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VIP

Preparation of Functionalized Organoindium Reagents by Means of Magnesium Insertion into Organic Halides in the Presence of $InCl_3$ at Room Temperature

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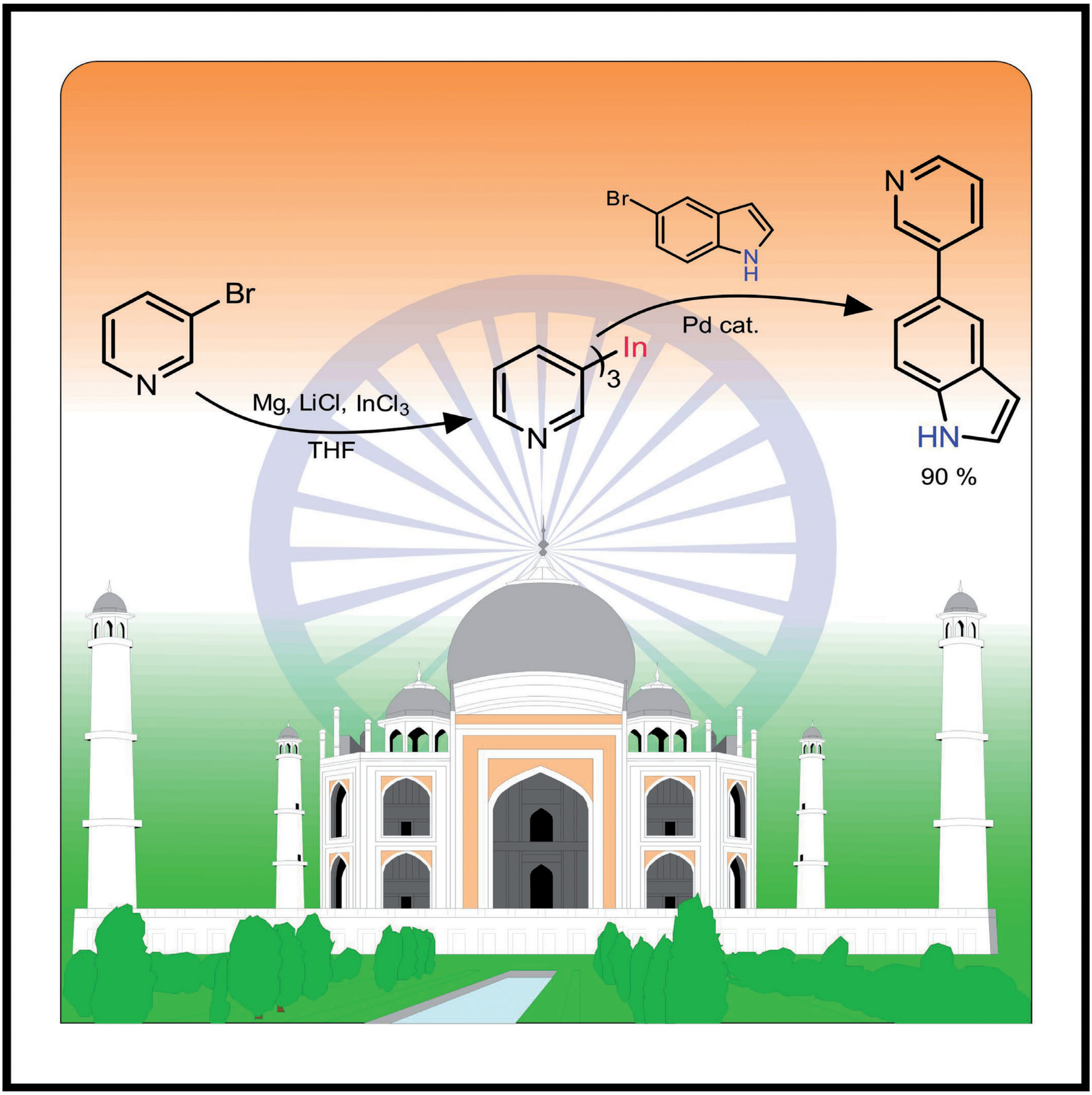
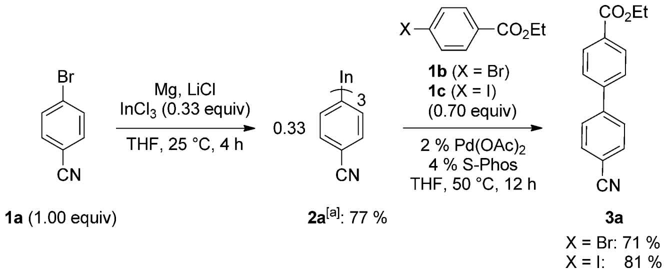


