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Electron-Rich, Bicyclic Biaryl-Like KITPHOS Monophosphines *via* [4+2] Cycloaddition between 1-Alkynylphosphine Oxides and Anthracene: Highly Efficient Ligands for Palladium-Catalysed C–N and C–C Bond Formation

Simon Doherty,[a,*] Julian G. Knight,[a,*] Catherine H. Smyth,[a,*] and Graeme A. Jorgenson[a]

[a] School of Natural Sciences, Chemistry, Bedson Building, Newcastle University, Newcastle upon Tyne, NE1 7RU, U.K.
Fax: (+44)-191-222-6929; e-mail: simon.doherty@ncl.ac.uk

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Abstract: Electron-rich, bicyclic biaryl-like KITPHOS monophosphines have been prepared *via* Diels–Alder cycloaddition between 1-alkynylphosphine oxides and anthracene in an operationally straightforward and highly modular synthetic protocol that will allow access to an architecturally and electronically diverse family of ligands. Palladium complexes of these ligands are highly efficient catalysts for the Buchwald–Hartwig amination and Suzuki–Miyaura coupling of a wide range of aryl chlorides, which for the vast majority of substrate combinations outperform their *o*-(dicyclohexylphosphino)biphenyl-based counterparts.

Keywords: aminations; aryl chlorides; biaryl-like compounds; electron-rich species; phosphines; Suzuki–Miyaura coupling

Palladium-catalysed C–C and C–heteroatom bond formation has evolved into an exceptionally powerful tool which has found widespread use in many areas of organic synthesis.[1] While the first catalysts for these transformations were typically based on a source of palladium and either a triarylphosphine or a chelating diphosphine such as 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (BINAP) or 1,1′-bis(diphenylphosphino)-ferrocene (dppf), high temperatures were often required to achieve acceptable levels of efficiency and they were generally unreactive towards aryl chloride substrates.[2] However, recent advances in catalyst development have led to the discovery that electron-rich biaryl monophosphines such as **1** and **2**, and their derivatives (Figure 1), form highly efficient catalysts for C–N as well as C–C and C–O bond formation with a wide range of aryl chlorides, often at room temperature and at very low catalyst loadings.[3] The efficiency of these catalyst systems has been attributed to a combination of factors, the first of which is their highly electron-rich character which facilitates oxidative addition of less reactive aryl chlorides.[3a,b] Recent studies also suggest that the steric bulk of these biaryl phosphines is critical to achieving high activity by promoting the formation of the monophosphine complex.[4] Finally, computational and experimental studies reveal that a weak interaction between palladium and the *ortho*-carbon atom of the non-phosphine-containing ring of the ligand stabilises the catalyst when the palladium is not involved in a step within the catalytic cycle.[5]

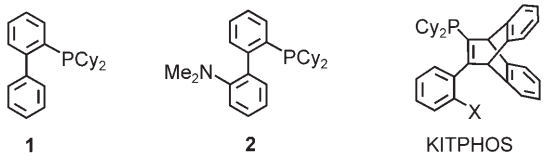
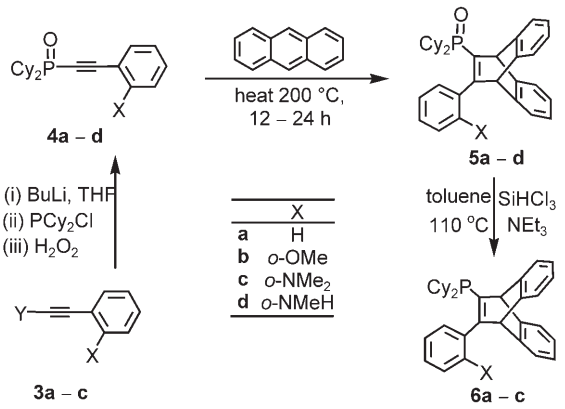


Figure 1. Biaryl monophosphines **1** and **2** and KITPHOS monophosphines.

