Palladium-Catalyzed Methylation of Aryl and Vinyl Halides by Stabilized Methylaluminum and Methylgallium Complexes

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The intramolecularly stabilized mono- and dialkylaluminum complexes **1a**, **2**, **3**, **4a**, **5a**, **5c**, **6a**, **6c**, **7**, **8**, and **9** in the presence of palladium catalysts, cross-alkylate aryl, vinyl, and benzyl bromides and iodides under mild standard laboratory conditions. Aryl bromides with carbonyl substituents or benzylic halides are converted partially into dialkyl compounds. Under similar conditions, the analogous stabilized dimethylgallium complexes **1b**, **4b**, **5b**, **6b**, and **10** methylate aryl and vinyl bromides and iodides in a highly selective manner. Substituted bromobenzenes XC_6H_4Br, where X = CHO, COPh, CO_2Et, CN, NO_2, Cl, CH_2Br, or CH=CHCOPh, are methylated by the organogallium reagents usually only at the aromatic ring halogen atom to give substituted toluenes as single products. The methylation rates were shown to depend on the nature of the chelating ligands, on the solvent, and on the type of palladium catalyst employed.

Introduction

Although palladium-catalyzed cross-alkylation of aryl and alkenyl halides and pseudohalogenides can be carried out with the aid of a variety of metal and metalloidalkyls,[1] only a few examples for such alkylations by trialkylaluminum reagents have been reported.[2] The fact that just a very small number of scientists have investigated these reactions is probably associated with the pyrophoric nature of these alkylating agents. Recently,[3] we have demonstrated that the air sensitivity of the trialkylaluminum compounds can be reduced by replacement of one alkyl group of R_3Al by a chelating ligand L and that the resulting dialkyl complexes $(R_2AlL)_n$, where $n = 1$ or 2, efficiently alkylate ketones, aldehydes, and activated C=C in aromatic solvents under standard laboratory conditions. However, in contrast to some conventional metal alkyls, the aluminum complexes were found neither to alkylate aryl and aroyl chlorides nor to affect any other types of halides under our reaction conditions. In this paper we report that the stabilized aluminum compounds do alkylate aryl and vinyl bromides and iodides in the presence of palladium catalysts (eq 1) and that the analogous stabilized gallium complexes cross-alkylate these halides in a highly selective manner.

$$RX \xrightarrow[(3)\ \text{aq HCl}]{(1)\ [\text{Pd}],\ (2)\ R'_2AlL} RR' + AlCl_2X + L' \qquad (1)$$

R = aryl, vinyl, benzyl R′ = alkyl
X = Br, I L = chelating ligand
L′ = lignad residue after hydrolysis

Results and Discussion

[(3-Dimethylamino)propyl]dimethylaluminum (**1a**)[4] (obtained from Me_2AlCl and $Me_2N(CH_2)_3Li$[5]) which served in our previous work as the standard methylation agent for transformation of ketones and aldehydes to the respective methyl carbinols[3] has been employed also in the present research. When, for example, a solution of 1 mmol of 1-bromonaphthalene and 2×10^{-2} mmol of $PdCl_2(PPh_3)_2$ in dry benzene was heated at 50−85 °C under N_2 for 30 min, followed by treatment with 0.505 mmol of **1a** in the same solvent at 80−90 °C for 12 h and quenching with cold 2% aqueous hydrochloric acid, 98% of 1-methylnaphthalene was obtained. Although both methyl groups in **1a** were shown to take part in the alkylation process (vide infra), the reaction time could be reduced to 2 h if the molar ratio aluminum complex: bromide was further increased to 1:1. Under similar experimental conditions a variety of other aryl bromides and iodides could be converted into the respective methylated products. Some representative results are summarized in Table 1 (experiments 1−10). It has been shown that the methylation of dihalides proceeds step-

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Table 1. Palladium-Catalyzed Methylation of Representative Aryl, Benzyl, and Vinyl Bromides and Iodides by 1a[a]

expt	substrate	time, h[b]	products (yield, %)
1	bromobenzene	8	toluene (97)
2	iodobenzene	1	toluene (91)
3	1-bromonaphthalene	12	1-methylnaphthalene (98)
4	2-bromonaphthalene	8	2-methylnaphthalene (98)
5	9-bromoanthracene	2	9-methylanthracene (92)[6]
6	2-iodobromobenzene		*o*-xylene (80), 2-bromotoluene (13)
7	1,8-diiodonaphthalene	3	1,8-dimethylnaphthalene (84),[7] 1-iodo−8-methylnaphthalene (7),[8] 1-iodonaphthalene (0.5), 1-methylnaphthalene (0.5)
8	2,2′-diiodo−1,1′-biphenyl	6.5	2,2′-dimethyl−1,1′-biphenyl (99)[9]
9	bis(2-iodophenyl)methane	6	bis(2-methylphenyl)methane (87)[10]
10	3,4-dibromothiophene	3	3-bromo−4-methyltiophene (76),[11] 3,4-dimethylthiophene (14)[12]
11	benzyl bromide	3	ethylbenzene (99)
12	9-bromo−9-phenylfluorene	12	9-methyl−9-phenylfluorene (100)[13]
13	(1-naphthyl)phenylbromomethane	6[c]	α-(1-naphthyl)ethylbenzene (60)[14]
14	(*E*)-β-bromostyrene	5	(*E*)−1-phenyl−1-propene (97)
15	(*Z*)-α-bromostilbene	8	(*Z*)-α-methylstilbene (96)
16	2-bromoindene	2	2-methylindene (88),[15] indene (<1), 2,3-dimethylindene (<1)[16]

