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Palladium-Catalysed Amination of Aryl- and Heteroaryl Halides Using *tert*-Butyl Tetraisopropylphosphorodiamidite as an Easily Accessible and Air-Stable Ligand

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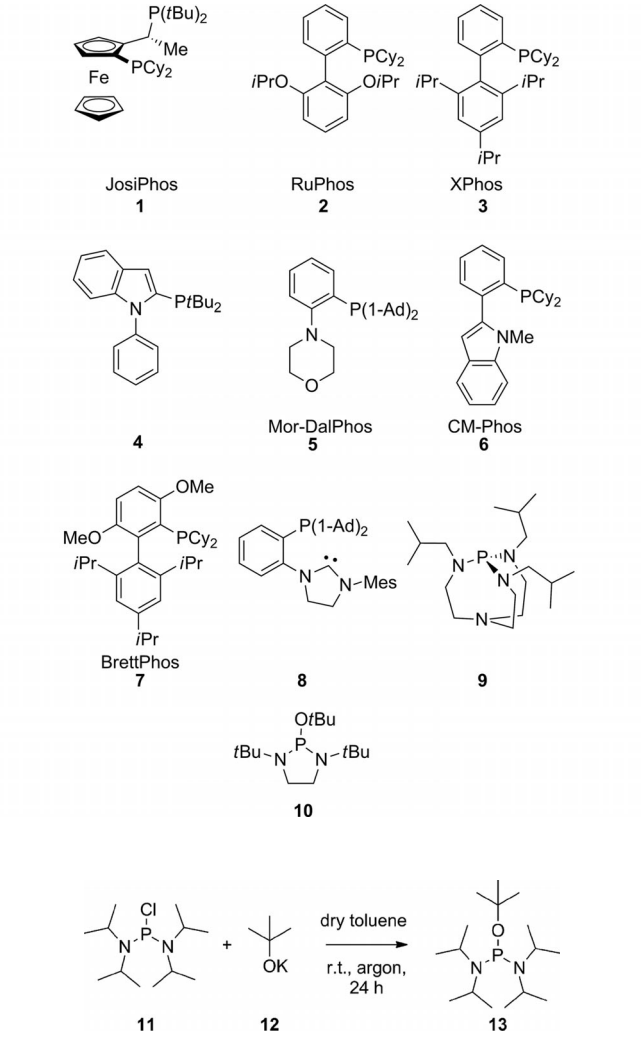
The phosphorus compound *tert*-butyl tetraisopropylphosphorodiamidite, prepared from bis(diisopropylamino)chlorophosphine, is an excellent ligand for palladium-catalysed Buchwald–Hartwig amination of aryl- and heteroaryl chlorides and bromides. Based on its ready accessibility and air-stability, this amination protocol is a practical approach to the synthesis of industrially important aryl- and heteroarylamines.

Introduction

The Pd-catalysed Buchwald–Hartwig amination of aryl and heteroaryl halides is a prominent transformation in modern synthetic chemistry.[1] The efficiency of this industrially important C–N bond-forming reaction is highly dependent on the nature of the ligands. In contrast to the "standard" phosphorus ligand, Ph_3P, which leads to poor yields, bulky tertiary phosphines such as **1**,[2] **2**,[3] **3**,[3a,4] **4**,[5] **5**,[6] **6**,[7] **7**,[3b,8] and **8**[9] ensure high yields for a variety of structurally different substrates. *N*-Heterocyclic carbene (NHC) ligands have also been used, phosphine-functionalized NHC **9** being a recent example.[10] All of these ligands require multi-step syntheses. Phosphorus compounds that lack P–C bonds are generally quite air-stable; ligands **9**[10] and **10**[11] are examples of such compounds that have also been used in Buchwald–Hartwig aminations.

In a patent, we recently disclosed preliminary results regarding the use of P-ligands of type **13** bearing two bulky amino groups and a sterically demanding alkoxy moiety at phosphorus.[12] The synthesis of this compound, which was originally used as a phosphorylating agent for biomolecules, has been described briefly in the literature, but spectroscopic data are lacking.[13] Our synthetic strategy is straightforward and is based on the reaction of commercially available bis(diisopropylamino)chlorophosphine (**11**) with potassium *tert*-butoxide (**12**) (Scheme 1). The fact that the material is readily available in sufficiently large amounts by this method, and the observation that it is easily handled



Scheme 1. Synthesis of ligand **13**.

