Palladium-Catalyzed Cross-Methylation of Haloarenes Possessing Active Hydrogen Atoms by Intramolecularly Stabilized Dimethylindium and Dimethylaluminum Reagents

Nimer Jaber,[a] Dmitri Gelman,[a] Herbert Schumann,*[b] Sebastian Dechert,[b] and Jochanan Blum*[a]

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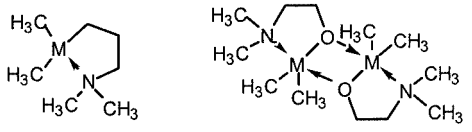
While the intramolecularly stabilized aluminum complex $[(CH_3)_2AlOCH_2CH_2N(CH_3)_2]_2$ (**2a)** reacts readily with 4-bromophenol to give methane and $[(4\text{-}BrC_6H_4O)_2AlOCH_2CH_2N(CH_3)_2]_2$ (**7**), the demethylation of the analogous indium complex $[(CH_3)_2InOCH_2CH_2N(CH_3)_2]_2$ **2c** is very slow. This inertness of **2c** enables it to cross-methylate bromophenols and other bromoarenes with active hydrogen atoms in the presence of soluble palladium phosphane catalysts. The cross-methylation by **2c** can be carried out under an ambient atmosphere. The ring-bound bromine atoms in **7** are replaced by CH_3 groups when treated with an excess of the methylation reagent **2a**, and the resulting aluminum cresolate liberates 4-methylphenol upon hydrolysis.

Introduction

In the course of our studies on cross-coupling processes by intramolecularly stabilized group 13-metal alkylating agents,[1–5] we found that in the presence of palladium catalysts, aryl chlorides, bromides and triflates react readily with the aluminum reagents **1a** and **2a** to give the corresponding methylarenes. Aryl halides and pseudohalides that have vulnerable substituents such as aldehyde, ketone or bromomethyl moieties, however, undergo cross-methylation in a nonselective fashion as both reactive groups are affected by the reagents. The gallium analogs of **1a** and **2a** (i.e. **1b** and **2b**) do not attack carbonyl, cyano, bromomethyl or nitro groups,[1] but react rather slowly as cross-coupling reagents, and are often deactivated by electron-releasing groups located in the *ortho* or *para* positions.[4] The application of intramolecularly stabilized indium complexes was shown to overcome these shortcomings. Complexes **1c** and **2c** were found to react nearly as fast as the aluminum compounds, they are not deactivated by ring-bonded alkyl or alkoxyl groups, and do not attack vulnerable groups other than the ring-attached halide or triflate functions.[4] Diminished reactivity and the ability to withstand the presence of active functional groups that are known to destroy alkylmetal compounds have lately been observed also with some other organoindium complexes that, under oxygen-free conditions, are quite stable, even in the presence of water.[6] Takami et al.[7] found that triphenyl- and trivinylindium, as well as bis(4-methoxyphenyl)indium chloride, react in wet THF with iodo- and bromoarenes that have active hydrogen atoms. Trimethylindium, however, was found to form only traces (3%) of methylated products. We now report on the conditions for the smooth, selective cross-methylation of haloarenes with active hydroxyl, carboxyl and amino groups under an ambient atmosphere by the intramolecularly stabilized complexes **1c** and **2c**.



