC_6H_4OTf$	**1b**	$Pd(PPh_3)_4$	4-$MeCOC_6H_4Me$	57
27	4-$MeCOC_6H_4OTf$	**3b**	$Pd(PPh_3)_4$	4-$MeCOC_6H_4Me$	15
28	4-$MeCOC_6H_4OTf$	**3c**	Pd(PPh3)4	4-$MeCOC_6H_4Me$	51[e]

[a] Reaction conditions as described in the Section 2 for 20 h (unless stated otherwise).

[b] The yields given are average of at least two experiments with similar results. Except for entries 23, 24 and 28 the missing percentage reflects the unreacted triflate.

[c] Freshly prepared catalyst.

[d] 1 h.

[e] 24 h.

[f] 90°C.

[g] In C_6D_6 instead of C_6H_6. The yield was determined by ^1H NMR analysis.

[h] Contaminated with substantial amount of condensation products.

is remarkable that in spite of the fact that the key catalyst in the cross-coupling in aryl bromides and probably also in the reaction of triflates is a Pd(0) species [7], the Pd(II) complexes $PdCl_2(PPh_3)_2$ and $Pd(binap)(OAc)_2$ are usually better catalysts than $Pd(PPh_3)_4$ for the conversion of 2-naphthyl triflate into 2-methylnaphthalene. This observation may be associated with the liberation of two molecules of free PPh_3 during the dissolution of $Pd(PPh_3)_4$. Triphenylphosphine was found to act as an inhibitor in our cross-coupling processes, e.g. the addition of one half equivalent of PPh_3 to the reaction mixture of entry 18 of Table 1, diminishes the rate so that only 19% of 2-methylnaphthalene are formed after 20 h. The high catalytic activity of $Pd(binap)(OAc)_2$ is rationalized by the formation of a charge transfer complex between the bicyclic substrate and the polycyclic catalyst that may facilitate the approach of the palladium atom to the site of reaction.

In analogy to the cross-methylation of 2-naphthyl triflate, 1-naphthyl triflate is converted to 1-methylnaphthalene. The comparative experiments summarized in Table 1 show that the isomeric triflates react at different rates and depend on the nature of the methylating agent. While the dimeric methylating reagent **3a** reacts faster with 2-naphthyl triflate than with the isomer whose triflic group is located at the sterically hindered a-position (see entries 15–20), the monomeric oxygen-free reagents **1a**, **1b** and **1c** usually methylate 1-naphthyl triflate faster than the 2-triflate (entries 2, 3 and 5–12). The reactions of 1- and 2-naphthyl triflates with **1c** in the presence of Pd(binap(OAc)$_2$ are exceptions (entries 13 and 14). The order of activity in the alkylations with the smaller reagents may be rationalized by a combination of steric and electronic effects where the latter one is dominant.

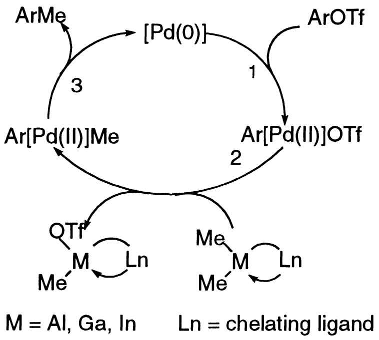
A more pronounced electronic effect has been observed in the cross-methylation of substituted phenyl triflates. Table 2 reveals that in the presence of palladium catalysts 4-nitro-, 4-cyano-, 4-chloro- and 4-bromophenyl triflates (in which the substituents are electron attracting) react smoothly with the dimethylaluminum, -gallium and -indium reagents **1a**, **1b**, **1c** and **3a** (entries 6–19). Complex $PdCl_2(PPh_3)_2$ is usually the best catalyst in these reactions. This complex is somewhat more efficient than $Pd(PPh_3)_4$. Pd(binap)(OAc)$_2$ has here no special advantage as it does not form charge transfer complexes with the monocyclic substrates. 4-Formylphenyl triflate also undergoes cross-methylation but not as fast as the other phenyl triflates with electron-attracting groups. Furthermore, during the workup, both the 4-tolualdehyde and the unreacted starting material undergo in part, a Cannizzaro-type disproportionation. Therefore, we conducted the cross-coupling of this aldehyde in benzene-d_6 and skipped the quenching by aqueous HCl (entries 20–22). Under such conditions the ^{1}H NMR analysis did not trace any carboxylic acids or alcohols. The reaction of 4-(trifluoromethanesulfonyloxy)acetophenone with the gallium reagents **1b** and **3b** formed pure 4-methylacetophenone. However, during the cross-coupling by the aluminum complex **1a** (but not by the gallium reagent **1b**) substantial amounts of condensation compounds were formed along with only 12% of the expected product (entries 23 and 24). The indium methylation agent formed in addition to 4-methylacetophenone also 5–12% of undesired macromolecules. It is notable that unlike 4-bromobenzaldehyde and 4-bromoacetophenone [7], the corresponding triflates do not form with **1a** any methyl carbinols during the cross-coupling process.

