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A phosphine-free, heterogeneous palladium-catalyzed atom-efficient carbonylative cross-coupling of triorganoindiums with aryl halides leading to unsymmetrical ketones

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The first phosphine-free heterogeneous palladium-catalyzed carbonylative cross-coupling of aryl halides with triorganoindiums has been developed that proceeds smoothly under 1 or 2.5 atm of carbon monoxide in THF at 68 ºC and provides a general and powerful tool for the synthesis of various valuable unsymmetrical ketones with high atom-economy, good yield, and recyclability of the catalyst. Our system not only avoids the use of phosphine ligands, but also solves the basic problem of palladium catalyst recovery and reuse.

Introduction

Aryl ketones[1] and α,β-acetylenic ketones[2] are important building blocks for a large number of natural products and pharmaceutical compounds. One general method for the preparation of aryl ketones is the Friedel-Crafts acylation of substituted aromatic rings.[3] The crucial disadvantage of traditional Friedel-Crafts acylation is the use of more than a stoichiometric amount of anhydrous $AlCl_3$, which is incompatible with many functional groups and produces a large amount of waste. A common approach

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to α,β-acetylenic ketones involves the acylation of alkynylmetal reagents such as silver,[4] copper,[5] lithium,[6] zinc,[7] silicon,[8] and tin[9] with acid chlorides. Generally, the preparation of unsymmetrical ketones by transition-metal-catalyzed cross-coupling reaction is severely limited, since the organometallic partners often react with the product ketone. The transition metal-catalyzed carbonylative cross-coupling reaction of organic electrophiles with organometallics in the presence of carbon monoxide has provided a straightforward and convenient route to unsymmetrical ketones.[10] A variety of organometallics including magnesium,[11] aluminum,[12] silicon,[13] tin,[14] zinc,[15] boron,[16] and bismuth[17] reagents have been reported to undergo the carbonylative cross-coupling reactions, but the utility of this route is limited by requirements of a high temperature or a high pressure of carbon monoxide, the transfer of only one of the organic groups attached to the metal, and β-hydride elimination. Recently, we reported a phosphine-free heterogeneous palladium-catalyzed atom-efficient carbonylative cross-coupling of aryl iodides with triarylbismuths leading to biaryl ketones, however, the developed method was not applicable to the synthesis of alkyl aryl ketones and α,β-acetylenic ketones.[18] Besides these traditional organometallic reagents, triorganoindium reagents (R_3In) are increasingly gaining attention as efficient partners for transition-metal-catalyzed cross-couplings.[19] The high efficiency, versatility, atom-economy, and chemoselectivity of these organoindium reagents make them useful alternatives to other organometallic compounds in cross-coupling reactions. Lee and Sarandeses reported the palladium(0)-catalyzed carbonylative cross-coupling reactions of triorganoindium compounds with aryl (or alkenyl) halides (or

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pseudohalides) and CO, providing a new and efficient route for the synthesis of unsymmetrical ketones.[20] The reaction was carried out in refluxing THF under 1 or 2.5 atm of CO with 4-5 mol% $Pd(PPh_3)_4$ as catalyst. However, homogeneous $Pd(PPh_3)_4$ is air and moisture-sensitive, expensive, cannot be recycled, and difficult to separate from the product mixture, which may have a very serious negative impact on their possible industrial applications, especially the pharmaceutical industry. Therefore, from the viewpoint of green and sustainable chemistry, the development of a recyclable palladium catalyst that allows for highly efficient synthesis of unsymmetrical ketones from a wide range of substrates (aryl halides and triorganoindiums) is highly desirable.

Immobilization of homogeneous catalysts through covalent bond formation with functional groups on various porous materials is usually the method of choice since the supported catalysts can be easily separated from the reaction mixture by simple filtration and reused in successive reactions provided that the active sites have not become deactivated. Moreover, heterogeneous catalysis also helps decrease wastes derived from reaction workup, contributing to development of green and sustainable chemical process.[21] Mesoporous material MCM-41 has recently emerged as a promising solid support for immobilization because of its large and uniform pore size, ultrahigh surface area, big pore volume and rich silanol groups in the inner walls.[22] So far, some functionalized MCM-41-immobilized transition-metal catalysts such as palladium,[18,23] rhodium,[24] molybdenum,[25] gold[26] and copper[27] complexes have been successfully used as potentially green and sustainable catalysts in organic reactions. Recently, we reported the first synthesis of an MCM-41-immobilized palladium(II)-

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Schiff base complex [MCM-41-N,N-Pd(OAc)$_2$] and its successful application to the atom-efficient cross-coupling of triarylbismuths with aryl iodides.[28] In continuing our efforts to develop greener synthetic pathways for organic transformations,[23c,d,26d,27] herein we wish to report the first phosphine-free heterogeneous palladium-catalyzed carbonylative cross-coupling of aryl halides with triorganoindiums by using MCM-41 -N,N-Pd(OAc)$_2$ complex as a recyclable catalyst. The reactions proceeded smoothly in THF at 68 ºC under 1 or 2.5 atm of carbon monoxide, yielding a variety of unsym-metrical ketones in good yields with high atom-economy and recyclability of the catalyst.

Results and discussion

Although phosphine ligands can stabilize palladium and influence its reactivity, the simplest and cheapest palladium catalysts are of course the phosphine-free systems. Furthermore, the procedure for synthesizing the immobilized phosphine palladium complexes is rather complicated since the preparation of the heterogeneous phosphine ligands requires multi-step sequences. Therefore, the development of phosphine-free supported palladium complex catalysts having a high activity and good stability is a topic of enormous importance. The MCM-41-immobilized palladium(II)-Schiff base complex [MCM-41-N,N-Pd(OAc)$_2$] was easily synthesized starting from mesoporous material MCM-41, 3-aminopropyltriethoxysilane, pyridine-2-carboxaldehyde, and Pd(OAc)$_2$ as shown in Scheme 1 according to our previous precedure.[28] Firstly, the condensation of 3-aminopropyltriethoxysilane with MCM-41 in toluene at 100 °C for