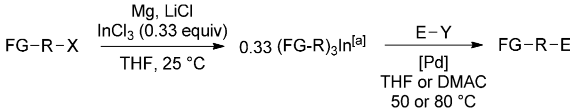
The conversion of organic halides to organometallics by direct metal insertion (the Grignard reaction) is a very general method. The LiCl-mediated insertion of Mg,[1] Zn,[2] Al,[3] Mn,[4] and In[5] has proven to be especially effective and provides access to a range of functionalized organometallic reagents that can readily be applied to cross-coupling[6] and other reactions with electrophiles.[7] Nevertheless, some functionalized halides, such as 4-bromobenzonitrile (**1a**), do not insert magnesium under standard conditions and require specific optimization because of radical side-reactions. Takai and Ikawa first reported the beneficial effect of indium(III) halides on the insertion of aluminum metal into allylic halides.[8] This observation solved the problem of the erratic behavior of the direct insertion of magnesium into the bromonitrile **1a** and led us to develop a new, general one-pot procedure for the preparation of triorganoindium compounds of type **2**, **5**, **8**, and **11**, starting from various organic halides (chlorides and bromides).

Organoindium compounds are versatile organometallic intermediates for organic synthesis because they display a high functional group tolerance and are mainly prepared by transmetalation reactions.[9] A direct insertion of indium powder is only possible with activated organic halides and requires a large excess of this expensive metal.[5,10] However, the treatment of **1a** (1.00 equiv) with magnesium turnings (2.50 equiv) in the presence of LiCl (2.50 equiv) and InCl$_3$ (0.33 equiv) at room temperature in THF for 4 h leads to the corresponding triorganoindium reagent (**2a**) in good yield (77 %; Scheme 1). No excess of indium(III) is necessary under these conditions. Iodolysis followed by gas-chromatographic analysis showed complete conversion and more importantly the absence of significant amounts of side products. Sarandeses and co-workers pioneered and further established Pd-catalyzed cross-couplings with organoindium reagents.[11] Interestingly, a Pd-catalyzed cross-coupling of tri(4-cyanophenyl)indium (**2a**) with the Buchwald ligand (2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl (S-Phos))[12] led to a smooth reaction with ethyl 4-bromobenzoate (**1b**; THF, 50 °C, 12 h), providing the desired biphenyl **3a** in 71 % yield. Ethyl 4-iodobenzoate (**1c**) was also used instead of **1b** as an electrophile, which resulted in an increased yield of **3a** (81 %; Scheme 1).



Scheme 1. Preparation of tri(4-cyanophenyl)indium (**2a**) from 4-bromobenzonitrile (**1a**) by means of Mg insertion in the presence of LiCl and InCl$_3$ and subsequent Pd-catalyzed cross-coupling. [a] Complexed LiCl and magnesium halides are omitted for clarity.

Herein, we report that this method is general and applies to aryl, heteroaryl, and alkyl bromides, as well as benzyl chlorides. In all cases, the resulting indium reagents react with aryl halides in the presence of a palladium catalyst (Scheme 2).



Scheme 2. Preparation of triorganoindium reagents by means of Mg insertion in the presence of LiCl and InCl$_3$. X = Br, Cl; Y = Br, I; R = aryl, heteroaryl, benzyl, alkyl; E = aryl, heteroaryl; FG = functional group; [Pd] = Pd(OAc)$_2$ (2 %), S-Phos (4 %) or [PdCl$_2$(PPh$_3$)$_2$] (4 %); DMAC = *N*,*N*-dimethylacetamide. [a] Complexed LiCl and magnesium halides are omitted for clarity.

Therefore, ethyl 4-bromobenzoate (**1b**) could also be smoothly converted to the corresponding triarylindium reagent, **2b**, in 4 h at 25 °C with Mg/LiCl (2.5 equiv) and InCl$_3$ (0.33 equiv). Subsequent cross-coupling with 3-iodobenzonitrile (**1d**) or 4-bromoanisole (**1e**; Table 1, entries 1 and 2, respectively) in THF at 50 °C with Pd(OAc)$_2$ (2 %) and S-Phos (4 %),[12] as the catalytic system, led to the corresponding biphenyl, **3b** or **3c**, in 57–67 % yield after 12 h. Moreover, tri(4-chlorophenyl)indium **2c** could be efficiently prepared by a selective insertion of Mg into the C–Br bond of 1-bromo-4-chlorobenzene (**1f**) and was coupled to bromobenzocaine (**1g**) in 82 % yield (Table 1, entry 3). The electron-rich tri(*para*-anisyl)indium (**2d**) and tri(*ortho*-dimethylaminophenyl)indium (**2e**) were also accessible from substrates **1e** and **1i** under mild conditions (25 °C, 4 h) and underwent cross-couplings with 4-iodonitrobenzene (**1h**) and **1a** in 69–84 % yield (Table 1, entries 4 and 5, respectively). Moreover, tri{[(diethylcarbamoyl)oxy]phenyl}indium (**2f**) was prepared from the corresponding bromoarene (**1j**) and could be reacted with **1a**, the bromobenzamide (**1k**), or the unprotected bromoindole (**4a**) in 64–87 % yield (Table 1, entries 6–8) under the coupling conditions developed (Pd(OAc)$_2$/S-Phos; THF, 50 °C). In several cases, it was found that a smaller amount of magnesium turnings (1.5 instead of 2.5 equiv) lead to similar results (Table 1, entries 6–8).