1 **2**

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

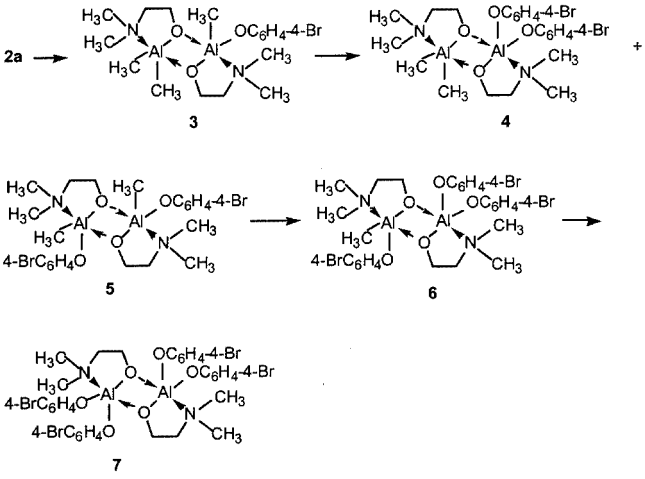
[a] Department of Organic Chemistry, Hebrew University, Jerusalem 91904, Israel
Fax: (internat.) + 972-2/651-3832
E-mail: jblum@chem.ch.huji.ac.il
[b] Institut für Chemie, Technische Universität Berlin, 10623 Berlin, Germany
Fax: (internat.) + 49-(0)30/3142-2168
E-mail: schumann@chem.tu-berlin.de

Results and Discussion

When the aluminum cross-methylation reagent **1a** was treated with halophenols, it reacted readily with the active hydrogen atoms to give methane. Consequently, the ability of **1a** to participate in palladium-catalyzed cross-methyl-

ation was destroyed. The analogous indium reagent **1c**, however, was found to convert 4-bromophenol, under oxygen-free conditions, in the presence of $[Pd(PPh_3)_4]$, into 4-methylphenol in quantitative yield. The dimethylaluminum aminoethoxide derivative **2a** was found to react with 4-bromophenol, similarly to complex **1a**, to give methane. However, the aluminum-containing product still proved capable of taking part in cross-coupling reactions in the presence of an excess of methylation reagent. After quenching with hydrochloric acid the expected 4-methylphenol was formed. The dimethylindium aminoethoxide derivative **2c** cross-methylates 4-bromophenol under an ambient atmosphere even when a relatively low [reagent]:[phenol] ratio was used (see Table 1). The different behavior of **2a** and **2c** towards 4-bromophenol is rationalized in terms of two phenomena: (i) the difference in rate of the reactions of the reagents with the phenol, and (ii) the different mechanisms by which **2a** and **2c** react. In a series of comparative experiments, we have monitored the rate of methane formation from 4-bromophenol and **2a, 2b** and **2c** by gasometric analysis. Initially, we treated a benzene solution of 0.38 mmol of **2a** at room temperature with 0.152 mmol of 4-bromophenol (i.e. 4 mol of the phenol was added for each mol of the dialuminum reagent). The reaction, which started immediately, afforded the first two equivalents (17 mL) of methane within 6 min, and the remaining two equivalents within the next 18 min. Realizing the difference in rate between the reaction of the first and the second aluminum-attached CH_3 groups, we repeated the experiment with just 0.76 mmol of 4-bromophenol per 0.38 mmol of the bimetallic reagent. The calculated amount of 17 mL of methane was now evolved within 7 min. Replacement of **2a** by the indium complex **2c** led to the formation of 17 mL of methane only after 5 h. The gallium reagent **2b** proved to react even more slowly, and furnished only 8 mL of gas (47% of the calculated amount) after 15 h.

During the evolution of methane in the reaction of **2a** and 4-bromphenol ([**2a**]:[4-BrC_6H_4OH] = 1:4) the four CH_3 groups are gradually replaced by 4-BrC_6H_4O moieties, as outlined in Scheme 1. When the evolution of methane is complete pure **7** remains as the only product. The mixture of the transient reaction intermediates **3**−**6** has not been separated, although the formation of these methylaluminum compounds has been confirmed by recording the ^1H NMR spectra of reaction mixtures of **2a** in C_6D_6 during gradual addition of limited quantities of 4-bromophenol. While the CH_3 signal of **2a** at $\delta = -0.57$ decreases, signals at $\delta = -0.556$, -0.559, -0.560 (**5**), -0.561, and -0.63 (**3**) appear and then disappear until, after addition of four equivalents of the phenol, no CH_3 signals are left. During this operation, four transient AB quadruplets of **3**−**6** centered at $\delta = 7.048$, 7.109, 7.165, and 7.396 are formed, and ultimately converted into the AB quadruplet of **7**, centered at $\delta = 7.035$.