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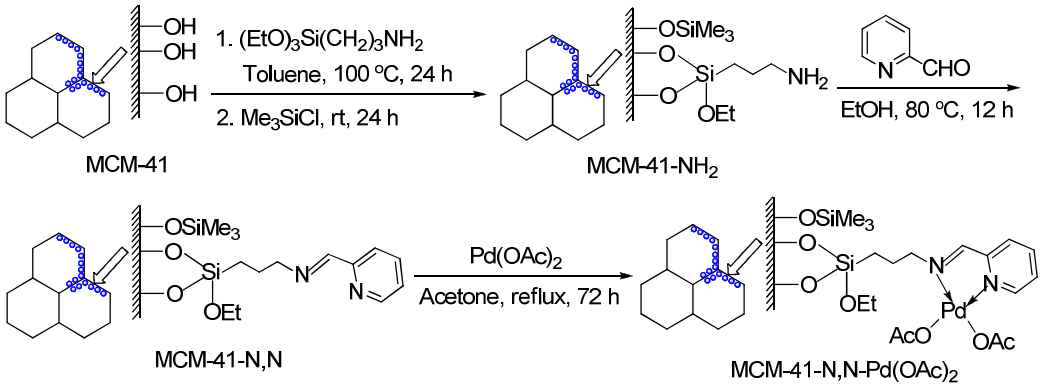
24 h, followed by the silylation with Me_3SiCl in toluene at room temperature for 24 h gave 3-aminopropyl-functionalized MCM-41 material(MCM-41-NH_2). The latter was subsequently treated with pyridine-2-carboxaldehyde in dry ethanol at 80 °C for 12 h to afford the Schiff base-functionalized MCM-41 (MCM-41-N,N), which was then reacted with $Pd(OAc)_2$ in acetone under reflux for 72 h to generate the MCM-41-immobilized palladium(II)-Schiff base complex [MCM-41-N,N-$Pd(OAc)_2$] as a light yellow powder.



Scheme 1. Preparation of MCM-41-N,N-$Pd(OAc)_2$ complex.

The MCM-41-immobilized palladium(II)-Schiff base complex [MCM-41-N,N-$Pd(OAc)_2$] was then used as the catalyst for the carbonylative cross-coupling of aryl halides with triorganoindiums. In our initial screening experiments, the carbonylative cross-coupling of 4-iodotoluene with Me_3In (0.37 equiv.) in the presence of 1.0 mol% MCM-41-N,N-$Pd(OAc)_2$ was chosen as the model reaction to optimize the reaction conditions and the results are summarized in Table 1. Of the optimized reaction conditions screened, the best result was obtained with 0.37 equiv of Me_3In and 1.0 mol% of MCM-41-N,N-$Pd(OAc)_2$ in THF at 68 ºC under atmospheric pressure of CO

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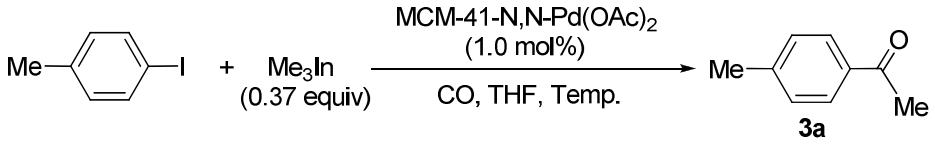
gas, and the desired 4'-methylacetophenone **3a** was produced in 81% yield (Table 1, entry 1). This result means that all of the methyl groups attached to the indium were clearly entered into the product. Surprisingly, however, a decreased yield of **3a** was observed under higher pressure (5 and 10 atm) of CO gas (entries 2 and 3). The carbonylative cross-coupling reaction did not occur at 25 ºC even under 5 atm of CO gas (entries 4 and 5). Lowering the reaction temperature to 50 ºC resulted in a decreased yield (entries 6 and 7). When 4 mol% of $Pd(PPh_3)_4$ was used as catalyst,[20a] the desired product **3a** was obtained in 72 % yield after 4 h (entry 8), indicating that the phosphine-free heterogeneous palladium catalyst exhibited higher activity than $Pd(PPh_3)_4$. Increasing the amount of the catalyst to 2.0 mol% could shorten the reaction time, but did not improve the yield significantly (entry 9). Reducing the amount of the catalyst to 0.5 mol% resulted in a decreased yield and required a longer reaction time (entry 10).

Table 1 Carbonylative cross-coupling reaction of 4-iodotoluene with Me_3In (0.37 equiv.) in different conditions.[a]



Entry	Pressure of CO (atm)	Temp. (ºC)	Time (h)	Isolated yield (%)
1	1	68	2	81
2	5	68	2	63
3	10	68	2	49
4	1	25	6	0
5	5	25	6	0
6	1	50	6	31

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7	5	50	6	34
8[b]	1	68	4	72
9[c]	1	68	1	82
10[d]	1	68	5	65

[a] All reactions were performed using 1.0 mmol of 4-iodotoluene, 0.37 mmol of Me_3In in 4.0 mL of THF. [b] 4 mol% $Pd(PPh_3)_4$ was used. [c] 2 mol% of MCM-41-N,N-$Pd(OAc)_2$ was used. [d] 0.5 mol% of MCM-41-N,N-$Pd(OAc)_2$ was used.

To examine the scope for this heterogeneous carbonylative cross-coupling reaction, we have investigated the reaction using a variety of aryl halides and different triorganoindiums as the substrates under the optimized reaction conditions (Scheme 2) and the results are outlined in Table 2. As shown in Table 2, the carbonylative cross-coupling reactions of Me_3In with a variety of aryl iodides bearing either electron-donating or electron-withdrawing groups proceeded smoothly under the optimized conditions, giving the corresponding substituted acetophenones **3b-3e** in 80-87% yields (entries 2-5). The results indicate that the electronic nature of the substituent on the benzene ring has limited influence on this heterogeneous palladium-catalyzed carbonylative cross-coupling reaction. Reactions of sterically hindered 2-iodotoluene and bulky 1-iodonaphthalene also proceeded effectively to furnish the desired 2'-methylacetophenone **3f** and 1-acetylnaphthalene **3g** in 79 and 83% yield, respectively (entries 6 and 7). Heteroatoms turned out to be compatible with the employed reaction conditions, the reaction of 2-iodothiophene with Me_3In and CO produced the desired 2-acetylthiophene **3h** in 80% yield (entry 8). Tri-*n*-butylindium exhibited a similar reactivity with trimethylindium. Both electron-deficient and electron-rich aryl iodides could undergo the carbonylative cross-coupling reactions with *n*-Bu_3In under atmos-

