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Cobalt-Catalyzed Electrophilic Amination of Aryl- and Heteroaryl-Zinc Pivalates with *N*-Hydroxylamine Benzoates

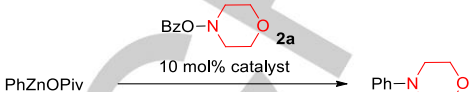
Yi-Hung Chen[+], Simon Graßl[+], and Paul Knochel*

Abstract: Aryl- and heteroaryl-zinc pivalates are aminated with *O*-benzoylhydroxylamines at 25 °C within 2-4 h in the presence of 2-5% $CoCl_2$·2LiCl furnishing the corresponding tertiary arylated or heteroarylated amines in good yields. This electrophilic amination provides also an access to diarylamines and aryl(heteroaryl)amines. A new tuberculosis drug candidate (Q203) was prepared in 6 steps and 56% overall yield using this cobalt-catalyzed amination as the key step.

Functionalized aromatic amines are widely found in pharmaceuticals, natural products, and agricultural chemicals.[1] Thus, general aromatic C-N bond forming reactions are required. Over the past two decades, the development of palladium catalyzed Buchwald-Hartwig nucleophilic aminations[2] allowed a facile synthesis of aryl amines. However, these reactions usually require expensive catalysts and ligands. Moreover, elevated temperatures and stoichiometric amounts of base are often necessary. In 2004, Johnson reported an alternative electrophilic amination using diarylzinc reagents and *O*-benzoylhydroxylamine derivatives to afford tertiary amines under mild conditions.[3] This amination[4] has been extended to organometallics derived from Mg,[3d] Zn,[5] Al,[6] B,[7] Si[8] and Cu[9] using Cu or Ni as catalysts. Despite the impressive progress made, the use of air sensitive reagents, ligands or toxic Ni-catalysts still represent drawbacks. Recently, we reported a new class of highly functionalized organozinc reagents with enhanced air- and moisture-stability.[10-12] These reagents were used to improve the efficiency of cobalt-catalyzed Negishi cross-coupling[11] and were useful for biological active molecule syntheses[12] and high-throughput screenings.[13] Herein, we describe the first cobalt-catalyzed electrophilic amination of organozinc pivalates with *O*-benzoylhydroxylamines. The reaction scope is especially broad, allowing the preparation of tertiary diarylalkylamines not available by copper- or nickel-catalyzed aminations. Also, the utility of this amination method was demonstrated by the synthesis of a potent clinical candidate for the treatment of tuberculosis.[14]

Preliminary studies showed that phenylzinc pivalate (**1a**) is aminated with benzoylhydroxylmorpholine (**2a**) in the presence of various catalysts at room temperature (Table 1). ArZnCl·Mg(OPiv)$_2$·LiCl is abbreviated as ArZnOPiv for the sake of clarity.[15] When using iron(II) or copper(I) catalysts, the main product is the corresponding homodimer (e.g. biphenyl, Table 1, entries 1-3). Better results are obtained with Ni(II)-catalysts (entries 4-5). Interestingly, THF soluble $CoCl_2$·2LiCl proved to be the most effective catalyst and afforded *N*-phenylmorpholine (**3a**) in 93% isolated yield (entry 7). The relative lower toxicity of $CoCl_2$ compared to $NiCl_2$ is the advantage of using this metallic salt.[16] In this study, we also found that considerably more homodimer was generated using phenylzinc chloride compared to phenylzinc pivalate.[17] Further optimizations showed that 2.5% $CoCl_2$·2LiCl as well as 1.1 equiv of PhZnOPiv were sufficient to achieve a complete conversion.

Table 1: Catalyst screening for the electrophilic amination.



1a **3a**

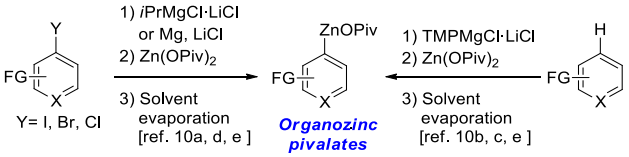
Entry	Catalyst	Yield (%)[a]
1	$Fe(acac)_2$	31
2	CuI	36
3	$Cu(OTf)_2$	40
4	$NiCl_2$	84
5	$NiCl_2(PPh_3)_2$	72
6	$Co(acac)_2$	61
7	$CoCl_2$· 2LiCl	98 (93)[b]

[a] GC yield using undecane as internal standard. [b] Isolated yield.

