



Coupling of acyl chlorides with triarylbismuths catalyzed by palladium bipyridyl complex anchored on nanosized MCM-41: A recyclable and atom-efficient catalytic process for the synthesis of diaryl and alkyl aryl ketones

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ABSTRACT

The coupling reactions of acyl chlorides with triarylbismuths catalyzed by a palladium bipyridyl complex anchored on nanosized mesoporous silica MCM-41 gave diaryl and alkyl aryl ketones in good to high yields. The amount of triarylbismuths required for the cross-coupling could be up to half the molar ratio relative to the acyl chlorides for the completion of the reaction; the catalyst could be recovered and re-used after the reaction, providing both an atom-efficient and catalyst-recyclable process for the synthesis of diaryl and alkyl aryl ketones.

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1. Introduction

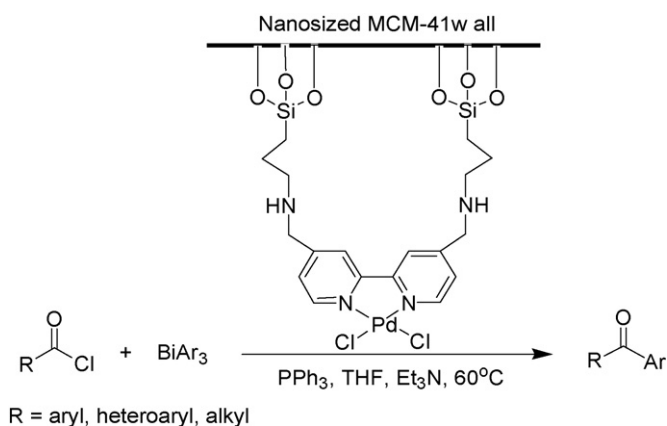
Friedel–Crafts acylation in the presence of Lewis acids is one of the most useful synthetic methods for the preparation of aromatic ketones [1,2]. Because the substituents on the aromatic ring affect the rate of Friedel–Crafts acylation and the regioselectivity, transition-metal-catalyzed formation of aromatic ketones seems to be a better strategy for this purpose [3]. Among many methods, the palladium-catalyzed coupling reaction of acyl chlorides with organometallic reagents is one of the most efficient methods for aromatic ketone synthesis. The mechanism involves the oxidative addition of acyl chlorides to palladium, the transmetalation of the organic group from organometallic reagent to an acyl palladium species, and subsequent reductive elimination, giving the aromatic ketone. Organoboron [4–13], organotin [14,15] and organozinc [1,2] reagents have been used as organometallic reagents for the synthesis of ketones. Although these reagents are well-documented with regards to their use in transmetalation, only one equivalent of the organic group can be used for the cross-coupling reaction. Recently, triarylbismuths have been employed to couple with acyl chlorides on the basis of atom-efficient considerations, as three equivalents of the aryl groups on bismuth can be transferred to the transi-

tion metal [16–18]. For this reason, less than equivalent quantity of triarylbismuth is needed for the cross-coupling reaction.

Because of economic concerns, the development of a recyclable catalyst, as well as the use of atom-efficient triarylbismuths, for the synthesis of ketones is much desired. Previously, Zhang's group has reported the use of a recyclable palladium catalyst system in PEG or ionic liquid to obtain ketones by the coupling of carboxylic anhydrides or acyl chlorides and arylboronic acids, stoichiometric amounts of arylboronic acids are required [12]. On the other hand, ordered mesoporous silica (OMS) is a good choice as a solid support for the purpose of recovery and recyclability. OMS materials with a uniform pore diameter, high surface area, and large number of silanol groups are ideal supports for immobilizing transition metal complexes, and the heterogenized catalysts may be easily separated from the reaction mixture [19–32]. The catalyst-immobilization techniques of recyclable palladium complexes for C–C bond formation have been developed for the Mizoroki–Heck reaction [33–43], Suzuki–Miyaura reaction [44–48], Sonogashira coupling [49–51], indole formation [52], Kumada–Tamao–Corriu reaction [53], and Migita–Kosugi–Stille reaction [54]. We have previously reported that the nanosized OMS-grafted palladium bipyridyl complex NS-MCM-41-Pd is a highly efficient and recyclable catalyst for the Mizoroki–Heck [39] and Kumada–Tamao–Corriu [53] reactions. The fundamental advantage of this catalyst is that the short and highly connected wormhole-like channels of nanosized MCM-41 lead to easy exchange of reactants, salts and products through-

