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Remarkably Effective Phosphanes Simply with a PPh_2 Moiety: Application to Pd-Catalysed Cross-Coupling Reactions for Tetra-*ortho*-substituted Biaryl Syntheses

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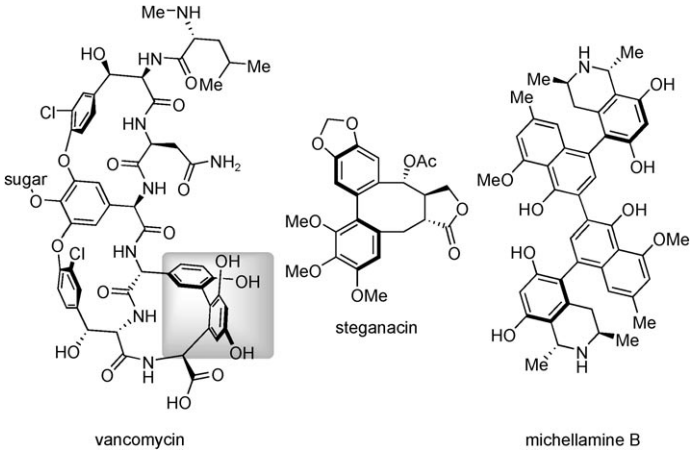
Dedicated to Professor Albert S. C. Chan on the occasion of his 60th birthday

ortho-Substituted biaryl compounds are important structural motifs present in a number of natural products from various origins and have a wide range of biological properties.[1,2] The biaryl substructures in vancomycin, a glycopeptide antibiotic from *Streptomyces orientalis*,[3] steganacin, a cytotoxic tubulin-binding dibenzocyclootadiene lignan from *Steganotaenia araliacea*,[4] and michellamine B, an anti-HIV naphthylisoquinoline alkaloid from *Ancistrocladus abbreviatus*,[5] have aroused the interest of many synthetic chemists within the field of sterically congested biaryl synthesis.

However, the ability to prepare extremely hindered asymmetric biaryl compounds by using Suzuki–Miyaura coupling reactions has proven to be an extremely difficult task. Recent superb findings by the Buchwald group have demonstrated that PCy_2-substituted phenanthrene-based phosphanes[6] and 2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl (S-Phos)[7] are effective ligands for the synthesis of tetra-*ortho*-substituted biaryl compounds, mainly from aryl bromides (Figure 1). To date, in the exploration of phosphane ligands, only the ruthenocenylphosphane R-Phos developed by Hoshi/Hagiwara[8] and, very recently, the diazaphospholidine chloride disclosed by Ackermann[9] allowed the successful synthesis of tetra-*ortho*-substituted biaryls from unactivated aryl chlorides (Figure 1). Besides phosphanes, carbene IBiox12·OTf with a tuneable ring size, "flexible-steric-bulk" PEPPSI-IPent and phenanthryl-based H_2-ICP·HCl, reported by Glorius,[10] Organ[11] and Ma/Andrus,[12] respectively, are also appropriate for sterically congested couplings (Figure 1).



The lore in the field of demanding cross-coupling reactions reveals that successful phosphane ligands often contain dialkylphosphane groups, such as PCy_2 or $PtBu_2$ (Figure 1). In contrast to $ArPCy_2$ and $ArPtBu_2$ ligands, the corresponding $ArPPh_2$ compounds have received less attention due to the accepted rationale indicating that they are less electron-rich and less bulky than the corresponding $ArPCy_2$ and $ArPtBu_2$ compounds (Figure 2)[13] and, thus, provide a less favourable outcomes for the oxidative addition and reductive elimination steps in unactivated aryl chloride couplings.[14–16]

However, triarylphosphanes are attractive compounds as they are reasonably air stable and can be readily prepared from the relatively inexpensive Ph_2PCl.[17] Herein, we report an unexpected finding that advances coupling technology by showing that the previously omitted triarylphosphane family can effectively deal with difficult coupling reactions. We disclose their ability to perform the most difficult biaryl cou-