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pheric pressure of CO gas smoothly to afford the corresponding *n*-butyl aryl ketones **3i-3m** in 81-86% yields (entries 9-13). In addition, bulky 1-iodonaphthalene and 2-iodothiophene gave the expected products **3n** and **3o** in good yields (entries 14 and 15). Tri-*sec*-butylindium could also react with iodobenzene under an atmospheric pressure of CO to produce the desired 2-methyl-1-phenylbutan-1-one **3p** in 76% yield (entry 16). However, the reaction did not work with tricyclopropylindium (*c*-Pr_3In). Besides trialkylindiums, triaryl- and trialkynylindiums also proved to be suitable coupling partners. However, under the reaction conditions optimized for Me_3In, the carbonylative cross-coupling reactions of Ph_3In or trialkynylindiums with aryl iodides afforded only moderate yields of unsymmetrical ketones due to the easy formation of the direct cross-coupling products. To our delight, the direct cross-coupling reactions of aryl iodides with Ph_3In or trialkynylindiums could be greatly suppressed by increasing the pressure of CO from 1 to 2.5 atm. For example, the reactions of Ph_3In with aryl iodides bearing various substituents, regardless of their electronic properties and substitution positions, produced the desired diaryl ketones **3q-3u** in 68-88% yields (entries 17-21). It is noteworthy that under the optimized reaction conditions, bulky 1-iodonaphthalene and heteroaryl iodides such as 2-iodothiophene and 3-iodo-pyridine could undergo the carbonylative cross-coupling reactions with Ph_3In effectively, affording the desired products **3v-3x** in good yields (entries 22-24). The reactions of tri(phenylethynyl)indium and tri(hex-1-ynyl)indium with various aryl iodides also proceeded smoothly under 2.5 atm of CO to furnish the corresponding aryl alkynyl ketones **3y-3c'** in 74-86% yields (entries 25-29). Interestingly, 4-chloro-

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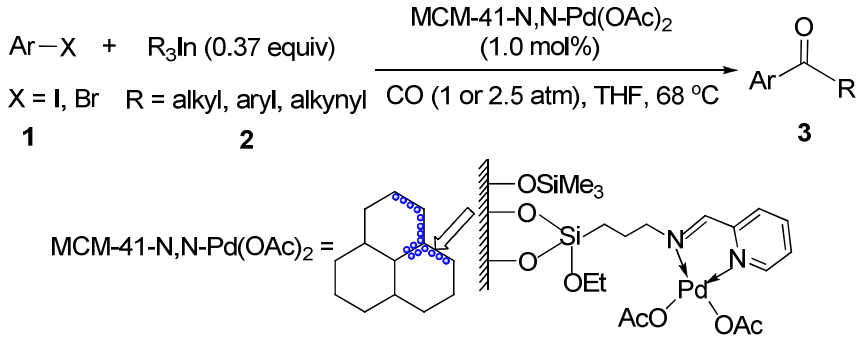
iodobenzene was selectively subjected to carbonylative cross-coupling reactions to produce the desired 4'-chloroacetophenone **3d**, 1-(4-chlorophenyl)pentan-1-one **3k**, and 1-(4-chlorophenyl)-3-phenylprop-2-yn-1-one **3z** in high yields (entries 4, 11 and 26). The present method provides a quite general and practical route for the synthesis of a variety of unsymmetrical ketones. A wide range of electron-donating and electron -withdrawing groups such as methyl, methoxy, chloro, fluoro, trifluoromethyl, cyano, ketone and ester on aryl iodides were well tolerated.



Scheme 2. Heterogeneous carbonylative cross-coupling of aryl halides with R_3In.

Encouraged by the above results, the carbonylative cross-coupling reactions of triorganoindiums with a variety of aryl bromides were then examined under optimized reaction conditions and the results are also listed in Table 2. Generally, the reactivity of aryl bromides was lower than that of aryl iodides. The reactions of electron-deficient aryl bromides with trialkylindiums could proceed smoothly to afford the desired alkyl aryl ketones in good yields (entries 30-33), whilst electron-rich aryl bromides gave only low yields (entries 34 and 35). Similarly, the reactions of bromo-benzene and electron-deficient aryl bromides with Ph_3In or trialkynylindiums could give moderate yields of the desired products (entries 36-40), but the electron-rich aryl

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bromides were poor substrates (entries 41 and 42). We also applied the present protocol to dihalogenated aromatic compounds to prepare diacylbenzenes, which can be used effectively in materials and dendrimer sciences (Scheme 3). Reaction of 1,4-diiodobenzene with 1.1 equiv of tri-*n*-butylindium under 1 atm of CO gas for 3 h produced the expected 1,1'-(1,4-phenylene)dipentan-1-one **4a** in 70% yield. We were pleased to observe that treatment of 1,4-diiodobenzene with 1.1 equiv of tri(4-fluoro-phenyl)indium under 2.5 atm of CO gas for 3 h afforded the desired 1,4-bis(4-fluorobenzoyl)benzene **4b** in 72% yield.

Table 2 Synthesis of a variety of unsymmetrical ketones.[a]

Entry	Ar-X	R	Time (h)	Product	Yield (%)[b]
1	4-MeC_6H_4I	Me	2	**3a**	81
2	4-MeOC_6H_4I	Me	2.5	**3b**	87
3	4-FC_6H_4I	Me	2	**3c**	82
4	4-ClC_6H_4I	Me	2	**3d**	80
5	4-MeOCOC_6H_4I	Me	1.5	**3e**	82
6	2-MeC_6H_4I	Me	3	**3f**	79
7	1-iodonaphthalene	Me	2.5	**3g**	83
8	2-iodothiophene	Me	2	**3h**	80
9	3-MeC_6H_4I	*n*-Bu	2	**3i**	82
10	4-MeOC_6H_4I	*n*-Bu	2.5	**3j**	86
11	4-ClC_6H_4I	*n*-Bu	2	**3k**	81
12	4-MeCOC_6H_4I	*n*-Bu	1.5	**3l**	83
13	4-NCC_6H_4I	*n*-Bu	1.5	**3m**	81
14	1-iodonaphthalene	*n*-Bu	2.5	**3n**	75
15	2-iodothiophene	*n*-Bu	2	**3o**	78
16	C_6H_5I	*sec*-Bu	2.5	**3p**	76
17[c]	C_6H_5I	Ph	2	**3q**	84

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18[c]	4-$MeOC_6H_4I$	Ph	2.5	**3r**	88
19[c]	4-$MeOCOC_6H_4I$	Ph	1.5	**3s**	85
20[c]	3-$CF_3C_6H_4I$	Ph	2	**3t**	80
21[c]	2-MeC_6H_4I	Ph	3	**3u**	68
22[c]	1-iodonaphthalene	Ph	2.5	**3v**	79
23[c]	2-iodothiophene	Ph	2	**3w**	77
24[c]	3-iodopyridine	Ph	2	**3x**	71
25[c]	4-$CH_3C_6H_4I$	PhC≡C	2	**3y**	86
26[c]	4-ClC_6H_4I	PhC≡C	2	**3z**	83
27[c]	C_6H_5I	*n*-BuC≡C	2	**3a'**	74
28[c]	4-$CH_3C_6H_4I$	*n*-BuC≡C	2	**3b'**	79
29[c]	4-$MeOC_6H_4I$	*n*-BuC≡C	2	**3c'**	85
30	4-$MeOCOC_6H_4Br$	Me	2.5	**3e**	71
31	4-ClC_6H_4Br	Me	3	**3d**	63
32	4-$MeCOC_6H_4Br$	*n*-Bu	2.5	**3l**	67
33	4-NCC_6H_4Br	*n*-Bu	2.5	**3m**	69
34	4-$CH_3C_6H_4Br$	Me	4	**3a**	43
35	4-$MeOC_6H_4Br$	*n*-Bu	6	**3j**	29
36[c]	C_6H_5Br	Ph	3	**3q**	50
37[c]	C_6H_5Br	*n*-BuC≡C	4	**3a'**	46
38[c]	4-$MeCOC_6H_4Br$	Ph	3	**3d'**	59
39[c]	4-NCC_6H_4Br	Ph	3	**3e'**	61
40[c]	4-ClC_6H_4Br	PhC≡C	4	**3z**	51
41[c]	4-$MeOC_6H_4Br$	Ph	6	**3r**	26
42[c]	4-$CH_3C_6H_4Br$	PhC≡C	5	**3y**	32