The method could also be applied to the preparation of heteroaromatic indium reagents. Thus, 3-bromopyridine (**4b**) was reacted with Mg turnings, LiCl, and InCl$_3$ (1.50, 1.50, and 0.33 equiv, respectively) at 25 °C in THF and after 4 h full conversion to the corresponding organometallic reagent (**5a**) was detected by GC-MS analysis of a reaction

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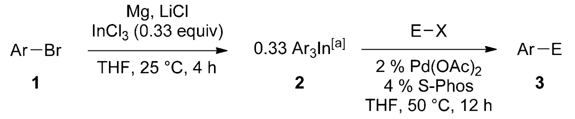
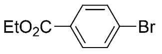
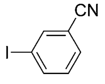
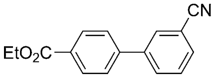
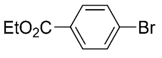
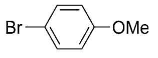
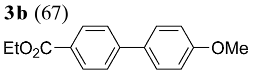
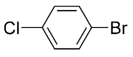
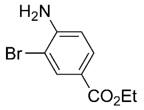
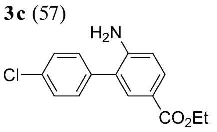
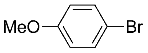
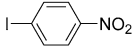
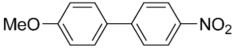
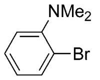
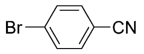
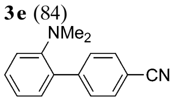
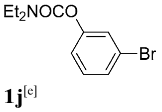
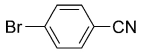
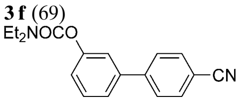
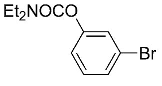
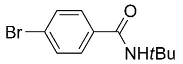
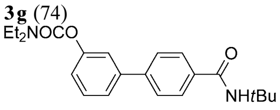
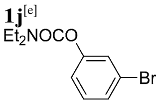
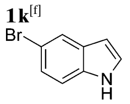
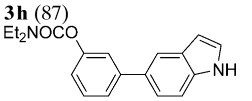
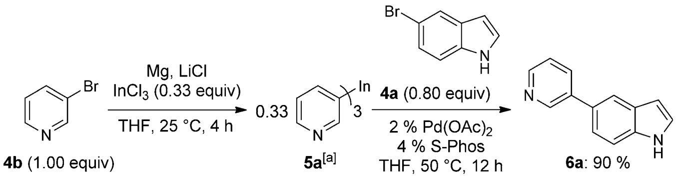
Table 1. Cross-coupling of triarylindium reagents of type **2**, obtained from aryl bromides **1** by Mg insertion in the presence of LiCl and $InCl_3$, with different organic halides as electrophiles.



Entry	Ar−Br	E−X	Product (Yield [%])[b]
1	 **1b**[c]	 **1d**[d]	 **3b** (67)
2	 **1b**[c]	 **1e**[d]	 **3c** (57)
3	 **1f**[c]	 **1g**[d]	 **3d** (82)
4	 **1e**[c]	 **1h**[d]	 **3e** (84)
5	 **1i**[c]	 **1a**[d]	 **3f** (69)
6	 **1j**[e]	 **1a**[f]	 **3g** (74)
7	 **1j**[e]	 **1k**[f]	 **3h** (87)
8	 **1j**[e]	 **4a**[f]	 **3i** (64)

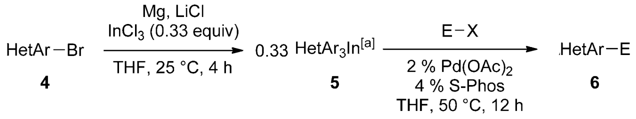
[a] Complexed LiCl and magnesium halides are omitted for clarity. [b] Yields of the isolated, analytically pure, product. [c] Mg turnings (2.50 equiv), LiCl (2.50 equiv), $InCl_3$ (0.33 equiv) were applied to the preparation of the triarylindium reagent. [d] 0.70 equivalents of electrophile were used. [e] Mg turnings (1.50 equiv), LiCl (1.50 equiv), $InCl_3$ (0.33 equiv) were applied to the preparation of the triarylindium reagent. [f] 0.80 equivalents of electrophile were used.

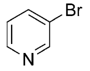
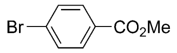
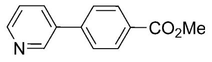
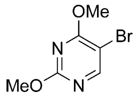
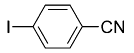
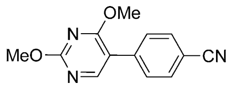
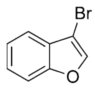
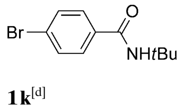
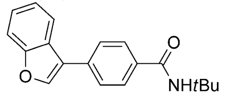
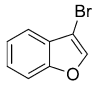
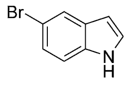
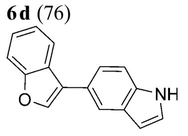
aliquot. The tri(3-pyridyl)indium reagent **5a** could be coupled with the unprotected 5-bromoindole (**4a**) by using $Pd(OAc)_2$ (2%) and S-Phos (4%), leading to the heteroarylated indole **6a** in 90% yield (Scheme 3).