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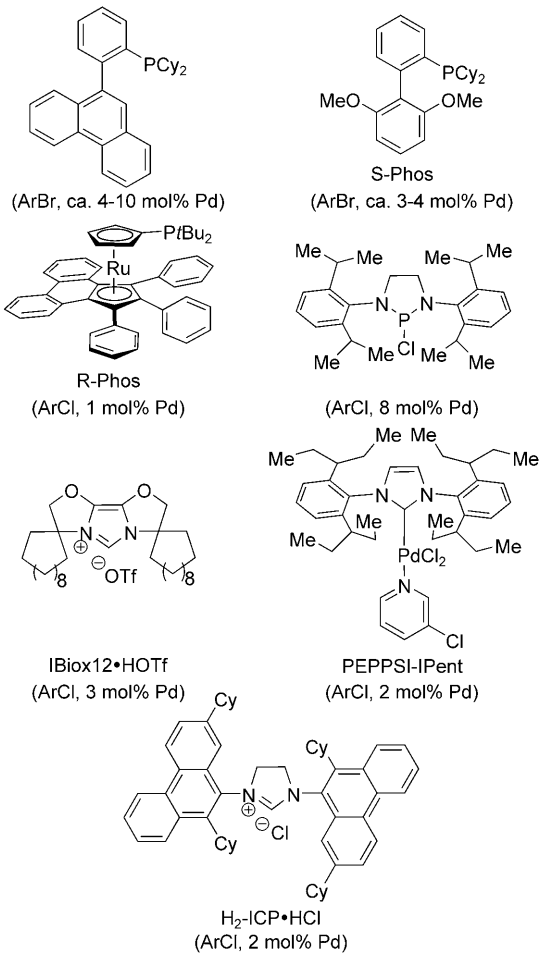


Figure 1. Phosphanes and carbenes used in Pd-catalysed Suzuki-type syntheses of asymmetric tetra-*ortho*-substituted biaryls.

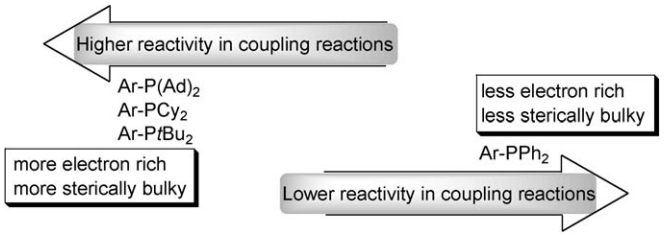


Figure 2. The normal reactivity of aryldialkylphosphane and triarylphosphane ligands in cross-coupling processes.

plings, forming tetra-*ortho*-substituted compounds from unactivated aryl chlorides, for the first time.

We recently disclosed a series of indolyl N–P-bonded aminophosphane[18] and C–P-bonded phosphane ligands,[19] which were prepared by straightforward Fischer indolisation and phosphonation (Figure 3). The CM-phos ligand succeeded in catalysing the challenging aryl mesylate coupling reactions.[20] In order to show the attractive features of this modular ligand synthesis, we communicate, herein, the assembly of a new series of C–P-type ligands, in which the phosphane