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in air, led us to consider it as a possible ligand in Buchwald–Hartwig amination. In this paper, we report the results of a more extensive study.

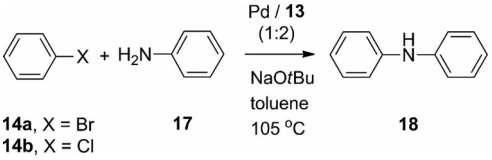
Results and Discussion

Optimization Experiments

Initial exploratory optimization experiments were carried out using the amination of bromobenzene (**14a**) with morpholine (**15**) to give **16** as the model reaction. As shown in Table 1 (see also Tables S1 and S2 for additional examples), the reaction is best performed under an inert atmosphere in toluene as the solvent. Various Pd sources may be used. Other solvents such as THF, DME (dimethoxyethane), or dioxane can also be used, but they seem to give somewhat less efficient reactions. The best bases are NaO*t*Bu and KO*t*Bu.

Exploratory optimization experiments were also carried out for the reaction between bromobenzene (**14a**) and aniline (**17**) to give amination product **18** (Table 2; see also Tables S2–S5 for additional examples). At a catalyst loading of 5 mol-% and a reaction temperature of 105 °C, complete conversion was observed after 30 min (Table 2, entry 1). Therefore, the reaction was repeated, this time taking samples at two-minute intervals. We found that complete conversion was reached within the first two minutes, with only traces of the respective triarylamine being detected (<1%; Table 2, entry 2). When the reaction was continued for 20 h at this concentration, the amount of triarylamine increased, but it stayed below 10%. Furthermore, the reaction could even be performed under an atmosphere of air. Under such conditions, full conversion was achieved at 105 °C within

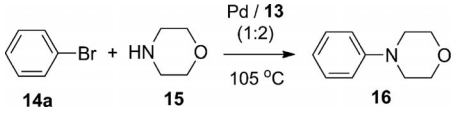
Table 2. Exploratory experiments the Pd-catalysed amination **14a/14b** + **17**→**18**.[a]



Entry	Halide	Pd source	Pd [mol-%]	*t*	Conv. [%]
1	**14a**	$Pd(dba)_2$	5	30 min	100
2	**14a**	$Pd(dba)_2$	5	2 min	100
3	**14a**	$Pd(dba)_2$	5	1 h[b]	100
4	**14a**	$Pd(dba)_2$	1	1 h[b]	100
5	**14a**	$Pd(dba)_2$	0.5	20 h	54
6	**14a**	$Pd(COD)Cl_2$	0.5	20 h	19
7	**14a**	$PdCl_2$	0.5	20 h	7
8	**14a**	$Pd(OAc)_2$	0.5	20 h	10
9	**14a**	$Pd(acac)_2$	0.5	20 h	8
10	**14b**	$Pd(dba)_2$	1	24 h	63
11	**14b**	$Pd(dba)_2$	2	24 h	91
12	**14b**	$Pd(dba)_2$	3	24 h	100

[a] Same conditions as for Table 1. [b] Reactions carried out under an air atmosphere.

Table 1. Optimization experiments of the Pd-catalysed amination **14a** + **15**→**16**.[a]