[a] Reaction was carried out with R_3In (0.37 mmol), aryl halide (1.0 mmol), and 1 mol% MCM-41-N,N-$Pd(OAc)_2$ in THF (4 mL) at 68 °C under atmospheric pressure of CO gas. [b] Isolated yields. [c] Under 2.5 atm of CO.

To verify whether the observed catalysis was due to the MCM-41-N,N-$Pd(OAc)_2$ complex or to a leached palladium species in solution, we performed the hot filtration

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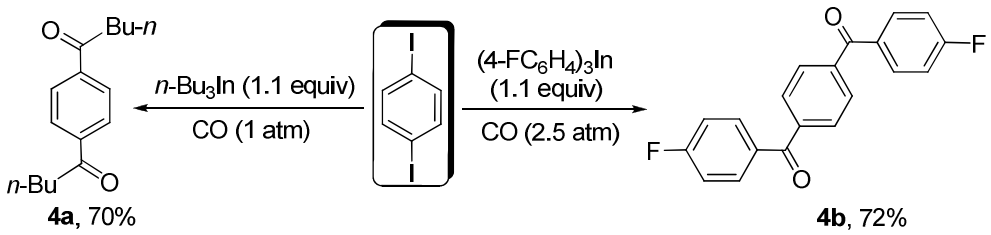
test.[29] We focused on the carbonylative cross-coupling reaction of 4-iodotoluene with Me_3In. We filtered off the MCM-41-N,N-Pd$(OAc)_2$ complex after 0.5 h of reaction time and allowed the filtrate to react further. The catalyst filtration was performed at the reaction temperature (68 °C) to avoid possible recoordination or precipitation of soluble palladium upon cooling. We found that, after this hot filtration, no significant increase in conversion of 4-iodotoluene was observed and the desired **3a** was isolated in only 39% yield, demonstrating that leached palladium species from the supported catalyst (if any) are not responsible for the observed catalytic activity. It was confirmed by ICP-AES analysis that no palladium species could be detected in the filtrate (below the detection limit). These results rule out any contribution to the observed catalysis from a homogeneous palladium species indicating that the catalyst was stable during the reaction and the observed catalysis was intrinsically heterogeneous.



Scheme 3. Heterogeneous double carbonylative cross-coupling of 1,4-diiodobenzene
Reaction conditions: 2 mol% MCM-41-N,N-Pd$(OAc)_2$, THF, 68 °C, 3 h.

A plausible mechanism for this heterogeneous palladium-catalyzed carbonylative cross-coupling of triorganoindiums with aryl halides is illustrated in Scheme 4.[20b] First, the MCM-41-N,N-Pd$(OAc)_2$ complex is reduced by CO gas[30] or R_3In to the MCM-41-N,N-Pd(0) complex. Oxidative addition of Ar-X (**1**) to the MCM-41-N,N-

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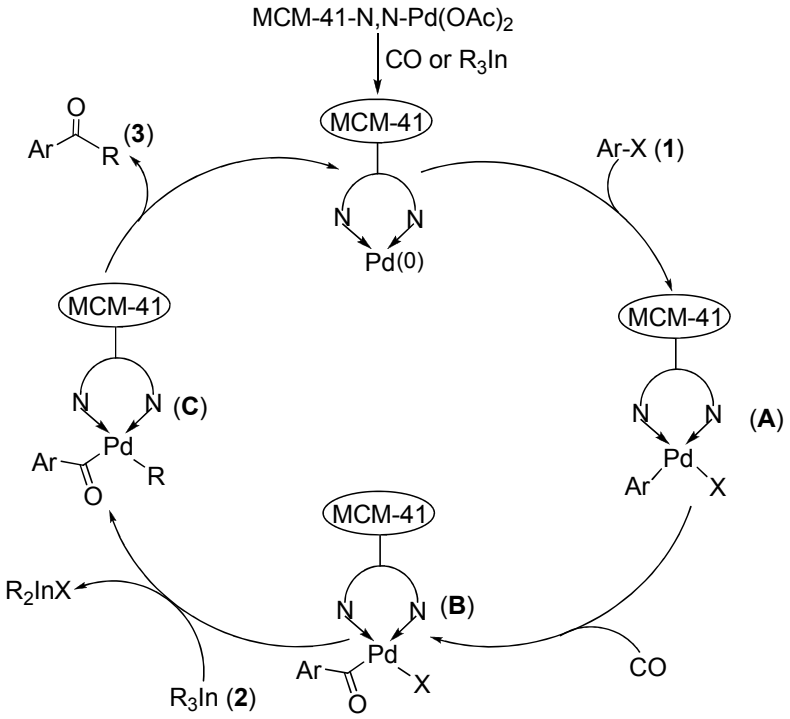
Pd(0) complex provides an MCM-41-bound arylpalladium(II) complex (**A**), which is followed by migratory insertion of carbon monoxide to afford an MCM-41-bound acylpalladium(II) complex (**B**). Transmetalation between intermediate **B** and triorganoindium reagent (**2**) gives intermediate (**C**), which undergoes reductive elimination to afford the expected unsymmetrical ketone (**3**) and regenerate the MCM-41-N,N-Pd(0) complex.



Scheme 4. Proposed catalytic cycle.

For a supported precious metal catalyst, it is important to examine its ease of separation, recoverability and reusability. The MCM-41-N,N-Pd(OAc)$_2$ complex can be easily separated and recovered by a simple filtration of the reaction solution. We next investigated the recyclability of the catalyst by using the carbonylative cross-

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coupling reaction of 4-iodoanisole with Me_3In. After carrying out the reaction, the catalyst was recovered by simple filtration and washed with DMF and diethyl ether. After being air-dried, it can be reused directly without further purification. It should be noted that the palladium in the recovered catalyst is in Pd(0) form. The recovered palladium catalyst was used in the next run, and almost the same yield of **3b** was obtained for 8 consecutive cycles (Figure 1). In addition, palladium leaching in the heterogeneous catalyst was also determined by ICP-AES analysis on the recovered catalyst after eight consecutive runs and the palladium content of the recovered catalyst was found to be 0.41 mmol/g, which revealing almost the same palladium content as the fresh one. In our opinion, the high catalytic activity and excellent reusability of the palladium catalyst relates to the efficient site isolation, to the optimal dispersion of the active sites on the inner channel walls and to the relatively strong interaction between bidentate Schiff base ligand and the palladium centre supported on the MCM-41. The result is important from the standpoint of green and sustainable chemistry.

