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Nickel-catalyzed cross-coupling of *O*,*N*-chelated diarylborinates with aryl chlorides and mesylates†

Chao Ren, Jingshu Zeng and Gang Zou *

A practical nickel catalyst system consisting of readily available components, *trans*-NiCl(Ph)(PPh_3)$_2$/[Iprmim]I/K_3PO_4·$3H_2O$ in toluene, has been developed for efficient cross-coupling of 3-dimethylaminopropyl diarylborinates with aryl chlorides and mesylates. A small amount of water has been found to be crucial in achieving high efficiency in the system. The nickel catalyst system displayed remarkably higher activities to aryl chlorides and mesylates than the corresponding tosylates in cross-coupling with not only diarylborinates but also diarylborinic acids, arylboronic acids, anhydrides and trifluoroborates as indicated in control experiments. A variety of electronically various biaryls could be obtained in excellent yields by using 3–5 mol% loading of the nickel catalyst while sterically hindered biaryls were obtained in comparably lower yields.

Introduction

The physiochemical properties, in particular stability and reactivities, of diarylborinates not only depend on their aryl groups but also could be finely tuned by coordination of the boron center. As one of the most stable types of arylboron compounds, chelate stabilized four-coordinate diarylborinates are almost infinitely air- and moisture-stable yet have tunable reactivities *via* the chelating ligands, therefore finding increasing importance in chemical,[1] material[2] and biological sciences.[3] As part of our on-going research on practical synthetic methodology for biaryls,[4] we have recently reported that 3-dimethylaminopropyl diarylborinates featuring a six-membered *O*,*N*-chelated boron ring displayed a delicately balanced stability and reactivity *via* the so-called through-bond interactions[5] in palladium catalyzed Suzuki coupling of aryl chlorides.[4e] Although less popular than palladium, homogeneous nickel catalysis has attracted increasing interests,[6] because nickel is not only more cost-effective and less toxic but also has proven to be more versatile in catalyzing Suzuki coupling of less reactive electrophiles, such as sulfonates,[7] nitriles,[8] ammonium salts,[9] ethers,[10] esters,[11] amides,[11c,d,12] fluorides,[13] sulfamates,[14] and carbamates.[11c,15] However, the nickel-catalyzed Suzuki coupling is still much less used in practical synthesis than the palladium-catalyzed one. One of the major causes to this disparity is the requirement of either strong reducing conditions to activate the inexpensive Ni(II) precatalysts, *e.g.* nickel halide ($NiX_2(L)_2$), or highly air- and light-sensitive Ni(0) precursors, most commonly Ni(cod)$_2$, which is expensive and must be stored, handled and used under rigorously light- and air-free conditions.[16] To solve this problem, air-stable, yet easily activated (Ar)NiCl(L) precatalysts supported by phosphine, N-heterocyclic carbene (NHC), or chelating diamine ligands have been developed by Yang,[17] Percec,[18] Jamison,[19] Hartwig,[20] Buchwald,[21] and many others[22] and have proven to be highly active for specific reactions.

To develop practical nickel catalyst systems for Suzuki coupling of cost-effective substrates, we report herein a highly efficient nickel catalyst system based on *trans*-NiCl(Ph)(PPh_3)$_2$ and sterically unsymmetrical N-heterocyclic carbenes for Suzuki coupling of shelf-stable *O*,*N*-chelated diarylborinates with aryl chlorides and mesylates for synthesis of biaryls.

Results and discussion

Coupling with aryl chlorides

Initially, the cost-effective, readily available and air-stable $NiCl_2(PPh_3)_2$/[Bmim]Br catalyst system,[4b] which we have established for cross-coupling of aryl (pseudo)chlorides with diarylboronic acids, was used in the model reaction of 3-dimethylaminopropyl diphenylborinate (**1a**) with 4-chloroactetophenone (**2a**) (Table 1, entry 1). The desired biaryl product **3aa** was obtained in a modest yield (73%) significantly lower than the almost quantitative yield (98%) in the control reaction of the corresponding borinic acid (anhydride). The decrease in catalysis efficiency could be partly attributed to the increased stability of chelated diarylborinates than free borinic acids, thus the decreased ability in activation of Ni(II) chloride precatalyst. Therefore, the easily activated organonickel complex *trans*-NiCl(Ph)(PPh_3)$_2$ was tested as the precatalyst and the yield

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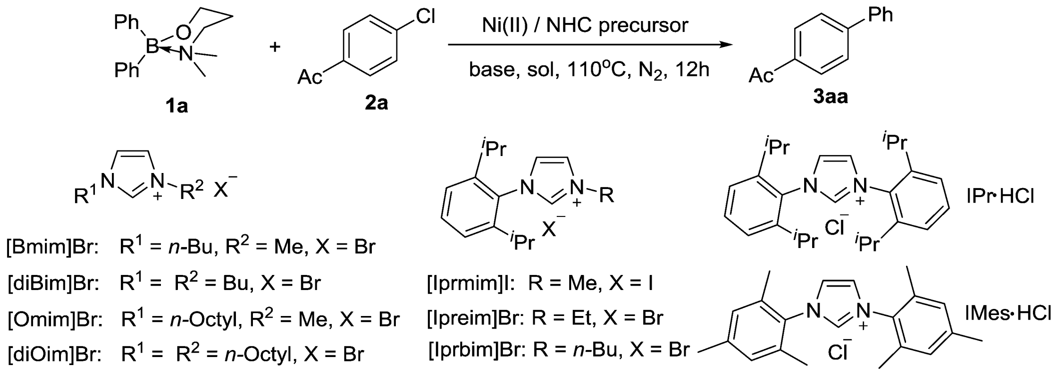
† Electronic supplementary information (ESI) available: Experimental procedure, characterization data for products, and copies of NMR spectra. See DOI: 10.1039/c8nj05503c

Table 1 Optimization of Ni-catalyzed cross-coupling of diarylborinate **1a** with aryl chloride **2a**[a]



