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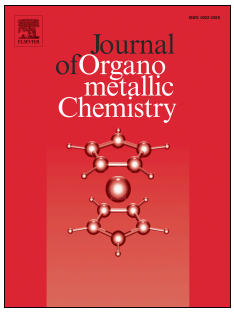

[P,N]-phosphinobenzimidazole ligands in palladium-catalyzed C-N cross-coupling reactions: The effect of the *N*-substituent of the benzimidazole scaffold on catalyst performance

Joseph P. Tassone, Gregory J. Spivak

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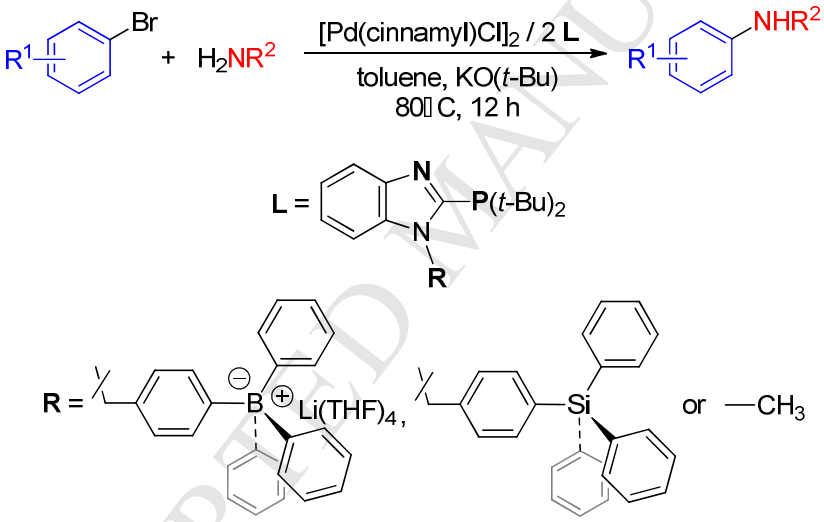
Table of Contents graphic:



[P,N]-Phosphinobenzimidazole Ligands in Palladium-Catalyzed C-N Cross-Coupling Reactions: The Effect of the *N*-Substituent of the Benzimidazole Scaffold on Catalyst Performance

Joseph P. Tassone and Gregory J. Spivak*

Department of Chemistry, Lakehead University, Thunder Bay, Ontario, P7B 5E1, CANADA

E-mail: greg.spivak@lakeheadu.ca

Abstract

A series of [P,N]-phosphinobenzimidazole ligands is reported in which the charge (anionic *vs.* neutral) and size of the *N*-substituent of the benzimidazole scaffold has been varied. In order to evaluate the impact of the substituent's properties on the performance of the metal in catalytic reactions, each ligand was screened for its ability to promote the cross-coupling of aryl bromides with various primary aryl amines using palladium as the metal source. In general, the ligands formed active cross-coupling catalysts with palladium. Moreover, the ligand variants containing larger *N*-substituents boosted the efficiency of the cross-coupling reaction considerably, while their charge (either anionic or neutral) appeared to have no significant impact.

Keywords: anionic phosphines; tetraphenylborate; [P,N]-phosphinobenzimidazole; Buchwald-Hartwig cross-coupling; palladium

Introduction

The palladium-catalyzed cross-coupling application continues to serve as a remarkably powerful tool for the synthesis of new carbon-carbon and carbon-heteroatom bonds.[1] Significant improvements in catalyst design have propelled the technology forward in recent years. Central to these advancements has been the evolution of designer ligands which have allowed access to new catalyst systems that are capable of linking a broader range of coupling partners to carbon under milder reaction conditions and/or with lower catalyst loadings. Many of the more versatile ligands include monodentate and bidentate phosphine ligands,[2] however, more recently, strategically designed heterobifunctional bidentate phosphine ligands containing a strongly donating phosphine anchor paired with a contrasting weaker, more labile donor centre have also shown significant promise.[3] For example, several classes of heterobifunctional [P,N]-ligands have been developed, and, when paired with palladium, have proven to form very effective and versatile cross-coupling catalysts.[4] We recently reported on the synthesis and hemilabile character of an anionic, tetraphenylborate-functionalized, [P,N]-phosphinobenzimidazole ligand[5] and have since wondered of the extent to which the tetraphenylborate substituent (*i.e.*, its anionicity, size and location[6]) impacts the donor centres of the ligand, and ultimately catalytic performance. Indeed, other related bulky, negatively charged ligands have proven to be effective supporting ligands in palladium cross-coupling applications.[7]