Scheme 1

The structure of **7** has been determined by X-ray diffraction analysis. The compound is dimeric in the solid state, bridged by the oxygen atoms of the aminoethoxy ligand (see Figure 1). The coordination number of aluminum is five and the coordination geometry corresponds to a distorted trigonal bipyramid with the coordinating oxygen and nitrogen atoms in the axial positions. The equatorial positions are occupied by the two oxygen atoms of the 4-bromophenoxy ligand and the bridging alkoxide oxygen of the aminoethoxy ligand. The shortest Al−O distances are

Table 1. Effect of the molar ratio [substrate]:[methylation reagent] in cross-methylation of 4-BrC_6H_4OH with complexes of type **2** in the presence of $PdCl_2(PPh_3)_2$[a]

Entry	Methylation reagent	Molar ratio reagent:4-BrC_6H_4OH[b]	Reaction time (h)	Isolated 4-methylphenol (%)
1	**2a**	0.5	24	0
2	**2a**	1	2	<1[c]
3	**2a**	1.5	2	57
4	**2a**	2	2	96
5	**2b**	3	24	0
6	**2c**	0.5	2	15
7	**2c**	1	2	37
8	**2c**	1.5	2	54
9	**2c**	2	2	75
10	**2c**	3	2	96

[a] Reaction conditions: 0.38 mmol 4-BrC_6H_4OH; ratio of [substrate]:[$PdCl_2(PPh_3)_2$] = 1:25, 2.2 mL benzene; 80 °C. [b] "Molecular weights" of monometallic rather than dimetallic reagents are used. [c] <2% after 24 h.