Scheme 3. Preparation of tri(3-pyridyl)indium (**5a**) from 3-bromopyridine (**4b**) by means of Mg insertion in the presence of LiCl and $InCl_3$ and subsequent Pd-catalyzed cross-coupling. [a] Complexed LiCl and magnesium halides are omitted for clarity.

Table 2. Cross-coupling of triheteroarylindium reagents of type **5**, obtained from heteroaryl bromides **4** by Mg insertion in the presence of LiCl and $InCl_3$, with different organic halides as electrophiles.



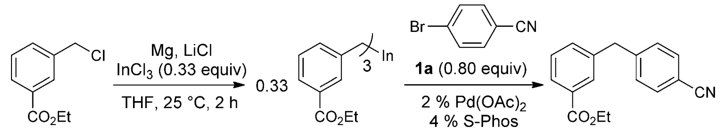
Entry	HetAr−Br	E−X	Product (Yield [%])[b]
1	 **4b**[c]	 **1l**[d]	 **6b** (82)
2	 **4c**[e]	 **1m**[f]	 **6c** (68)
3	 **4d**[c]	 **1k**[d]	 **6d** (76)
4	 **4d**[c]	 **4a**[d]	 **6e** (69)

[a] Complexed LiCl and magnesium halides are omitted for clarity. [b] Yield of isolated, analytically pure, product. [c] Mg turnings (1.50 equiv), LiCl (1.50 equiv), and $InCl_3$ (0.33 equiv) were applied to the preparation of the triheteroarylindium reagent. [d] 0.80 equivalents of electrophile were used. [e] Mg turnings (2.50 equiv), LiCl (2.50 equiv), and $InCl_3$ (0.33 equiv) were applied to the preparation of the triheteroarylindium reagent. [f] 0.70 equivalents of electrophile were used.

In a similar manner, the tripyridylindium derivative **5a** was coupled with 4-bromomethylbenzoate (**1l**) in 82% yield (Table 2, entry 1). Starting from 5-bromo-2,4-dimethoxypyrimidine (**4c**), the tripyrimidylindium reagent **5b** was accessible and was arylated with 4-iodobenzonitrile (**1m**) in 68% yield (Table 2, entry 2). The insertion of Mg into 3-bromobenzofuran (**4d**) in the presence of $InCl_3$/LiCl yielded the corresponding tribenzofurylindium reagent **5c**, which reacted with the bromobenzamide **1k** and indole **4a** in 69–76% yields (Table 2, entries 3 and 4) under Pd catalysis.

The one-pot, in situ, Mg/LiCl/$InCl_3$ transmetalation procedure was also applied to the preparation of tribenzylindium compounds (**8**) starting from benzyl chlorides and bromides (**7**). Thus, the reaction of Mg turnings (1.50 equiv) with ethyl 3-(chloromethyl)benzoate (**7a**) in the presence of LiCl (1.50 equiv) and $InCl_3$ (0.33 equiv) in THF led to the tri[3-(ethoxycarbonyl)benzyl]indium reagent **8a** after 2 h at 25 °C. Direct cross-coupling in THF with 4-bromobenzonitrile (**1a**) with $Pd(OAc)_2$ (2%) and S-Phos (4%) as the catalytic system gave a 74% yield of the diarylmethane **9a** (Scheme 4) after 12 h.

Tribenzylindium (**8b**), prepared from benzyl chloride (**7b**), reacted with ethyl 4-iodobenzoate (**1c**) and 3-bromopyridine (**4b**) and the coupling products were obtained in 75–88% yield (Table 3, entries 1 and 2) after 12 h. For these



7a **8a**[a] **9a**: 74 %

Scheme 4. Preparation of tri[3-(ethoxycarbonyl)benzyl]indium (**8a**) from ethyl 3-(chloromethyl)benzoate (**7a**) by means of Mg insertion in the presence of LiCl and $InCl_3$ and subsequent Pd-catalyzed cross-coupling. [a] Complexed LiCl and magnesium halides are omitted for clarity.