Results and discussion

The anionic, [P,N]-phosphinobenzimidazole ligand central to this investigation (**1**, abbreviated as $[Li(THF)_4][P^{t\text{-}Bu}NBPh_4]$) is illustrated in Figure 1. Ligand **1** was strategically designed to contain a sterically large and exceptionally powerful donor anchor (*i.e.*, the $-P(t\text{-}Bu)_2$ group) – an important feature of the supporting ligand in palladium-catalyzed cross-coupling

applications – attached in the 2-position of a benzimidazole backbone, the latter of which is expected to interact dynamically with the metal centre under conditions of catalysis (*vide infra*). The ligand is rendered anionic upon introducing the borate group. For comparative purposes, the essentially isosteric, but neutral variant 2-(di-*tert*-butylphosphino)-1-(4-(triphenylsilyl)benzyl)benzimidazole (**2**, abbreviated as $P^{t\text{-}Bu}NSiPh_4$), along with its *N*-methyl analogue 2-(di-*tert*-butylphosphino)-1-methylbenzimidazole (**3**, abbreviated as $P^{t\text{-}Bu}NMe$) were also synthesized and employed in parallel studies (Figure 1; see the Supporting Information for details regarding the syntheses of **1**, **2** and **3**). Lithium ion exchange of **1** with Ph_4P^+ (*i.e.*, to give the Ph_4P^+ salt **1'**, abbreviated as $[Ph_4P][P^{t\text{-}Bu}NBPh_4]$) is readily accomplished in CH_2Cl_2. ^1H NMR spectral integrations, and the very similar (<1 ppm difference) ^{31}P NMR chemical shifts of both **1** and **1'**, suggest the ligand is not coordinated to Li^+ in **1**, which is in contrast to related systems.[5]

In order to determine whether or not the benzimidazole *N*-substituents of the [P,N]-phosphinobenzimidazole ligands impact the catalytic performance of a metal to which the ligand is attached, we utilized the Buchwald-Hartwig amination coupling as a test reaction.[8] This cross-coupling strategy has arguably seen the greatest success in applications which employ the Buchwald class of electron-rich biaryl phosphines as supporting ligands.[2b,9] In this context, the ligands examined in this study share some common structural and electronic features with the Buchwald ligands, including a bulky and powerful electron-donating phosphine anchor, and a dynamic, secondary palladium-arene interaction[10] (Buchwald) or strained, hemilabile benzimidazole chelate[5] (**1**/**1'**, **2** and **3**), both of which serve to stabilize the metal during catalysis, and also help to suppress β-hydrogen elimination and prevent dimerization via halide bridges.

Using aniline and bromobenzene as test substrates, we initially focussed on determining the optimal coupling conditions by screening the various parameters essential to the reaction, including the palladium source, base, solvent, temperature and time (see Table S1 of the Supporting Information). A precatalyst formed from $[Pd(cinnamyl)Cl]_2$[11] and ligand **1** (in 1:2) proved to be an effective combination, and essentially quantitative conversions to diphenylamine were observed in toluene at 80 °C within 12 hours using KO(*t*-Bu) as base.