Entry	Ni(II) (mol %)	L (mol %)	Base	Sol.	Yield[b] (%)
1	NiCl$_2$(PPh$_3$)$_2$ (3)	[Bmim]Br (3)	$K_3PO_4{\cdot}3H_2O$	Tol	73
2	*trans*-NiCl(Ph)(PPh$_3$)$_2$ (3)	[Bmim]Br (3)	$K_3PO_4{\cdot}3H_2O$	Tol	81
3	NiCl$_2$ (3)	[Bmim]Br (3)	$K_3PO_4{\cdot}3H_2O$	Tol	19
4	*trans*-NiCl(Ph)(PPh$_3$)$_2$ (3)	—	$K_3PO_4{\cdot}3H_2O$	Tol	49
5	*trans*-NiCl(Ph)(PPh$_3$)$_2$ (3)	[diBim]Br (3)	$K_3PO_4{\cdot}3H_2O$	Tol	84
6	*trans*-NiCl(Ph)(PPh$_3$)$_2$ (3)	IPr·HCl (3)	$K_3PO_4{\cdot}3H_2O$	Tol	89
7	*trans*-NiCl(Ph)(PPh$_3$)$_2$ (3)	IMes·HCl (3)	$K_3PO_4{\cdot}3H_2O$	Tol	76
8	*trans*-NiCl(Ph)(PPh$_3$)$_2$ (3)	[diOim]Br (3)	$K_3PO_4{\cdot}3H_2O$	Tol	80
9	*trans*-NiCl(Ph)(PPh$_3$)$_2$ (3)	[Omim]Br (3)	$K_3PO_4{\cdot}3H_2O$	Tol	89
10	*trans*-NiCl(Ph)(PPh$_3$)$_2$ (3)	[Iprmim]I (3)	$K_3PO_4{\cdot}3H_2O$	Tol	97
11	*trans*-NiCl(Ph)(PPh$_3$)$_2$ (3)	[Ipreim]Br (3)	$K_3PO_4{\cdot}3H_2O$	Tol	90
12	*trans*-NiCl(Ph)(PPh$_3$)$_2$ (3)	[Iprbim]Br (3)	$K_3PO_4{\cdot}3H_2O$	Tol	86
13	*trans*-NiCl(Ph)(PPh$_3$)$_2$ (3)	[Mesmim]I (3)	$K_3PO_4{\cdot}3H_2O$	Tol	86
14	*trans*-NiCl(Ph)(PPh$_3$)$_2$ (1)	[Iprmim]I (1)	$K_3PO_4{\cdot}3H_2O$	Tol	85
15	*trans*-NiCl(Ph)(PPh$_3$)$_2$ (1)	[Iprmim]I (2)	$K_3PO_4{\cdot}3H_2O$	Tol	83
16	*trans*-NiCl(Ph)(PPh$_3$)$_2$ (3)	[Iprmim]I (3)	$K_3PO_4{\cdot}3H_2O$	Tol	94[c]
17	*trans*-NiCl(*o*-Tol)(PPh$_3$)$_2$ (3)	[Iprmim]I (3)	$K_3PO_4{\cdot}3H_2O$	Tol	91
18	*trans*-NiCl(1-Naph)(PPh$_3$)$_2$ (3)	[Iprmim]I (3)	$K_3PO_4{\cdot}3H_2O$	Tol	60
19	*trans*-NiCl(Ph)(PCy$_3$)$_2$ (3)	[Iprmim]I (3)	$K_3PO_4{\cdot}3H_2O$	Tol	84
20	*trans*-NiCl(*o*-Tol)(PCy$_3$)$_2$ (3)	[Iprmim]I (3)	$K_3PO_4{\cdot}3H_2O$	Tol	77
21	*trans*-NiCl(*o*-Tol)(dppf) (3)	[Iprmim]I (3)	$K_3PO_4{\cdot}3H_2O$	Tol	30
22	*trans*-NiCl(Ph)(PPh$_3$)$_2$ (3)	[Iprmim]I (3)	$K_3PO_4{\cdot}3H_2O$	Tol/25% H$_2$O	53
23	*trans*-NiCl(Ph)(PPh$_3$)$_2$ (3)	[Iprmim]I (3)	K_3PO_4	Tol	53
24	*trans*-NiCl(Ph)(PPh$_3$)$_2$ (3)	[Iprmim]I (3)	K_3PO_4 + H_2O	Tol	75
25	*trans*-NiCl(Ph)(PPh$_3$)$_2$ (3)	[Iprmim]I (3)	K_3PO_4 + $5H_2O$	Tol	95
26	*trans*-NiCl(Ph)(PPh$_3$)$_2$ (3)	[Iprmim]I (3)	K_3PO_4 + $10H_2O$	Tol	61
27	*trans*-NiCl(Ph)(PPh$_3$)$_2$ (3)	[Iprmim]I (3)	NaOH	Tol	47
28	*trans*-NiCl(Ph)(PPh$_3$)$_2$ (3)	[Iprmim]I (3)	KOH	Tol	43
29	*trans*-NiCl(Ph)(PPh$_3$)$_2$ (3)	[Iprmim]I (3)	KO^{t}Bu	Tol	Trace
30	*trans*-NiCl(Ph)(PPh$_3$)$_2$ (3)	[Iprmim]I (3)	K_2CO_3	Tol	35
31	*trans*-NiCl(Ph)(PPh$_3$)$_2$ (3)	[Iprmim]I (3)	$K_3PO_4{\cdot}3H_2O$	DMF	45
32	*trans*-NiCl(Ph)(PPh$_3$)$_2$ (3)	[Iprmim]I (3)	$K_3PO_4{\cdot}3H_2O$	Dioxane	74
33	*trans*-NiCl(Ph)(PPh$_3$)$_2$ (3)	[Iprmim]I (3)	$K_3PO_4{\cdot}3H_2O$	DMSO	20
34	*trans*-NiCl(Ph)(PPh$_3$)$_2$ (3)	[Iprmim]I (3)	$K_3PO_4{\cdot}3H_2O$	CH$_3$CN	13[d]

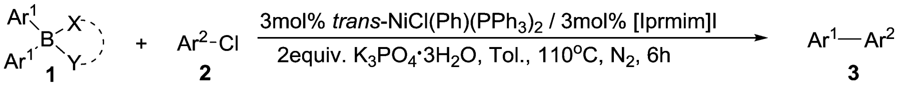
[a] Reaction conditions: **1a** (0.65 mmol), **2a** (1 mmol), base (2 mmol), solvent (5 mL), N$_2$, 12 h, reflux. [b] Isolated yields. [c] 6 h. [d] At reflux.

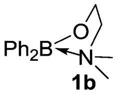
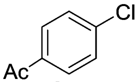
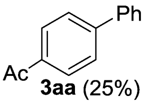
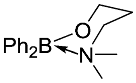
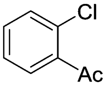
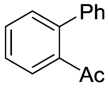
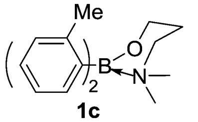
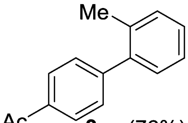
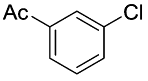
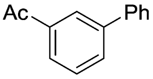
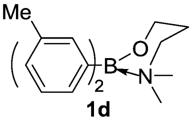
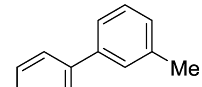
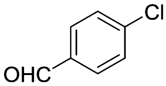
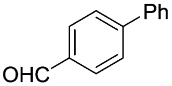
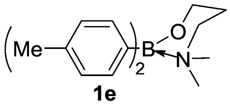
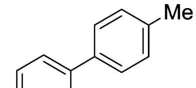
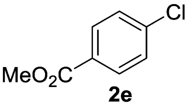
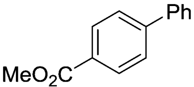
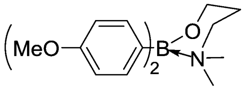
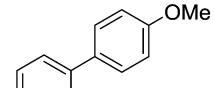
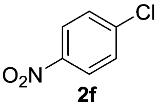
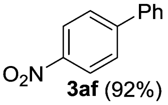
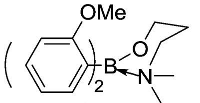
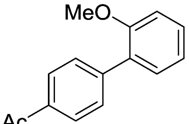
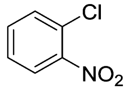
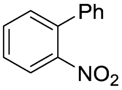
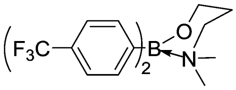
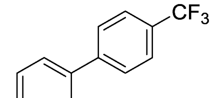
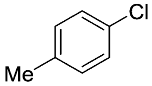
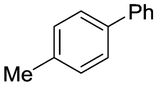
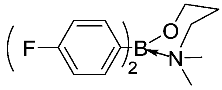
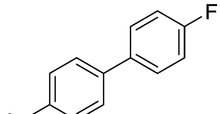
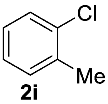
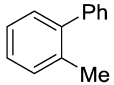
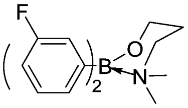
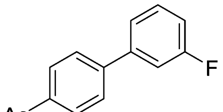
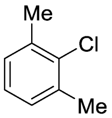
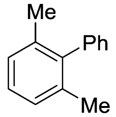
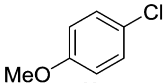
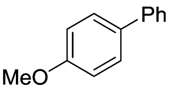
of **3aa** was increased to 81% (Table 1, entry 2). The *in situ* generated NHC ligand also proved to be necessary since the *trans*-NiCl(Ph)(PPh$_3$)$_2$ in the absence of [Bmim]Br gave only 49% yield (Table 1, entry 4). Screening of a variety of NHC precursors revealed an unusual steric effect of the NHC ligand on the catalysis efficiency, that is sterically unsymmetrical NHC appeared to match the precursor *trans*-NiCl(Ph)(PPh$_3$)$_2$ better.