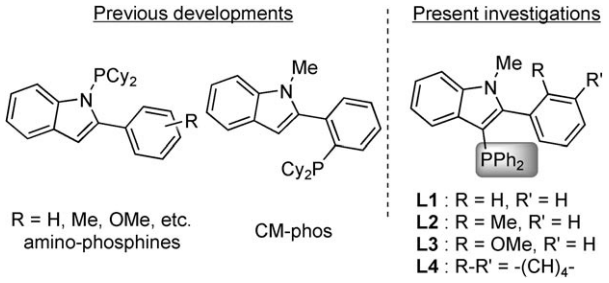
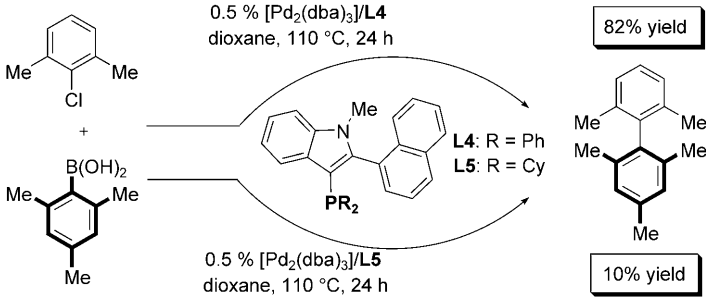


Figure 3. Exploration of a series of modular indolylphosphanes.

group is incorporated within the indole ring (**L1–L4**; Figure 3).

With our newly developed ligands in hand, we attempted one of the most difficult coupling reactions, the synthesis of tetra-*ortho*-biaryl compounds (Scheme 1). 2-Chloro-*meta*-xylene and 2-mesitylboronic acid were initially used as

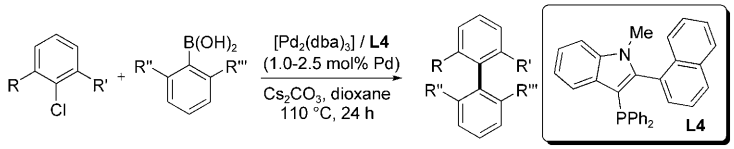


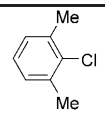
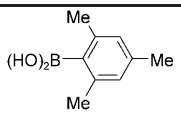
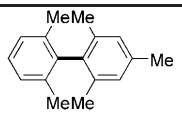
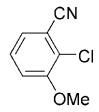
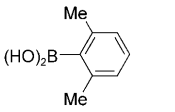
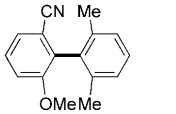
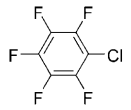
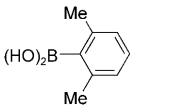
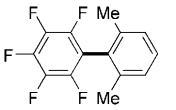
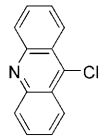
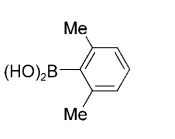
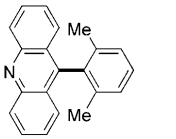
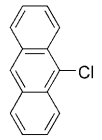
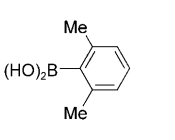
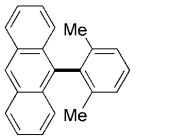
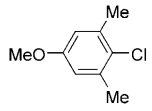
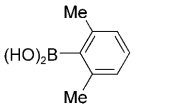
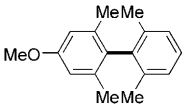
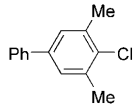
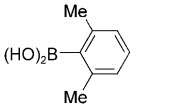
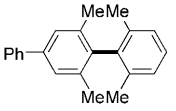
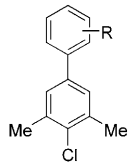
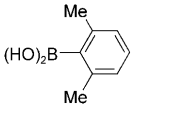
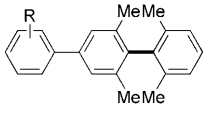
Scheme 1. Unusual reactivity difference between triarylphosphane **L4** and aryldialkylphosphane **L5** ligands; dba = 1,5-diphenylpenta-1,4-dien-3-one.

model substrates. **L4** gave a slightly better conversion than **L3**. To our surprise, the allegedly more reactive aryldialkylphosphane **L5** showed an inferior outcome, yet the ligand **L4**, in which the scaffold consists of the PPh_2 group, gave a superior coupling-product yield (Scheme 1).