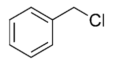
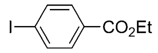
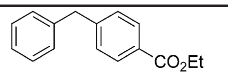
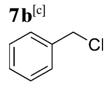
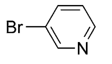
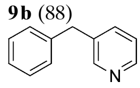
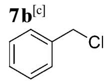
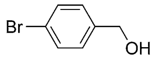
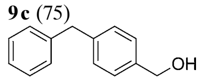
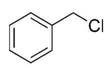
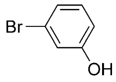
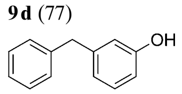
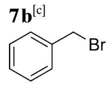
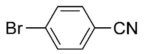
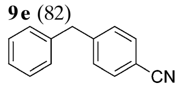
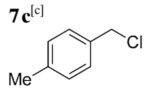
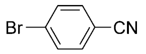
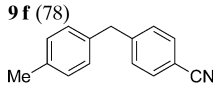
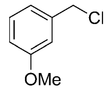
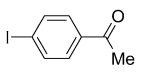
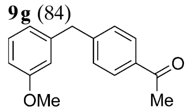
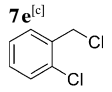
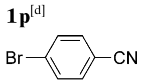
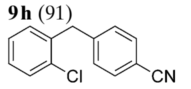
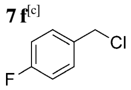
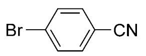
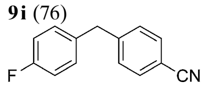
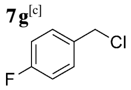
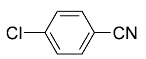
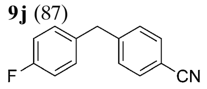
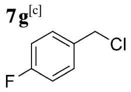
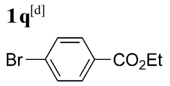
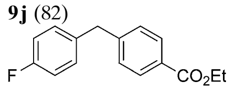
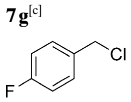
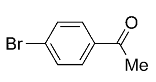
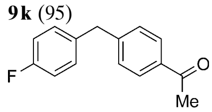
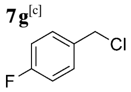
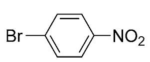
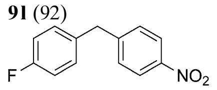
insertions, the use of smaller amounts of magnesium turnings (1.2 equiv) proved to be sufficient. For these reactions *N,N*-dimethylacetamide (DMAC) was the solvent, the reaction temperature was raised to 80 °C and $[PdCl_2(PPh_3)_2]$ (4 %) was applied as the catalytic system. These reaction conditions proved superior to the use of the combination $Pd(OAc)_2$/S-Phos/THF/50 °C and were also applied to the subsequently described coupling reactions in Table 3.[13] Remarkably, tribenzylindium (**8b**) could also be coupled with (4-bromophenyl)methanol (**1n**; 0.80 equiv with respect to benzyl chloride (**7b**) was applied to the preparation of **8b**) and 3-bromophenol (**1o**; 0.60 equiv with respect to benzyl chloride (**7b**) was applied to the preparation of **8b**) in 77–82 % yield under the optimized reaction conditions (Table 3, entries 3 and 4). The acidic proton of the alcohol functionality does not disturb the cross-coupling. Moreover, tribenzylindium (**8b**) was efficiently generated from benzyl bromide (**7c**) and, after cross-coupling, yielded the benzonitrile **9f** in 78 % yield (Table 3, entry 5). In the same manner, the tri(4-methylbenzyl)indium **8c** was arylated with 4-bromobenzonitrile (**1a**) in 84 % yield (Table 3, entry 6). The 3-methoxybenzyl- and 2-chlorobenzylindium reagents **8d** and **8e** could also be prepared and coupled in good yields (76–91 %; Table 3, entries 7 and 8). The tri(4-fluorobenzyl)indium **8f** also proved to be accessible under the conditions developed and reacted with a variety of aryl bromides and 4-chlorobenzonitrile (**1q**) in 81–95 % yield (Table 3, entries 9–13).

The treatment of alkyl bromides with magnesium turnings in the presence of $InCl_3$ and LiCl also gives access to trialkylindium reagents (**11**). Thus, tri(5-cyano-5-methylhexyl)indium (**11a**) was prepared from 6-bromo-2,2-dimethylhexanenitrile (**10a**) in 2 h at 25 °C in THF with 1.20 equivalents of Mg/LiCl. Cross-coupling with (4-bromophenyl)methanol (**1n**) in DMAC with $[PdCl_2(PPh_3)_2]$ (4 %) as catalyst afforded the alkylated benzyl alcohol derivative **12a** in 67 % yield (Scheme 5).

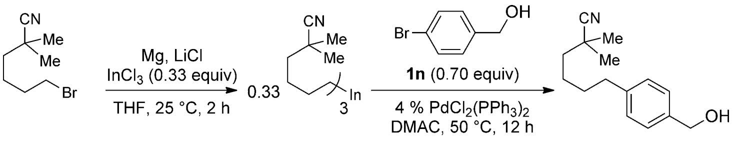
Moreover, tri(5-cyano-5-methylhexyl)indium (**11a**) was coupled with a range of aryl bromides, as well as 4-chloro-

Table 3. Cross-coupling of tribenzylindium reagents (**8**), obtained from benzyl halides (**7**) by Mg insertion in the presence of LiCl and $InCl_3$, with different organic halides as electrophiles.