Entry	Pd source	Pd [mol-%]	Solvent	Base	*t*	Conv.[b] [%]
1	$Pd(dba)_2$	5	toluene	NaO*t*Bu	1 h	100
2	$Pd(dba)_2$	5	THF	NaO*t*Bu	1 h	89
3	$Pd(dba)_2$	5	DME	NaO*t*Bu	1 h	94
4	$Pd(dba)_2$	5	dioxane	NaO*t*Bu	1 h	85
5	$Pd(dba)_2$	5	toluene	KO*t*Bu	3 h	92
6	$Pd(dba)_2$	5	toluene	K_2CO_3	3 h	3
7	$Pd(dba)_2$	5	toluene	Cs_2CO_3	3 h	7
8	$Pd(dba)_2$	5	toluene	K_3PO_4	3 h	18
9	$Pd(dba)_2$	5	toluene	NaO*t*Bu	0.5 h	100
10	$Pd(dba)_2$	5	toluene	NaO*t*Bu	2 min	100
11	$Pd(dba)_2$	2	toluene	NaO*t*Bu	0.5 h	100
12	$Pd(dba)_2$	2	toluene	NaO*t*Bu	0.5 h	100
13	$Pd(COD)Cl_2$	2	toluene	NaO*t*Bu	0.5 h	100
14	$PdCl_2$	2	toluene	NaO*t*Bu	0.5 h	100
15	$Pd(OAc)_2$	2	toluene	NaO*t*Bu	0.5 h	100
16	$Pd(acac)_2$	2	toluene	NaO*t*Bu	0.5 h	98
17	$Pd(CH_3CN)Cl_2$	2	toluene	NaO*t*Bu	0.5 h	85
18	$Pd(dba)_2$	1	toluene	NaO*t*Bu	1 h	100
19	$Pd(dba)_2$	0.5	toluene	NaO*t*Bu	20 h	95
20	$Pd(dba)_2$	0.25	toluene	NaO*t*Bu	20 h	34

[a] Reaction conditions: **14a** (1 mmol), **15** (2 mmol), base (2 mmol), Pd: *tert*-butyl tetraisopropylphosphorodiamidite (1:2), dry toluene (3 mL), 105 °C, argon. [b] Conversions to coupling product, based on **14a**, determined by GC. dba = dibenzylideneacetone, COD = cyclooctadiene, acac = acetoacetate.

1 h, provided 5 mol-% catalyst loading was used (Table 2, entries 3 and 4). Several experiments were also performed with the cheaper chlorobenzene (**14b**), which also proved to be successful (Table 2, entries 10–12). In many previous amination studies, undesired reduction of the aryl halide was observed to a small extent, and this side-reaction also occurs in the present catalyst system (typically <5%).

Scope and Limitations

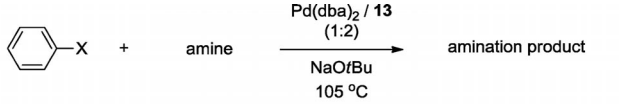
Following the optimization experiments, other amines **19**–**21** were tested with phenyl halides **14a** and **14b**. Table 3 summarizes the best results using all amines tested to date. Here and in subsequent tables, conversion values refer to amination product formation based on ArX, as determined by GC, taking into account dehalogenation (reduction) and homocoupling reactions. It is clear that ligand **13** can be used to make up a fairly effective and general catalyst system. In the case of morpholine (**15**), a catalyst loading of 1 mol-% was sufficient to achieve complete conversion within 1 h when using **14a**, while in the case of chlorobenzene (**14b**), complete conversion required 24 h at the same catalyst loading (Table 3, entries 1 and 2). Aniline needed a higher catalyst loadings with **14b**, but the reaction was completely selective, and no triphenylamine as an undesired by-product was detected. In addition to further secondary amines **19**–**20**, primary amines such as benzylamine (**21**) similarly reacted readily (Table 3, entries 10 and 11). Even though the reactions went to completion, small amounts of the respective tertiary amines (9%) were formed as by-products.

We then turned to other aryl halides **25a**–**34a**, **25b**–**31b**, and **33b** as reaction components, and discovered that these also react smoothly with morpholine (**15**) and aniline (**17**) (Table 4). Here again, in almost all reactions, minor amounts of aromatic compounds corresponding to the reduction products (<5%) of the aryl halides were observed. Unfortunately, in the case of sterically hindered halides **31** and **32**, this side-reaction dominated, indicating the limitations of the method (Table 4, entries 13–15). The reaction between 1-bromo-4-(*tert*-butyl)benzene (**28a**) and morpholine (**15**) (Table 4, entry 7) was scaled up (10 mmol), and the high yield of 95% obtained after column chromatography demonstrates the feasibility of this method based on ligand **13**. Vinyl bromides could also be aminated similarly. For example, (bromomethylene)cyclohexane (**34a**) reacted smoothly with morpholine within 2 h at a catalyst loading of 1 mol-%.