To further probe and ensure the effectiveness of the Pd–**L4** catalytic system, an array of sterically congested aryl chlorides and arylboronic acids were examined in this reaction (Table 1). The slightly activated 2,6-dimethoxyphenyl- and 2-methoxy-6-substituted-phenylboronic acids were not used in our investigations.[21] The **L4** ligand showed slightly higher activity than **L3** in promoting the extremely hindered biaryl synthesis (Table 1, entries 1 vs. 2). Cs_2CO_3 provided a better substrate conversion than $K_3PO_4 \cdot H_2O$ (Table 1, entries 2 vs. 3). Tetra-*ortho*-substituted biaryl coupling in the presence of cyano and methoxy groups was also accomplished in excellent yield (Table 1, entry 4). Anthracenyl chlorides furnished the coupling products smoothly (Table 1, entries 6 and 7).[22] In particular, 2,6-dimethyl-4-chloroanisole could be coupled smoothly to afford the desired product in moderate to good yield (Table 1, entry 8). The impediments to this particular transformation are not only due

Table 1. Tetra-*ortho*-substituted biaryl synthesis catalysed by the Pd–**L4** catalytic system.[a]



Entry	ArCl	Ar′B(OH)$_2$	Product	Pd [mol %]	Yield [%][b]
1[c]				2.0	82
2				1.0	82
3[d]				4.0	34[e]
4				1.0	94
5				1.0	82
6				1.0	96
7				2.0	48
8				2.5	68
9				1.0	88
10			R = 3-C(O)Me	1.0	82
11			 R = 4-COOMe	1.0	80

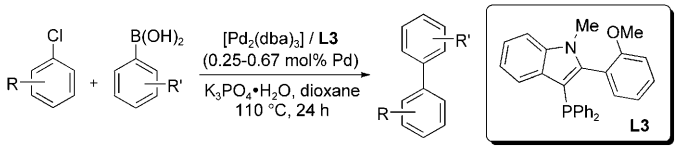
[a] Reaction conditions: ArCl (1.0 mmol), Ar′B(OH)$_2$ (2.0 mmol), [Pd$_2$(dba)$_3$] (mol % as indicated), ligand (Pd/L, 1:4), Cs_2CO_3 (3.0 mmol) and dioxane (3.0 mL), under N_2 at 110 °C for 24 h (reaction times for each substrate were not optimised). [b] Isolated yields are reported. [c] **L3** was used instead of **L4**. [d] $K_3PO_4 \cdot H_2O$ was used as the base. [e] GC yield is reported.

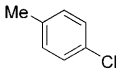
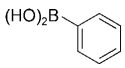
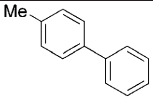
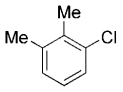
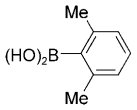
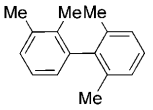
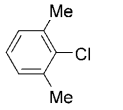
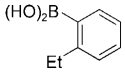
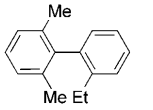
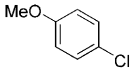
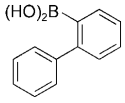
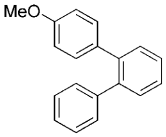
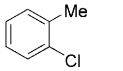
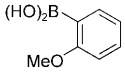
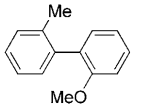
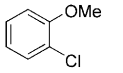
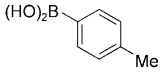
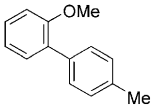
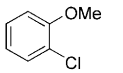
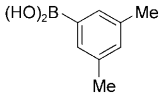
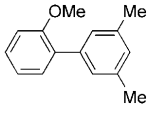
to the steric encumbrance of both the aryl chloride and the arylboronic acid, but also to the very electron-rich nature of the aryl chloride. Functional groups such as a methyl ester or ketone groups were also compatible with these reaction conditions (Table 1, entries 10 and 11).