$$\underset{\mathbf{7}}{\text{Bn}-\text{X}} \xrightarrow[\text{THF, 25 °C, 2 h}]{\text{Mg, LiCl, InCl}_3\text{ (0.33 equiv)}} 0.33\ \underset{\mathbf{8}}{\text{Bn}_3\text{In}^{[a]}} \xrightarrow[\text{4 \% PdCl}_2(\text{PPh}_3)_2\text{, DMAC, 80 °C, 12 h}]{\text{E}-\text{X}} \underset{\mathbf{9}}{\text{Bn}-\text{E}}$$

Entry	Bn−X	E−X	Product (Yield [%])[b]
1	 **7b**[c]	 **1c**[d]	 **9b** (88)
2	 **7b**[c]	 **4b**[d]	 **9c** (75)
3	 **7b**[c]	 **1n**[d]	 **9d** (77)
4	 **7b**[c]	 **1o**[e]	 **9e** (82)
5	 **7c**[c]	 **1a**[d]	 **9f** (78)
6	 **7d**[c]	 **1a**[d]	 **9g** (84)
7	 **7e**[c]	 **1p**[d]	 **9h** (91)
8	 **7f**[c]	 **1a**[d]	 **9i** (76)
9	 **7g**[c]	 **1a**[d]	 **9j** (87)
10	 **7g**[c]	 **1q**[d]	 **9j** (82)
11	 **7g**[c]	 **1b**[d]	 **9k** (95)
12	 **7g**[c]	 **1r**[d]	 **9l** (92)
13	 **7g**[c]	 **1s**[d]	 **9m** (81)

[a] Complexed LiCl and magnesium halides are omitted for clarity. [b] Yield of isolated, analytically pure, product. [c] Mg turnings (1.20 equiv), LiCl (1.20 equiv), and $InCl_3$ (0.33 equiv) were applied to the preparation of the tribenzylindium reagent. [d] 0.80 equivalents of electrophile were used. [e] 0.60 equivalents of electrophile were used.

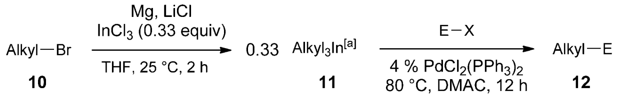


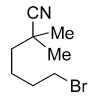
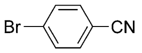
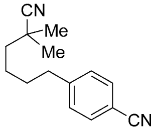
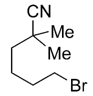
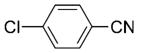
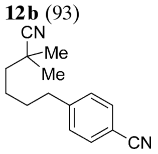
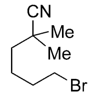
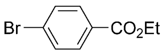
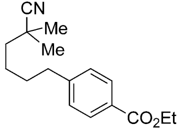
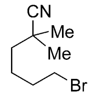
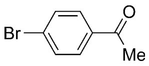
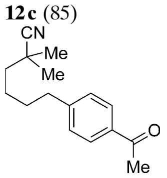
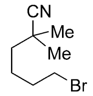
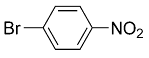
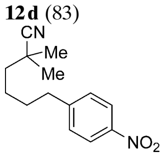
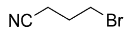
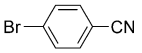
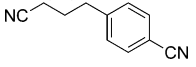
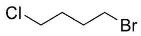
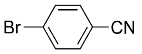
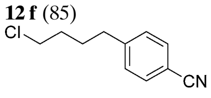
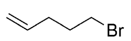
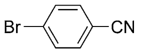
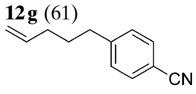
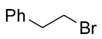
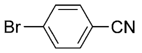
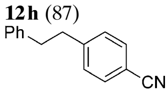
10a **11a**[a] **12a**: 67 %

Scheme 5. Preparation of tri(5-cyano-5-methylhexyl)indium (**11a**) from 6-bromo-2,2-dimethylhexanenitrile (**10a**) by means of Mg insertion in the presence of LiCl and $InCl_3$ and subsequent Pd-catalyzed cross-coupling. [a] Complexed LiCl and magnesium halides are omitted for clarity.

benzonitrile (**1q**), in 75–93 % yield (Table 4, entries 1–5). Tri(3-cyanopropyl)indium (**11b**) and tri(4-chlorobutyl)indium (**11c**) could also be efficiently generated from the corresponding alkyl bromides **10b** and **10c** and reacted in a cross-coupling reaction with 4-bromobenzonitrile (**1a**; 61–85 % yield; Table 4, entries 6–7). Furthermore, tri(pent-4-en-1-yl)indium (**11d**) and tri(phenylethyl)indium (**11e**) were arylated with 4-bromobenzonitrile (**1a**) in 87–94 % yield (Table 4, entries 8–9).

Table 4. Cross-coupling of trialkylindium reagents of type (**11**), obtained from alkyl bromides (**10**) by Mg insertion in the presence of LiCl and $InCl_3$, with different organic halides as electrophiles.