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Scheme 1. NS-MCM-41-Pd-catalyzed coupling of acyl chlorides with triarylbi-muths.

out the nanochannels. Thus, a very low catalyst loading can be applied in the reaction. In this report, we present a diaryl and alkyl aryl ketone synthesis procedure that not only uses triarylbi-muths as atom-efficient organometallic reagents but also employs a nanosized MCM-41 supported palladium bipyridyl complex as a recyclable catalyst (Scheme 1).

2. Experimental

2.1. General information

All reactions involving air- and moisture-sensitive conditions were carried out in a dry nitrogen atmosphere. The chemicals were purchased from commercial suppliers and were used

Table 1

Optimization of reaction conditions for the coupling of benzoyl chloride with triphenylbismuth^a.

Entry	Solvent	Base (equivalent)	T (°C)	Yield (%) ^b
1	THF	Et ₃ N (2)	60	70
2	THF	Bu ₃ N (2)	60	65
3	DME	Et ₃ N (2)	80	45
4	1,4-Dioxane	Et ₃ N (2)	80	24
5	Toluene	Et ₃ N (2)	100	58
6 ^c	THF	Et ₃ N (2)	60	99
7 ^c	THF	Et ₃ N (2)	rt	0
8 ^c	THF	Et ₃ N (1)	60	50
9 ^c	THF	Et ₃ N (3)	60	70
10 ^c	THF	Et ₃ N (4)	60	45
11 ^c	THF	K ₂ CO ₃ (2)	60	83
12 ^c	THF	NaOAc (2)	60	57
13 ^{c,d}	THF	Et ₃ N (2)	60	5
14 ^{c,e}	THF	Et ₃ N (2)	60	88

^a Reaction conditions: [C₆H₅COCl]:[Ph₃Bi]:[PPh₃]:[Pd] = 100:35:2:1. Reaction time = 12 h.

^b GC yields.

^c [C₆H₅COCl]:[Ph₃Bi]:[PPh₃]:[Pd] = 100:50:2:1.

^d In the absence of PPh₃.

^e PdCl₂(bpy) was used as the catalyst.

without further purification. THF, 1,4-dioxane, DME and toluene were distilled from sodium benzophenone ketyl. Et₃N, Bu₃N, and diisopropylethylamine were dried over KOH and then distilled. 4,4'-Bis(bromomethyl)-2,2'-bipyridine [55,56], PdCl₂(PhCN)₂ [57], triarylbi-muth [58,59], and nanosized MCM-41 [60] were prepared according to known procedures. The detailed procedure for the preparation of NS-MCM-41-Pd was reported in our previously published paper [53]. Melting points were recorded using melting point apparatus and were uncorrected. Powder X-ray diffraction patterns were acquired on a PANalytical X'Pert PRO (45 kV, 40 mA) with Cu

Table 2

NS-MCM-41-Pd-catalyzed coupling of acyl chlorides with triarylbi-muths^a.