Once a set of optimized reaction conditions had been established, we then investigated the scope of the coupling reaction with aniline by varying the aryl bromide coupling partner (Table 1). The reactions of aryl bromides bearing weakly electron-donating alkyl groups proceeded efficiently (Table 1, entries 2 and 3), and even tolerated the more sterically demanding 2-bromotoluene. The strongly-deactivating methoxy group of 4-bromoanisole led to only moderate isolated yields (Table 1, entry 4), but this could be remedied by increasing the catalyst loading. Aryl bromides bearing electron-withdrawing substituents, including the base-sensitive ketone group, were well-tolerated, affording the coupled products in excellent yields (Table 1, entries 5 and 6). The notable exception was 1-bromo-4-nitrobenzene, which did not react with aniline under these conditions (Table 1, entry 7), perhaps due to competitive *in situ* reduction of the nitro substituent to yield the strongly deactivated, electron-rich 4-bromoaniline.[12] The reaction of 2-bromopyridine with aniline proceeded with only moderate yields (Table 1, entry 8), possibly because of competing reactions of the substrate, or the coupled product *N*-phenylpyridin-2-amine, to the palladium centre. Notably, in all instances, only the monoarylation product was observed, highlighting the selectivity of this catalyst system.

One of the primary objectives of this investigation was to explore the impact of the tetraphenylborate substituent of **1** on catalytic efficiency. In parallel with the catalytic studies

involving ligand **1**, we also investigated how the *N*-substituent's charge (*i.e.*, **1** *vs.* **2**) and size (*i.e.*, **2** *vs.* **3**) might also impact the cross-coupling reaction under the same reaction conditions (Table 2). We found it interesting that a catalyst system composed of either anionic ligand **1** or its sterically comparable, but neutral counterpart **2** yielded fairly similar cross-coupling results, despite the differences in ligand charges. Thus, the negative charge of the tetraphenylborate substituent in **1** does not appear to boost overall catalytic efficiency. The impact of the anionic charge on the donor atoms of **1** is likely limited, in part, by its conjugative isolation. Moreover, the proximity[6] of the tetraphenylborate substituent to the donor atoms perhaps also diminishes the impact of the anionic charge on the electronic properties of **1**. In contrast, catalyst systems employing either **1** or **2** as a supporting ligand outperformed the catalyst system utilizing the sterically smaller **3**, often by a significant margin (Table 2). This includes when electron-donating or electron-withdrawing substituents were present on the aryl bromide (Table 2, entries 1-4), or when bulky anilines were employed (Table 2, entries 5 and 6). It was also clear that the catalyst system employing ligand **3** did not tolerate the use of cyclohexylamine as well (Table 2, entry 7). Perhaps the added bulk introduced by the tetraphenylborate and tetraphenylsilyl groups increases the overall steric profile of their respective ligands, which in turn helps promote the reductive elimination of cross-coupled products from Pd(II) intermediates during catalysis by offering a relief in steric congestion about the metal.[13] We also found it noteworthy that the identity of the counterion of the anionic phosphine ligand does not appear to have a significant impact on catalysis, as the reactions employing either the lithium salt **1** or the Ph_4P^+ salt **1'** each gave reproducibly comparable yields.

Similar results were obtained when, instead of *in situ*-generated palladium catalyst systems, preformed[14] palladium catalysts were used. In separate reactions (Scheme 1), ligands **1'**,