Entry	Alkyl–Br	E–X	Product (Yield [%])[b]
1	 **10a**[c]	 **1a**[d]	 **12b** (93)
2	 **10a**[c]	 **1q**[d]	 **12b** (75)
3	 **10a**[c]	 **1b**[d]	 **12c** (85)
4	 **10a**[c]	 **1r**[d]	 **12d** (83)
5	 **10a**[c]	 **1s**[d]	 **12e** (77)
6	 **10b**[c]	 **1a**[d]	 **12f** (85)
7	 **10c**[c]	 **1a**[d]	 **12g** (61)
8	 **10d**[c]	 **1a**[d]	 **12h** (87)
9	 **10e**[c]	 **1a**[d]	 **12i** (94)

[a] Complexed LiCl and magnesium halides are omitted for clarity. [b] Yield of isolated, analytically pure, product. [c] Mg turnings (1.20 equiv), LiCl (1.20 equiv), $InCl_3$ (0.33 equiv) were applied to the preparation of the trialkylindium reagent. [d] 0.70 equivalents of electrophile were used.

In conclusion, we have developed a new, efficient, one-pot procedure that enables the direct preparation of triorganoindium reagents from organic halides by means of a magnesium insertion in the presence of $InCl_3$ and LiCl. Starting from functionalized aryl, heteroaryl, and alkyl bromides, as well as benzyl chlorides, the corresponding organoindium reagents are accessible at 25 °C within 4 h in good yields. Moreover, the organoindium reagents obtained underwent Pd-catalyzed cross-coupling reactions.

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Keywords: cross-coupling · indium · insertion · magnesium · palladium

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[1] a) F. M. Piller, P. Appukkuttan, A. Gavryushin, M. Helm, P. Knochel, *Angew. Chem.* **2008**, *120*, 6907–6911; *Angew. Chem. Int. Ed.* **2008**, *47*, 6802–6806; b) F. M. Piller, A. Metzger, M. A. Schade, B. A. Haag, A. Gavryushin, P. Knochel, *Chem. Eur. J.* **2009**, *15*, 7192–7202; c) A. Metzger, F. M. Piller, P. Knochel, *Chem. Commun.* **2008**, 5824–5826; d) T. D. Blümke, F. M. Piller, P. Knochel, *Chem. Commun.* **2010**, *46*, 4082–4084.

[2] a) A. Krasovskiy, V. Malakhov, A. Gavryushin, P. Knochel, *Angew. Chem.* **2006**, *118*, 6186–6190; *Angew. Chem. Int. Ed.* **2006**, *45*, 6040–6044; b) N. Boudet, S. Sase, P. Sinha, C.-Y. Liu, A. Krasovskiy, P. Knochel, *J. Am. Chem. Soc.* **2007**, *129*, 12358–12359; c) A. Metzger, M. A. Schade, P. Knochel, *Org. Lett.* **2008**, *10*, 1107–1110.

[3] a) T. D. Blümke, Y.-H. Chen, Z. Peng, P. Knochel, *Nat. Chem.* **2010**, *2*, 313–318; b) L.-N. Guo, H. Gao, P. Mayer, P. Knochel, *Chem. Eur. J.* **2010**, *16*, 9829–9834; c) Z. Peng, T. D. Blümke, P. Mayer, P. Knochel, *Angew. Chem.* **2010**, *122*, 8695–8698; *Angew. Chem. Int. Ed.* **2010**, *49*, 8516–8519; d) T. D. Blümke, K. Groll, K. Karaghiosoff, P. Knochel, *Org. Lett.* **2011**, *13*, 6440–6443.

[4] Z. Peng, P. Knochel, *Org. Lett.* **2011**, *13*, 3198–3201.

[5] a) Y.-H. Chen, P. Knochel, *Angew. Chem.* **2008**, *120*, 7760–7763; *Angew. Chem. Int. Ed.* **2008**, *47*, 7648–7651; b) V. Papoian, T. Minehan, *J. Org. Chem.* **2008**, *73*, 7376–7379; c) Y.-H. Chen, M. Sun, P. Knochel, *Angew. Chem.* **2009**, *121*, 2270–2273; *Angew. Chem. Int. Ed.* **2009**, *48*, 2236–2239.

[6] a) *Metal-Catalyzed Cross-Coupling Reactions*, 2nd ed. (Eds.: A. de Meijere, F. Diederich), Wiley-VCH, Weinheim, **2004**; b) C. C. C. Johansson Seechurn, M. O. Kitching, T. J. Colacot, V. Snieckus, *Angew. Chem.* **2012**, *124*, 5150–5174; *Angew. Chem. Int. Ed.* **2012**, *51*, 5062–5085; c) V. F. Slagt, A. H. M. de Vries, J. G. de Vries, R. M. Kellog, *Org. Process Res. Dev.* **2010**, *14*, 30–47.

[7] *Handbook of Functionalized Organometallics* (Ed.: P. Knochel), Wiley-VCH, Weinheim, **2005**.