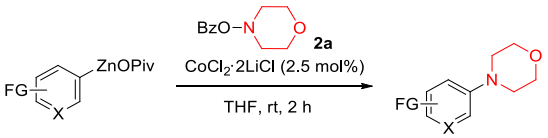
Using *O*-benzoylhydroxylmorpholine (**2a**) as typical amination reagent, we have determinated the scope of the amination of organozinc pivalates (Table 2). We have noticed that both electron-rich, electron-poor or sterically hindered arylzinc pivalates **1b-e** are aminated with benzoylhydroxylmorpholine (**2a**) smoothly to afford the desired products **3b-e** in 81-97% yield (entries 1-4).

Table 2: The scope of organozinc pivalates for electrophilic amination.

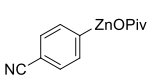
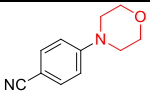
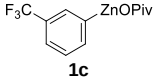
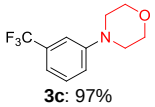
1) Preparation of organozinc pivalates



2) Electrophilic amination with organozinc pivalates



1 **3**

Entry	(Hetero)arylzinc pivalate	Product[a]
1	 **1b**	 **3b**: 93%
2	 **1c**	 **3c**: 97%

[*] Dr. Y.-H. Chen, S. Graßl, Prof. Dr. P. Knochel Ludwig-Maximilians-Universität München, Department Chemie
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[+] These authors contributed equally to this work.
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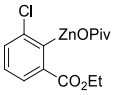
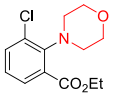
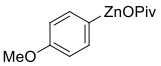
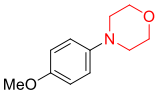
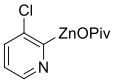
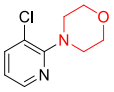
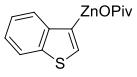
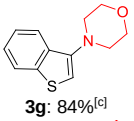
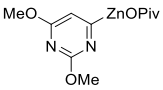
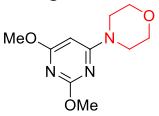
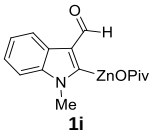
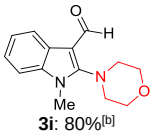
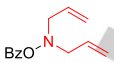
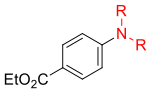
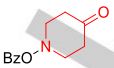
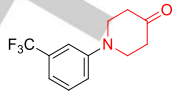
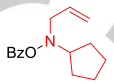
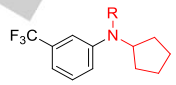
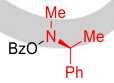
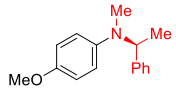
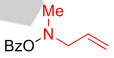
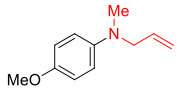
3		**1d**	 **3d**: 81%[b]
4		**1e**	 **3e**: 96%
5		**1f**	 **3f**: 95%[b]
6		**1g**	 **3g**: 84%[c]
7		**1h**	 **3h:** 91%[b]
8		**1i**	 **3i**: 80%[b]

[a] Isolated yields of analytically pure products. [b] TMEDA (5 mol%) was added. [c] Reaction time: 12 h.

This electrophilic amination was extended to heteroarylzinc pivalates bearing a pyridine, benzylthiophene, pyrimidine and indole ring. Thus, heteroarylzinc pivalates **1f-i** were aminated with **2a** in 80-95% yield (entries 5-8). Surprisingly, we observed that organozinc pivalates which were prepared via directed metallation using TMPMgCl·LiCl[18] or TMPZnCl·LiCl,[19] (TMP = 2,2,6,6-tetramethylpiperidyl) did not undergo the amination reaction. We assume that a strong coordination of TMP-base to the cobalt center deactivates the catalyst.[17] Interestingly, the addition of 5% TMEDA (tetramethylethylenediamine) avoids this deactivation.