As palladium-catalysed aminations and cross-couplings are pivotal to the synthesis of important intermediates and building blocks for the fine chemicals industry there is immense interest in using this design concept to develop alternative ligands that are easy to prepare, highly modular and cost effective.[6] Ideally, these ligands should have a broad substrate scope, be capable of activating chloride-based substrates under mild conditions, facilitate the coupling of hindered substrates and allow for scale-up and process development. These monophosphines are typically prepared either by modification of an existing biaryl precursor

or *via* addition of an aryl-Grignard reagent to a benzyne intermediate.[3e,7] Recently though, cycloaddition methodology has evolved as a potentially versatile approach for constructing the biaryl fragment in monophosphines. For example, Diels–Alder cycloaddition between 1-alkynylphosphine oxides and various 1,3-dienes[8] as well as rhodium-catalysed [2+2+2]cycloaddition of tethered diynes with 1-alkynylphosphine sulfides have both been used to prepare biaryl-based monophosphines.[9] In this regard, we have recently used the double Diels–Alder cycloaddition between 1,4-bis(diphenylphosphinoyl)buta-1,3-diyne and anthracene to construct the skeletal framework of the biaryl-like diphosphine CATPHOS, which forms a highly efficient catalyst for the Buchwald–Hartwig amination of a wide range of aromatic bromides as well as the α-arylation of ketones.[10] This approach has now been extended to include the corresponding [4+2]cycloaddition between 1-alkynylphosphine oxides and anthracene to generate an entirely new family of electron-rich biaryl-like monophosphine, KITPHOS. These ligands form highly active catalysts for the Buchwald–Hartwig amination and Suzuki–Miyaura coupling of a range of aryl chlorides which, for the vast majority of substrate combinations, outperform their *o*-(dicyclohexylphosphino)biphenyl-based counterparts. Key features of these KITPHOS monophosphines include their operationally straightforward synthesis in good to excellent yield from inexpensive starting materials and their highly modular synthesis which allows the substitution pattern of the 1-alkynylphosphine oxide aryl group to be systematically varied, the steric bulk and basicity of the phosphino group to be fine-tuned, and the biaryl-like fragment to be modified by performing the cycloaddition with a substituted anthracene or its equivalent.

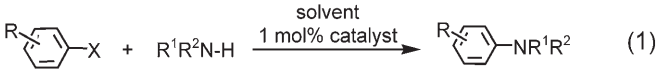
Our interest in KITPHOS monophosphines **6a–c** began after recognising the close similarity of their basic structural architecture with that of the dialkylphosphanylbiphenyls developed by Buchwald and coworkers. Monophosphines **6a–c** were prepared from the corresponding 1-alkynylphosphines oxides **3a–c** in three experimentally easy steps, according to the procedure outlined in Scheme 1. 1-Alkynylphosphine oxides **4a–c** were prepared by reaction of chlorodicyclohexylphosphine with the corresponding 1-lithio-1-alkyne, generated either from the terminal alkyne (Y=H) or *via* desilylation (Y=$SiMe_3$), followed by oxidation prior to work-up and purification.[11] The biaryl-like skeleton was constructed *via* the Diels–Alder reaction between 1-alkynylphosphine oxides **4a–c** and anthracene, which gave **5a** and **b** in excellent yield after purification. Unfortunately, competing *N*-demethylation during the reaction between **4c** and anthracene resulted in the formation of a significant amount of **4d** and **5d** as by-products and as a result **5c** could only be isolated in poor yield. Further studies



Scheme 1. Synthesis of electron-rich biaryl-like monophosphines **6a–c**.

are currently underway to develop an alternative more efficient synthesis of **5c**. Reduction of these phosphine oxides was achieved by heating a toluene solution of **5a–c**, trichlorosilane and triethylamine at 110 °C for 48 h to afford the desired KITPHOS monophosphines **6a–c** (Scheme 1).[12]

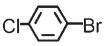
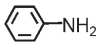
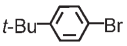
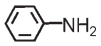
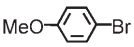
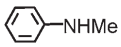
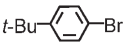
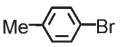
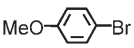
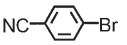
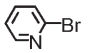
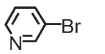
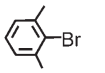
Since palladium(0) complexes of electron-rich biaryl monophosphines are highly efficient catalysts for the amination of bromides, chlorides and triflates[3b] as well as Suzuki coupling reactions[3c,e,13] of a wide range of aryl and heteroaryl compounds, often at low catalyst loadings, we chose these two reactions with which to undertake a comparative study. Preliminary reactions focused on the amination of a range of aryl and heteroaryl bromides with primary and secondary amines [Eq. (1)] using Pd(0)/**6a** (1.0 mol% Pd/