Another set of unactivated aryl chlorides was also examined (Table 2). In contrast to the specifically tetra-*ortho*-substituted biaryl couplings, Pd–**L3** showed a slightly better reactivity than Pd–**L4** for these reactions. During the course of our investigation, the complete conversion of the ArCls was generally observed if 0.5 mol % Pd was used. The coupling of sterically hindered substrates (both electrophilic and nucleophilic partners) that generate tri-*ortho*-substituted biaryl compounds was also accomplished (Table 2, entries 3 and 4**)**. This result represents the lowest catalyst loading achieved so far for tri-*ortho*-substituted biaryl coupling in which a phosphane ligand with a PPh_2 moiety is used. A deactivated aryl chloride also smoothly coupled with 2-biphenylboronic acid (Table 2, entry 5).

In addition to unactivated aryl chlorides, the Pd–**L3** catalyst system was applied to functionalised aryl chloride couplings (Table 3). Catalyst loading for these reactions could

Table 2. Palladium–$ArPPh_2$-catalysed Suzuki–Miyaura couplings of unactivated aryl chlorides.[a]



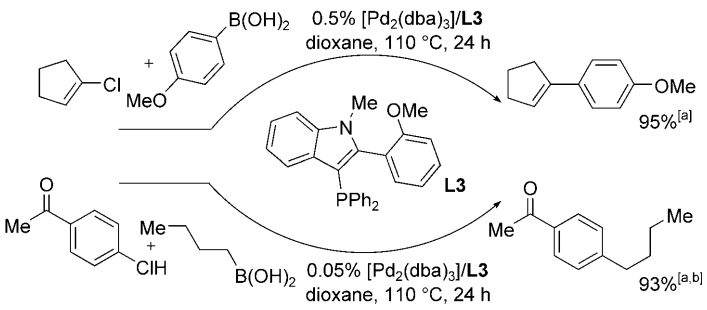
Entry	ArCl	$Ar'B(OH)_2$	Product	Pd [mol%]	Yield [%][b]
1				0.5	97
2				0.25	82[c]
3				0.67	87
4				0.67	92
5				0.5	80
6				0.5	84
7				0.4	95
8				0.4	92

[a] Reaction conditions: ArCl (1.0 mmol), $Ar'B(OH)_2$ (1.5 mmol), $[Pd_2(dba)_3]$ (mol% as indicated), ligand (Pd/L, 1:4), $K_3PO_4{\cdot}H_2O$ (3.0 mmol) and dioxane (3.0 mL), under N_2 at 110 °C for 24 h (reaction times for each substrate were not optimised). [b] Isolated yields are reported. [c] GC yield is reported.

be reduced to 0.02 mol% Pd at 90 °C. In order to show the efficiency of the newly developed system, we avoided using the "privileged" phenylboronic acid as the substrate, but instead used challenging electron-deficient[23] or sterically hindered arylboronic acids as the nucleophilic partners. Excellent product yields were obtained when 3-nitrophenylboronic acid was used (Table 3, entries 1 and 2). A 2,6-disubstituted-arylboronic acid also furnished the coupling products in an almost quantitative yield (Table 3, entries 3 and 4). Common functional groups, such as enolisable ketones, aldehydes, methyl esters and cyano groups, were all compatible with these reaction conditions (Table 3, entries 1 and 4–8). Nitrogen heterocycles, such as pyridine, isoquinoline and unprotected indole, proved to be proficient at affording their corresponding products in excellent yields (Table 3, entries 9–13).

In addition to the aryl coupling partners, the reactions of vinyl chlorides and alkylboronic acids were also tested (Scheme 2).[24] Cyclopentenyl chloride coupled with *para*-anisylboronic acid in good yield. Catalyst loading can be reduced to 0.1 mol% Pd for the coupling of *n*-butylboronic acid with an aryl chloride (Scheme 2).

