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Suzuki−Miyaura Coupling of Aryl Tosylates Catalyzed by an Array of Indolyl Phosphine−Palladium Catalysts

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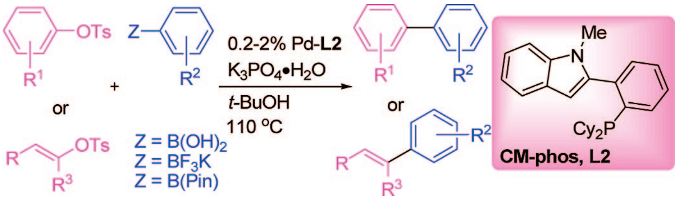

A family of indolyl phosphine ligands was applied to Suzuki−Miyaura cross-coupling of aryl tosylates. Catalyst loading can be reduced to 0.2 mol % for coupling of nonactivated aryl tosylate. A challenging example for room temperature coupling is realized. The scope of this highly active Pd/**L2** system can be extended to other boron nucleophiles, including trifluoroborate salts and boronate esters. The ligand structural comparisons toward the reactivity in tosylate couplings are also described.

Introduction

The Suzuki−Miyaura reaction employing organoboron nucleophiles represents one of the most effective methods for the construction of C(sp^2)−C(sp^2) linkages,[1] and constitutes numerous applications in pharmaceutical and material chemistry.[2] Aryl iodides, bromides, triflates, nonaflates, and more recently chlorides[3] are commonly used for the synthesis of substituted arenes. In fact, aryl tosylates are less expensive than the corresponding triflates and nonaflates and are therefore desirable alternatives.[4] Moreover, aryl tosylates are more convenient to use because they are more stable toward hydrolysis than corresponding triflates and usually have high crystallinity. Although they have several beneficial features, their superior stability translates into an inferior reactivity in palladium-catalyzed coupling processes.[5] However, nickel-catalyzed aryl tosylate couplings have been reported.[6]

Considerable efforts have been undertaken by researchers in both academia and industry over the past decade to expand the feasibility on difficult aryl/alkenyl tosylate couplings.[7,8] To our knowledge, there are only two publications to date on the Pd-catalyzed Suzuki−Miyaura coupling of aryl tosylates.[7a,b] On the contrary to aryl chloride coupling reactions,[9] we speculate that tosylate coupling reactions are particularly sensitive to the nature and skeleton of the supporting phosphine ligands. For example, Josiphos-type ligands[10] were reported by Hartwig and co-workers to be effective for Kumada coupling of aryl tosylates,[7c] but they were ineffective in the corresponding

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(1) (a) de Meijere, A.; Diederich, F., Eds. *Metal-Catalyzed Cross-Coupling Reactions*, 2nd ed.; Wiley-VCH: Weinheim, Germany, 2004; Vols. *1*−*2*. (b) Beller, M.; Bolm, C. *Transition Metals for Organic Synthesis, Building Blocks and Fine Chemicals*, 2nd ed.; Wiley-VCH: Weinheim, Germany, 2004; Vols. *1*−*2*. (c) Nigeshi, E., Ed. *Handbook of Organopalladium for Organic Synthesis*; Wiley-Interscience: Chichester, UK, 2002; Vols. *1*−*2*. (d) Hassan, J.; Sévignon, M.; Gozzi, C.; Schulz, E.; Lemaire, M. *Chem. Rev.* **2002**, *102*, 1359. (e) Tsuji, J. *Palladium Reagents and Catalysts*, 2nd ed.; Wiley: Chichester, UK, 2004. (f) Yin, L.; Liebscher, J. *Chem. Rev.* **2007**, *107*, 133. (g) Corbet, J.-P.; Mignani, G. *Chem. Rev.* **2006**, *106*, 2651. (h) Roglans, A.; Pla-Quintana, A.; Moreno-Manas, M. *Chem. Rev.* **2006**, *106*, 4622.