2 or **3** each cleanly react with either $[Pd(cinnamyl)Cl]_2$ or $PdCl_2(COD)$ to give $[Ph_4P][PdCl(\eta^3\text{-cinnamyl})(\kappa^1\textit{P}\text{-P}^{t\text{-Bu}}NBPh_4)]$ (**4**), $[PdCl(\eta^3\text{-cinnamyl})(\kappa^1\textit{P}\text{-P}^{t\text{-Bu}}NR)]$ (R = $SiPh_4$, **5**; R = Me, **6**), $[Ph_4P][PdCl_2(\kappa^2\text{-P}^{t\text{-Bu}}NBPh_4)]$ (**7**) and $[PdCl_2(\kappa^2\text{-P}^{t\text{-Bu}}NR)]$ (R = $SiPh_4$, **8**; R = Me, **9**), and were characterized by NMR spectroscopy and using microanalytical data. The signal pattern observed for the cinnamyl ligand in the ^{1}H NMR spectra of **4**-**6** suggest an η^3-coordination mode.[15] Moreover, the downfield ^{31}P NMR chemical shifts observed for **4**-**6** (~47 ppm) compared to **7**-**9** (~36 ppm) are consistent with a monodentate (ring-opened) coordination mode for each ligand.[5] The room temperature ^{31}P NMR spectra of complexes **5** and **6** each display multiple, closely spaced signals attributed to the coordinated phosphine ligand, and suggests a number of discrete species exist in solution for each complex, perhaps isomers arising from restricted Pd-P rotation. This is not uncommon in $[PdX(allyl)(PR_3)]$ (X = anionic ligand) complexes containing sterically large phosphine ligands.[15a] The signals in the ^{31}P NMR spectrum of **6** coalesce into a single, sharp peak at elevated temperatures (50 °C; see the Supporting Information), while those of complex **5** undergo little change up to 60 °C. Interestingly, the room temperature ^{31}P NMR spectrum of **4** shows only a single, sharp peak attributed to its phosphine ligand.

Within the context of our catalytic studies, we were especially interested in complexes **4**-**6** since they perhaps represent intermediate species which form *in situ* upon mixing the [P,N]-phosphinobenzimidazole ligands with the $[Pd(cinnamyl)Cl]_2$ precursor. In fact, like the *in situ*-generated catalyst systems derived from the bulkier ligands **1'** or **2**, the corresponding preformed counterparts **4** and **5** also proved to be superior catalysts compared to complex **6** under the same catalytic conditions, again illustrating the impact of the size of the *N*-substituent of the benzimidazole scaffold. Thus, using bromobenzene and aniline again as test substrates, complexes **4** and **5** outperformed **6** (containing the sterically smaller ligand **3**) as cross-coupling

catalysts, with each reaching essentially complete conversion within 12 hours as determined by NMR spectroscopy, compared to less than 50% conversion when using catalyst **6** (see the Supporting Information).

Summary

We have prepared a series of 2-(di-*tert*-butylphosphino)benzimidazole ligands in which the charge and size of the *N*-substituent of the benzimidazole scaffold has been varied, and examined their utility in Buchwald-Hartwig amination reactions. Interestingly, the identity of the *N*-substituent of the [P,N]-phosphinobenzimidazole ligand exerts a considerable impact on the activity of the palladium catalyst with which it is paired, with sterically larger groups producing more active catalysts. This steric effect is particularly interesting in these studies considering the position of the substituents relative to the donor centres of the ligand.

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Table of Contents entry and synopsis:

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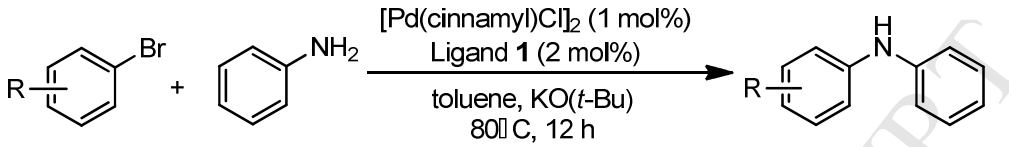
Joseph P. Tassone and Gregory J. Spivak*

Department of Chemistry, Lakehead University, Thunder Bay, Ontario, Canada P7B 5E1;

email: greg.spivak@lakeheadu.ca

A series of 2-(di-*tert*-butylphosphino)benzimidazole ligands have been prepared in which the charge and size of the *N*-substituent of the benzimidazole scaffold was varied. The Buchwald-Hartwig amination reaction was used to screen the ability of each [P,N]-phosphinobenzimidazole ligand to promote the cross-coupling of aryl bromides with primary aryl amines, and the impact of the *N*-substituent of the benzimidazole scaffold on catalytic performance was assessed.