In contrast to phenyl triflates with electron-attracting substituents at the *p* position, those with electron releasing groups (CH_3, OCH_3) do not react at all with the aluminum and gallium reagents, although, the indium complex **1c** leads to slow methylation (entry 4). Even unsubstituted phenyl triflate is usually refractory to **1a** and **1b** under our standard reaction conditions. It reacts, however, with **1c** (entry 3) as well as with **1a** in the presence of freshly prepared $PdCl_2(PPh_3)_2$ (vide supra).

As expected 2-chlorophenyl triflate, in which the site of reaction is sterically hindered reacts slower than the 4-chloro-isomer with **3a** (compare entries 6 and 8). Owing to the diminished mesomeric effect of the *m* oriented chlorine atom in 3-chlorophenyl triflate, this compound hardly reacts under similar conditions (entry 7). For the same reason 3-ethylphenyl triflate forms 3-ethyltoluene in good yield (entry 5).

The observation that 4-bromophenyl triflate reacts with the aluminum, gallium and indium reagents to give 4-bromotoluene free of any 4-methylphenyl triflate (entries 10–14) is unexpected in light of the fact that aryl bromides undergo usually faster palladium-catalyzed cross-methylation than the respective aryl triflates (compare, e.g. the reaction of 2-bromonaphthalene that forms with **1a** 98% of 2-methylnaphthalene after 8 h [7] and the reaction of 2-naphthyl triflate that give 81% of this product after 20 h under similar conditions). Moreover, one would predict a certain C–Br bond weakening in 4-BrC_6H_4OTf by the triflate moiety in analogy to the weakening of this bond in 4-BrC_6H_4Cl [8].

Although, we have not performed detailed mechanistic studies, the evidence at hand are compatible with a mechanism similar to that of the cross-alkylation of aryl bromides [7] (Scheme 1). The fact that electron-attracting substituents at the *p* position of the substrates enhance the reaction and vice versa, electron donating groups slow the reaction down, suggest that the oxidative addition (step 1) is rate limiting. In the methylation of aryl chlorides with our alkylating reagents in the presence of electron-rich palladium catalysts, however, step 2 is rate determining [28]. We have already proven that in the cross-methylation of aryl chlorides and bromides both methyl groups of the methylating reagents may take part in the process



Scheme 1. Proposed mechanism for palladium catalyzed cross-methylation of aryl triflates by stabilized dimethyl-aluminum, -gallium and -indium reagents.

and therefore, one half mole of complexes **1a**, **1b** and **1c** or one quarter mole of complexes **3a**, **3b**, **3c** and **4** is sufficient for the methylation of each mole of aryl bromide. In the cross-methylation of aryl triflates only one methyl group of the reagents is applicable. Thus, when, e.g. 1 mmol of 4-bromophenyl triflate and 0.5 mmol of dimeric **3a** (i.e. substrate: Al = 1:1) are reacted in the presence of 0.02 mmol of $PdCl_2(PPh_3)_2$ for 120 h 4-bromotoluene is formed in quantitative yield. If however, the amount of the reagent is reduced to 0.25 mmol (i.e. substrate: Al = 2:1) the maximum yield is 50% even after 10 days at 80°C.

In conclusion, the cross-methylation of aryl triflates depends on the structural features of all the components of the process. The aluminum reagents react usually faster than the gallium and indium complexes. The gallium compounds are the slowest but the most selective ones, substituted phenyl triflates are best activated by $PdCl_2(PPh_3)_2$ while naphthyl triflates give best results in the presence of $Pd(binap)(OAc)_2$. This enables to select the reaction system according to need by adequate variations in the substrate, the alkylating agent or the catalyst.

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