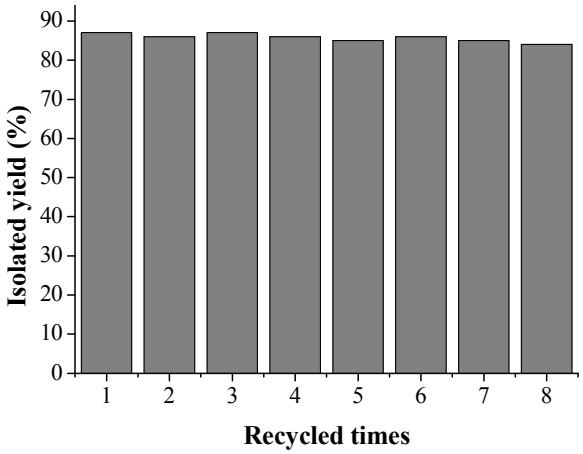

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Fig. 1 Recycle of the MCM-41-N,N-Pd(OAc)$_2$ complex.

Conclusion

In summary, we first developed the heterogeneous carbonylative cross-coupling reaction of readily available, stable and environmentally benign triorganoindium compounds with various aryl halides leading to a variety of unsymmetrical ketones in good yields. This heterogeneous carbonylative cross-coupling has many attractive features, such as: (1) triorganoindiums act as low toxic and atom-efficient coupling reagents; (2) 1 equiv of triorganoindiums gives 3 equiv of carbonylative coupling products; (3) the reaction is tolerant of a wide range of functional groups; (4) only 1 mol% of MCM-41-N,N-Pd(OAc)$_2$ is used compared with 4-5 mol% of Pd(PPh$_3$)$_4$ in homogeneous reaction; (5) this phosphine-free heterogeneous palladium catalyst can easily be prepared from commercially available reagents and recovered by a simple filtration of the reaction solution, and recycled at least eight times without significant loss of activity.

Experimental

General comments

All chemicals were reagent grade and used as purchased. All solvents were dried and distilled before use. The MCM-41-N,N-Pd(OAc)$_2$ catalyst was prepared according to our previous procedure,[28] the palladium content was determined to be 0.42 mmol/g.

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The products were purified by flash chromatography on silica gel. Mixture of EtOAc and hexane was generally used as eluent. All carbonylative cross-coupling products were characterized by comparison of their spectra and physical data with authentic samples. ^{1}H NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer with TMS as an internal standard in $CDCl_3$ as solvent. ^{13}C NMR spectra (100 MHz) were recorded on a Bruker Avance 400 MHz spectrometer in $CDCl_3$ as solvent. HRMS spectra were recorded on a Q-Tof spectrometer with micromass MS software using electrospray ionization (ESI). Melting points are uncorrected. Palladium content was determined with inductively coupled plasma atom emission Atomscan16 (ICP-AES, TJA Corporation).

General procedure for preparation of triorganoindium reagents

A 25 mL round-bottomed flask containing a stirrer bar was charged with $InCl_3$ (0.37 mmol) and dried under vacuum with a heat gun. The flask was cooled, a positive argon pressure was established and anhydrous THF (2 mL) was added. The resulting solution was cooled to –78 ºC and a solution of RLi or RMgBr (1.1 mmol, 1.0-2.5 M in hexane, THF, or Et_2O) was slowly added (15-30 min). The reaction mixture was stirred for 30 min, the cooling bath was removed, and the mixture was warmed to room temperature over 30 min.

General procedure for the heterogeneous palladium-catalyzed carbonylative cross-coupling of aryl halides with trialkylindiums

A solution of Me_3In or *n*-Bu_3In (0.37 mmol, ca. 0.18 M in dry THF) was added to a mixture of MCM-41-N,N-$Pd(OAc)_2$ (24 mg, 1 mol%) and aryl halide (1 mmol) in

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THF (2 mL) under argon atmosphere. The resulting mixture was bubbled with CO gas for 5 min at room temperature to flush out argon, then a positive CO pressure was established. The reaction mixture was warmed to 68 ºC over 30 min and stirred under atmospheric pressure of CO gas for 1.5-6 h at 68 ºC. After being cooled to room temperature, the mixture was diluted with Et_2O (20 mL) and filtered. The palladium catalyst was washed with DMF (2 × 5 mL), Et_2O (2 × 5 mL) and reused in the next run. The filtrate was washed with sat. aq $NaHCO_3$ (5 mL), water (3 × 5 mL) and dried ($MgSO_4$), filtered, and concentrated under vacuum. The residue was purified by flash column chromatography on silica gel (EtOAc:hexane = 1:25) to give the carbony-lative cross-coupling product.

4'-Methylacetophenone 3a. Colorless oil.[31] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85 (d, J = 8.0 Hz, 2H), 7.25 (d, J = 8.0 Hz, 2H), 2.57 (s, 3H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.7, 143.8, 134.7, 129.2, 128.4, 26.4, 21.6.

4'-Methoxyacetophenone 3b. White solid, m.p. 36–37 °C (ref.[31] m.p. 36–38 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.93 (d, J = 8.4 Hz, 2H), 6.93 (d, J = 8.8 Hz, 2H), 3.86 (s, 3H), 2.55 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.7, 163.5, 130.6, 130.4, 113.7, 55.5, 26.3.

4'-Fluoroacetophenone 3c. Colorless oil.[31] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.99 (dd, J = 8.8, 5.6 Hz, 2H), 7.13 (t, J = 8.6 Hz, 2H), 2.59 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.4, 165.7 (d, $^1J_{C\text{-}F}$ = 251.9 Hz), 133.6, 130.9 (d, $^3J_{C\text{-}F}$ = 9.3 Hz), 115.6 (d, $^2J_{C\text{-}F}$ = 21.8 Hz), 26.4.

4'-Chloroacetophenone 3d. Colorless oil.[31] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89 (d,

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J = 8.8 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 2H), 2.59 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.6, 139.4, 135.3, 129.7, 128.8, 26.4.

Methyl 4-acetylbenzoate 3e. White solid, m.p. 87–89 °C (ref.[32] m.p. 89–91 °C). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.07 (s, 4H), 3.90 (s, 3H), 2.64 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 198.1, 166.0, 140.6, 133.7, 129.9, 128.9, 52.9, 27.4.