When aniline (**17**) was used as the amine, higher amounts of catalyst were required for good conversions, but the undesired reduction of the respective aryl halide was minimized (Table 4, entries 31–33). In the case of the sterically hindered aryl halide 2-bromo-1,3-dimethylbenzene (**32a**), excellent results were observed (97% conversion to the desired amine; Table 4, entry 33). Thus, halide **32a** appears to be more reactive than 2-bromo-1,3,5-trimethylbenzene (**31a**) at the same catalyst loading. A similar reactivity pattern was noticed in the reactions of aryl halides with amines **19**–**21** (Table S6). In addition to the desired amination reaction, in some cases traces of C–C homocoupling compounds derived from the aryl halides were observed (<3%; see GC chromatograms in the Supporting Information).

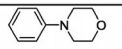
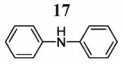
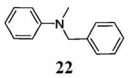
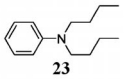
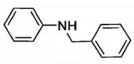
Finally, a few heteroaryl halides **54a**–**58a** and **54b**–**58b** were tested. Table 5 shows that 2- and 3-bromosubstituted pyridines have different reactivities in their reactions with morpholine (**15**) and aniline (**17**). Unexpectedly, chloro-substituted pyridines reacted faster than their bromo analogues. For example, 3-bromopyridine (**55a**) reacted with morpholine to give 4-(pyridin-3-yl)morpholine (**60**) with a 48% conversion after 24 h, whereas 3-chloropyridine was completely converted into the desired amine (i.e., **60**) within 4 h (Table 5, entries 3 and 4). The same behaviour was noticed for 2-halo-substituted quinolines **57a** and **57b** (Table 5, entries 6 and 7). A scaled-up procedure gave 4-(quinolin-2-yl)morpholine (**62**) after column chromatography in a very good yield (93%), underlining once more the practical utility of ligand **13** (Table 5, entry 7). When aniline (**16**) was used as the amine, increased catalyst loadings proved to be necessary, but even then the reactions did not reach completion (Table 5, entries 10–14). Furthermore,

Table 3. Amination of phenyl halides **14a** and **14b** using amines **15**,[a] **17**, and **19**–**21**.[b]



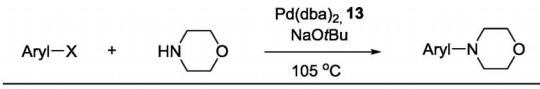
14a, X = Br
14b, X = Cl

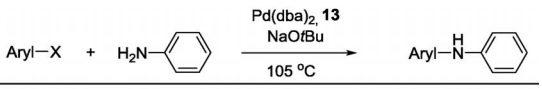
15, morpholine — **16**
17, aniline — **18**
19, *N*-benzylmethylamine — **22**
20, dibutylamine — **23**
21, benzylamine — **24**

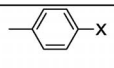
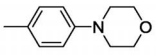
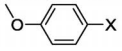
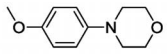
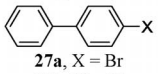
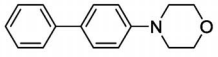
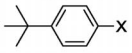
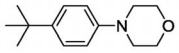
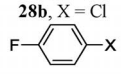
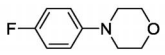
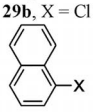
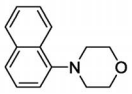
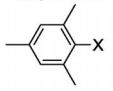
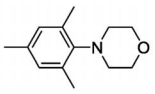
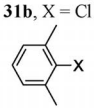
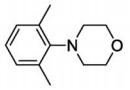
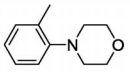
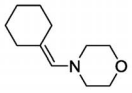
Entry	Halide	$Pd(dba)_2$ [mol-%]	Amine	*t* [h]	Product	Conv.[c] [%]
1	**14a**	1	**15**	1		100
2	**14b**	1	**15**	24		99
3	**14a**	1	**17**	1	 **17**	100
4	**14b**	3	**17**	24		100
5	**14a**	0.5	**19**	20	 **18**	100
6	**14b**	5[d]	**19**	20	**22**	100
7	**14a**	0.5	**20**	20		64
8	**14a**	5[d]	**20**	20	**23**	98
9	**14b**	5[d]	**20**	20		100
10	**14a**	5[d]	**21**	20		91[e]
11	**14b**	5[d]	**21**	20	**24**	91[e]