[a] Standard reaction conditions: 1 mmol of halide, 2×10^{-2} mmol of $PdCl_2(PPh_3)_2$, in 4 mL of benzene at 50 °C for 30 min; addition of 0.505 mmol of **1a** in 3 mL of the same solvent at 80 °C, N_2 or Ar atmosphere. [b] The time does not include the initial heating at 50 °C. [c] A longer reaction period resulted in the formation of substantial amounts of side products.

Table 2. Palladium-Catalyzed Methylation of Some Functionalized Aryl Bromides by 1a[a]

expt	substrate	time, h[b]	products (yield, %)
1	4-Br C_6H_4CHO[b]	8	4-MeC_6H_4CHO (62), 4-Me$C_6H_4CH_2OH$ (18), 4-Me$C_6H_4CO_2H$ (18)
2	4-Br C_6H_4COPh	19	4-MeC_6H_4C(Me)(Ph)OH (17), 4-MeC_6H_4COPh (3)
3	2-Br $C_6H_4CO_2Et$	12	2-Me$C_6H_4CO_2Et$ (13), $C_6H_5CO_2Et$ (18)
4	3-Br $C_6H_4CO_2Et$	12	3-Me$C_6H_4CO_2Et$ (40), $C_6H_5CO_2Et$ (6)
5	4-Br $C_6H_4CO_2Et$	12	4-Me$C_6H_4CO_2Et$ (75), $C_6H_5CO_2Et$ (10)
6	4-Br C_6H_4CN[b]	8	4-MeC_6H_4CN (81)
7	4-Br $C_6H_4CH_2Br$[b]	3	4-MeC_6H_4Et (16)[c]
8	4-Br $C_6H_4CH{=}CHCOPh$[b]	8	4-Me$C_6H_5CH{=}CHCOPh$ (85)
9	2-Br $C_6H_4C{\equiv}CC_6H_4$−2-Br	3	2-Me$C_6H_4C{\equiv}CC_6H_4$−2-Me (96)[17]

[a] Standard reaction conditions: 1 mmol of bromide in 4 mL of benzene, 2×10^{-2} mmol of $PdCl_2(PPh_3)_2$, in 4 mL of benzene; heating for 30 min at 80 °C; addition of 0.505 mmol of **1a** in 3 mL of the same solvent at 85 °C. [b] Substrate:**1a**:catalyst = 50:50:1. [c] Contaminated with ca. 80% of a variety of bi- and polyphenyl and bi- and polybenzyl derivatives.

wise, i.e., the starting materials are converted initially into the monomethylated products which give dimethylarenes in the second step. Thus, when the dimethylated products start to accumulate, most of the starting dihalides have already been consumed.

Experiments 11−13 indicate that primary benzyl bromides react in a similar fashion. The secondary bromide (1-naphthyl)phenylbromomethane gives however only 60% of the α-(1-naphthyl)ethylbenzene together with undesired side products.

Vinyl bromides could also be methylated by **1a** in high yields. Under the conditions of Table 1, the reactions proceeded with retention of configuration (see experiments 14 and 15). However, when an equimolar rather than a catalytic amount of the palladium complex had been employed, some *Z*−*E* isomerization of the double bond took place. Excess of the palladium compound led also to some hydrogenolysis of the halogen atoms by which nonmethylated hydrocarbons were formed.

Since **1a** affects also carbonyl groups,[3] we have investigated the behavior of the methylation agent toward substituted aryl bromides with vulnerable functional groups (see Table 2). Usually, though not always, both the aromatic halogen and the second function underwent methylation. When only one function had been methylated it was usually the aromatic ring bromide. An exception was 4-bromobenzyl bromide (Table 2, experiment 7) which gave, in addition to a poor yield of *p*-methylethylbenzene, a variety of coupling compounds including bromobibenzyl derivatives. The methylation of the bromobenzaldehyde by the basic reagent (experiment 1) was found to be accompanied by products of a Cannizzaro-like reaction (cf. ref 3). Comparison of experiments 3 and 4 in Table 1 and experiments 3−5 in Table 2 indicates that the methylation processes are affected by steric constraints.