For example, a remarkable increase in yields of **3aa** was observed from symmetrical NHC precursors, [diBim]Br, IPr·HCl, IMes·HCl and [diOim]Br (76–89%), to unsymmetrical analogs, [Omim]Br, [Ipreim]Br, [Iprbim]Br, [Mesmim]I and [Iprmim]I (86–97%), among which [Iprmim]I performed best to give an excellent yield (Table 1, entries 5–13). In fact, **3aa** could be obtained in 94% yield within half reaction time (6 h) albeit the yields deceased significantly to 83–85% with a lower (1 mol%) *trans*-NiCl(Ph)(PPh$_3$)$_2$ loading (Table 1, entries 14–16). The tests of structurally various analogs of *trans*-NiCl(Ph)(PPh$_3$)$_2$ with respect to aryl and phosphine ligands showed no improvement on the catalytic efficiency. For example, only *trans*-NiCl(*o*-Tol)(PPh$_3$)$_2$ gave a comparable yield (91%) (Table 1, entry 17) while naphthyl complex *trans*-NiCl(1-Naph)(PPh$_3$)$_2$, tricyclohexylphosphine complexes, *trans*-NiCl(Ph)(PCy$_3$)$_2$ and *trans*-NiCl(*o*-Tol)(PCy$_3$)$_2$ and 1,1′-bis(diphenylphosphino) ferrocene complex *trans*-NiCl(*o*-Tol)(dppf) gave significantly lower yields (Table 1, entries 18–21).

Use of anhydrous K_3PO_4 led to a remarkably lower yield (53%) than that with trihydrate one ($K_3PO_4 \cdot 3H_2O$), in consistent with the observed positive effects of small amount of water on nickel catalysis in literaure,[12a,23] although large amount of water was deleterious (Table 1, entries 22, 24 and 26). Base and solvent screening failed to improve the reaction compared

Table 2 Scope of the Ni-catalyzed cross-coupling of *O*,*N*-chelated diarylborinates with aryl chlorides[a]



Entry	Borinate (**1**)	Chloride (**2**)	Biaryl (**3**)	Entry	Borinate (**1**)	Chloride (**2**)	Biaryl (**3**)
1	 **1b**	 **2a**	 **3aa** (25%)	10	 **1a**	 **2b**	 **3ab** (85%)
2	 **1c**	**2a**	 **3ca** (76%)	11	**1a**	 **2c**	 **3ac** (90%)
3	 **1d**	**2a**	 **3da** (92%)	12	**1a**	 **2d**	 **3ad** (92%)
4	 **1e**	**2a**	 **3ea** (91%)	13	**1a**	 **2e**	 **3ae** (93%)
5	 **1f**	**2a**	 **3fa** (90%)	14	**1a**	 **2f**	 **3af** (92%)
6	 **1g**	**2a**	 **3ga** (74%)	15	**1a**	 **2g**	 **3ag** (77%)
7	 **1h**	**2a**	 **3ha** (68%)	16	**1a**	 **2h**	 **3ah** (84%, 95%[b])
8	 **1i**	**2a**	 **3ia** (94%)	17	**1a**	 **2i**	 **3ai** (71%, 80%[b])
9	 **1j**	**2a**	 **3ja** (91%)	18	**1a**	 **2j**	 **3aj** (15%, 40%[b])
				19	**1a**	 **2k**	 **3ak** (82%, 93%[b])

[a] Reaction conditions: **1** (0.65 mmol), **2** (1 mmol), 3 mol% *trans*-$NiCl(Ph)(PPh_3)_2$/3 mol% [Iprmim]I, $K_3PO_4 \cdot 3H_2O$ (2 mmol), toluene (5 mL), N_2, 6 h, reflux. [b] 5 mol% *trans*-$NiCl(Ph)(PPh_3)_2$/5 mol% [Iprmim]I, 12 h.

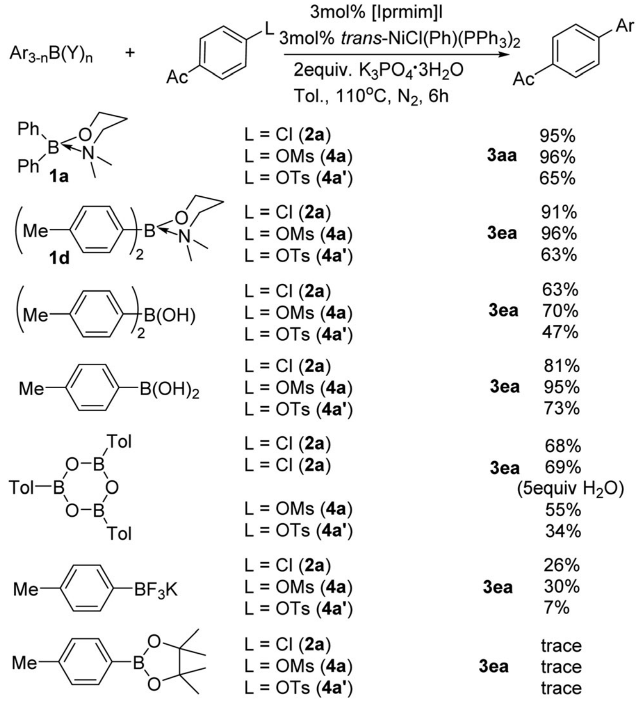
with the $K_3PO_4 \cdot 3H_2O$ in toluene system (Table 1, entries 27–34). For example, use of NaOH or KOH led to much lower yields while the system deactivated totally with KO^tBu (Table 1, entries 27–29). Low to modest yields were obtained in the common solvents, *e.g.* DMF, dioxane, DMSO and CH_3CN (Table 1, entries 31–34). Therefore, the optimal condition was set as 3 mol% *trans*-NiCl(Ph)$(PPh_3)_2$/[Iprmim]I in toluene using $K_3PO_4 \cdot 3H_2O$ as base.