Encouraged by these results, we have extended the scope of this amination to various *O*-benzoylhydroxylamines affording trisubstituted aniline derivatives **3j-n** in 78-97% yield (Table 3, entries 1-5). Notably, the reaction is compatible with benzoylhydroxylpiperidone (**2c**) bearing a sensitive ketone function and acidic alpha-protons. The cleavage of the allyl group was realized under mild conditions, affording either primary or secondary aniline derivatives **4a-b** in 91-93% yield (entries 1 and 3).[20]

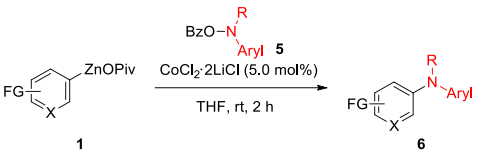
Table 3: Amination of arylzinc pivalates with various *O*-benzoylhydroxylamines of type **2**.

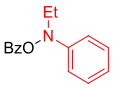
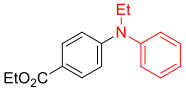
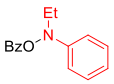
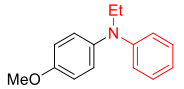
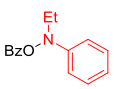
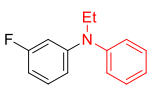
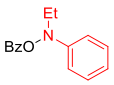
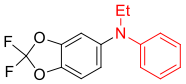
Entry	Organozinc pivalate of type **1**	Electrophile **2**	Product[a]
1	FG= *p*-CO_2Et **1j**	 **2b**	 **3j**: R = allyl; 81% **4a**: R = H; 91%
2	FG= *m*-CF_3 **1c**	 **2c**	 **3k:** 81%
3	FG= *m*-CF_3 **1c**	 **2d**	 **3l:** R = allyl; 78% **4b:** R = H; 93%
4	FG= *p*-OMe **1e**	 **2e**	 **3m**: 97%
5	FG= *p*-OMe **1e**	 **2f**	 **3n**: 89%

[a] Isolated yields of analytically pure products.

In contrast to previous electrophilic aminations, the reaction between arylzinc and benzoylhydroxylaniline derivatives proceeds also well. Thus, the amination of arylzinc pivalates **1e** and **1j-m** with *O*-benzoylhydroxylaniline (**5a**)[21] led to the diarylamines **6a-e** under standard conditions in 61-89% yield (Table 4, entries 1-5). Also anisylzinc pivalate (**1e**) underwent amination with the *O*-benzoyl hydroxylanilines **5b-c** leading to diarylamines **6f-g** in 68-78% yield (entries 6-7).

Table 4: Amination of arylzinc pivalates with various *O*-benzoylhydroxylanilines.



Entry	Organozinc pivalate of type **1**	Electrophile **5**	Product[a]
1	FG= *p*-CO_2Et **1j**	 **5a**	 **6a**: 89%
2	FG= *p*-OMe **1e**	 **5a**	 **6b**: 79%
3	FG= *m*-F **1k**	 **5a**	 **6c**: 84%
4	FG= CF_2O_2 **1l**	 **5a**	 **6d**: 66%

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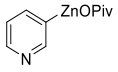
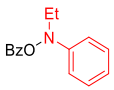
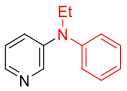
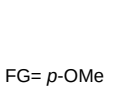
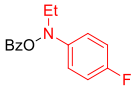
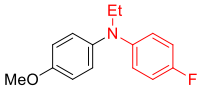
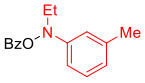
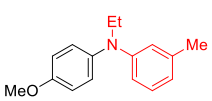
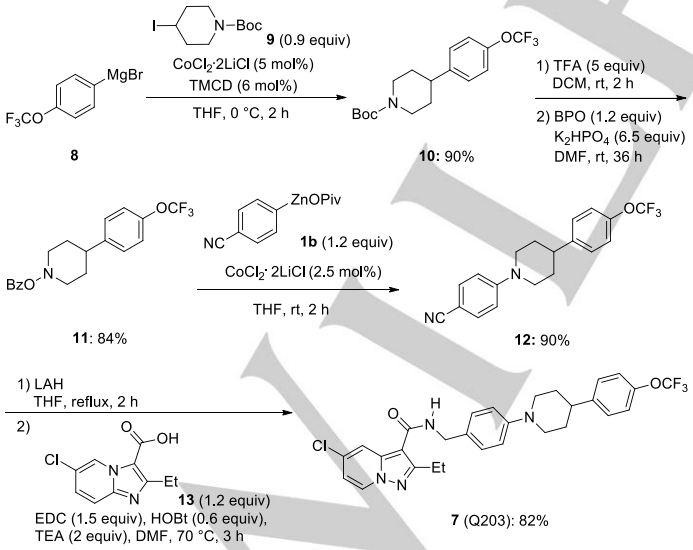
5	 **1m**	 **5a**	 **6e:** 61%[b]
6	FG= *p*-OMe  **1e**	 **5b**	 **6f**: 78%
7	FG= *p*-OMe **1e**	 **5c**	 **6g:** 68%

[a] Isolated yields of analytically pure products. [b] **1m** (2 equiv); THF:NMP = 3:1; 12 h reaction time.