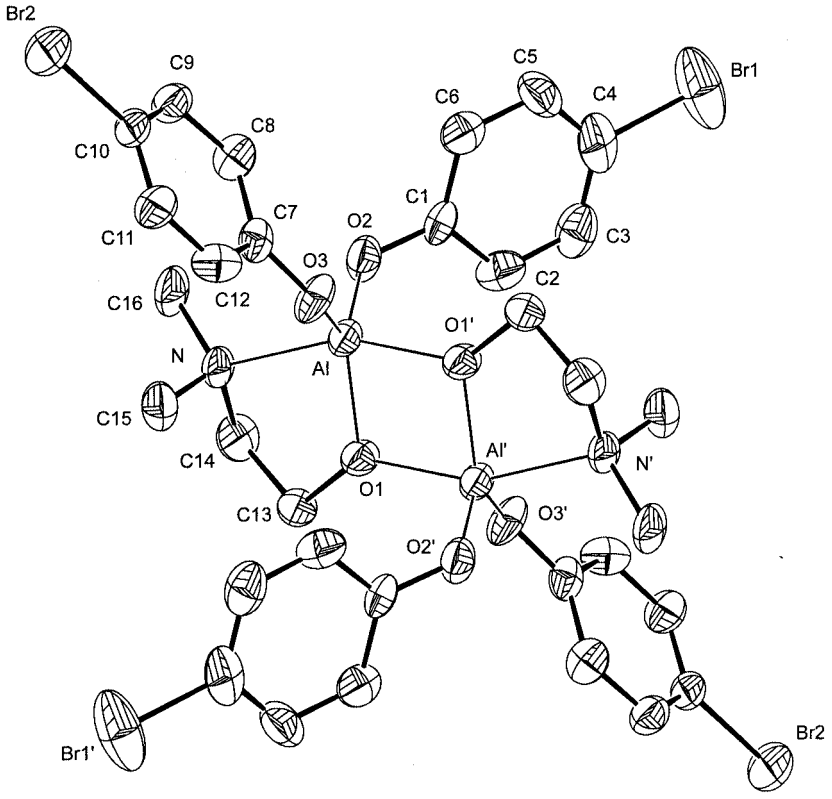


Figure 1. ORTEP diagram of **7**; thermal ellipsoids are shown at the 30% probability level; hydrogen atoms are omitted for clarity; selected bond lengths (Å) and bond angles (°): Al−O(1) 1.813(8), Al−O(1′) 1.879(8), Al−O(2) 1.727(9), Al−O(3) 1.726(8), Al−N 2.097(9); Al−O(1)−Al′ 104.5(4), O(1)−Al−N 81.5(4), O(1)−Al−O(2) 120.2(4), O(1)−Al−O(3) 121.8(4), O(1)′−Al−N 157.0(4), O(1)′−Al−O(2) 100.6(4), O(1)′−Al−O(3) 93.0(4), O(2)−Al−O(3) 118.0(4), N−Al−O(2) 91.5(4), N−Al−O(3) 98.6(4); symmetry transformation used to generate equivalent atoms: (′)$-x + 1, -y + 1, -z + 1$

found for the aluminum phenoxy bonds (1.73 Å) and are similar to the bond lengths reported for similar compounds.[8] The central Al_2O_2 ring is perfectly planar. The two Al−O distances within the ring are different (Al−$O_{equat.}$ 1.81 Å/Al−O_{axial} 1.88 Å). This is a typical feature of five-coordinate dimeric aluminum alkoxides.[9] The Al−N distance (2.10 Å) and the O_{axial}−Al−N bond angle (157.0°) are similar to the values found for [Me_2Al-(μ-$OCH_2CH_2NMe_2$)]$_2$ (2.13 Å/151.7°).[10]

In the presence of a palladium catalyst the bromine atoms in the bromophenoxy complexes **3**−**7** can react with excess **2a**. Hydrolysis of the resulting aluminum-derived cre-

Table 2. Palladium-catalyzed cross-methylation of some halo- and pseudohaloarenes possessing active hydrogen atoms by the indium reagent **2c**[a]

Entry	Substrate	Ratio of [**2c**]:[substrate]	Product	Yield after 2 h (%)[b]
1	2-bromophenol	2	2-methylphenol	33
2	3-bromophenol	2	3-methylphenol	99
3	4-bromophenol	2	4-methylphenol	75
4	4-iodophenol	2	4-methylphenol	33
5	4-hydroxyphenyl trifluoromethenesulfonate	2	4-methylphenol	8[c]
6	4-bromo-1,3-benzenediol	3	4-methyl-1,3-benzenediol[11]	40
7	4-bromobenzyl alcohol	1	4-methylbenzyl alcohol	39[d]
8	4-bromobenzoic acid	2	4-methylbenzoic acid	100
9	5-bromo-2-hydroxybenzoic acid[3]	3	5-methyl-2-hydroxybenzoic acid [12]	96
10	2-bromo-3,5-hydroxybenzoic acid[e]	4	2-methyl-3,5-hydroxybenzoic acid[13]	[f]
11	4-bromoaniline	3	4-methylaniline	93[g]
12	5-bromo-2-aminobenzoic acid[d]	4	5-methyl-2-aminobenzoic acid[14]	90[g]

[a] Reaction conditions as in Table 1; 2 h. [b] The remaining percentage reflect on unchanged substrate. [c] After 20 h. [d] 96% after 22 h. [e] In THF. [f] 9% after 73 h. [g] The free amine was obtained after neutralization of the reaction mixture.

solates gives 4-methylphenol. Thus, the successful formation of cresol from 4-bromophenol and **2a** requires more than one molecule of the reagent for every two molecules of the bromophenol. Unlike the cross-methylation of 4-bromophenol with **2a**, the reaction with the indium complex **2c** seems to proceed by the general mechanism outlined previously for cross-coupling of non-hydroxylated aryl halides and triflates with reagents of type **1** and **2**.[1−4] Because of the slow reaction of the indium complex with the OH group not much indium phenolate is formed. The cross-methylation is not conditioned either by the presence of excessive reagent or by hydrolysis of the In−OAr bonds. Indeed, while the monitoring of $[PdCl_2(PPh_3)_2]$-catalyzed cross-methylation of 4-bromophenol by **2c** in C_6D_6 by ^1H NMR spectroscopy revealed a gradual accumulation of 4-methylphenol during the process, no phenolic product could be detected in the analogous reaction with **2a** prior to quenching with aqueous hydrochloric acid.