Table 1. Palladium-catalyzed amination of aryl bromides using ligand **1**.[a]



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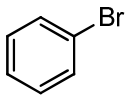
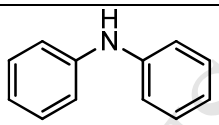
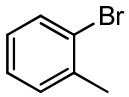
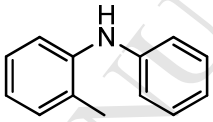
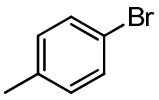
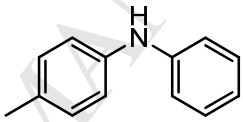
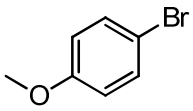
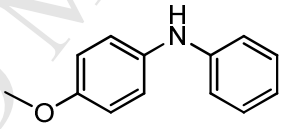
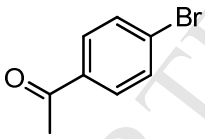
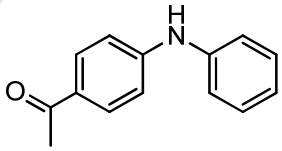
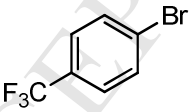
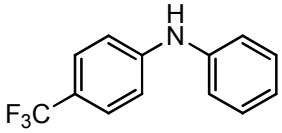
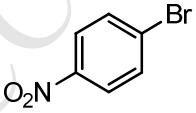
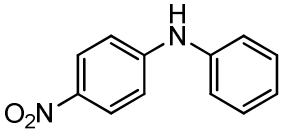
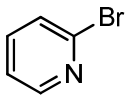
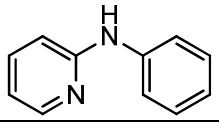
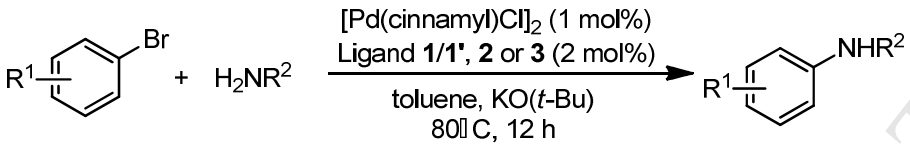
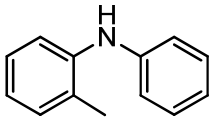
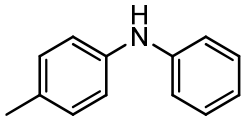
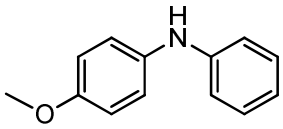
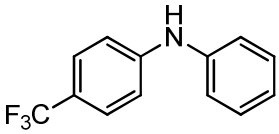
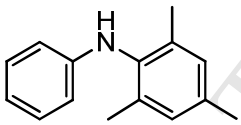
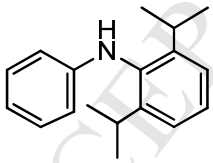
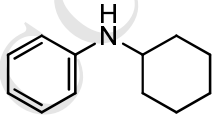
1			92
2			96
3			97
4			57 (71)[c]
5			91
6			86
7			0
8			36

[a] Reaction conditions: 0.6 mmol aryl bromide, 0.72 mmol aniline, 1 mol% $[Pd(cinnamyl)Cl]_2$, 2 mol% **1**, 0.72 mmol KO(*t*-Bu), 2 mL toluene. [b] Isolated yield (average of two runs). [c] 1.5 mol% $[Pd(cinnamyl)Cl]_2$ and 3 mol% **1** were used.

Table 2. Palladium-catalyzed cross-coupling of aryl bromides with various amines using **1**/**1'**, **2** or **3** as a supporting ligand.[a]



		Yield (%)[b]			
Entry	**Product**	**1**	**1'**	**2**	**3**
1		96	96	93	70
2		97	-	94	40
3		57	62	41	11
4		86	-	96	46
5		73	-	84	55
6		76	72	82	30
7		72	70	70	33

[a] Reaction conditions: 0.6 mmol aryl bromide, 0.72 mmol amine, 1 mol% $[Pd(cinnamyl)Cl]_2$, 2 mol% ligand, 0.72 mmol KO(*t*-Bu), 2 mL toluene. [b] Isolated yield (average of two runs).