(2) (a) King, A. O.; Yasuda, N. In *Organometallics in Process Chemistry*; Larsen, R. D., Ed.; Springer-Verlag: Berlin Heidelberg, 2004; pp. 205−245. (b) Miyaura, N. *Top. Curr. Chem.* **2002**, *219*, 11. (c) Suzuki, A. In *Modern Arene Chemistry*; Astruc, D., Ed.; Wiley-VCH: Weinheim, Germany, 2002; pp 53−106. (d) Suzuki, A. *J. Organomet. Chem.* **2002**, *653*, 54.

(3) For a pertinent review on aryl chloride couplings, see: Littke, A. F.; Fu, G. C. *Angew. Chem., Int. Ed.* **2002**, *41*, 4176.

(4) The prices of the sulfonating agent are as follows: TsCl, approximately 0.05 USD/g; Tf$_2$O, approximately 5 USD/g, from commercial suppliers in 2005−2006. Note: TsCl is a solid form and is sold in an ordinary reagent bottle, while Tf$_2$O is a moisture-sensitive liquid and is usually sold in an ampule.

(5) For mechanistic studies on oxidative addition of aryl tosylates by Pd-complexes, see: Roy, A. H.; Hartwig, J. F *Organometallics* **2004**, *23*, 194.

(6) For Ni-catalyzed Suzuki cross-coupling of aryl tosylates, see: (a) Zim, D.; Lando, V. R.; Dupont, J.; Monteiro, A. L. *Org. Lett.* **2001**, *3*, 3049. (b) Tang, Z. Y.; Hu, Q. S. *J. Am. Chem. Soc.* **2004**, *126*, 3058. (c) Percec, V.; Golding, G. M.; Smidrkal, J.; Weichold, O. *J. Org. Chem.* **2004**, *69*, 3447. (d) Percec, V.; Bae, J.-Y.; Hill, D. H. *J. Org. Chem.* **1995**, *60*, 1060. (e) Percec, V.; Bae, J.-Y.; Hill, D. H. *J. Org. Chem.* **1995**, *60*, 1066. (f) Percec, V.; Bae, J.-Y.; Hill, D. H. *J. Org. Chem.* **1995**, *60*, 6895. (g) Ueda, M.; Saitoh, A.; Oh-tani, S.; Miyaura, N. *Tetrahedron* **1998**, *54*, 13079. (h) Kobayashi, Y.; Mizojiri, R. *Tetrahedron Lett.* **1996**, *37*, 8531. (i) Tang, Z.-Y.; Spinella, S.; Hu, Q.-S. *Tetrahedron Lett.* **2006**, *47*, 2427. (j) Lipshutz, B. H.; Butler, T.; Swift, E. *Org. Lett.* **2008**, *10*, 697.

10.1021/jo8014819 CCC: $40.75

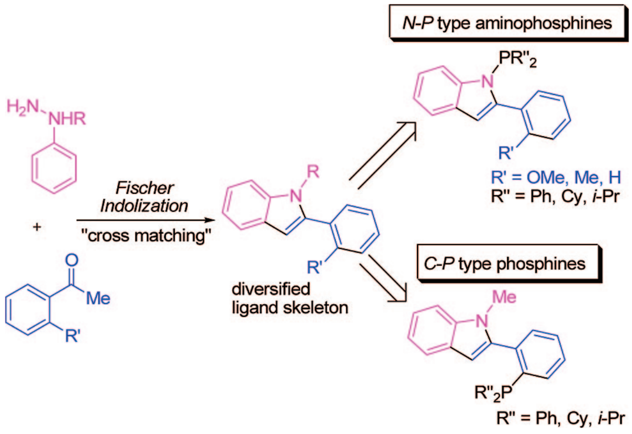
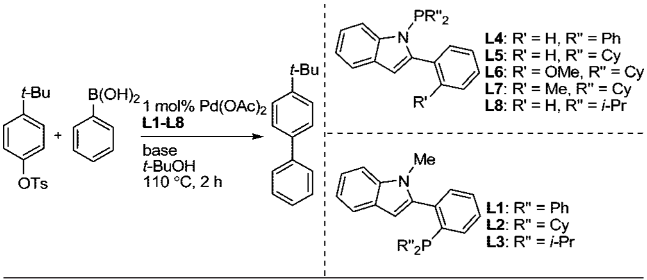


FIGURE 1. Ligand diversification from the 2-arylindole template.