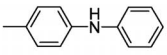
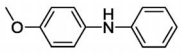
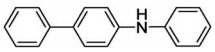
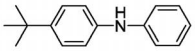
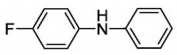
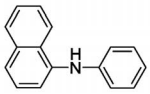
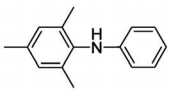
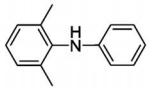
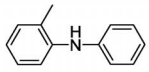
[a] Morpholine (2 mmol) was used. [b] Reaction conditions: ArX (1 mmol), amine (1.2 mmol), NaO*t*Bu (2 mmol), $Pd(dba)_2$:**13** (1:2), dry toluene (3 mL), 105 °C, argon. [c] Conversions to amination product based on ArX as determined by GC, taking into account dehalogenation (reduction) and homocouping reactions. [d] Non-optimized catalyst loadings. [e] Complete conversion, but with 9% of the tertiary amine as by-product.

Table 4. Amination of aryl halides **25a**,**b**–**34a**.[a,b]





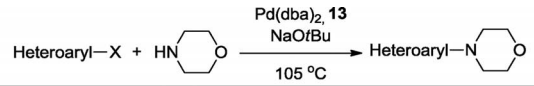
Entry	Halide	Product	Pd(dba)$_2$ [mol-%]	t [h]	Conv.[c] [%]
1			1	1	100
2	**25a**, X = Br **25b**, X = Cl	**35**	2	8	100
3			1	2	95
4	**26a**, X = Br **26b**, X = Cl	**36**	1	9	91
5			1	2	93
6	**27a**, X = Br **27b**, X = Cl	**37**	1	8	95
7			1	1	96/95[d]
8	**28a**, X = Br **28b**, X = Cl	**38**	1	19	96
9			1	7	94
10	**29a**, X = Br **29b**, X = Cl	**39**	1	22	93
11			1	2	94
12	**30a**, X = Br **30b**, X = Cl	**40**	2	2	90
13			5	5	21/79/0[e]
14	**31a**, X = Br **31b**, X = Cl	**41**	6	24	31/69/0[e]
15			5	6	20/36/44[e]
	32a, X = Br	**42**			
16			1	1	100
17	**33a**, X = Br **33b**, X = Cl	**43**	1	5	100
18			1	2	86
	34a	**44**			

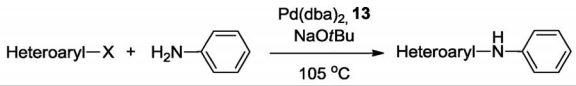
Entry	Product	Pd(dba)$_2$ [mol-%]	t [h]	Conv.[c] [%]
19		2	1	100
20	**45**	5	24	95
21		3	5	93
22	**46**	8	24	74
23		2	1	99
24	**47**	4	24	97
25		2	1	100
26	**48**	5	24	98
27		5	1	96
28	**49**	6	24	85
29		3	1	98
30	**50**	5	24	97
31		7.5	20	82
32	**51**	4	24	75
33		7.5	20	97
	52			
34		2	1	100
35	**53**	6	24	97

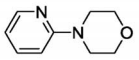
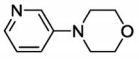
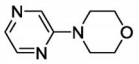
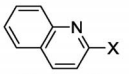
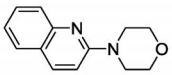
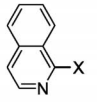
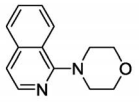
[a] Reaction conditions: aryl halide (1 mmol), amine (1.2 mmol), NaO*t*Bu (2 mmol), Pd(dba)$_2$:**13** (1:2), dry toluene (3 mL), 105 °C, argon. [b] In the case of morpholine (**15**), 2 mmol was used. [c] Conversions to coupling product based on aryl halide determined by GC. Conversion values related to amination product are based on the reaction of ArX as determined by GC, taking into account dehalogenation (reduction) and homocouping reactions (from average of at least three independent experiments). [d] Corrected GC conversion/yield after column chromatography of scaled up reaction (10 mmol starting halide). [e] Ratio amination product/reduced substrate/starting aryl halide. Selectivities were determined by GC, taking into account dehalogenation (reduction) and homocoupling reactions.