(1)

2.5 mol% phosphine) in toluene at 80 °C with NaO-*t*-Bu, full details of which are given in Table 1. Under these conditions, Pd(0)/**6a** catalysed the amination of a range of electron-deficient and electron-rich substrates as well as sterically hindered 2,6-dimethylbromobenzene, the latter achieving 70% conversion after 2 h compared with 50% when catalysed by Pd(0)/**1**, in the same time (entries 19–20). Notably, for the vast majority of substrate combinations tested Pd(0)/**6a** either rivalled or outperformed its biphenyl counterpart Pd(0)/**1**, *in our laboratory under the same conditions.* The difference in performance between the catalysts based on **6a** and **1** was most evident in the amination of electron-deficient substrates particularly for the reaction between 1-bromo-4-chlorobenzene and aniline (entries 1 and 2). Bromopyridine substrates also proved to be effective coupling partners with the amination between 2-bromopyridine and morpholine

Table 1. Palladium-catalysed amination of aryl bromides using ligands **6a** and **1**.[a]

Entry	L	Aryl bromide	Amine	Time [h]	Conversion [%][b]
1	**6a**			3	94
2	**1**			3	36
3	**6a**			2	62
4	**1**			3	37
5	**6a**			1	100
6	**1**			1	97
7	**6a**			1	99
8	**1**			1	99
9	**6a**			1	80
10	**1**			1	77
11	**6a**			1	90
12	**1**			1	77
13	**6a**			6	40
14	**1**			23	30
15	**6a**			1	100
16	**1**			1	76
17	**6a**			2	68
18	**1**			1	99
19	**6a**			2	70
20	**1**			2	50

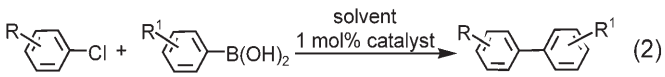
[a] *Reaction conditions:* 1.0 equiv. of Ar-Br, 1.1 equiv. of amine, 1.4 equiv. of NaO-*t*-Bu, 0.5 mol% $Pd_2(dba)_3$, 2.5 mol% **6a** or **1**, toluene , 80 °C.

[b] Conversions determined by GC analysis of the reaction mixture and based on aryl bromide. Average of three runs.

reaching completion within 1 h with Pd(0)/**6a** compared to only 76% conversion for its biphenyl counterpart (entries 15 and 16).

Having firmly established the efficacy of KITPHOS monophosphine **6a** in the palladium-catalysed amination of aryl bromides, catalyst testing was extended to include chloride substrates. Gratifyingly, under our conditions, Pd(0)/**6a** catalysed the amination of a range of aryl chlorides with a variety of amine coupling partners including cyclic secondary alkylamines, secondary anilines and primary alkylamines, in the majority of cases giving good to excellent conversions at 100 °C with 1 mol% palladium (Table 2). As for the aryl bromides described above, Pd(0)/**6a** consistently outperformed its biaryl counterpart for all substrate combinations tested, in some cases by a significant margin. With the aim of developing a family of KITPHOS monophosphines capable of transforming a wide range of substrate combinations, the performance of catalysts generated from **6a–c** were compared against the corresponding systems based on **1** and **2**, for the amination of selected aryl chlorides. Table 3 reveals that the introduction of an *ortho*-OMe or -NMe_2 substituent results in a significant and in some cases substantial enhancement in catalyst performance, with all four substrate combinations giving markedly higher conversions for catalysts derived from **6b** and **6c** compared to their unsubstituted counterpart. The beneficial influence of the *ortho* substituent is particularly evident in the reaction between chlorobenzene and pyrrolidine which reached 97% conversion with Pd(0)/**6c** compared with only 44% for the Pd(0)/**6a** system. Similarly, Pd(0)/**6c** gave complete conversion for the amination of 2,6-dimethylchlorobenzene with morpholine while Pd(0)/**6a** gave only 52% conversion in the same time.