2'-Methylacetophenone 3f. Colorless oil.[31] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.68 (d, *J* = 8.4 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.27-7.21 (m, 2H), 2.56 (s, 3H), 2.52 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.7, 138.4, 137.7, 132.0, 131.5, 129.3, 125.7, 29.5, 21.5.

1-Acetylnaphthalene 3g. Colorless oil.[31] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.74 (d, *J* = 8.4 Hz, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.91 (d, *J* = 7.2 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.61-7.58 (m, 1H), 7.57-7.45 (m, 2H), 2.72 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.8, 135.5, 134.0, 133.0, 130.2, 128.7, 128.5, 128.1, 126.5, 126.1, 124.4, 30.0.

2-Acetylthiophene 3h. Colorless oil.[31] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70 (d, *J* = 4.0 Hz, 1H), 7.64 (d, *J* = 5.2 Hz, 1H), 7.13 (t, *J* = 4.4 Hz, 1H), 2.57 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.7, 144.5, 133.8, 132.5, 128.1, 26.8.

1-(*m*-Tolyl)pentan-1-one 3i. Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.78-7.73 (m, 2H), 7.37-7.31 (m, 2H), 2.95 (t, *J* = 7.4 Hz, 2H), 2.41 (s, 3H), 1.76-1.66 (m, 2H), 1.46-1.35 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 200.9, 138.3, 137.2, 133.6, 128.6, 128.4, 125.3, 38.4, 26.6, 22.5, 21.4, 13.9. HRMS calcd for $C_{12}H_{16}O^+$ [M^+]: 176.1201, found 176.1206.

1-(4-Methoxyphenyl)pentan-1-one 3j. Pale yellow oil.[20a] ^{1}H NMR (400 MHz,

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$CDCl_3$): δ = 7.94 (d, J = 8.4 Hz, 2H), 6.93 (d, J = 8.8 Hz, 2H), 3.87 (s, 3H), 2.91 (t, J = 7.4 Hz, 2H), 1.75-1.67 (m, 2H), 1.45-1.36 (m, 2H), 0.95 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 199.3, 163.3, 130.3, 130.2, 113.7, 55.4, 38.0, 26.8, 22.5, 13.9.

1-(4-Chlorophenyl)pentan-1-one 3k. Pale yellow oil.[20a] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.89 (d, J = 8.4 Hz, 2H), 7.42 (d, J = 8.4 Hz, 2H), 2.93 (t, J = 7.4 Hz, 2H), 1.74-1.66 (m, 2H), 1.45-1.35 (m, 2H), 0.95 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 199.2, 139.3, 135.4, 129.5, 128.8, 38.3, 26.4, 22.4, 13.9.

1-(4-Acetylphenyl)pentan-1-one 3l. Pale yellow oil.[20a] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.96 (s, 4H), 2.93 (t, J = 7.4 Hz, 2H), 2.58 (s, 3H), 1.71-1.62 (m, 2H), 1.40-1.30 (m, 2H), 0.89 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 200.1, 197.6, 140.2, 140.0, 128.5, 128.3, 38.8, 26.9, 26.3, 22.4, 14.0.

1-(4-Cyanophenyl)pentan-1-one 3m. Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.97 (d, J = 8.4 Hz, 2H), 7.70 (d, J = 8.0 Hz, 2H), 2.92 (t, J = 7.4 Hz, 2H), 1.70-1.61 (m, 2H), 1.38-1.30 (m, 2H), 0.89 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 199.1, 140.0, 132.5, 128.5, 118.0, 116.2, 38.7, 26.1, 22.4, 13.9. HRMS calcd for $C_{12}H_{13}NO^+$ [M^+]: 187.0997, found 187.0995.

1-(Naphthalen-1-yl)pentan-1-one 3n. Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.54 (d, J = 8.0 Hz, 1H), 7.94 (d, J = 8.0 Hz, 1H), 7.86-7.80 (m, 2H), 7.58-7.44 (m, 3H), 3.03 (t, J = 7.4 Hz, 2H), 1.79-1.71 (m, 2H), 1.46-1.38 (m, 2H), 0.95 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 205.1, 136.5, 134.0, 132.3, 130.2, 128.4, 127.8, 127.1, 126.4, 125.8, 124.4, 42.1, 26.9, 22.5, 14.0. HRMS calcd for $C_{15}H_{16}O^+$

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[M^+]: 212.1201, found 212.1207.

1-(Thiophen-2-yl)pentan-1-one 3o. Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.73-7.69 (m, 1H), 7.62 (t, J = 4.8 Hz, 1H), 7.16-7.10 (m, 1H), 2.89 (t, J = 7.4 Hz, 2H), 1.79-1.70 (m, 2H), 1.47-1.36 (m, 2H), 0.96 (t, J = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.5, 144.5, 133.3, 131.6, 128.0, 39.2, 26.9, 22.5, 13.9. HRMS calcd for $C_9H_{12}OS^+$ [M^+]: 168.0609, found 168.0612.

2-Methyl-1-phenylbutan-1-one 3p. Colorless oil.[20a] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.95 (dd, J = 8.4, 1.2 Hz, 2H), 7.54-7.48 (m, 1H), 7.45-7.40 (m, 2H), 3.42-3.36 (m, 1H), 1.87-1.79 (m, 1H), 1.52-1.44 (m, 1H), 1.18 (dd, J = 6.8, 1.2 Hz, 3H), 0.90 (t, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 204.2, 136.8, 132.7, 128.5, 128.2, 42.0, 26.6, 16.7, 11.7.

General procedure for the heterogeneous palladium-catalyzed carbonylative cross-coupling of aryl halides with triphenylindium or trialkynylindiums

In a Schlenk tube, a solution of Ph_3In or $(RC{\equiv}C)_3In$ (0.37 mmol, ca. 0.18 M in dry THF) was added to a mixture of MCM-41-N,N-Pd$(OAc)_2$ (24 mg, 1 mol%) and aryl halide (1 mmol) in THF (2 mL). The tube was charged with CO (2.5 atm) and the resulting mixture was warmed to 68 ºC over 30 min and stirred for 1.5-6 h at 68 ºC. After being cooled to room temperature, the pressure was released and the mixture was diluted with Et_2O (20 mL) and filtered. The palladium catalyst was washed with DMF (2 × 5 mL), Et_2O (2 × 5 mL) and reused in the next run. The filtrate was washed with sat. aq $NaHCO_3$ (5 mL), water (3 × 5 mL) and dried ($MgSO_4$), filtered, and concentrated under vacuum. The residue was purified by flash column chromato-

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graphy on silica gel (EtOAc:hexane = 1:25) to give the carbonylative cross-coupling product.