The synthetic utility of this electrophilic amination for the preparation of medicinally valuable molecules was demonstrated by a concise synthesis of the potential anti-tuberculosis drug candidate Q203 (**7**)[14] (Scheme 1). The synthesis began with a cobalt-catalyzed cross-coupling of commercial available 4-iodopiperidine (**9**) with Grignard reagent **8**[22] under conditions reported by Yorimitsu, Oshima[23] and Cossy[24] providing the piperidine **10** in 90% yield. The Boc-protecting group was removed using trifluoroacetic acid followed by oxidation with BPO to afford hydroxylamine **11** in 84% yield (2 steps). The key step in the construction of diarylpiperidine **12** was the electrophilic amination with 4-cyanophenylzinc pivalate (**1b**) in the presence of 2.5% $CoCl_2$·2LiCl generating piperidine **12** in 90% yield. With the core skeleton in hand, benzonitrile **12** was reduced with LAH (lithium aluminum hydride) and further coupled with acid **13** furnishing the amide Q203 (**7**) in 82% yield (6 steps, 56% overall yield).



Scheme 1. Synthesis of Q203 (**7**) with cobalt-catalyzed C-C and C-N bond forming reactions. TMCD= (*R*,*R*)-tetramethylcyclohexanediamine; BPO= benzoyl peroxide; EDC= 1-[3-(dimethylamino)propyl]-3-ethylcarbodimide hydrochloride; HOBt= 1-hydroxylbenzotriazole.

In summary, we have reported the first cobalt-catalyzed electrophilic amination with aryl- and heteroaryl-zinc pivalates and *O*-benzoylhydroxylamine derivatives under very mild conditions. The amination was further extended to *O*-benzoylhydroxylanilines which previously were not appropriate substrates using Cu-catalysis. Finally, the concise synthesis of Q203 (**7**) demonstrates the utility of our method. Preliminary mechanistic studies indicate that the amination proceeds via a non-radical pathway.[17] Further investigations towards a more general and practical preparation of various amines[25] to expand the scope are currently underway in our laboratories.

Acknowledgements

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Keywords: electrophilic amination • organozinc pivalate • cobalt catalysis • cross-coupling • tuberculosis

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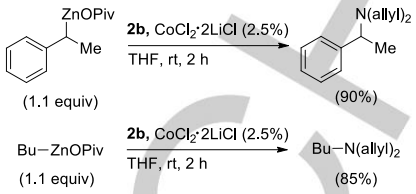
[25] Both alkyl and benzylic zinc pivalates also undergo this cobalt-catalyzed amination reaction.



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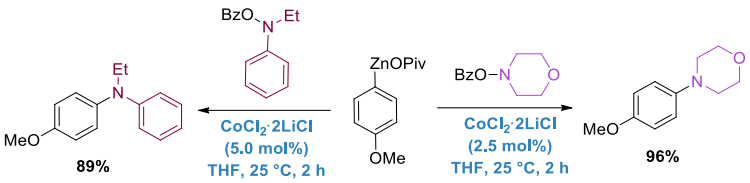

Cobalt-catalyzed aminations. A range of aryl- and heteroaryl-zinc pivalates underwent cobalt-catalyzed electrophilic aminations with *O*-benzoylhydroxylamines in good yields under mild conditions. This reaction can be applied to prepare tertiary, secondary, primary arylamines or diarylamines. Also we have prepared Q203, a new tuberculosis drug candidate, in 6 steps and 56% overall yield using the cobalt-catalyzed amination as key step.

Yi-Hung Chen[+], *Simon Graßl*[+], *Paul Knochel**

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Cobalt-Catalyzed Electrophilic Amination of Aryl- and Heteroaryl-zinc Pivalates with *N*-Hydroxylamine Benzoates