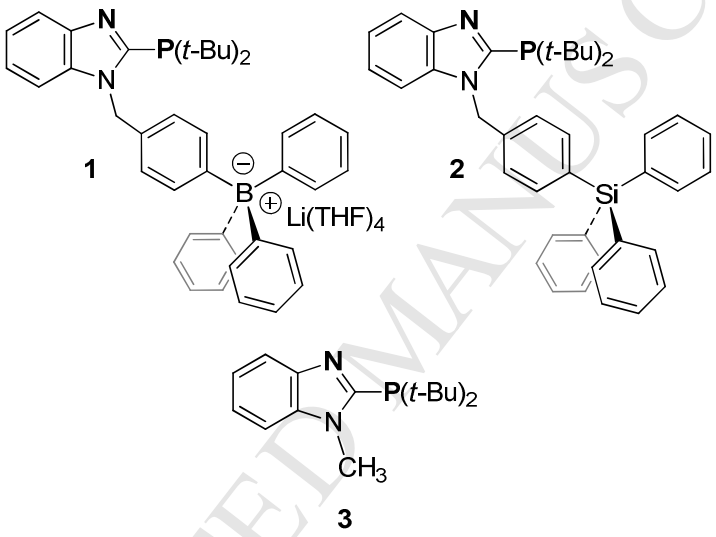
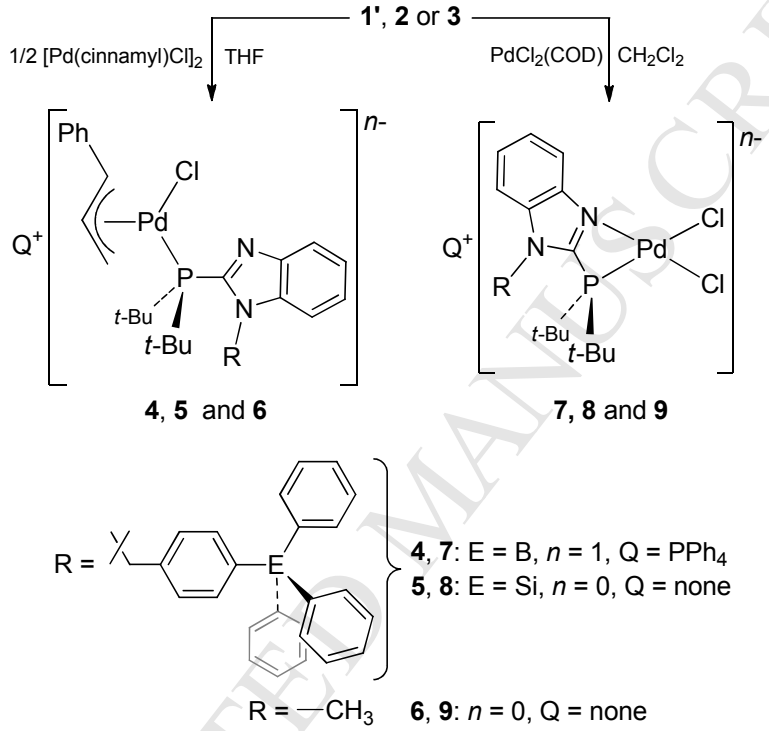


Figure 1. [P,N]-Phosphinobenzimidazole ligands examined in this study



Scheme 1. Synthesis of complexes **4**-**9**.

Highlights:

- A series of [P,N]-phosphinobenzimidazole ligands is described
- The ligands promote the palladium-catalyzed amination of aryl bromides
- Larger *N*-substituents on the benzimidazole scaffold boost catalytic performance