Benzophenone 3q. White solid, m.p. 46–47 °C (ref.[18] m.p. 47–48 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.81 (d, J = 7.2 Hz, 4H), 7.59 (t, J = 7.6 Hz, 2H), 7.49 (t, J = 7.6 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.8, 137.6, 132.4, 130.1, 128.3.

4-Methoxybenzophenone 3r. White solid, m.p. 60–61 °C (ref.[18] m.p. 59–60 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85-7.82 (m, 2H), 7.77-7.74 (m, 2H), 7.58-7.54 (m, 1H), 7.47 (t, J = 7.6 Hz, 2H), 6.96 (dd, J = 8.8, 2.0 Hz, 2H), 3.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.6, 163.2, 138.3, 132.6, 131.9, 130.1, 129.8, 128.2, 113.6, 55.5.

Methyl 4-benzoylbenzoate 3s. White solid, m.p. 107–108 °C (ref.[18] m.p. 108–109 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.15 (dd, J = 6.6, 1.8 Hz, 2H), 7.84 (dd, J = 6.8, 2.0 Hz, 2H), 7.81 (d, J = 8.0 Hz, 2H), 7.65-7.60 (m, 1H), 7.50 (t, J = 7.6 Hz, 2H), 3.97 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.0, 166.3, 141.3, 137.0, 133.2, 133.0, 130.1, 129.8, 129.5, 128.5, 52.5.

3-(Trifluoromethyl)benzophenone 3t. White solid, m.p. 48–49 °C (ref.[18] m.p. 50–51 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07 (s, 1H), 7.98 (d, J = 7.6 Hz, 1H), 7.85 (d, J = 7.6 Hz, 1H), 7.81-7.77 (m, 2H), 7.69-7.60 (m, 2H), 7.52 (t, J = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.1, 138.3, 136.8, 133.1, 133.0, 131.0 (q, $^2J_{C\text{-}F}$ = 36.4 Hz), 130.0, 128.9, 128.8 (q, $^3J_{C\text{-}F}$ = 3.6 Hz), 128.6, 126.7 (q, $^3J_{C\text{-}F}$ = 3.8 Hz), 123.5 (q, $^1J_{C\text{-}F}$ = 272.0 Hz).

2-Methylbenzophenone 3u. Colorless oil.[18] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80 (d,

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J = 7.6 Hz, 2H), 7.57 (d, *J* = 7.6 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.33-7.24 (m, 3H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.1, 138.2, 137.3, 136.2, 132.6, 130.5, 129.7, 129.6, 128.0, 127.9, 124.7, 19.5.

1-Benzoylnaphthalene 3v. Colorless oil.[18] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.09 (d, *J* = 7.6 Hz, 1H), 7.95 (d, *J* = 8.4 Hz, 1H), 7.89–7.83 (m, 3H), 7.56–7.37 (m, 7H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.0, 138.4, 136.5, 133.8, 133.3, 131.3, 131.1, 130.5, 128.5, 128.4, 127.8, 127.3, 126.5, 125.8, 124.4.

2-Benzoylthiophene 3w. White solid, m.p. 52–53 °C (ref.[18] m.p. 54–55 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88-7.85 (m, 2H), 7.74–7.71 (m, 1H), 7.66–7.64 (m, 1H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.18–7.15 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 188.2, 143.7, 138.2, 134.8, 134.2, 132.3, 129.2, 128.4, 128.0.

3-Benzoylpyridine 3x. White solid, m.p. 40–41 °C (ref.[18] m.p. 39–41 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.02 (s, 1H), 8.83 (s, 1H), 8.13 (d, *J* = 8.0 Hz, 1H), 7.81 (d, *J* = 7.6 Hz, 2H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 2H), 7.48-7.44 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.7, 152.5, 150.7, 137.3, 136.7, 133.2, 130.0, 128.6, 127.6, 123.5.

1-(4-Methylphenyl)-3-phenylpropynone 3y. White solid, m.p. 105–106 °C (ref.[33] m.p. 106–107 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.12 (d, *J* = 8.0 Hz, 2H), 7.68 (d, *J* = 6.8 Hz, 2H), 7.48 (t, *J* = 6.8 Hz, 1H), 7.42 (t, *J* = 7.2 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 177.7, 145.2, 134.7, 133.0, 130.7, 129.7, 129.4, 128.7, 120.3, 92.6, 87.0, 21.8.

1-(4-Chlorophenyl)-3-phenylpropynone 3z. White solid, m.p. 85–86 °C (ref.[33] m.p.

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86–87 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.16-8.13 (m, 2H), 7.69-7.66 (m, 2H), 7.52-7.40 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 176.7, 140.7, 135.4, 133.1, 131.0, 130.9, 129.0, 128.8, 119.9, 93.7, 86.6.

1-Phenylhept-2-yn-1-one 3a'. Pale yellow oil.[33] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.14 (d, J = 7.2 Hz, 2H), 7.59 (t, J = 7.2 Hz, 1H), 7.47 (t, J = 7.6 Hz, 2H), 2.52-2.47 (m, 2H), 1.69-1.61 (m, 2H), 1.54-1.46 (m, 2H), 0.98-0.94 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 178.2, 136.9, 133.9, 129.5, 128.5, 96.8, 79.7, 29.8, 22.1, 18.9, 13.5.

1-(4-Methylphenyl)hept-2-yn-1-one 3b'. Pale yellow oil.[33] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.03 (d, J = 8.0 Hz, 2H), 7.26 (d, J = 7.6 Hz, 2H), 2.49 (t, J = 7.2 Hz, 2H), 2.42 (s, 3H), 1.68-1.61 (m, 2H), 1.54-1.46 (m, 2H), 0.96 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 177.9, 144.9, 134.6, 129.6, 129.2, 96.3, 79.7, 29.9, 22.1, 21.7, 18.9, 13.5.

1-(4-Methoxyphenyl)hept-2-yn-1-one 3c'. Pale yellow oil.[33] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.10 (dd, J = 7.2, 1.8 Hz, 2H), 6.95 (d, J = 8.8 Hz, 2H), 3.88 (s, 3H), 2.49 (t, J = 7.2 Hz, 2H), 1.69-1.62 (m, 2H), 1.54-1.46 (m, 2H), 0.96 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 176.9, 164.3, 131.9, 130.4, 113.7, 95.9, 79.7, 55.5, 29.9, 22.1, 18.9, 13.5.

4-Acetylbenzophenone 3d'. White solid, m.p. 82–83 °C (ref.[18] m.p. 83–84 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.06 (dd, J = 6.6, 1.8 Hz, 2H), 7.87 (dd, J = 6.6, 1.8 Hz, 2H), 7.81 (d, J = 7.6 Hz, 2H), 7.65-7.61 (m, 1H), 7.51 (t, J = 7.6 Hz, 2H), 2.68 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.5, 196.0, 141.4, 139.6, 136.9, 133.0, 130.1,

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DOI: 10.1039/C7NJ02969A

130.0, 128.5, 128.2, 26.9.