In conclusion, we have prepared a new set of easily accessible and tuneable triarylphosphane ligands.[25] These ligands significantly expand the scope of Pd-catalysed cross-couplings by enabling the use of non-electron-rich boranes for the coupling of aryl chlorides. Notably, we have succeeded in achieving the most difficult Pd-catalysed cross-coupling, the synthesis of tetra-*ortho*-substituted asymmetric biaryl compounds, by using an arylphosphane ligand possessing a PPh_2 group. These unusual findings highlight the versatility of triarylphosphanes and indicate that the PCy_2 or $PtBu_2$ moieties are not necessary to deal with difficult coupling processes. We anticipate that further enhancements of the reactivity of the previously unexplored triarylphosphane family towards a variety of coupling reactions are attainable.

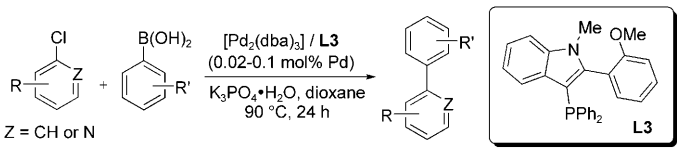


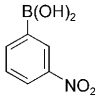
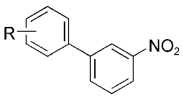
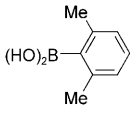
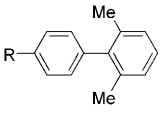
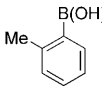
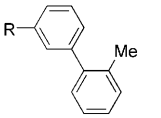
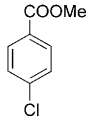
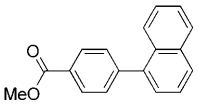
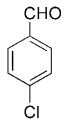
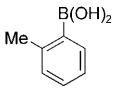
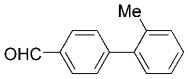
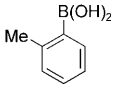
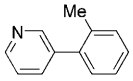
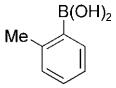
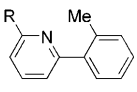
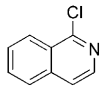
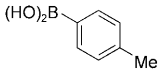
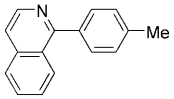
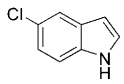
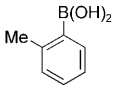
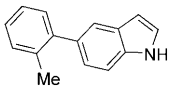
Scheme 2. The feasibility of the Pd–triarylphosphane-catalysed Suzuki coupling of vinyl chloride and alkylboronic acid. [a] Isolated yields. [b] 3 equivalents of $RB(OH)_2$ was used (with respect to the ArCl).

Experimental Section

General experimental procedures are given in the Supporting Information.

Table 3. Palladium-catalysed cross-couplings of functionalised ArCl.[a]



Entry	ArCl	$Ar'B(OH)_2$	Product	Pd [mol%]	Yield [%][b]
1	R = 3-C(O)Me			0.1	98
2	R = 4-C(O)Ph			0.067	95
3	R = C(O)Ph			0.05	99
4	R = COOMe			0.05	91
5	R = COOMe			0.05	92
6	R = CN			0.025	97
7				0.02	84
8[c]				0.1	96
9[c]				0.1	82
10[c]	R = H			0.01	97
11[c]	R = Me			0.01	95
12[c]				0.01	96
13[c]				1.5	70

[a] Reaction conditions: ArCl (1.0 mmol), $Ar'B(OH)_2$ (1.5 mmol), $[Pd_2(dba)_3]$ (mol% as indicated), ligand (Pd/L, 1:4), $K_3PO_4{\cdot}H_2O$ (3.0 mmol) and dioxane (3.0 mL), under N_2 at 90 °C for 24 h (reaction times for each substrate were not optimised). [b] Isolated yields are reported. [c] Reaction temperature = 110 °C.