Scope and limitations of the nickel-catalyzed cross-coupling of *O*,*N*-chelate stabilized diarylborinates with aryl chlorides were briefly explored (Table 2). A low yield (25%) was obtained with dimethylaminoethyl diarylborinate (**1b**) confirming the privilege of the six-membered *O*,*N*-chelated boron ring with 3-dimethyl aminopropanol for the reactivity of *O*,*N*-chelated diarylborinates. Electron-donating 3-Me (**1d**, 92%), 4-Me (**1e**, 91%), 4-MeO (**1f**, 90%), or withdrawing 4-F (**1i**, 94%), 3-F (**1j**, 91%), except for 4-CF_3 (**1h**, 68%), groups at the phenyl ring of diarylborinates appeared not to significantly affect their reactivity in cross-coupling with **2a** while an *ortho*-group, *e.g.* 2-Me (**1c**, 76%) or 2-OMe (**1g**, 74%), decreased the yields of biaryls remarkably (Table 2, entries 2–9). In contrast, both electronic and steric factors of aryl chlorides affected their cross-coupling with diarylborinates. For example, 4-chlorobenzaldehyde (**2d**, 92%), methyl 4-chlorobenzoate (**2e**, 93%), 3-chloroactetophenone (**2c**, 90%) and 4-chloronitrobenzene (**2f**, 92%) reacted similarly to **2a**, while 2-chloroactetophenone (**2b**) and 2-chloronitrobenzene (**2g**) gave the corresponding products in comparable lower yields (85%) and (77%), respectively (Table 2, entries 10–15). An electron-donating group, *e.g.* 4-Me (**2h**, 84%) and 4-OMe (**2k**, 82%), significantly decreased the reactivity of aryl chorides, in particular, at *ortho*-position of the aryl ring, *e.g.* 2-Me (**2i**, 71%), therefore higher loading (5 mol%) of the catalyst and longer reaction time were required to obtain satisfactory yields (Table 2, entries 16, 17 and 19). However, reaction of sterically demanding 2,6-dimethyl phenyl chloride (**2j**) with **1a** still gave a low yield (40%) even with 5mol% catalyst loading (Table 2, entry 18).

Coupling with aryl mesylates

Although aryl halides have been recognized as the standard electrophile counterpart in Suzuki coupling for construction of biaryl structure, the required halides are sometimes difficult, even extremely challenging, to access. Therefore, many efforts have been made to use readily accessible phenol derivatives, in particular sulfonates,[24] *i.e.* triflates, tosylates and mesylates. Among these sulfonates, tosylates have been most intensively used since they possess low cost, fair stability and good reactivity. Comparably, the closely related mesylates were hampered by the poorer leaving ability of the mesylate group. However, mesylates have better environmentally friendly profile than tosylates, *e.g.* higher atom economy and natural biodegradation of by-product.[25] Having established the nickel-based catalyst system for cross-coupling of O,N-chelated diarylborinates with aryl chlorides, we further investigated its performance in the corresponding coupling with aryl mesylates (Scheme 1).

Surprisingly, 4-acetylphenyl mesylate (**4a**) displayed significantly higher reactivity than its tosylate (**4a′**) in the *trans*-NiCl(Ph)$(PPh_3)_2$/[Iprmim]I catalyzed cross-coupling with **1a**, possibly due to the steric factor given the fact that the latter is generally more electronically active than the former. Control experiments with 3-dimethylaminopropyl di(*p*-tolyl)borinate (**1d**) and the corresponding free borinic acids, di(*p*-tolyl)borinic acid, which is dehydration-resisting, thus more accurate in stoichiometry than its phenyl analog ($Ph_2B(OH)$), as well as *p*-tolyl boronic acid, anhydride (boroxine) and trifluoroborate carried under otherwise identical conditions confirmed the privilege of aryl mesylates as electrophiles, irrespective of nucleophile counterparts although the reacivities of the latter two boron reagents appeared to be significantly lower. No reaction was observed with pinacol *p*-tolylboronate in all cases.



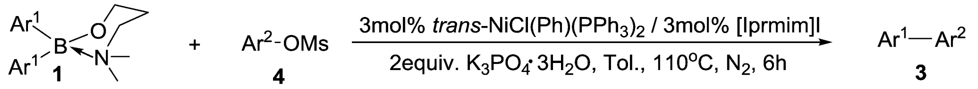
Scheme 1 Reactivities of aryl chlorides and sulfonates in the nickel-catalyzed cross-coupling with arylborons.

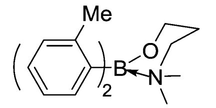
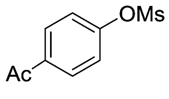
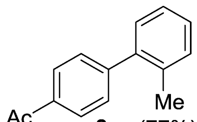
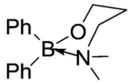
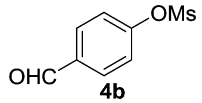
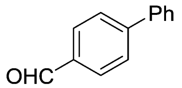
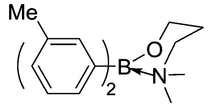
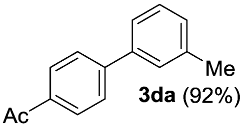
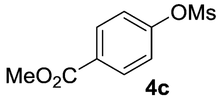
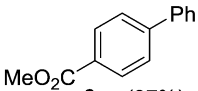
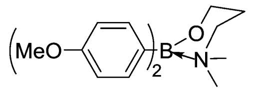
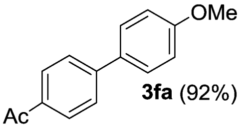
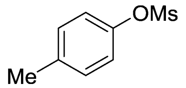
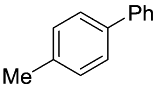
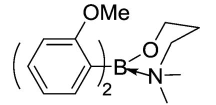
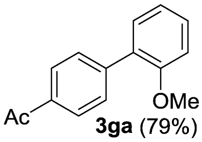
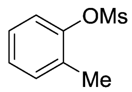
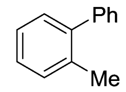
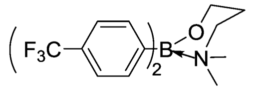
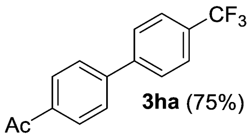
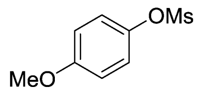
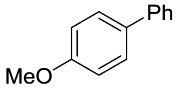
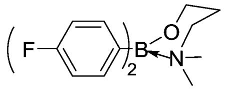
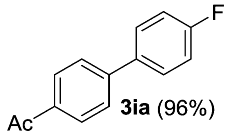
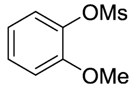
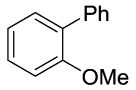
Investigation on the scope of the cross-coupling of *O*,*N*-chelated diarylborinates with aryl mesylates revealed that the electronic and steric influences from both nucleophile and electrophile counterparts are similar to those observed in the reaction of aryl chlorides (Table 3). For example, diarylborinates bearing 3-Me (**1d**, 92%), 4-MeO (**1f**, 92%) or 4-F (**1i**, 96%) group at phenyl rings coupled with **4a** giving the diaryls **3ca-3ia** in excellent yields, while the 2-Me (**1c**, 77%) or 2-OMe (**1g**, 79%) substituent decreased the biaryl yields (Table 3, entries 1–6). Electronically deficient aryl mesylates with 4-CHO (**4b**, 91%) or 4-CO_2Me (**4c**, 97%) group gave higher yields than those of electron-rich ones **4f** (4-OMe, 84%) and **4d** (4-Me, 87%) (Table 3, entries 7–9 and 11). Similar to chlorides, an *ortho*-substituent also decreased the reactivity of aryl mesylates.