Stabilized alkylaluminum complexes other than **1a** could also be used successfully in the palladium-catalyzed cross-alkylation reactions. The dialkyl complexes **2**, **3**, **4a**, **5a**, **5c**, **6a**, **6c**, **7**, and **8**, as well as the monomethyl compound **9** (Chart 1), have been prepared from R_3Al, R_2AlCl, $RAlCl_2$, or $AlCl_3$ by the general routes used previously in our and other laboratories.[4,18,19] The vari-

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(8) Experimental data: separated from the reaction mixture by a 2 m long GC column packed with 10% OV-101 on Chromosorb W; pale yellow semisolid; 300-MHz ^1H NMR ($CDCl_3$) δ 3.20 (s, 3), 7.37 (dd, 1, $J_{6,7}$ = 5 Hz, $J_{5,7}$ = 1.5 Hz), 7.26−7.38 (m, 2), 7.70 (dd, 1, $J_{5,6}$ = 9 Hz, $J_{5,7}$ = 1.5 Hz), 7.79 (dd, 1, $J_{2,4}$ = 1 Hz, $J_{3,4}$ = 9 Hz), 8.29 (dd, 1, $J_{2,3}$ = 7 Hz, $J_{2,4}$ = 1 Hz); GC-MS (70 eV), 150°) *m/z* (rel intensity) 268 ($M^{\bullet+}$), 100), 141 ($C_{11}H_9^+$, 43), 139 ($C_{11}H_7^+$, 12), 115 ($C_9H_7^+$, 18). Anal. Calcd for $C_{11}H_9I$: C, 49.28; H, 3.38. Found: C, 49.09; H, 3.20.
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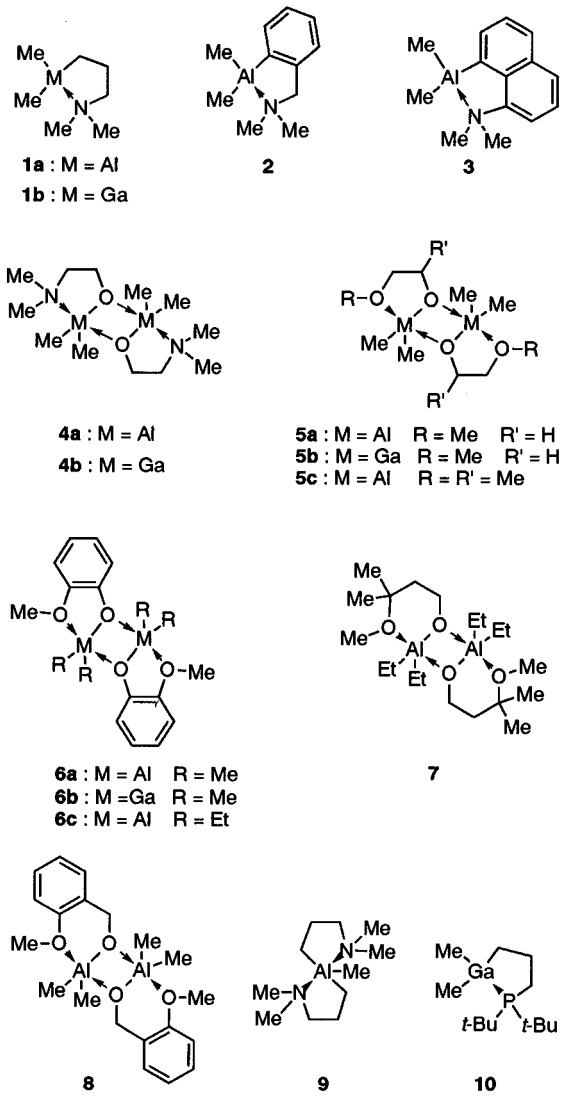
Chart 1



ous aluminum alkoxide derivatives were shown by mass spectral and by X-ray diffraction analyses to exist as dimers, while all the oxygen-deficient complexes proved to be monomers[20] The efficiencies of the stabilized dimethylaluminum complexes were found to vary significantly and to depend in the first place on the structural features of the chelating ligands (vide infra). There has also been observed a substantial difference in activity between the dimethyl- and the diethylaluminum compounds. In general, the stabilized methylaluminum complexes reacted faster than the ethyl analogues and gave in most cases clean methylated products in high yields. The ethylating agents **6c** and **7** formed considerable amounts of ethyl-free parent compounds, in addition to the expected products. For example, upon interaction of **6c** with 9-bromoanthracene for 12 h under our standard conditions, 80% of 9-ethylanthracene and 9% of anthracene were obtained. Similarly **7** and 1-bromonaphthalene gave after 24 h a mixture of 61% of 1-ethylnaphthalene, 19% of naphthalene, and 17% of unreacted starting material. The formation of the dehalogenated arenes can be rationalized either by thermal dissociation

Table 3. Dependence of the Initial Rate of Methylation of 1-Bromonaphthalene by 5a on the Nature of the Palladium Catalyst[a]

palladium catalyst	rel rate	palladium catalyst	rel rate
$Pd(PPh_3)_4$	1.00	$PdCl_2$	0.15
$PdCl_2(PPh_3)_2$	0.93	$Pd(CN)_2$	0.03
$[NH_4]_2[PdCl_4]$	0.40	$Pd(OAc)_2$	0.02

[a] Reaction conditions: 1 mmol of substrate, 2×10^{-2} mmol of palladium compound in 4 mL of benzene for 30 min at 88 °C in a sealed ampule; then addition of 0.252 mmol of **5a** in 3 mL of benzene at the same temperature.