4-Cyanobenzophenone 3e'. White solid, m.p. 109–111 °C (ref.[18] m.p. 110– 112 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88 (d, J = 8.8 Hz, 2H), 7.81-7.77 (m, 4H), 7.65 (t, J = 7.6 Hz, 1H), 7.52 (t, J = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.5, 140.7, 135.9, 132.8, 131.7, 129.7, 129.5, 128.1, 117.5, 115.2.

General procedure for the heterogeneous palladium-catalyzed double carbonylative cross-coupling of 1,4-diiodobenzene with *n*-Bu_3In or (4-$FC_6H_4)_3$In

In a Schlenk tube, a solution of *n*-Bu_3In or (4-$FC_6H_4)_3$In (1.1 mmol, ca. 0.18 M in dry THF) was added to a mixture of MCM-41-N,N-Pd$(OAc)_2$ (48 mg, 2 mol%) and 1,4-diiodobenzene (1 mmol) in THF (1 mL). The tube was charged with CO (1 or 2.5 atm) and the resulting mixture was warmed to 68 ºC over 30 min and stirred for 3 h at 68 ºC. After being cooled to room temperature, the mixture was diluted with Et_2O (20 mL) and filtered. The palladium catalyst was washed with DMF (2 × 5 mL), Et_2O (2 × 5 mL) and reused in the next run. The filtrate was washed with sat. aq $NaHCO_3$ (5 mL), water (3 × 5 mL) and dried ($MgSO_4$), filtered, and concentrated under vacuum. The residue was purified by flash column chromatography on silica gel (EtOAc: hexane = 1:25) to give the expected product.

1,1'-(1,4-Phenylene)dipentan-1-one 4a. Pale yellow oil.[20a] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.02 (s, 4H), 2.99 (t, J = 7.4 Hz, 4H), 1.76-1.68 (m, 4H), 1.46-1.37 (m, 4H), 0.96 (t, J = 7.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 200.0, 140.1, 128.2, 38.7, 26.3, 22.4, 13.9.

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DOI: 10.1039/C7NJ02969A

1,4-Bis(4-fluorobenzoyl)benzene 4b. White solid, m.p. 207-209 °C (ref.[34] m.p. 209–210 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.91-7.86 (m, 8H), 7.20 (t, J = 8.6 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.4, 165.7 ($^{1}J_{C\text{-}F}$ = 255.6 Hz), 140.7, 133.2 ($^{4}J_{C\text{-}F}$ = 3.0 Hz), 132.8 ($^{3}J_{C\text{-}F}$ = 10.1 Hz), 129.6, 115.7 ($^{2}J_{C\text{-}F}$ = 22.1 Hz).

The experimental procedure for the hot filtration test

A 25 mL round-bottomed flask equipped with a gas inlet tube, a reflux condenser, and a magnetic stirring bar was charged with MCM-41-N,N-Pd(OAc)$_2$ (24 mg, 1 mol%) and 4-iodotoluene (1.0 mmol) under Ar. The flask was flushed with carbon monoxide for 5 min and a positive CO pressure was established. THF (2 mL) and a solution of Me_3In (0.37 mmol, ca. 0.18 M in dry THF) were then added via syringe. After being stirred at 68 °C for 0.5 h under CO (1 atm), the reaction mixture was filtered at 68 °C to remove the supported palladium catalyst and the filtrate was transferred to another 25 mL round-bottomed flask under Ar. The hot filtration solution was bubbled with CO gas at room temperature for 5 min to flush out argon and then stirred at 68 °C under CO (1 atm) for 3 h. After being cooled to room temperature, the mixture was diluted with Et_2O (20 mL). The ether solution was washed with sat. aq $NaHCO_3$ (5 mL), water (3 × 5 mL) and dried ($MgSO_4$), filtered, and concentrated under vacuum. The residue was purified by flash column chromatography on silica gel (EtOAc: hexane = 1:25) to give the desired **3a** (52.3 mg, 39%).

The experimental procedure for the recycle of the catalyst

View Article Online
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A solution of Me_3In (0.37 mmol, ca. 0.18 M in dry THF) was added to a mixture of MCM-41-N,N-Pd$(OAc)_2$ (24 mg, 1 mol%) and 4-iodoanisole (1 mmol) in THF (2 mL) under Ar. The resulting mixture was bubbled with CO gas for 5 min at room temperature to flush out argon and then stirred at 68 ºC under CO (1 atm) for 2.5 h. After being cooled to room temperature, the mixture was diluted with Et_2O (20 mL) and filtered. The palladium catalyst was washed with DMF (2 × 5 mL), Et_2O (2 × 5 mL) and air-dried. The filtrate was washed with sat. aq $NaHCO_3$ (5 mL), water (3 × 5 mL) and dried ($MgSO_4$), filtered, and concentrated under vacuum. The residue was purified by flash column chromatography on silica gel (EtOAc:hexane = 1:25) to give the desired **3b** in 87% yield. The recovered palladium catalyst was subjected to a second run of the reaction by using the same substrates (4-iodoanisole and Me_3In) under the same conditions and the procedure was repeated up to seven times.

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Graphical Abstract

A phosphine-free, heterogeneous palladium-catalyzed atom-efficient carbonylative cross-coupling of triorganoindiums with aryl halides leading to unsymmetrical ketones

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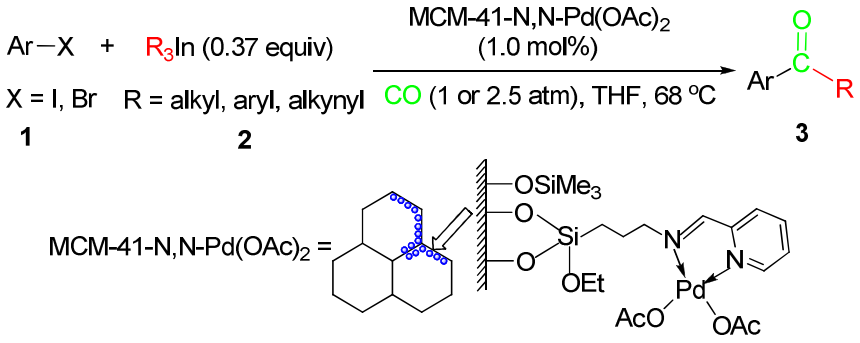

A phosphine-free heterogeneous palladium-catalyzed carbonylative cross-coupling of triorganoindiums with aryl halides for the synthesis of unsymmetrical ketones has been described.