Mechanistic discussion

Although the general M^0/M^{2+} cycle has been widely accepted for both nickel- and palladium-catalyzed Suzuki coupling the

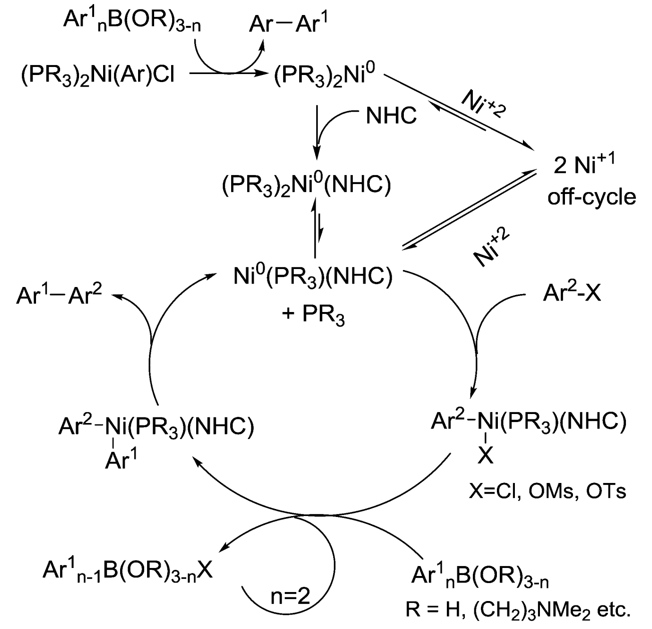
Table 3 Scope of the Ni-catalyzed cross-coupling of *O,N*-chelated diarylborinates with aryl mesylates[a]



Entry	Borinate (1)	Mesylate (4)	Biaryl (3)	Entry	Borinate (1)	Mesylate (4)	Biaryl (3)
1	 **1c**	 **4a**	 **3ca** (77%)	7	 **1a**	 **4b**	 **3ad** (91%)
2	 **1d**	4a	 **3da** (92%)	8	1a	 **4c**	 **3ae** (97%)
3	 **1f**	4a	 **3fa** (92%)	9	1a	 **4d**	 **3ah** (87%, 96%[b])
4	 **1g**	4a	 **3ga** (79%)	10	1a	 **4e**	 **3ai** (75%, 82%[b])
5	 **1h**	4a	 **3ha** (75%)	11	1a	 **4f**	 **3ak** (84%, 94%[b])
6	 **1i**	4a	 **3ia** (96%)	12	1a	 **4g**	 **3al** (71%, 80%[b])

[a] Reaction conditions: **1** (0.65 mmol), **4** (1 mmol), 3 mol% *trans*-NiCl(Ph)$(PPh_3)_2$/3 mol% [Iprmim]I, $K_3PO_4 \cdot 3H_2O$ (2 mmol), toluene (5 mL), N_2, 6 h, reflux. [b] 5 mol% *trans*-NiCl(Ph)$(PPh_3)_2$/5 mol% [Iprmim]I, 12 h.

mechanism with nickel catalysts is much more complicated than that of palladium ones because of the redox diversity of nickel. Therefore, only a tentative explanation is given based on the Ni^0/Ni^{2+} cycle (Scheme 2). The $ArNiCl(PR_3)_2$ precatalysts are reduced to Ni(0) species by transmetalation with aryl boron species followed by reductive elimination, which depends on not only the $ArNiCl(PR_3)_2$ structure, *i.e.* Ar and PR_3, but also the reaction conditions as well as activity of the arylboron species. The inactivity of pinacol borate in the reaction could be reasonably attributed to the failure of precatalyst activation due to its low activity in transmetalation. The delicate balance between availability, stability and activity of the catalytically active Ni(0) species determines the efficiency of the catalyst system. Presence of the *in situ* generated sterically unsymmetrical NHC ligand helps to prevent the active Ni(0) species from deactivation *via* comproportionation with Ni(II) species yet reserves their reactivity, therefore performing best. The two-coordinate nickel(0) complex co-supported by phosphine and NHC, $Ni^0(PR_3)(NHC)$, generated *via* PR_3/NHC ligand exchange should be the most active Ni(0) species since both NHC



Scheme 2 A plausible mechanistic explanation.

and PPh_3 have proven to be necessary to achieve the optimal catalyst system.

The key role played by the NHC/PR_3 co-supported Ni(0) species in the catalytic cycle is also consistent with the observation of the decreased catalytic efficiency using nickel precursors $ArNiCl(PR_3)_2$ with electron-rich PCy_3 or chelating diphosphine dppf ligand since their exchange with NHC should be slower than that of PPh_3, in particular in the case of dppf. The observed differences in reactivities of mesylates vs tosylates as well as various arylboron derivatives, *i.e.* 3-dimethylaminopropyl diarylborinates, diarylborinic acids, arylboronic acid and derivatives, *e.g.* boroxine(anhydride), pinacol borate and trifluoroboronate, in control experiments implies that both oxidative addition of aryl sulfonates to the $Ni^0(PR_3)(NHC)$ and the following aryl transmetalation from boron should be involved in rate-determining steps in the catalytic cycle.

Conclusions

In summary, a triphenylphosphine and NHC co-supported organonickel-based catalyst system, *trans*-$NiCl(Ph)(PPh_3)_2$/[Iprmim]I/$K_3PO_4{\cdot}3H_2O$ in toluene, has been developed for cross-coupling of shelf-stable *O*,*N*-chelate stabilized 3-dimethylaminopropyl diarylborinates with aryl chlorides and mesylates. A small amount of water appeared to play an important role in the catalysis, which could be readily introduced by use of trihydrate potassium phosphate. Sterically unsymmetrical NHCs appeared to match the organonickel precursor better than the symmetrical ones. The nickel-based catalyst system showed remarkably higher activity to the environmentally friendly aryl mesylates than the corresponding tosylates in cross-coupling with diarylborinates, which was unmistakably confirmed in control experiments of diarylborinic acids and the traditional arylboronic acid derivatives. A variety of electronically various biaryls could be obtained in excellent yields by using 3–5 mol% loading of the nickel catalyst while a significant steric effect was observed from both diarylborinates and aryl chlorides and mesylates.