Suzuki−Miyaura reactions as reported by the Buchwald group.[7a] In addition to aryl tosylates, aryl mesylates are attractive but difficult substrates. We recently disclosed the first general amination of aryl mesylates[11] using the indolyl phosphine **L2** (**CM-phos**) as the supporting ligand.[12] In fact, it is desirable to develop a series of ligands that can be easily fine-tuned in dealing with the narrow window for these challenging substrates. Herein, we report our efforts on the application of a series indolyl phosphine ligands in tackling the tosylate substrates in Suzuki−Miyaura coupling. These ligands displayed excellent catalytic activity in coupling of aryl/alkenyl tosylates with different organoboron nucleophiles.

Results and Discussion

TABLE 1. Investigations on the Effectiveness of the Indolyl Phosphine Ligands L1−L8 in Suzuki−Miyaura Coupling of Nonactivated ArOTs[a]



entry	ligand	base	% yield[b]
1	**L1** (R″ = Ph)	$K_3PO_4\cdot H_2O$	<1
2	**L2** (R″ = Cy)	$K_3PO_4\cdot H_2O$	93
3	**L3** (R″ = *i*-Pr)	$K_3PO_4\cdot H_2O$	86
4	no ligand	$K_3PO_4\cdot H_2O$	0
5[c]	**L2** (R″ = Cy)	$K_3PO_4\cdot H_2O$	99
6	**L2** (R″ = Cy)	Cs_2CO_3	85
7	**L2** (R″ = Cy)	Na_2CO_3	<1
8	**L2** (R″ = Cy)	KO*t*-Bu	14
9	**L4** (R′ = H, R″ = Ph)	$K_3PO_4\cdot H_2O$	<1
10	**L5** (R′ = H, R″ = Cy)	$K_3PO_4\cdot H_2O$	<1
11	**L6** (R′ = OMe, R″ = Cy)	$K_3PO_4\cdot H_2O$	2
12	**L7** (R′ = Me, R″ = Cy)	$K_3PO_4\cdot H_2O$	<1
13	**L8** (R′ = H, R″ = *i*-Pr)	$K_3PO_4\cdot H_2O$	<1
14[d]	**L6** (R′ = OMe, R″ = Cy)	$K_3PO_4\cdot H_2O$	2

[a] Reaction conditions: ArOTs (1.0 mmol), $PhB(OH)_2$ (2.0 mmol), base (3.0 mmol), $Pd(OAc)_2$ (0.01 mmol, 1.0 mol%), **L1**−**L3** (0.04 mmol), *t*-BuOH (3.0 mL), at 110 °C under N_2 for 2 h (see the Supporting Information for experimental details). [b] Calibrated GC yields were reported with dodecane as the internal standard. [c] DMF solvent was used. [d] Toluene solvent was used.

We recently reported a series of N−P bound amino-phosphine ligands which can be easily accessed by Fischer indolization[13] from commercially available starting materials (Figure 1).[14] They showed the highest activity achieved so far for the Suzuki−Miyaura coupling of aryl chlorides employing amino-phosphine ligands. On the basis of the attractive feature of this ligand synthesis that the ligand framwork can be easily tuned by a cross matching of two starting materials, we developed another series of C−P bound phosphine ligands for our further investigations,[15] especially in the area of aryl arenesulfonate couplings (Figure 1). These ligands can be simply purified by single crystallization (without tedious chromatographic purification throughout the whole synthetic process) and showed exceptionally high air-stability in both solid and solution states.[16]