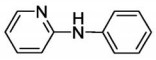
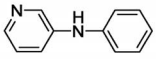
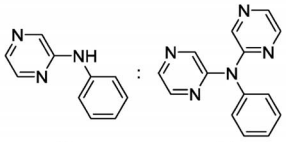
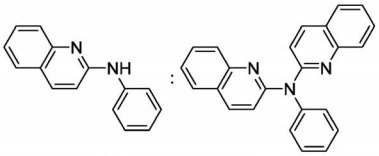
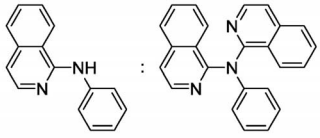
in the reactions of 2-bromo- and 2-chloroquinolines (**57a** and **57b**), different product ratios resulted. Optimized experiments carried out with 2-bromoquinoline gave a mixture of mono- (**68**) and diarylated (**69**) products in a 1:3 ratio (Table 5, entry 15). The same trend was observed in the reaction of 2-bromoisoquinoline, but in this case the

Table 5. Amination of heteroaryl halides **54a**–**58a** and **54b**–**58b**.[a]





Entry	Halide	Product	$Pd(dba)_2$ [mol-%]	t [h]	Conv. [%]
1			1	24	65
2	**54a**, X = Br **54b**, X = Cl	**59**	1	19	83
3			1	24	48
4	**55a**, X = Br **55b**, X = Cl	**60**	1	4	100
5	 **56a**, X = Br **56b**, X = Cl	 **61**	5	2	86[b]
6			1	3	99
7	**57a**, X = Br **57b**, X = Cl	**62**	1	1	98/ 93[e]
8			2	4	99
9	**58a**, X = Br **58b**, X = Cl	**63**	2	4	99

Entry	Product	$Pd(dba)_2$ [mol-%]	t [h]	Conv. [%]
10		2	24	33
11	**64**	2	24	56
12		5	1	84
13	**65**	5	24	75
14	 **66** **67**	5	20	50[d] (5:1)[e]
15		5	20	87 (1:3)[e]
16	**68** **69**	2	24	73 (11:1)[e]
17		5	20	73 (1:5)[e]
18	**70** **71**	2	24	81 (26:1)[e]

[a] Similar conditions to Table 3. [b] MeONa was used as base in this case. [c] Corrected GC conversion/yield after column chromatography, scaled up reaction (10 mmol starting halide). [d] Yield after column chromatography. [e] Ratio of diaryl- to triarylamine as determined by GC.

selectivity for the diarylated product (i.e., **71**) was higher (1:5 ratio; Table 5, entry 17). Completely different behaviour was observed in the reactions of 2-chloroquinoline (**57b**) and 2-chloroisoquinoline (**58b**). In these cases, monoarylation was preferred, and selectivities of 11:1 (**68**/**69**) and 26:1 (**70**/**71**), respectively, were observed (Table 5, entries 16 and 18). In addition to the aminated quinolines, small amounts of *tert*-butylated quinoline derivatives were detected in some cases, in yields of up to 22%. Heteroaryl halides were found to behave similarly in their reactions with amines **19**–**21** (Table S6).