Table 4. Dependence of the Initial Rate of Methylation of 1-Bromonaphthalene by 5a on the Nature of the Reaction Medium[a]

solvent	rel rate	solvent	rel rate
benzene	1.00	ether	0.26
toluene	0.80	chloroform	0.15
heptanes	0.74	1,2-dichloroethane	0.12
chlorobenzene	0.71	tetrahydrofuran	0.11
cyclohexane	0.50	dimethyl sulfoxide	negligible

[a] Reaction conditions as in Table 3 except that the catalyst was $PdCl_2(PPh_3)_2$ and that instead of benzene various dried solvents were used.

of the higher dialkylaluminum complexes into ethylene-aluminum complexes and molecular hydrogen or by their transformation to aluminum hydrides.[21] Since dissociation of the dimethylaluminum complexes is less common, dehalogenation in **1a**-mediated reactions has been observed only in a few cases (see Table 2, experiments 3−5).

The cross-alkylation could be catalyzed by several different palladium compounds. The results of a set of comparative experiments using **5a** as methylating agent are summarized in Table 3. Similar relative rates were observed when dimeric **5a** was replaced by monomeric **1a**. In addition to the palladium catalysts listed in Table 3, we were able to use a sample of 10% Pd/C (that had been purchased from Industrie Engelhard, Rome) for **1a**-mediated methylation of 9-bromoanthracene and (*Z*)-α-bromostilbene under the conditions of Table 1. Both the rate and the selectivity were found to be lower than those in experiments with the homogeneous palladium catalysts. The bromoarene gave after 12 h 9-methylanthracene in 61% yield, and the stilbene derivative formed a mixture of 53% of (*Z*)- and 7% of (*E*)-α-methylstilbene. This discrepancy could be eliminated by pretreatment of the palladium with 2−3 equiv of PPh_3. Under such conditions (*Z*)-α-bromostilbene afforded exclusively the (*Z*)-product in 95% yield. When, however, these experiments were repeated with three other brands of Pd/C, no methylation whatsoever took place (even upon increasing the temperature to 155 °C or increasing the amount of the supported palladium).

The methylations proved to take place in a variety of solvents. The rate was found, however, to depend strongly on the nature of the media. The efficiency of methylation of 1-bromonaphthalene by **5a** in some common solvents is listed in Table 4. Noncoordinating aromatic solvents were shown to be the most effective ones.

Trimethylgallium could be stabilized by the same method as the corresponding aluminum compounds.[4] Complexes **1b**, **4b**, **5b**, **6b**, and **10** have been prepared

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(20) X-ray diffraction analyses of the alkylaluminum and -gallium complexes that have not been described previously will be published in a separate paper.
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Table 5. Palladium-Catalyzed Methylation of Aryl and Vinyl Bromides by Two Stabilized Dimethylgallium Complexes[a]

expt	substrate	gallium complex	time, h[b]	products (yield, %)
1	bromobenzene	**1b**	7	toluene (100)
2	bromobenzene	**5b**	12	toluene (90)
3	4-bromotoluene	**1b**	3[c]	*p*-xylene (48)
4	4-bromoanisole	**1b**	3[d]	4-methoxytoluene (31), 4,4′-dimethoxy−1,1′-biphenyl (5)
5	1-bromonaphthalene	**1b**	15	1-methylnaphthalene (99)
6	1-bromonaphthalene	**5b**	17	1-methylnaphthalene (95), naphthalene (3)
7	(*Z*)-α-bromostilbene	**1b**	3	(*Z*)-α-methylstilbene (89), (*E*)-α-methylstilbene (6)
8	(*Z*)-α-bromostilbene	**5b**	12	(*Z*)-α-methylstilbene (100)

[a] Reaction conditions: 1 mmol of halide, 2×10^{-2} mmol of $PdCl_2(PPh_3)_2$ in 4 mL of benzene; heating for 30 min at 80 °C; addition of 0.505 mmolar equiv of the gallium complex in 3 mL of benzene and heating at the same temperature. [b] At 100% conversion, except when stated otherwise. [c] At 49% conversion. [d] At 40% conversion.