The efficacy of both N−P bound and C−P bound indolyl phosphine ligands on Suzuki−Miyaura coupling of tosylate substrate was investigated. We used the nonactivated 4-*tert*-butylphenyl tosylate and phenylboronic acid as the model substrates for our trial runs (Table 1). We initially applied 1 mol % of $Pd(OAc)_2$ with 4 equiv of ligands for the prototypical reactions. It is obvious that ligand **L1** with a diphenylphosphino moiety did not provide any substrate conversion. In contrast, the more electron-rich dicyclohexylphosphino **L2** (**CM-phos**) and diisopropylphosphino **L3** analogues showed good to excellent catalytic activity (entries 1−3). Control experiment revealed that the supporting ligand was necessary for the successful transformation (entries 2 vs 4). The use of *t*-BuOH and DMF as the reaction solvent gave comparable results (entries 2 and 5),[17] while dioxane and THF provided moderate product yields. Upon screening of commonly used inorganic bases, we found

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(7) For ArOTs substrates, Suzuki coupling, see: (a) Nguyen, H. N.; Huang, X.; Buchwald, S. L. *J. Am. Chem. Soc.* **2003**, *125*, 11818. (b) Zhang, L.; Meng, T.; Wu, J. *J. Org. Chem.* **2007**, *72*, 9346. (c) Roy, A. H.; Hartwig, J. F. *J. Am. Chem. Soc.* **2003**, *125*, 8704. (d) Limmert, M. E.; Roy, A. H.; Hartwig, J. F. *J. Org. Chem.* **2005**, *70*, 9364. (e) Ackermann, L.; Althammer, A. *Org. Lett.* **2006**, *8*, 3457. (f) Huang, X.; Anderson, K. W.; Zim, D.; Jiang, L.; Klapars, A.; Buchwald, S. L. *J. Am. Chem. Soc.* **2003**, *125*, 6653. (g) Hamann, B. C.; Hartwig, J. F. *J. Am. Chem. Soc.* **1998**, *120*, 7369. (h) Gelman, D.; Buchwald, S. L. *Angew. Chem., Int. Ed.* **2003**, *42*, 5993. (i) Fernández-Rodríguez, M. A.; Shen, Q.; Hartwig, J. F. *J. Am. Chem. Soc.* **2006**, *128*, 2180. (j) Munday, R. H.; Martinelli, J. R.; Buchwald, S. L. *J. Am. Chem. Soc.* **2008**, *130*, 2754.

(8) For alkenyl-OTs substrates, Suzuki coupling, see: (a) Steinhuebel, D.; Baxter, J. M.; Palucki, M.; Davies, I. W. *J. Org. Chem.* **2005**, *70*, 10124. (b) Klapars, A.; Campos, K. R.; Chen, C.-y.; Volante, R. P. *Org. Lett.* **2005**, *7*, 1185. (c) Hansen, A. L.; Skrydstrup, T. *Org. Lett.* **2005**, *7*, 5585. (d) Hansen, A. L.; Ebran, J.-P.; Ahlquist, M.; Norrby, P.-O.; Skrydstrup, T. *Angew. Chem., Int. Ed.* **2006**, *45*, 3349.

(9) For a recent review on the development and application of bulky electron-rich phosphines for Pd-catalyzed cross-coupling reaction of aryl halides and sulfonates, notably through the work of Beller, Buchwald, Fu, and Hartwig groups, see: Zapf, A.; Beller, M. *Chem. Commun.* **2005**, 431.

(10) For Josiphos-type ligands, see:Togni, A.; Breutel, C.; Schnyder, A.; Spindler, F.; Landert, H.; Tigani, A. *J. Am. Chem. Soc.* **1994**, *116*, 4062.

(11) So, C. M.; Zhou, Z.; Lau, C. P.; Kwong, F. Y. *Angew. Chem., Int. Ed.* **2008**, *47*, 6402.