The effect of the molar ratio [substrate]:[methylating reagent] in the cross-methylation of 4-bromophenol with reagents **2** has been demonstrated by a series of experiments that are summarized in Table 1.

This table indicates that cross-methylation with **2a** takes place at an appreciable rate only when [Al]:[bromophenol] is greater than 1.5, whereas the indium reagent **2c** yields 15% of 4-methylphenol after 2 h even when the ratio is 0.5.

At a [catalyst]:[substrate] ratio above 1:25 the cross-methylation processes is independent of the amount of catalyst. The rate depends to some extent, however, on the structure and oxidation state of the palladium complex. Comparative cross-methylation experiments of 4-bromophenol by **2c** at 80 °C in the presence of $[PdCl_2(PPh_3)_2]$, $[Pd(PPh_3)_4]$, $[Pd(OAc)_2(dppp)]$ and $[Pd(dppp)_2]$ under identical conditions formed, after 2 h, 75, 68, 60, and 0% cresol, respectively.

Complex **2c** cross-methylates not only halo-monophenols and hydroxy triflates, but also derivatives of resorcinol and phloroglucinol, as well as other substrates with active hydrogen, such as benzylic alcohols, carboxylic acids and primary amines. Some representative results are listed in Table 2. Since the indium reagent reacts only slowly with the active hydrogen atoms, the nature of the active function has no big effect on the yield. In fact the cross-methylation of 4-bromophenol, 4-bromobenzoic acid, 4-bromoaniline and bromobenzene with **2c** leads to similar yields of methylated products under identical conditions.

Attempts to block the OH group in 4-bromophenol with lithium, sodium or potassium lowered the rate of the cross-coupling, probably owing to the low solubility of the resulting phenolates. Entries 1−3 in Table 2 indicate the existance of a mild electronic effect on the rate. A more pronounced influence proved to be caused by steric constraints (see entries 1, 6 and 10).

For comparison we examined the possibility to cross-methylate 4-bromophenol (under argon) with trimethylindium. The pure reagent gave only 4% of 4-methylphenol, and a reagent generated in situ from methyllithium and $InCl_3$, according to Pérez et al,[15] did not form cresol at all. In this regard we would like to draw attention to the fact that, in general, isolated trialkylindium compounds, prepared by conventional methods,[16] react considerably slower than those prepared in situ from organolithium or Grignard reagents.[15] For example, 4′-bromoacetophenone, in the presence of $[PdCl_2(PPh_3)_2]$, has been reported to yield 94% of 4′-methylacetophenone and 91% of 4′-butylacetophenone with trimethyl- and tributylindium (both prepared in situ), respectively,[15] but only 48 and 46% of the expected products under the reported experimental conditions with isolated pure trialkylindium reagents. The isolated reagents lead to the formation of considerable amounts (21−25%) of the homocoupling product 4,4′-bis(acetyl)-1,1′-biphenyl, along with unchanged starting material. Similar differences in yield between the expected cross-coupling products of in situ prepared, and of isolated, trialkylindium were observed in the $[NiCl_2(PPh_3)_2]$-catalyzed cross-coupling of 4′-chloroacetophenone. We therefore assume that the reactions of haloarenes with RLi (or RMgX) and $InCl_3$ are cross-coupling reactions of *alkyllithium* (or Grignard) reagents, probably catalyzed by the indium salt.