Conclusions

The P-ligand *tert*-butyl tetraisopropylphosphorodiamidite (**13**) is an easily prepared air-stable compound, accessible from bis(diisopropylamino)chlorophosphine (Scheme 1). It is a useful ligand in Pd-catalysed Buchwald–Hartwig amination reactions. The compound is generically related to ligand **10**, but the preparation of ligand **10** involves the laborious synthesis of the intermediate *N*,*N*-bis(*tert*-butyl)ethylenediamine. The amination reactions described in this paper using ligand **13** are also more efficient. Limitations became apparent when more hindered substrates were tested, and in these cases, undesired reduction constitutes the major reaction pathway. Moreover, when the catalyst loading was lowered to <0.5 mol-%, the reactions did not reach completion, presumably due to catalyst deactivation. Strangely enough, compound **13** has not been used in any transition-metal-catalysed reactions before. This study demonstrates that Buchwald–Hartwig amination of aromatic and heteroaromatic halides using this sterically demanding ligand is feasible, as shown, inter alia, by several examples of scaled-up transformations. This procedure competes well with many (but not all) previously reported protocols for amination based on more difficult to prepare, and thus more expensive, ligands such as **1**–**10**. Industrial applications appear to be possible, because ligand **13** (or its analogues) has a relatively low molecular weight, it is easily stored and handled, and its undesired oxidation by air is a very slow process. In fact, the amination can be carried out in air if a Pd catalyst loading of 5 mol-% is used. We also anticipate that this compound can serve as a useful ligand in other transition-metal-catalysed reactions.

Experimental Section

General Remarks: Unless otherwise stated, the reactions were performed under argon in a normal fume cupboard in 10 mL Schlenk tubes sealed with PTFE septa, using an oil bath heated at 105 °C. Reaction progress was monitored by GC, and compounds were identified by GC–MS or by ^{1}H and ^{13}C NMR spectroscopy using authentic samples. Bis(diisopropylamino)chlorophosphine (**11**) was bought from Sigma–Aldrich, and *tert*-butyl tetraisopropylphosphorodiamidite (**13**) was prepared as described below or was bought from Sigma–Aldrich and used without further purification (95%). Dry toluene was acquired from Sigma–Aldrich or TCI, and was used without further drying. All other reagents were purchased from Acros, Sigma–Aldrich, Alfa Aesar, and ABCR Chemicals, and were used without further purification. NMR spectra were recorded with Bruker Avance 300 and DRX 400 (^{1}H: 300 or 400 MHz, ^{13}C: 75 or 101 MHz) spectrometers using tetramethylsilane as internal standard (δ = 0 ppm). High-resolution EI mass spectra were measured with a Finnigan MAT 95S spectrometer. Conversions to the coupling product, based on aryl halide, were determined by GC. Reported yields are an average of three or more runs. Analytical thin-layer chromatography was carried out on Merck silica gel 60 F254q plates, and column chromatography was carried out using Merck silica gel 60 (230–400 mesh ASTM).

Catalyst Preparation: A stock solution of catalyst was prepared as follows: $Pd(dba)_2$ (1 equiv.) was added to a heat-gun-dried Schlenk tube under argon, and then *tert*-butyl tetraisopropylphosphorodiamidite (95%; 2 equiv.) was added. The tube was evacuated and backfilled with argon three times, and then dry toluene was added by syringe. The Schlenk tube was then capped with a PTFE septum, the solution was homogenised using an IKA MS2 mini shaker for 30 s, and then an argon-filled balloon was attached to the tube. The solution was stirred for at least 10 min before the catalyst was added to the reaction mixture. The calculated amount of freshly prepared catalyst was added using a 1 mL syringe. For each set of reactions, a new batch of the catalyst solution was prepared.

General Procedure for the Amination Reaction: NaO*t*Bu (2 mmol) and aryl halide (1 mmol; when solid) were added to an oven-dried Schlenk tube. The tube was evacuated and backfilled with argon three times, and then dry toluene, catalyst (volume calculated based on the desired concentration of catalyst), and amine (1.20 mmol) were added to reach a total volume of 3 mL. When an liquid aryl halide was used, this was added after the addition of the catalyst. The tube was then sealed with a PTFE septum, the suspension homogenized using an IKA MS2 mini shaker for 10–30 s, and the mixture was stirred in a preheated oil bath at 105 °C. Reaction progress was monitored by GC. After all the starting materials had been consumed, or when the reaction did not progress any more, the mixture was cooled down to room temperature, and then diethyl ether (7 mL) and saturated aqueous NaCl solution (10 mL) were added. The resulting suspension was transferred into a separatory funnel, the layers were separated, and the organic phase was washed with water (4 × 10 mL). The organic layer was dried with anhydrous Na_2SO_4, and then concentrated under reduced pressure. The crude residue was purified by column chromatography. The spectroscopic data of all known amination products are in agreement with literature values.