(12) **CM-phos**: CM represents the initial of the inventor. Particularly in this case, CM-phos has the meaning of the nature of the phosphine ligand, i.e., *C*arbene-*M*etal-*phos*phine.

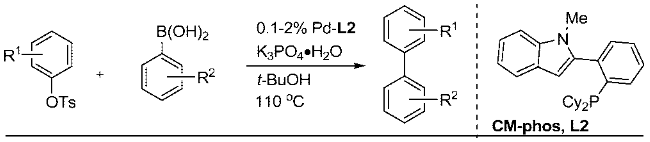
(13) For general indole syntheses, see: (a) Robinson, B. *The Fischer Indole Synthesis*; Wiley: Chichester, UK, 1982. For an alternative 2-arylindole synthesis, see:(b) Denmark, S.; Baird, J. D. *Org. Lett.* **2004**, *6*, 3649.

(14) So, C. M.; Lau, C. P.; Kwong, F. Y. *Org. Lett.* **2007**, *9*, 2795.

(15) For the first Pd-catalyzed Suzuki−Miyaura coupling of aryl mesylates, see: So, C. M.; Lau, C. P.; Kwong, F. Y. *Angew. Chem., Int. Ed.* **2008**, doi: 10.1002/anie.200803193.

(16) There were no detectable phosphine oxide signals of **L2** from ^{31}P NMR, when the solid-form ligand was allowed to stand either under air for 1 week or in solution-form for at least 3 days. In contrast, P*t*-Bu_3 has been shown to be destroyed in air within 2 h, see: (a) Wolfe, J. P.; Tomori, H.; Sadighi, J. P.; Yin, J.; Buchwald, S. L. *J. Org. Chem.* **2000**, *65*, 1158. (b) Barder, T. E.; Buchwald, S. L. *J. Am. Chem. Soc.* **2007**, *129*, 5096.

TABLE 2. Pd-Catalyzed Suzuki−Miyaura Coupling of Aryl Tosylates with Arylboronic Acids[a]



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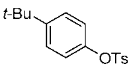
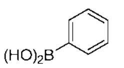
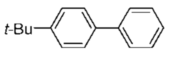
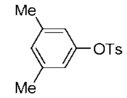
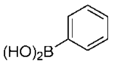
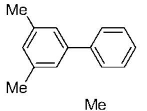
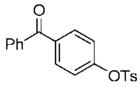
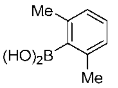
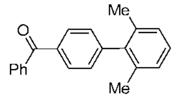
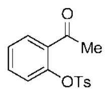
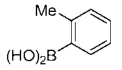
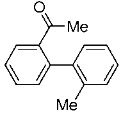
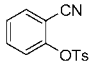
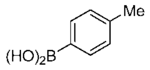
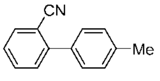
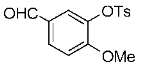
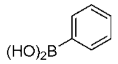
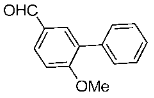
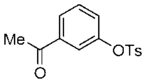
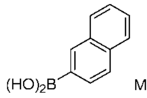
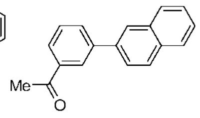
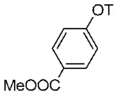
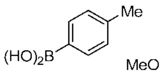
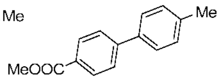
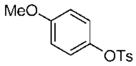
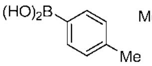
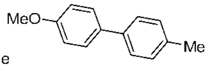
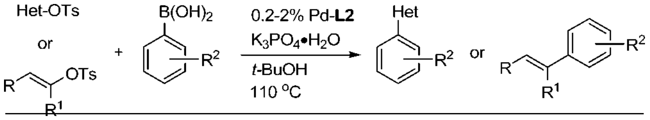
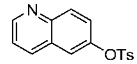
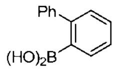
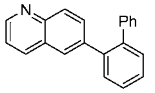
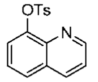
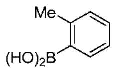
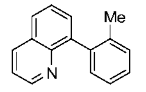
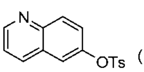
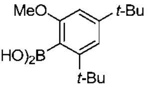
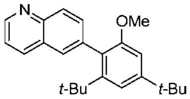
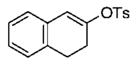
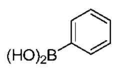
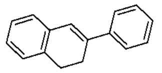
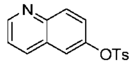
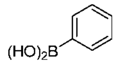
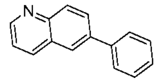
1				1%, 2 h	92
2				0.2%, 12.5 h	85
3				1%, 2 h	94
4				0.5%, 2 h	90
5				1%, 3.5 h	86
6				0.5%, 2 h	83
7				2%, 2 h	87
8				0.5%, 3 h	89
9				0.2%, 2 h	80
10				3%, 4 h	90