Experimental

General information

All reactions were carried out under nitrogen by using standard Schlenk techniques unless otherwise stated. Commercially available chemicals were used as received. $NiCl(Ph)(PPh_3)_2$,[26] $NiCl(Ph)(PCy_3)_2$,[27] NiCl(1-Nath)(PPh_3)2,[18c] $NiCl_2(PPh_3)_2$,[19b] NiCl(*o*-Tol)(PPh_3)$_2$,[19b] NiCl(*o*-Tol)(PCy_3)$_2$,[19b] NiCl(*o*-Tol)(dppf),[19b] **1a-1j**,[1f] **4a-4g**,[28] **4a′**,[28] N-heterocyclic carbene precursors of [Bmim]Br,[29] [Omim]Br,[29] [diOim]Br,[29] [diBim]Br,[29] IMes·HCl,[30] IPr·HCl,[30] [Iprmim]I,[31] [Ipreim]Br,[31] [Iprbim]Br,[32] [Mesmim]I[33] were prepared according to previously reported procedures. Column chromatograph was performed on 300–400 mesh silica gel. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ or DMSO-d_6 at ambient temperature. Chemical shifts in NMR are reported in ppm (δ), relative to the internal standard of tetramethylsilane (TMS) or residues of the deuterated solvents.

Typical procedure for cross-coupling

Under a N_2 atmosphere, to a 10 ml dry flask were added aryl chloride/mesylates (1 mmol), diarylborinates (0.65 mmol), *trans*-$NiCl(Ph)(PPh_3)_2$ (3 mol%), [Iprmim]I (3 mol%), $K_3PO_4{\cdot}3H_2O$ (2 mmol), and toluene (5 ml). The mixture was stirred at 110 °C for a given time or monitored by TLC until the starting material was completely consumed. The reaction mixture was diluted with CH_2Cl_2 (15 ml), followed by washing with H_2O (3 × 10 ml). The organic layer was dried over anhydrous Na_2SO_4, filtered, and evaporated under reduced pressure to give crude product, which was purified by column chromatography on silica gel to afford biaryl compound (see ESI† for details).

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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References

1 (*a*) E. Dimitrijević and M. S. Taylor, *ACS Catal.*, 2013, **3**, 945–962; (*b*) M. S. Taylor, *Acc. Chem. Res.*, 2015, **48**, 295–305; (*c*) K. A. D'Angelo and M. S. Taylor, *J. Am. Chem. Soc.*, 2016, **138**, 11058–11066; (*d*) K. A. D'Angelo and M. S. Taylor, *Chem. Commun.*, 2017, **53**, 5978–5980; (*e*) T. M. El Dine, D. Evans, J. Rouden and J. Blanchet, *Chem. – Eur. J.*, 2016, **22**, 5894–5898; (*f*) A. Chardon, T. M. El Dine, R. Legay, M. De Paolis, J. Rouden and J. Blanchet, *Chem. – Eur. J.*, 2017, **23**, 2005–2009.

2 For recent reviews: (*a*) Y.-L. Rao and S. Wang, *Inorg. Chem.*, 2011, **50**, 12263–12274; (*b*) D. Li, H. Zhang and Y. Wang, *Chem. Soc. Rev.*, 2013, **42**, 8416–8433; (*c*) A. Wakamya and S. Yamaguch, *Bull. Chem. Soc. Jpn.*, 2015, **88**, 1357–1377; (*d*) K. Tanaka and Y. Chujo, *NPG Asia Mater.*, 2015, **7**, e223For recent examples and references therein see: (*e*) Y. Qi, R. Kang, J. Huang, W. Zhang, G. He, S. Yin and Y. Fang, *J. Phys. Chem. B*, 2017, **121**, 6189–6199; (*f*) Z. Zhang, Z. Zhang, H. Zhang and Y. Wang, *Dalton Trans.*, 2018, **47**, 127–134.

3 (*a*) S. J. Baker, T. Akama, Y.-K. Zhang, V. Sauro, C. Pandit, R. Singh, M. Kully, J. Khan, J. J. Plattner, S. J. Benkovic, V. Lee and K. R. Maples, *Bioorg. Med. Chem. Lett.*, 2006, **16**, 5963–5967; (*b*) C. K. Colton and M. Zhu, *Handb. Exp Pharmacol.*, 2007, **179**, 173–187; (*c*) S. Ozaki, A. Z. Suzuki, P. O. Bauer, E. Ebisui and K. Mikoshiba, *Biochem. Biophys. Res. Commun.*, 2013, **441**, 286–290; (*d*) A. Hofer, G. Kovacs, A. Zappatini, M. Leuenberger, M. A. Hediger and M. Lochner, *Bioorg. Med. Chem.*, 2013, **21**, 3202–3213; (*e*) K. Song, H. Wang, G. B. Kamm, J. Pohle, F. C. Reis, P. Heppenstall, H. Wende and J. Siemens, *Science*, 2016, **353**, 1393–1398; (*f*) A. G. Baldwin, J. Rivers-Auty,

M. J. D. Daniels, C. S. White, C. H. Schwalbe, T. Schilling, H. Hammadi, P. Jaiyong, N. G. Spencer, H. England, N. M. Luheshi, M. Kadirvel, C. B. Lawrence, N. J. Rothwell, M. K. Harte, R. A. Bryce, S. M. Allan, C. Eder, S. Freeman and D. Brough, *Cell Chem. Biol.*, 2017, **24**, 1321–1335; (*g*) F. J. P. Kühn, W. Mathis, K. Cornelia, D. C. Hoffmann and A. Luckhoff, *Sci. Rep.*, 2017, **7**, 7245; (*h*) A. G. Baldwin, V. S. Tapia, T. Swanton, C. S. White, J. A. Beswick, D. Brough and S. Freeman, *ChemMedChem*, 2018, **13**, 312–320; (*i*) E. Redondo-Castro, D. Faust, S. Fox, A. G. Baldwin, S. Osborne, M. J. Haley, E. Karran, H. Nuthall, P. J. Atkinson, L. A. Dawson, C. Routledge, S. M. Allan, S. Freeman, J. Brownlees and D. Brough, *Sci. Rep.*, 2018, **8**, 5667.

4 (*a*) X. Chen, H. Ke, Y. Chen, C. Guan and G. Zou, *J. Org. Chem.*, 2012, **77**, 7572–7578; (*b*) H. Ke, X. Chen and G. Zou, *J. Org. Chem.*, 2014, **79**, 7132–7140; (*c*) H. Ke, X. Chen, Y. Feng and G. Zou, *Sci. China: Chem.*, 2014, **57**, 1126–1131; (*d*) X. Chen, H. Ke and G. Zou, *ACS Catal.*, 2014, **4**, 379–385; (*e*) N. Zhang, C. Wang, G. Zou and J. Tang, *J. Organomet. Chem.*, 2017, **842**, 54–58; (*f*) C. Wang, J. Zhang, J. Tang and G. Zou, *Adv. Synth. Catal.*, 2017, **359**, 2514–2519.

5 N. Farfán, D. Castillo, P. Joseph-Nathan, R. Contreras and L. V. Szentpály, *J. Chem. Soc., Perkin Trans. 2*, 1992, 527–532.