***tert*-Butyl Tetraisopropylphosphorodiamidite (13):** Bis(diisopropylamino)chlorophosphine (**11**; 1.0 g, 3.75 mmol) and potassium *tert*-butoxide (**12**; 0.504 g, 4.5 mmol) were placed in a Schlenk tube, which was then degassed. Dry toluene (40 mL) was added under an argon atmosphere. The reaction mixture was stirred at room temperature for 24 h, then it was washed with water (4×). The organic phase was dried and evaporated to give *tert*-butyl tetraisopropylphosphorodiamidite (**13**; 0.984 g, 86%) as a white crystalline solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.64–3.47 (m, 4 H), 1.32 (m, 9 H), 1.23–1.08 (m, 24 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 74.86 [d, $J_{P,C}$ = 15.6 Hz, $C(CH_3)_3$], 44.88 [d, $J_{P,C}$ = 13.5 Hz, 4 C, $CH(CH_3)_2$], 30.97 [d, $J_{P,C}$ = 8.2 Hz, 3 C, $C(CH_3)_3$], 24.63 [d, $J_{P,C}$ = 5.5 Hz, 4 C, $CH(CH_3)_2$], 24.23 [d, $J_{P,C}$ = 8.7 Hz, 4 C, $CH(CH_3)_2$] ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 99.74 ppm. HRMS (EI): calcd. for $C_{16}H_{37}N_2OP$ $[M]^+$ 304.2644; found 304.2644.

***N*-Phenyl-*N*-(pyrazin-2-yl)pyrazin-2-amine (67):** Following the general procedure, compound **67** was obtained as a white solid. R_f = 0.16 (EtOAc/petroleum ether, 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.41 (d, J = 1.3 Hz, 2 H), 8.27–8.17 (m, 4 H), 7.48 (t, J = 7.5 Hz, 2 H), 7.37 (t, J = 7.4 Hz, 1 H), 7.25 (d, J = 8.5 Hz, 2 H) ppm. HRMS (EI): calcd. for $C_{14}H_{11}N_5$ $[M]^+$ 249.1014; found 249.1016.

***N*-Phenyl-*N*-(quinolin-2-yl)quinolin-2-amine (69):** Following the general procedure, compound **69** was obtained as colourless crystals. R_f = 0.54 (EtOAc/petroleum ether, 1:4). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.00 (d, ^3J = 8.8 Hz, 2 H), 7.82–7.69 (m, 4 H), 7.62–7.56 (m, 2 H), 7.48–7.35 (m, 4 H), 7.35–7.23 (m, 5 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.72, 147.50, 144.65, 137.11, 129.61, 129.50, 128.28, 128.02, 127.32, 126.01, 125.80, 124.92, 117.92 ppm. HRMS (EI): calcd. for $C_{24}H_{17}N_3$ $[M]^+$ 347.1422; found 347.1423.

***N*-(*iso*-Quinolin-1-yl)-*N*-phenylisoquinolin-1-amine (71):** Following the general procedure, compound **71** was obtained as a white solid. R_f = 0.10 (EtOAc/petroleum ether, 1:4). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.23 (d, ^3J = 5.7 Hz, 2 H), 7.92–7.76 (m, 4 H), 7.58 (dt, ^3J = 7.6 Hz, 2 H), 7.50–7.43 (m, 2 H), 7.37–7.20 (m, 4 H), 7.10 (dt, ^3J = 7.4 Hz, 1 H), 7.00–6.90 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.69, 148.63, 141.93, 138.81, 129.98, 129.47, 127.31, 125.93, 124.54, 124.08, 118.67 ppm. HRMS (EI): calcd. for $C_{24}H_{17}N_3$ $[M]^+$ 347.1422; found 347.1414.

Supporting Information (see footnote on the first page of this article): Selected spectroscopic characterization of known amination products; copies of the ^{1}H and ^{13}C NMR spectra; GC chromatograms.

Acknowledgments

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