Conclusions

Direct $[PdCl_2(PPh_3)_2]$-catalyzed cross-methylation of halophenols and other haloarenes with active hydrogen atoms, is a unique feature of the intramolecularly stabilized dimethylindium reagent **2c**. At about 80 °C the interaction of the reagent with the active hydrogen function is slow enough to allow preferential attack at the ring-bound halogen atom. The reagent also withstands the presence of air and can therefore be used under ambient atmospheric conditions. Unlike the indium reagent, the analogous aluminum compound **2a** is both air sensitive and reacts rapidly with phenols to give methane and phenoxyaluminum derivatives. Nevertheless it can also be utilized as a cross-coupling reagent of bromophenol in the presence of an excess of the dimethylaluminum complex, which initially serves as an OH-protecting group. In the aluminum-induced cross-methylation, methylated aluminum phenoxides are formed and the liberation of the aluminum-free products takes place only after hydrolysis.

Experimental Section

General: ^1H and ^{13}C NMR spectra were recorded on Bruker AMX-200, AMX-300, and AMX-400 instruments. MS measurements were performed on a Hewlett−Packard model 4989A mass spectrometer with an HP gas chromatograph model 5890 series II. IR spectra were recorded on a Bruker model Vector 22 FTIR instrument, and HPLC separations were performed on a Jasco TRI-ROTAR IV machine equipped with a DG-3510 degasser and UVIDEC 100-VI UV spectrophotometer. Trimethylindium,[16] tri-*n*-butylindium,[16] [3-(dimethylamino)propyl-*C,N*]dimethylaluminum (**1a**),[17] [3-(dimethylamino)propyl-*C,N*]dimethylgallium (**1b**),[18] [3-(dimethylamino)propyl-*C,N*]dimethylindium (**1c**),[18] bis{μ-[2-(dimethylamino)ethanolato-*N,O:O*]}tetramethyldi-

aluminum (**2a**),[19] bis{μ-[2-(dimethylamino)ethanolato-*N,O:O*]}-tetramethyldigallium (**2b**),[20] and bis{μ-[2-(dimethylamino)ethanolato-*N,O:O*]}tetramethyldiindium (**2c**)[21] were prepared as described in the literature. 4-Hydroxyphenyl trifluoromethanesulfonate was synthesized from 4-aminophenol via the diazonium tetrafluoroborate.[22,23]

Bis{μ-[2-(dimethylamino)ethanolato-*N,O:O*]}tetrakis(4-bromophenoxy)dialuminum (7): A solution of freshly recrystallized 4-bromophenol (2.81 g, 16.24 mmol) in a mixture of 15 mL of benzene and 15 mL of hexane was added dropwise under argon at room temperature to a stirred solution of **2a** (1.19 g, 4.10 mmol) in 15 mL n-hexane. Vigorous evolution of a gas started immediately. After ca 30 min the formation of the methane was complete. The heavy precipitate of colorless **7** was collected and recrystallized from toluene. Yield 3.27 g (87%); m.p. (sealed capillary) 231 °C.; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.35 (s, 12 H, CH_3), 2.55 (t, J = 6.0 Hz, 4 H, NCH_2), 3.73 (t, J = 6.0 Hz, 4 H, OCH_2), 6.81, 7.30 (ABq, J_{AB} = 9 Hz, 16 H, ArH). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ = 45.31, 56.84, 58.17, 109.82, 120.98, 132.28, 159.21. $C_{32}H_{36}Al_2Br_4N_2O_6$ (918.2): calcd. C 41.86, H 3.95, N 3.05; found C 41.88, H 4.02, N 2.86.