6 For recent reviews see: (*a*) F.-S. Han, *Chem. Soc. Rev.*, 2013, **42**, 5270–5298; (*b*) J. Yamaguchi, K. Muto and K. Itami, *Eur. J. Org. Chem.*, 2013, 19–30; (*c*) S. Z. Tasker, E. A. Standley and T. F. Jamison, *Nature*, 2014, **509**, 299–309; (*d*) A. P. Prakasham and P. Ghosh, *Inorg. Chim. Acta*, 2015, **431**, 61–100; (*e*) E. A. Standley, S. Z. Tasker, K. L. Jensen and T. F. Jamison, *Acc. Chem. Res.*, 2015, **48**, 1503–1514; For a most recent example, (*f*) P.-A. Payard, L. A. Perego, I. Ciofini and L. Grimaud, *ACS Catal.*, 2018, **8**, 4812–4823 references therein.

7 (*a*) V. Percec, J.-Y. Bae and D. H. Hill, *J. Org. Chem.*, 1995, **60**, 1060–1065; (*b*) D. Zim, V. R. Lando, J. Dupont and A. L. Monteiro, *Org. Lett.*, 2001, **3**, 3049–3051; (*c*) Z.-Y. Tang and Q.-S. Hu, *J. Am. Chem. Soc.*, 2004, **126**, 3058–3059; (*d*) T. A. Butler, E. C. Swift and B. H. Lipshutz, *Org. Biomol. Chem.*, 2008, **6**, 19–25; (*e*) C.-H. Xing, J.-R. Lee, Z.-Y. Tang, J. Zheng and Q.-S. Hu, *Adv. Synth. Catal.*, 2011, **353**, 2051–2059.

8 (*a*) D. Yu, M. Yu, B. Guan, B. Li, Y. Zheng, Z. Wu and Z. Shi, *Org. Lett.*, 2009, **11**, 3374–3377; (*b*) M. G. Hanson, N. M. Olson, Z. Yi, G. Wilson and D. Kalyani, *Org. Lett.*, 2017, **19**, 4271–4274.

9 (*a*) S. B. Blakey and D. W. C. MacMillan, *J. Am. Chem. Soc.*, 2003, **125**, 6046–6047; (*b*) P. Maity, D. M. Shacklady-McAtee, G. P. A. Yap, E. R. Sirianni and M. P. Watson, *J. Am. Chem. Soc.*, 2013, **135**, 280–285.

10 (*a*) D. Yu, B. Li and Z. Shi, *Acc. Chem. Res.*, 2010, **43**, 1486–1495; (*b*) K. W. Quasdorf, A. Antoft-Finch, P. Liu, A. L. Silberstein, A. Komaromi, T. Blackburn, S. D. Ramgren, K. N. Houk, V. Snieckus and N. K. Garg, *J. Am. Chem. Soc.*, 2011, **133**, 6352–6363; (*c*) A. G. Sergeev, J. D. Webb and J. F. Hartwig, *J. Am. Chem. Soc.*, 2012, **134**, 20226–20229; (*d*) J. Li and Z. Wang, *Chem. Commun.*, 2018, **54**, 2138–2141.

11 (*a*) K. Amaike, K. Muto, J. Yamaguchi and K. Itami, *J. Am. Chem. Soc.*, 2012, **134**, 13573–13576; (*b*) S.-Q. Zhang, B. L. H. Taylor, C.-L. Ji, Y. Gao, M. R. Harris, L. E. Hanna, E. R. Jarvo, K. N. Houk and X. Hong, *J. Am. Chem. Soc.*, 2017, **139**, 12994–13005; (*c*) P. Lei, G. Meng, S. Shi, Y. Ling, J. An, R. Szostak and M. Szostak, *Chem. Sci.*, 2017, **8**, 6525–6530; (*d*) R. Takise, K. Muto and J. Yamaguchi, *Chem. Soc. Rev.*, 2017, **46**, 5864–5888; (*e*) Y. Li, K. Wang, Y. Ping, Y. Wang and W. Kong, *Org. Lett.*, 2018, **20**, 921–924; (*f*) A. H. Dardir, P. R. Melvin, R. M. Davis, N. Hazari and M. M. Beromi, *J. Org. Chem.*, 2018, **83**, 469–477.

12 (*a*) N. A. Weires, E. L. Baker and N. K. Garg, *Nat. Chem.*, 2016, **8**, 75–79; (*b*) Y. Gao, C.-L. Ji and X. Hong, *Sci. China: Chem.*, 2017, **60**, 1413–1424; (*c*) J. E. Dander and N. K. Garg, *ACS Catal.*, 2017, **7**, 1413–1423; (*d*) A. Chatupheeraphat, H.-H. Liao, W. Srimontree, L. Guo, Y. Minenkov, A. Poater, L. Cavallo and M. Rueping, *J. Am. Chem. Soc.*, 2018, **140**, 3724–3735; (*e*) T. B. Boit, N. A. Weires, J. Kim and N. K. Garg, *ACS Catal.*, 2018, **8**, 1003–1008.

13 (*a*) T. Schaub, M. Backes and U. Radius, *J. Am. Chem. Soc.*, 2006, **128**, 15964–15965; (*b*) M. Tobisu, T. Xu, T. Shimasaki and N. Chatani, *J. Am. Chem. Soc.*, 2011, **133**, 19505–19511.

14 (*a*) K. W. Quasdorf, M. Riener, K. V. Petrova and N. K. Garg, *J. Am. Chem. Soc.*, 2009, **131**, 17748–17749; (*b*) M. M. Beromi, A. Nova, D. Balcells, A. M. Brasacchio, G. W. Brudvig, L. M. Guard, N. Hazari and D. J. Vinyard, *J. Am. Chem. Soc.*, 2017, **139**, 922–936.

15 (*a*) A. Antoft-Finch, T. Blackburn and V. Snieckus, *J. Am. Chem. Soc.*, 2009, **131**, 17750–17752; (*b*) A. Ohtsuki, K. Yanagisawa, T. Furukawa, M. Tobisu and N. Chatani, *J. Org. Chem.*, 2016, **81**, 9409–9414; (*c*) Q. Chen, A. Wu, S. Qin, M. Zeng, Z. Le, Z. Yan and H. Zhang, *Adv. Synth. Catal.*, 2018, **360**, 3239–3244.

16 A paraffin-capsule strategy has been recently developed for handling air sensitive catalysts by Buchwald and Garg groups. (*a*) A. C. Sather, H. G. Lee, J. R. Colombe, A. Zhang and S. L. Buchwald, *Nature*, 2015, **524**, 208–211; (*b*) J. E. Dander, N. A. Weires and N. K. Garg, *Org. Lett.*, 2016, **18**, 3934–3936.

17 (*a*) C. Chen and L.-M. Yang, *J. Org. Chem.*, 2007, **72**, 6324–6327; (*b*) C.-Y. Gao and L.-M. Yang, *J. Org. Chem.*, 2008, **73**, 1624–1627; (*c*) X.-H. Fan and L.-M. Yang, *Eur. J. Org. Chem.*, 2010, 2457–2460; (*d*) J.-H. Huang and L.-M. Yang, *Org. Lett.*, 2011, **13**, 3750–3753; (*e*) X.-H. Fan and L.-M. Yang, *Eur. J. Org. Chem.*, 2011, 1467–1471; (*f*) X.-H. Fan, G. Li and L.-M. Yang, *J. Organomet. Chem.*, 2011, **696**, 2482–2484; (*g*) Q. Chen, X.-H. Fan, L.-P. Zhang and L.-M. Yang, *RSC Adv.*, 2014, **4**, 53885–53890; (*h*) Q. Chen, X.-H. Fan, L.-P. Zhang and L.-M. Yang, *RSC Adv.*, 2015, **5**, 15338–15340.