Acknowledgements

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Keywords: biaryls · cross-coupling · palladium · phosphane ligands · Suzuki–Miyaura coupling

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[16] To the best of our knowledge, no example of the use of the [Ar_3PPd] catalyst system for tri-*ortho*-substituted biaryl coupling with *o*-substituents larger than tri-*ortho*-methyl has been reported.

[17] For [Ph_2PCl], 500 g, USD = 298.0; for [Cy_2PCl], 5 g, USD = 162.8, from the Aldrich catalogue 2006.

[18] a) C. M. So, C. P. Lau, F. Y. Kwong, *Org. Lett.* **2007**, *9*, 2795; for indolylphosphane independently developed by Beller and co-workers, see: b) F. Rataboul, A. Zapf, R. Jackstell, S. Harkal, T. Riermeier, A. Monsees, U. Dingerdissen, M. Beller, *Chem. Eur. J.* **2004**, *10*, 2983; for a related imidazolylphosphane, see: c) S. Harkal, F. Rataboul, A. Zapf, R. Jackstell, T. Riermeier, M. Beller, *Adv. Synth. Catal.* **2004**, *346*, 1742; for other indolylphosphanes developed by our group, see: d) C. M. So, C. C. Yeung, C. P. Lau, F. Y. Kwong, *J. Org. Chem.* **2008**, *73*, 7803.

[19] C. M. So, Z. Zhou, C. P. Lau, F. Y. Kwong, *Angew. Chem.* **2008**, *120*, 6502; *Angew. Chem. Int. Ed.* **2008**, *47*, 6402.

[20] a) C. M. So, H. W. Lee, C. P. Lau, F. Y. Kwong, *Org. Lett.* **2009**, *11*, 317; b) C. M. So, C. P. Lau, F. Y. Kwong, *Angew. Chem.* **2008**, *120*, 8179; *Angew. Chem. Int. Ed.* **2008**, *47*, 8059; c) C. M. So, C. P. Lau, A. S. C. Chan, F. Y. Kwong, *J. Org. Chem.* **2008**, *73*, 7734.

[21] Electron-rich $ArB(OH)_2$ compounds are generally more nucleophilic and readily undergo transmetallation, see: a) reference [2a]. In contrast, electron-deficient $ArB(OH)_2$ compounds are less nucleophilic and undergo transmetallation at a slower rate than electron-neutral and -rich arylboronic acids. Hence, electron-deficient $ArB(OH)_2$ compounds are usually regarded as more challenging substrates. Moreover, electron-poor boronic acids are prone to homo-coupling side reactions, see: b) M. S. Wong, X. L. Zhang, *Tetrahedron Lett.* **2001**, *42*, 4087. Furthermore, electron-poor $ArB(OH)_2$ compounds are more susceptible to metal-catalysed protodeboronation, see: c) H. G. Kuivila, J. F. Reuwer, J. A. Mangravite, *J. Am. Chem. Soc.* **1964**, *86*, 2666.

[22] The GC yield of Table 1, entry 7 was significantly higher than the isolated yield. The moderate isolated yield obtained is due to the difficultly in chromatographically separating the desired product from some dechlorinated anthracene. Note: commercially available 9-chloroanthracene consists of 1–4 % anthracene impurity.

[23] Electron-deficient $ArB(OH)_2$ compounds are less nucleophilic and undergo transmetallation at a slower rate than electron-neutral and -rich arylboronic acids. Hence, they are usually regarded as more challenging substrates.

[24] For a recent review on alkylboronic acid couplings, see: H. Doucet, *Eur. J. Org. Chem.* **2008**, 2013.

[25] For all steps in new the ligand synthesis, products were simply purified by washing or crystallisation. No tedious column chromatography is required.

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