Table 6. Relative Initial Rates of Methylation of 1-Bromonaphthalene by Various Stabilized Aluminum and Gallium Complexes in the Presence of $PdCl_2(PPh_3)_2$ under Comparable Conditions[a]

methylating agent	rel initial rate	methylating agent	rel initial rate
5a	1.00	**4b**	0.30
5c	0.87	**1b**	0.20
2	0.80	**5b**	0.04
3	0.70	**10**	0.04
8	0.56	**9**	0.03
4a	0.47	**6a**	0.03
1a	0.35	**6b**	<0.01

[a] Reaction conditions: 1 mmol of halide, 2×10^{-2} mmol $PdCl_2(PPh_3)_2$; heating in a sealed ampule in 4 mL of benzene for 30 min at 88 °C; then addition of 0.505 mmolar equiv of the alkylating agent in 3 mL of the same solvent; heating at 88 °C.

in the framework of this study, and their capability to act as methylating agents has been investigated. It was found that unlike the analogous aluminum complexes[3] they neither alkylate carbonyl functions nor activated double bonds. They do, however, react smoothly with aryl and alkenyl (but not benzyl) bromides and iodides. Some representative examples are listed in Table 5. The table indicates that **1b** and **5b** differ slightly in their activity and selectivity and that the rates are somewhat slower than those recorded with the aluminum complex **1a**.

In fact, we have compared the methylation potencies of the various aluminum and gallium compounds for 1-bromonaphthalene under comparable conditions and found that several gallium complexes are even superior to some dialkylaluminum compounds. The figures given in Table 6 reveal that while the best aluminum methylating agent is **5a** having an $-O(CH_2)_2OMe$ chelating ligand, the preferred gallium complex is bis[μ-[2-(dimethylamino)ethanolato]tetramethyldigallium (**4b**). It seems that one of the factors, though not the only one, that affects the methylation is steric hindrance. The guaiacol derivatives **6a** and **6b** are the slowest methylating agents among those studied. Since kinetic measurements revealed that the transfer of the first methyl group of the alkylating agents to the substrate is faster than the second one, we found it useful to employ at least equivalent quantities of the aluminum or gallium complexes and the substrate when rapid methylation is required. The monomethylaluminum complex **9** with two chelating $(CH_2)_3NMe$ groups reacts of course much slower than **1a** in which two active methyl groups exist.

Since, in contrast to the aluminum complexes, the gallium compounds do not methylate carbonyl as well as some other vulnerable functions, we were able to selectively substitute the bromine atoms of aryl bromides that have carbonyl, cyano, nitro, chloro,[22] and even benzylic bromo groups. Representative gallium-mediated methylation experiments of such functionalized aryl bromides are summarized in Table 7. To the best of our knowledge, no other current methylating agent affects aromatic bromine atoms in such high selectivity. Both the electronic and the steric structure of the second substituent on the aryl halide affect the rate but have little influence on the nature of the products. In no case did the side products (usually coupling compounds of the starting material) exceed 5%.

Under the conditions for methylation of ketones and aldehydes by **1a**, benzoyl chloride could not be alkylated.[3] Instead, the acid chloride and the chelating ligand residue formed undesired benzoyl derivatives. When, however, the reactions were performed in the presence of catalytic amounts of $PdCl_2(PPh_3)_2$, moderate yields of acetophenone were formed along with decomposition products of the chelating ligands. For example, reaction of 1 mmol of PhCOCl in benzene with 2×10^{-2} mmol of the palladium complex for 30 min at 80 °C, followed by heating for 12 h with either **5a** or **5b**, afforded 29% of the expected acetophenone and 57% of $PhCO_2(CH_2)_2OMe$.

Both the methylations by the aluminum and the gallium complexes must be preceded by interaction of the substrate and the palladium catalyst. Experiments in which the alkylating agent was either heated first with the organic halide or added right from the beginning to the reaction mixture gave unsatisfactory results. In some such cases none of the expected products was formed, at all. Thus, it seems to us that the reaction mechanism of the methylation of vinyl bromides (which differs from that of the Heck reaction[23]) consists of the steps shown in Scheme 1. It is thus reasonable that the first step in the methylation of vinyl bromides is the formation of a Pd(0) η^2-complex of the olefin.[23d] This complex is likely to undergo intramolecular oxidative addition to form a η^1-Pd(II) alkenyl complex. Thereafter, exchange of the palladium-bound bromine with one methyl group of the methylating agent takes place. The catalytic cycle is completed by reductive elimination, by which the methylated product and the starting Pd(0) catalyst are formed. The methylation of the aryl halides (shown in Scheme 2) is assumed to take place by a similar route, except that the addition of the substrate to the Pd(0) catalyst directly forms an η^1-Pd(II) compound rather than an η^2- or η^6-palladium intermediate. If a π-bound complex were formed in this stage, one would expect partial scrambling

(22) A method for activation of aromatic chlorine atoms by our alkylating agents will be reported in a separate paper.