18 (*a*) P. Leowanawat, N. Zhang, M. Safi, D. J. Hoffman, M. C. Fryberger, A. George and V. Percec, *J. Org. Chem.*, 2012, **77**, 2885–2892; (*b*) N. Zhang, D. J. Hoffman, N. Gutsche, J. Gupta and V. Percec, *J. Org. Chem.*, 2012,

77, 5956–5964; (*c*) R. L. Jezorek, N. Zhang, P. Leowanawat, M. H. Bunner, N. Gutsche, A. K. R. Pesti, J. T. Olsen and V. Percec, *Org. Lett.*, 2014, **16**, 6326–6329; (*d*) J. Malineni, R. L. Jezorek, N. Zhang and V. Percec, *Synthesis*, 2016, 2795–2807; (*e*) J. Malineni, R. L. Jezorek, N. Zhang and V. Percec, *Synthesis*, 2016, 2808–2815.

19 (*a*) E. A. Standley and T. F. Jamison, *J. Am. Chem. Soc.*, 2013, **135**, 1585–1592; (*b*) E. A. Standley, S. J. Smith, P. Muller and T. F. Jamison, *Organometallics*, 2014, **33**, 2012–2018; (*c*) S. Z. Tasker, A. C. Gutierrez and T. F. Jamison, *Angew. Chem., Int. Ed.*, 2014, **53**, 1858–1861; (*d*) J. M. Weber, A. R. Longstreet and T. F. Jamison, *Organometallics*, 2018, **37**, 2716–2722; (*e*) F. Strieth-Kalthoff, A. R. Longstreet, J. M. Weber and T. F. Jamison, *ChemCatChem*, 2018, **10**, 2873–2877; (*f*) H. Li, C. P. Breen, H. Seo, T. F. Jamison, Y.-Q. Fang and M. M. Bio, *Org. Lett.*, 2018, **20**, 1338–1341.

20 (*a*) S. Ge and J. F. Hartwig, *J. Am. Chem. Soc.*, 2011, **133**, 16330–16333; (*b*) S. Ge and J. F. Hartwig, *Angew. Chem., Int. Ed.*, 2012, **51**, 12837–12841; (*c*) R. A. Green and J. F. Hartwig, *Angew. Chem., Int. Ed.*, 2015, **54**, 3768–3772.

21 (*a*) N. H. Park, G. Teverovskiy and S. L. Buchwald, *Org. Lett.*, 2014, **16**, 220–223; (*b*) E. B. Corcoran, M. T. Pirnot, S. S. Lin, S. D. Dreher, D. A. DiRocco, I. W. Davies, S. L. Buchwald and D. W. C. MacMillan, *Science*, 2016, **353**, 279–283.

22 (*a*) X. Lei, K. A. Obregon and J. Alla, *Appl. Organometal. Chem.*, 2013, **27**, 419–424; (*b*) L. M. Guard, M. M. Beromi, G. W. Brudvig, N. Hazari and D. J. Vinyard, *Angew. Chem., Int. Ed.*, 2015, **54**, 13352–13356; (*c*) J. Magano and S. Monfette, *ACS Catal.*, 2015, **5**, 3120–3123; (*d*) J. D. Shields, E. E. Gray and A. G. Doyle, *Org. Lett.*, 2015, **17**, 2166–2169; (*e*) M. Mastalir, B. Stoeger, E. Pittenauer, G. Allmaier and K. Kirchner, *Org. Lett.*, 2016, **18**, 3186–3189; (*f*) M. Mastalir, E. Pittenauer, B. Stoeger, G. Allmaier and K. Kirchner, *Org. Lett.*, 2017, **19**, 2178–2181; (*g*) J. A. Kessler and V. M. Iluc, *Dalton Trans.*, 2017, **46**, 12125–12131; (*h*) P. M. MacQueen and M. Stradiotto, *Synlett*, 2017, 1652–1656; (*i*) S. Ando, H. Matsunaga and T. Ishizuka, *J. Org. Chem.*, 2017, **82**, 1266–1272; (*j*) R. S. Sawatzky and M. Stradiotto, *Synlett*, 2018, 799–804.

23 G. Li, S. Shi, P. Lei and M. Szostak, *Adv. Synth. Catal.*, 2018, **360**, 1538–1543.

24 For recent reviews: (*a*) D.-G. Yu, B.-J. Li and Z.-J. Shi, *Acc. Chem. Res.*, 2010, **43**, 1486–1495; (*b*) C. M. So and F. Y. Kwong, *Chem. Soc. Rev.*, 2011, **40**, 4963–4972; (*c*) B. M. Rosen, K. W. Quasdorf, D. A. Wilson, N. Zhang, A.-M. Resmerita, N. K. Garg and V. Percec, *Chem. Rev.*, 2011, **111**, 1346–1416; (*d*) T. Mesganaw and N. K. Garg, *Org. Process Res. Dev.*, 2013, **17**, 29–39; (*e*) M. Tobisu and N. Chatani, *Top. Curr. Chem.*, 2016, **374**, 41.

25 (*a*) S. C. Baker, D. P. Kelly and J. C. Murrell, *Nature*, 1991, **350**, 627–628; (*b*) T. P. Higgins, M. Davey, J. Trickett, D. P. Kelly and J. C. Murrell, *Microbiology*, 1996, **142**, 251–260; (*c*) C. E. Spiese, J. L. Sanford, M. N. Bowling, E. A. Tatarkov and A. L. Pinkney, *Aquat. Microb. Ecol.*, 2017, **78**, 177–185.

26 A. Zeller, E. Herdtweck and T. Strassner, *Eur. J. Inorg. Chem.*, 2003, 1802–1806.

27 A. Morvillo and A. Turco, *J. Organomet. Chem.*, 1981, **208**, 103–113.

28 X. Lei, A. Jalla, M. A. A. Shama, J. M. Stafford and B. Cao, *Synthesis*, 2015, 2578–2585.

29 Y. Chu, H. Deng and J. Cheng, *J. Org. Chem.*, 2007, **72**, 7790–7793.

30 M. S. Viciu, R. F. Germaneau, O. Navarro-Fernandez, E. D. Stevens and S. P. Nolan, *Organometallics*, 2002, **21**, 5470–5472.

31 A. Flahaut, S. Roland and P. Mangeney, *J. Organomet. Chem.*, 2007, **692**, 5754–5762.

32 S. Chessa, N. J. Clayden, M. Bochmann and J. A. Wright, *Chem. Commun.*, 2009, 797–799.

33 H. Su, L. M. Perez, S. Lee, J. H. Reibenspies, H. S. Bazzi and D. E. Bergbreiter, *Organometallics*, 2012, **31**, 4063–4071.