[a] Reaction conditions: ArOTs (1.0 mmol), Ar′B(OH)$_2$ (2.0 mmol), $K_3PO_4\cdot H_2O$ (3.0 mmol), Pd(OAc)$_2$ (mol % as indicated), Pd:L = 1:4, t-BuOH (3.0 mL), at 110 °C under N_2 for the indicated period of time (see the Supporting Information). [b] Isolated yields.

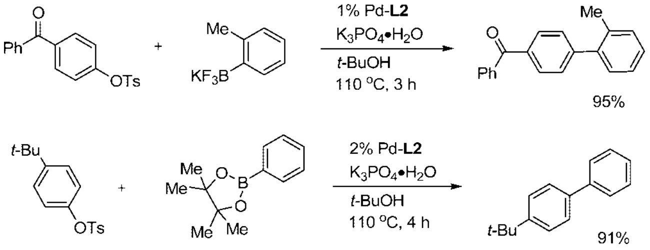
TABLE 3. Pd-Catalyzed Suzuki−Miyaura Coupling of Heteroaryl or Vinyl Tosylates with Arylboronic Acids[a]



entry	Het-OTs or VinylOTs	Ar'B(OH)$_2$	product	mol% Pd	% yield[b]
1				0.2%, 2 h	99
2				2%, 4.5 h	99
3				1%, 3 h	91
4				0.5%, 2 h	98
5[c]				4%, 78 h ***room temp.***	94

[a] Reaction conditions: Het-OTs or VinylOTs (1.0 mmol), Ar′B(OH)$_2$ (2.0 mmol), $K_3PO_4\cdot H_2O$ (3.0 mmol), Pd(OAc)$_2$ (mol % as indicated), Pd:L = 1:4, t-BuOH (3.0 mL), at 110 °C under N_2. [b] Isolated yields. [c] DMF solvent was used.

SCHEME 1. Suzuki−Miyaura Coupling of Aryl Tosylates with Other Organoboron Nucleophiles



that K_3PO_4 monohydrate and Cs_2CO_3 were suitable bases for this aryl tosylate coupling reaction (entries 6−8). In addition to phosphines **L1**−**L3**, an array of amino-phosphines **L4**−**L8** were examined. However, it seems amino-phosphines are not effective under these alcoholic reaction conditions (entries 9−13). We observed ligand decomposition (from hydrolysis of the N−P bond) during the course of the reactions. To eliminate the hydrolytic cleavage problem of amino-phosphines, we further investigated the applicability of these ligands using toluene as the reaction medium (entry 14). Although we did not observe any ligand decomposition, no significant conversion of the substrate was observed. Thus, the N−P bound amino-phosphines are generally inferior in tosylate coupling reactions.