Entry	Acyl chloride	Ar ₃ Bi	Pd (mol%) ^b	t (h)	Yield (%) ^c
1	Benzoyl chloride	(C ₆ H ₅) ₃ Bi	0.2	24	68 (61)
2	Benzoyl chloride	(4-MeC ₆ H ₄) ₃ Bi	1	12	93 (83)
3	Benzoyl chloride	(4-FC ₆ H ₄) ₃ Bi	1	24	75 (66)
4	<i>p</i> -Toluoyl chloride	(C ₆ H ₅) ₃ Bi	1	18	99 (83)
5	<i>p</i> -Toluoyl chloride	(4-MeC ₆ H ₄) ₃ Bi	0.2	32	72 (66)
6	<i>p</i> -Toluoyl chloride	(4-FC ₆ H ₄) ₃ Bi	1	9	73 (60)
7	<i>m</i> -Toluoyl chloride	(C ₆ H ₅) ₃ Bi	1	24	93 (82)
8	<i>m</i> -Toluoyl chloride	(4-MeC ₆ H ₄) ₃ Bi	1	24	99 (86)
9	<i>m</i> -Toluoyl chloride	(4-MeC ₆ H ₄) ₃ Bi	0.2	24	57 (52)
10	<i>m</i> -Toluoyl chloride	(4-FC ₆ H ₄) ₃ Bi	1	9	60 (47)
11	<i>o</i> -Toluoyl chloride	(C ₆ H ₅) ₃ Bi	1	24	65 (56)
12	<i>o</i> -Toluoyl chloride	(4-MeC ₆ H ₄) ₃ Bi	1	24	89 (74)
13	<i>o</i> -Toluoyl chloride	(4-FC ₆ H ₄) ₃ Bi	1	12	61 (51)
14	4-Methoxybenzoyl chloride	(C ₆ H ₅) ₃ Bi	1	12	84 (72)
15	4-Methoxybenzoyl chloride	(4-MeC ₆ H ₄) ₃ Bi	1	24	96 (91)
16	4-Methoxybenzoyl chloride	(4-MeC ₆ H ₄) ₃ Bi	0.2	48	88 (83)
17	4-Methoxybenzoyl chloride	(4-FC ₆ H ₄) ₃ Bi	1	12	70 (61)
18	4-Nitrobenzoyl chloride	(C ₆ H ₅) ₃ Bi	1	12	76 (68)
19	4-Nitrobenzoyl chloride	(C ₆ H ₅) ₃ Bi	0.2	48	61 (57)
20	4-Nitrobenzoyl chloride	(4-MeC ₆ H ₄) ₃ Bi	1	12	98 (91)
21	4-Nitrobenzoyl chloride	(4-FC ₆ H ₄) ₃ Bi	1	12	80 (66)
22	4-Chlorobenzoyl chloride	(C ₆ H ₅) ₃ Bi	1	9	90 (80)
23	4-Chlorobenzoyl chloride	(4-MeC ₆ H ₄) ₃ Bi	1	12	81 (70)
24	4-Chlorobenzoyl chloride	(4-MeC ₆ H ₄) ₃ Bi	0.2	32	72 (68)
25	4-Chlorobenzoyl chloride	(4-FC ₆ H ₄) ₃ Bi	1	12	54 (49)
26	2-Chlorobenzoyl chloride	(C ₆ H ₅) ₃ Bi	1	12	68 (62)
27	2-Chlorobenzoyl chloride	(4-MeC ₆ H ₄) ₃ Bi	1	12	65 (56)
28	2-Chlorobenzoyl chloride	(4-FC ₆ H ₄) ₃ Bi	1	12	70 (65)
29	4-Bromobenzoyl chloride	(C ₆ H ₅) ₃ Bi	1	12	82 (71)
30	4-Bromobenzoyl chloride	(4-MeC ₆ H ₄) ₃ Bi	1	12	89 (81)
31	4-Bromobenzoyl chloride	(4-FC ₆ H ₄) ₃ Bi	1	12	88 (78)

^a Reaction conditions: in THF at 60 °C. [Acyl chloride]:[Ar₃Bi]:[Et₃N] = 2:1:4.

^b Based on acyl chloride.

^c GC yields. Isolated yields are given in parentheses.

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