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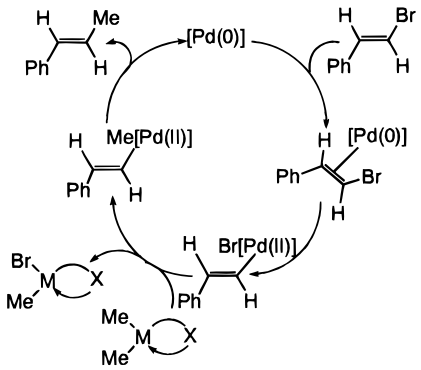
Table 7. Selective Methylation of Aryl Bromides with Vulnerable Substituents by Stabilized Dimethylgallium Complexes under Comparable Conditions[a]

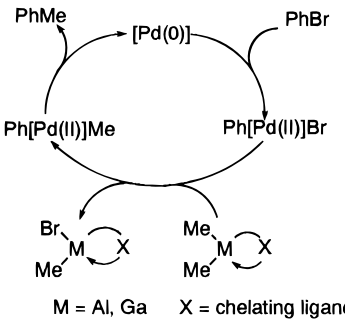
expt	substrate	gallium complex	products (yield, %)[b]
1	4-BrC_6H_4CHO	**1b**	4-MeC_6H_4CHO (95)
2	4-BrC_6H_4COPh	**5b**	4-MeC_6H_4COPh (100)
3	4-$BrC_6H_4CH{=}CHCOPh$	**1b**	4-$MeC_6H_4CH{=}CHCOPh$ (30)
4	4-$BrC_6H_4CO_2Et$	**1b**	4-$MeC_6H_4CO_2Et$ (98)
5	4-BrC_6H_4CN	**1b**	4-MeC_6H_4CN (82)
6	2-$BrC_6H_4NO_2$	**1b**	2-$MeC_6H_4NO_2$ (48)
7	4-$BrC_6H_4NO_2$	**1b**	4-$MeC_6H_4NO_2$ (61)
8	4-BrC_6H_4Cl	**1b**	4-MeC_6H_4Cl (70), (4-$MeC_6H_4)_2$ (5)
9	4-$BrC_6H_4CH_2Br$	**1b**	4-$MeC_6H_4CH_2Br$ (30)

[a] Reaction conditions: 1 mmol of substrate, 2×10^{-2} mmol of $PdCl_2(PPh_3)_2$, in 4 mL of benzene; heating at 85 °C for 30 min; addition of 1.1 mmol of **1b** or 0.505 mmol of **5b** of the gallium complex in 3 mL of benzene; heating at 85 °C for 3 h. [b] In no case, except in expt 8, has more than 2% side product been obtained. The missing percentage reflexes on the unreacted starting material.

Scheme 1



Scheme 2



of the methyl group in the product. Thus, both 1- and 2-bromonaphthalene should have formed mixtures of 1- and 2-methylnaphthalene, which was not the case.

In conclusion, we find the various intramolecularly stabilized dimethyl- and diethylaluminum complexes to be efficient reagents for palladium-catalyzed alkylation of aryl, benzyl, and vinyl bromides and iodides that operate in aromatic solvents under standard laboratory conditions. The analogous dimethylgallium compounds are of particular utility for selective methylation of aromatic bromides and iodides that have vulnerable functions that do not withstand other common organometallic alkylating agents.

Experimental Section

[3-(Dimethylamino)propyl-*C,N*]dimethylaluminum (**1a**),[24,25] [3-(dimethylamino)propyl-*C,N*]dimethylgallium (**1b**),[24−27] [2-[(dimethylamino)methyl]phenyl-*C,N*]dimethylaluminum (**2**),[19] bis[*μ*-[2-(dimethylamino)ethanolato-*N,O*:*O*]]tetramethyldialuminum (**4a**),[28] bis[*μ*-[2-(dimethylamino)ethanolato-*N,O*:*O*]]tetramethyldigallium (**4b**),[29] bis[*μ*-(2-methoxyethanolato-O^1:O^1,O^2)]tetramethyldialuminum (**5a**)[30,31] bis[*μ*-(2-methoxyethanolato-O^1:O^1,O^2)]tatramethyldigallium (**5b**),[4] bis[*μ*-(3-methoxy-2-propanolato-O^2:O^2,O^3)]tetramethyldialuminum (**5c**),[4] bis[*μ*-(2-methoxyphenolato-O^1:O^1,O^2)]tetramethyldialuminum (**6a**),[4,32] bis[*μ*-(2-methoxyphenolato-O^1:O^1,O^2)]tetramethyldigallium (**6b**),[4,32] bis[*μ*-(2-methoxyphenolato-O^1:O^1,O^2)]tetraethyldialuminum (**6c**),[32] and bis[*μ*-[(2-methoxyphenyl)methanolato-O^1:O^1,O^2]]tetramethyldialuminum (**8**)[4] have been prepared as described previously.