To test the effectiveness of the C−P bound indolyl phosphines, a range of aryl tosylates were examined, using the optimized reaction conditions (Table 2). In general, essentially complete conversions were observed within 2−4 h when 0.5−1 mol % of Pd was used. Homocoupled and reduction side-products were not observed from GC-MS analyses. Notably, the catalyst loading for the coupling of nonactivated aryl tosylate can be down to 0.2 mol % of Pd for the first time (entry 2). A variety of functional groups were compatible under these mild reaction conditions, including keto, nitrile, aldehyde, and ester (entries 4−9). For the first time, the electron-rich (deactivated) *p*-anisyl tosylate was demonstrated to be a feasible coupling partner (entry 10).

Apart from functionalized aryl tosylates, heteroaryl and vinyl tosylates were effective substrates in the Pd/**L2** catalytic system (Table 3). Sterically congested arylboronic acids were efficiently coupled with quinolyl tosylates in excellent yields (entries 1 and 2). It is noteworthy that the extremely hindered 2,4-di-*tert*-butyl-6-methoxyphenylboronic acid was found to be a capable coupling partner in this reaction (entry 3). The scope of tosylate coupling reactions can also be extended to vinyl tosylate (entry 4). Remarkably, an example of aryl tosylate coupling at room temperature reaction was realized (entry 5). These results indicate the palladium catalyst derived from **CM-phos** is highly active for tosylate coupling reactions.

Although boronic acids are widely used as the coupling nucleophiles, the exploration of other boronic acid surrogates

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(17) Although DMF provided slightly better product yield, *t*-BuOH was chosen for further study due to its relatively less toxicity.

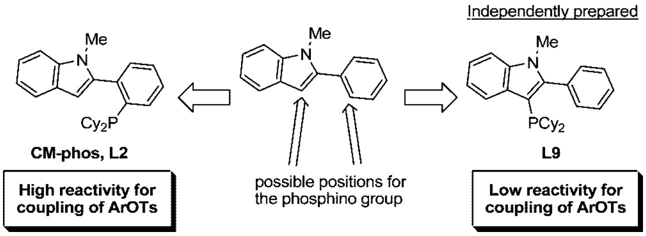

FIGURE 2. An investigation on an interplay of the phosphino group on the ligand scaffold toward the reactivity in tosylate couplings.

in this catalytic system is still needed.[18] An aryl trifluoroborate salt and a pinacol boronate ester were successfully coupled with aryl tosylates under our catalytic system (Scheme 1).

To study the importance of the phosphino group position on the indolyl ligand toward the efficiency of tosylate coupling reactions, we independently prepared a similar new phosphine ligand **L9** (Figure 2). However, we did not observe any reactivity of the catalyst when **L9** was subjected to the coupling of 4-*tert*-butylphenyl tosylate with phenylboronic acid. We were surprised that dramatic differences on reactivity were obtained when the position of the phosphino group was interchanged (but the ligand scaffold remained the same). Presumably the phosphino group on the aryl ring (instead of on the heterocyclic ring) provides better geometry of chelation to the palladium center and facilitates the oxidative addition of the Ar−OTs bond. Thus, tosylate couplings are likely sensitive to the structure of the ligand. Therefore, high ligand diversity is crucial to achieve problematic coupling reactions.

Conclusion

In conclusion, we reported our study on a series of simple indolyl phosphines to the Suzuki-type coupling of substituted arenesulfonates. A variety of aryl, heteroaryl, and vinyl tosylates were efficiently coupled with different organoboron nucleophiles. These easily accessible indolyl-type phosphine ligands in combination with Pd-complex precursor showed good activity (0.2 to 3.0 mol % Pd) in nonactivated tosylate coupling reactions. Particularly noteworthy is that the first example for room temperature Pd-catalyzed Suzuki−Miyaura cross-coupling of aryl tosylate was also successfully realized. This Pd/**CM-phos** catalyst provides a useful alternative system to the Buchwald-type biaryl phosphines,[19] which constitute effective Suzuki−Miyaura coupling of aryl tosylates.