A suitable crystal for X-ray diffraction analysis was obtained by slow recrystallization from toluene. The X-ray data were obtained by using a Siemens SMART-CCD diffractometer, ω-scans, Mo-K_α radiation (λ = 0.71093 Å), graphite monochromator, T = 293 K, SADABS[24] for absorption correction (T_{max} = 0.4080, T_{min} = 0.1493), structure solution with direct methods and refinement against F^2 (SHELX-97)[25] with anisotropic thermal parameters for all non-hydrogen atoms, hydrogen positions with fixed isotropic thermal parameters (U_{iso} = 0.08 Å^2) on calculated positions; crystal dimensions 0.54 × 0.36 × 0.10 mm, orthorhombic, space group *Pbca*, a = 12.6169(3) Å, b = 15.9490(2) Å, c = 18.9354(5) Å, V = 3810.31(14) Å^3, Z = 4, $\rho_{calcd.}$ = 1.601 × 10^3 kg m^{-3}, μ = 4.313 mm^{-1}, F(000) = 1824; data collection 4.3θ ≤ 2θ ≤ 48.0θ, -13 ≤ h ≤ 13, -18 ≤ k < 17, -21 ≤ l ≤ 6, 9549 data were collected, 2938 unique data (R_{int} = 0.1452), 1151 data with $I > 2\sigma(I)$, 210 refined parameters, GOF(F^2) = 1.007, final R indices ($R_1 = \Sigma||F_0| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_0^2 - F_c^2)^2/\Sigma w(F_0^2)^2]^{1/2}$), R_1 = 0.0898, wR_2 = 0.1736, max./min. residual electron density 0.688/−0.699 eÅ^{-3}. An ORTEP drawing of **7** is shown in Figure 1. CCDC-174124 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Monitoring of the Reaction of 4-Bromophenol with 2a, 2b and 2c: A round bottomed flask equipped with a gasometer was charged at 24 °C under oxygen-free conditions with a solution of the aluminum complex **2a** (110 mg, 0.38 mmol) in 3 mL of dry benzene. A solution of 4-bromophenol (263 mg, 1.52 mmol) in 6 mL of the same solvent was injected into this solution through a rubber septum. Evolution of the calculated volume of the first 0.76 mmol (17 mL) of methane took 6 min. The remaining 0.76 mmol of gas evolved during the next 18 min. Upon repetition of the experiment with just 0.76 mmol of 4-bromophenol the evolution of the gas was complete within 7 min.

The reaction of 0.76 mmol of 4-bromophenol with the indium complex **2c** (177 mg, 0.38 mmol) under the above conditions gave 17 mL (0.76 mmol) of methane within 5 h. In the reaction of the gallium reagent **2b** (143 mg, 0.38 mmol) with 0.76 mmol of the phenol, only 8 mL (4.7% of the calculated amount) of methane was formed during 15 h.

Cross-Coupling of 4-Bromophenol by 2c: In a typical experiment, a mixture of 4-bromophenol (165 mg, 0.955 mmol), **2c** (440 mg, 0.950 mmol), [$PdCl_2(PPh_3)_2$] (27 mg, 3.85 × 10^{-2} mmol) and 11 mL of dry benzene was refluxed for 2 h. The cooled reaction mixture was diluted with 50 mL of chloroform followed by acidification with 15% hydrochloric acid. After phase separation, extraction of the aqueous layer with chloroform, concentration of the organic phase, and chromatography on silica gel (using ether as eluent), 70 mg (68%) of 4-methylphenol and 38 mg (23%) of unchanged starting material were obtained.

Experiments with air-sensitive aluminum and gallium reagents, as well as those with bis(diphenylphosphanylpropane)palladium [Pd(dppp)$_2$], [$Pd(AcO)_2$(dppp)], and [$Pd(PPh_3)_4$] were conducted under argon in a thick-walled sealed pressure tube, thermostatted at 80 ± 0.2 °C. Some reactions were carried out in THF in the same manner as in benzene but the workup required removal of the solvent under reduced pressure prior to the quenching with hydrochloric acid. Representative results of the cross-methylation of 4-bromophenol under different conditions and the reaction of some other haloarenes with active hydrogen atoms are summarized in Table 1 and 2.

Acknowledgments

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