***[8-(Dimethylamino)naphthalen-1-yl-C,N]*dimethylaluminum (3).** To a stirred suspension of 16.3 g (64.9 mmol) of [8-(dimethylamino)naphthyl]lithium etherate[33] in 180 mL of Et_2O was added slowly under exclusion of air 7.00 g (64.9 mmol) of Me_2AlCl at −78 °C. After 60 min at this temperature the reaction mixture was allowed to warm to room temperature and stirred for further 18 h. Subsequently, the clear solution was decanted from the LiCl and the solvent was removed in vacuo. The residue was crystallized from a 2:5 mixture of toluene/hexane affording 9.4 g (64%) of **3** as colorless crystals: mp 62 °C; 200-MHz ^{1}H NMR (C_6H_6) δ −0.31 (s, 6), 2.18 (s, 6), 6.68 (dd, 1, $J_{5,7}$ = 1 Hz, $J_{6,7}$ = 7.5 Hz), 7.13 (dd, 1, $J_{5,6}$ = 8.2 Hz, $J_{6,7}$ = 7.5 Hz), 7.48 (dd, 1, $J_{2,3}$ = 6.3 Hz, $J_{3,4}$ = 8.2 Hz), 7.57 (dd, 1, $J_{5,6}$ = 8.2 Hz, $J_{5,7}$ = 1 Hz), 7.64 (dd, 1, $J_{2,4}$ = 1.3 Hz, $J_{3,4}$ = 8.2 Hz), 8.03 (dd, 1, $J_{2,3}$ = 6.3 Hz, $J_{2,4}$ = 1.3 Hz); 50-MHz ^{13}C{^{1}H} NMR (C_6H_6) δ −8.9, 48.8, 114.6, 124.7, 126.0, 127.8, 128.0, 128.3, 133.7, 134.6, 137.3, 151.2; 104-MHz ^{27}Al{^{1}H} NMR (C_6H_6) δ −180; EIMS (70 eV, 77 °C) *m/z* (rel intensity) 227 ($M^{\bullet+}$, 1, 212 [$(M - Me)^+$, 100], 197 [$(M - 2\,Me)^{\bullet+}$, 64], 154 ($C_{11}H_8N^+$, 7), 127 ($C_{10}H_7^+$, 5), 57 ($AlMe_2^+$, 2). Anal. Calcd for $C_{14}H_{15}AlN$: mol wt 227; C, 73.98; H, 7.98; N, 6.16. Found: mol wt (cryoscopy in C_6H_6) 207; C, 74.41; H, 7.94; N, 6.54.

Bis[*μ*-(3-methoxy-3-methylbutanolato-O^1:O^1,O^2)]tetraethyldialuminum (7). To a solution of 11.4 g (0.1 mol) of Et_3Al in 100 mL of pentane was added dropwise under Ar at −30 °C 118.g (0.1 mol) of freshly distilled 3-methoxy-3-methylbutanol. During the addition, a violent evolution of gas was observed. The resulting white suspension was stirred for an additional 2 h at −30 °C and afterwards allowed to warm to room temperature. After the solution was stirred for a further 12 h the solvent was removed in vacuo. The clear

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liquid residue was distilled to give 15.2 g (75%) of **7** as a colorless oil: bp 98−100 °C (0.1 mbar); 200-MHz ^{1}H NMR (C_6H_6) δ 0.20 (m, 4), 0.87 (s, 3), 1.02 (s, 3), 1.36 (m, 6), 1.69 (m, 1), 2.02 (m, 1), 2.93 (s, 3), 3.83 (m, 1), 4.08 (m, 1); 50-MHz ^{13}C{^{1}H} NMR (C_6H_6) δ −0.2, 9.6, 24.4, 24.8, 43.5, 43.9, 49.0, 59.3, 60.3, 73.3, 74.8; EIMS (70 eV, 77 °C) *m*/*z* (rel intensity) 404 ($M^{\bullet+}$, 1), 375 [$(M - Et)^+$, 33], 317 [$(M - 3Et)^+$, 4], 307 ($C_{14}H_{33}Al_2O_3^+$, 7), 287 ($C_{14}H_{33}Al_2O_2^+$, 25), 259 ($C_{11}H_{25}Al_2O_3^+$, 100), 245 ($C_{10}H_{23}Al_2O_3^+$, 58), 202 ($C_{10}H_{23}AlO_2^+$, 2), 173 ($C_8H_{18}AlO_2^{\bullet+}$, 25), 117 ($C_6H_{13}O_2^+$, 17), 85 ($C_4H_{10}Al^+$, 10). Anal. Calcd for $C_{20}H_{46}Al_2O_4$: C, 59.38; H, 11.46. Found: C, 59.03; H, 11.28.