Experimental Section

General Procedure for Suzuki−Miyaura Coupling of Aryl Tosylates. Pd(OAc)$_2$ (2.3 mg, 0.010 mmol) and ligand (0.040 mmol) were loaded into an oven-dried Schlenk tube equipped with a Teflon-coated magnetic stir bar. The tube was evacuated and flushed with nitrogen several times. Precomplexation was applied by adding freshly distilled dichloromethane and Et$_3$N into the tube. The solution was stirred and warmed with a hair dryer for about 1 to 2 min until the solvent started boiling. The solvent was then evaporated under high vacuum. Aryl tosylate (1.0 mmol), arylboronic acid (2.0 mmol), and K$_3$PO$_4$·H$_2$O (3.0 mmol) were loaded into the tube, and the system was further evacuated and flushed with nitrogen three times. The solvent *tert*-butanol (3.0 mL) was then added. The tube was stirred at room temperature for several minutes and then placed into a preheated oil bath (110 °C) for the time period as indicated in the tables. After completion of reaction as judged by GC analysis, the reaction tube was allowed to cool to room temperature and quenched with water and diluted with EtOAc. The organic layer was separated and the aqueous layer was washed with EtOAc. The filtrate was concentrated under reduced pressure. The crude products were purified by flash column chromatography on silica gel (230−400 mesh) to afford the desired product. 4-*tert*-Butylbiphenyl[20] (example from Table 2, entry 1): hexane, R_f 0.55; ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.72 (s, 9H), 7.64 (t, J = 7.4 Hz, 1H), 7.72−7.82 (m, 4H), 7.89−7.96 (m, 4H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 31.3, 34.4, 125.6, 126.7, 126.9, 128.6, 138.2, 140.9, 150.0; MS (EI) *m/z* (rel intensity) 210 (M$^+$, 35), 195 (100), 178 (20), 167 (30). 6-(2,4-Di-*tert*-butyl-6-methoxyphenyl)quinoline (example from Table 3, entry 3): EtOAc:hexane = 1:9, R_f 0.15; white solid, mp 136.4−138.1 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.19 (s, 9H), 1.42 (s, 9H), 3.56 (s, 3H), 6.92 (s, 1H), 7.24−7.31 (m, 4H), 8.02 (d, J = 7.9 Hz, 1H), 8.14 (d, J = 8.5 Hz, 1H), 8.87 (m, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 31.1, 32.5, 34.8, 36.6, 55.5, 105.7, 116.0, 120.5, 127.0, 127.2, 127.5, 129.2, 133.9, 135.5, 138.3, 147.0, 148.4, 149.6, 150.6, 157.3; MS (EI) *m/z* (rel intensity) 347 (M$^+$, 100), 332 (75), 317 (5), 302 (3), 290 (5), 276(75), 261(30); HRMS calcd for C$_{24}$H$_{29}$N: 347.2244, found 347.2253. (See the Supporting Information for experimental details.)

Acknowledgment. We thank the Research Grants Council of Hong Kong (Project No. CERG: PolyU 5005/07P) and University Grants Committee Areas of Excellence Scheme (Project No. AoE/P-10/01) for financial support.

Supporting Information Available: Detailed experimental procedures, characterization data, and copies of ^{1}H, ^{13}C, ^{31}P NMR, MS, HRMS, and IR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) For a review describing organotrifluoroborate salts in coupling reactions, see: Molander, G A.; Ellis, N. *Acc. Chem. Res.* **2007**, *40*, 275.

(19) To our best knowledge, there are only two publications to date on the effective Suzuki−Miyaura coupling of aryl tosylates. The ligand structures are the Buchwald-type phosphines. See refs 7a and 7b for 2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl and 2-dicyclohexylphosphino-2′,4′,6′-trimethoxylbiphenyl, respectively.

(20) Wolfe, J. P.; Singer, R. A.; Yang, B. H.; Buchwald, S. L. *J. Am. Chem. Soc.* **1999**, *121*, 9550.