[8] a) K. Takai, Y. Ikawa, *Org. Lett.* **2002**, *4*, 1727–1729; b) for the $InCl_3$-mediated preparation of 1,2-dimetallics, see also: T. D. Blümke, T. Klatt, K. Koszinowki, P. Knochel, *Angew. Chem.* **2012**, *124*, 10064–10068; *Angew. Chem. Int. Ed.* **2012**, *51*, 9926–9930.

[9] a) S. Araki, T. Hirashita in *Comprehensive Organometallic Chemistry III, Vol. 9* (Ed.: P. Knochel), Pergamon, Oxford, **2007**, pp. 649–751; b) P. Cintas, *Synlett* **1995**, 1087; c) C.-J. Li, T.-H. Chan, *Tetrahedron* **1999**, *55*, 11149; d) B. C. Ranu, *Eur. J. Org. Chem.* **2000**, 2347; e) T. P. Loh, G. L. Chua, *Chem. Commun.* **2006**, 2739–2749; f) J. Augé, N. Luben-Germain, J. Uziel, *Synthesis* **2007**, 1739.

[10] a) N. Fujiwara, Y. Yamamoto, *J. Org. Chem.* **1999**, *64*, 4095; b) N. W. E. Tyrra, *J. Fluorine Chem.* **2001**, *112*, 149; c) L. S. Chupak, J. P. Wolkowski, Y. A. Chantigny, *J. Org. Chem.* **2009**, *74*, 1388–1390; d) K. Koszinowski, *J. Am. Chem. Soc.* **2010**, *132*, 6032; e) Z. L. Shen, K. K. K. Goh, Y. S. Yang, Y. C. Lai, C. H. A. Wong, H. L. Cheong, T. P. Loh, *Angew. Chem.* **2011**, *123*, 531–534; *Angew. Chem. Int. Ed.* **2011**, *50*, 511–514; f) Z. L. Shen, K. K. K. Goh, C. H. A. Wong, Y. S. Yang, Y. C. Lai, H. L. Cheong, T. P. Loh, *Chem. Commun.* **2011**, *47*, 4778–4780; g) L. Adak, N. Yoshikai, *J. Org. Chem.* **2011**, *76*, 7563–7568.

[11] a) M. A. Pena, J. Pérez Sestelo, L. A. Sarandeses, *Synthesis* **2005**, 485–492; b) I. Pérez, J. Pérez Sestelo, L. A. Sarandeses, *Org. Lett.* **1999**, *1*, 1267–1269; c) I. Pérez, J. Pérez Sestelo, L. A. Sarandeses, *J. Am. Chem. Soc.* **2001**, *123*, 4155–4160; d) I. Pérez, J. Pérez Sestelo, L. A. Sarandeses, *Chem. Commun.* **2002**, 2246–2247; e) D. Rodríguez, J. Pérez Sestelo, L. A. Sarandeses, *J. Org. Chem.* **2004**, *69*, 8136–8139; f) R. Riveiros, D. Rodríguez, J. Pérez Sestelo, L. A. Sarandeses, *Org. Lett.* **2006**, *8*, 1403–1406; g) M. A. Pena, J. Pérez Sestelo, L. A. Sarandeses, *J. Org. Chem.* **2007**, *72*, 1271–1275; h) R. Riveiros, L. Saya, J. Pérez Sestelo, L. A. Sarandeses, *Eur. J. Org. Chem.* **2008**, 1959–1966; i) Á. Mosquera, R. Riveiros, J. Pérez Sestelo, L. A. Sarandeses, *Org. Lett.* **2008**, *10*, 3745–3748; j) L. Bouissane, J. Pérez Sestelo, L. A. Sarandeses, *Org. Lett.* **2009**, *11*, 1285–1288; k) M. Montserrat Martínez, M. Peña-López, J. Pérez Sestelo, L. A. Sarandeses, *Org. Biomol. Chem.* **2012**, *10*, 3892–3898.

[12] a) S. D. Walker, T. E. Barder, J. R. Martinelli, S. L. Buchwald, *Angew. Chem.* **2004**, *116*, 1907–1912; *Angew. Chem. Int. Ed.* **2004**, *43*, 1871–1876; b) T. E. Barder, S. D. Walker, J. R. Martinelli, S. L. Buchwald, *J. Am. Chem. Soc.* **2005**, *127*, 4685–4696; c) R. A. Altman, S. L. Buchwald, *Nat. Protoc.* **2007**, *2*, 3115–3121; d) R. Martin, S. L. Buchwald, *Acc. Chem. Res.* **2008**, *41*, 1461–1473.

[13] Because of the relatively low reactivity of benzylindium (ref. [5c]) and alkylindium reagents (ref. [10e]) as compared to the arylindium counterparts (ref. [5a]), a poor yield was obtained when the cross-coupling was carried out with the $Pd(OAc)_2$/S-Phos catalytic system in THF. Thus, the comparatively more robust catalytic system $[PdCl_2(PPh_3)_2]$/DMAC (ref. [10e]) was employed for the subsequent cross-coupling reactions with the tribenzylindium and trialkylindium reagents.

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