Bis[3-(dimethylamino)propyl-*C,N*]methylaluminum (9). To a stirred solution of 6.23 g (46.7 mmol) of $AlCl_3$ in 200 mL of Et_2O was added dropwise under Ar at −78 °C 4.32 (46.7 mmol) of Me_2AlCl. The suspension was allowed to warm slowly, refluxed for 1 h, and stirred for another 15 h at room temperature. The resulting solution was added dropwise to a stirred suspension of 17.4 g (0.187 m) of [3-(dimethylamino)-propyl]lithium[5] in 500 mL of pentane at −78 °C. The reaction mixture was warmed to room temperature, stirred for 15 h, and filtered, and the filtrate was concentrated under reduced pressure. Distillation gave 15.0 g (75%) of **9** as a colorless oil: bp 60 °C (0.02 mbar); 200-MHz ^{1}H NMR (C_6H_6) δ −0.67 (s, 3), 0.02 (m, 4), 1.73 (m, 4), 191 (s, 12), 204, (m, 4); 50-MHz ^{13}C{^{1}H} NMR (C_6H_6) δ −8.8, −3.8, 22.5, 45.6, 62.5; 104-MHz ^{27}Al{^{1}H} NMR (C_6H_6) δ 138; EIMS (70 eV, 80 °C) *m*/*z* (rel intensity) 214 ($M^{\bullet+}$, 3), 199 [$(M - Me)^+$, 42], 128 ($C_6H_{14}AlN^+$, 100), 86 ($C_5H_{12}N^+$, 20), 58 ($C_3H_8N^+$, 25). Anal. Calcd for $C_{11}H_{27}AlN_2$: C, 61.64; H, 12.70; N, 13.07. Found: C, 61.24; H, 12.63; N, 12.88.

[3-[Bis(1,1-dimethylethyl)phosphino]propyl-*C,P*]dimethylgallium (10). To a suspension of the Grignard reagent, prepared from 5.57 g (25.0 mmol) of 1-chloro-3-[bis-(1,1-dimethylethyl)phosphino]propane and 0.68 g (28.0 mmol) of Mg turnings in 30 mL of Et_2O, was added dropwise under exclusion of air a solution of 3.38 g (25.0 mmol) of Me_2GaCl in 30 mL of the same solvent. After the mixture was stirred for an additional 12 h at room temperature, the solvent was removed in vacuo, and 50 mL of pentane was added to the residue. The solution was filtered, and the filtrate was concentrated in vacuo to give 6.03 g (84%) of **10** as colorless crystals: mp (sealed capilary) >150 °C (dec); 200-MHz ^{1}H NMR (C_6H_6) δ 0.10 (d, 6, $^3J_{P,H}$ = 5.2 Hz), 0.58−0.69 (m, 2), 0.90 (d, 18, $^3J_{P,H}$ = 14.8 Hz), 1.14−1.26 (m, 2), 1.85−2.06 (m, 2); 50-MHz ^{13}C{^{1}H} NMR (C_6H_6) δ −4.7 (d, $^2J_{P,C}$ = 10.5 Hz), 15.1 (d, $^2J_{P,C}$ = 29.9 Hz), 22.3 (d, $^2J_{P,C}$ = 15.5 Hz), 26.2 (d, $^1J_{P,C}$ = 12.7 Hz), 28.9 (d, $^2J_{P,C}$ = 5.6 Hz), 32.3 (d, $^1J_{P,C}$ = 4.6 Hz); 81-MHz ^{31}P{^{1}H} NMR (C_6H_6) δ 20.33; EIMS (70 eV, 40 °C), *m*/*z* (rel intensity) 273/271 [$(M - Me)^+$, 100], 217/215 ($C_{18}H_{19}$-GaP^+, 18), 161/159 ($C_4H_{11}GaP^{\bullet+}$, 27), 101/99 ($C_2H_5Ga^+$, 16), 69/71 ($Ga^{\bullet+}$, 12), 57 ($C_4H_9^+$, 18). Anal. Calcd for $C_{13}H_{30}GaP$: mol wt 287; C, 54.39; H, 10.53; Ga, 24.29. Found: mol wt (cryoscopy in C_6H_6) 281; C, 4.49; H, 10.59; Ga, 24.18.

General Procedure for the Alkylation of Aryl, Benzyl, and Vinyl Halides. Typically, a solution of 1 mmol of the substrate and 2 × 10^{-2} mmol of the palladium catalyst in 4 mL of dry solvent is heated at 50−90 °C under N_2 in a reaction vessel for 30 min. When the solvent is benzene, a sealed pressure tube is used. To this solution is added 0.505 mmol of monomeric or 0.252 mmol of dimeric stabilized alkylaluminum or gallium complex in 3 mL of the same solvent, and the heating is continued at 70−90 °C for the required length of time. The cooled mixture is treated with excessive dilute (2−10%) hydrochloric acid. Phase separation and extraction of the product from the aqueous layer by an appropriate solvent are followed by concentration of the combined organic solutions and purification by column chromatography. All known products have been characterized by comparison with authentic samples obtained either from commercial sources or by the synthetic routes described in the literature cited in Tables 1 and 2.

Slow alkylation reactions could be enhanced by doubling the amount of the alkylating agent. When low-boiling products had been expected, the reactions were conducted in deuterated solvents (usually benzene-d_6) and the reaction mixtures analyzed by NMR prior to their isolation. Kinetic measurements were performed in reaction vessels equipped with sampling devices which were heated with the aid of oil baths that could be adjusted to ±0.2 °C within the range of the desired temperature. Samples were withdrawn from the reaction mixture each 2−10 min and worked up as described above, in a specially designed microapparatus. The final organic solutions were analyzed by gas chromatography (OV-17 on Chromosorb W).

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