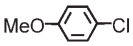
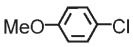
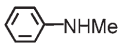
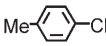
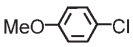
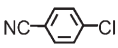
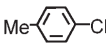
The encouraging performance of Pd(0)/**6a** catalyst for the amination of aryl chlorides prompted us to extend our studies to include Suzuki–Miyaura couplings [Eq. (2)], a reaction that is efficiently catalysed



(2)

by systems based on either $Pd_2(dba)_3$ or $Pd(OAc)_2$ and a biaryl monophosphine. Following a protocol described by Buchwald, the reaction between phenylboronic acid and a range of aryl chlorides was catalysed by $Pd(OAc)_2$/**6a**, **b** (Pd:**L**, 1:2.5) in either THF or toluene at 40–80 °C, details of which are presented in Table 4. Under these conditions, good to excellent conversions were obtained for each substrate combination, including those involving electron-donating and heteroaryl partners. While activated aryl chlorides typically gave good conversions at 40 °C, electron-rich and sterically demanding substrates required slightly higher temperatures (60–80 °C) to reach comparable conversions. Based on these preliminary stud-

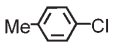
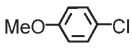
Table 2. Palladium-catalysed amination of aryl chlorides using ligands **6a** and **1**.[a]

Entry	L	Aryl chloride	Amine	Time [h]	Conversion [%][b]
1	**6a**			24	71
2	**1**			24	59
3	**6a**			24	48
4	**1**			24	32
5	**6a**			6	98
6	**1**			6	89
7	**6a**			2	>99
8	**1**			2	95
9	**6a**			2	96
10	**1**			2	69
11	**6a**			2	100
12	**1**			6	23
13	**6a**			1	100
14	**1**			1	100
15	**6a**			1	93
16	**1**			1	10
17	**6a**		nBuNH$_2$	6	96
18	**1**			6	40
19	**6a**			6	52
20	**1**			6	47

[a] *Reaction conditions:* 1.0 equiv. of Ar-Cl, 1.1 equiv. of amine, 1.4 equiv. of NaO-*t*-Bu, 0.5 mol% $Pd_2(dba)_3$, 2.5 mol% **6a** or **1**, toluene, 100 °C.

[b] Conversions determined by GC analysis of the reaction mixture and based on aryl chloride. Average of three runs.

Table 3. Comparison of the palladium-catalysed amination of aryl chlorides using ligands **6a–c**[a]

Entry	L	Aryl chloride	Amine	Time [h]	Conversion [%][b]
1	**6a**			6	44
2	**6b**			6	62
3	**6c**			6	97
5	**6a**			1	72
6	**6b**			1	87
7	**6c**			1	77
9	**6a**			1	64
10	**6b**			1	76
11	**6c**			1	73
13	**6a**			6	52
14	**6b**			6	89
15	**6c**			6	100

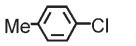
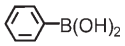
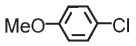
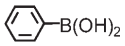
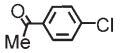
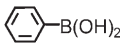
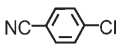
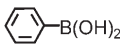
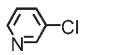
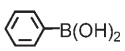
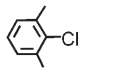
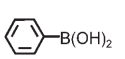
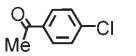
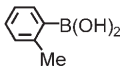
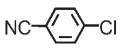
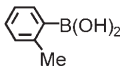
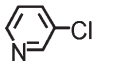
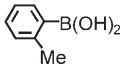
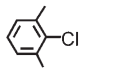
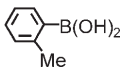
[a] *Reaction conditions:* 1.0 equiv. of Ar-Cl, 1.1 equiv. of amine, 1.4 equiv. of NaO-*t*-Bu, 0.5 mol% $Pd_2(dba)_3$, 2.5 mol% **6a–c**, toluene, 100 °C.

[b] Conversions determined by GC analysis of the reaction mixture and based on aryl chloride. Average of three runs.

ies a moderately hindered, more challenging combination was examined; the reaction between 2-methylphenylboronic acid and 1-chloro-2,6-dimethylbenzene. Gratifyingly, Pd(0)/**6a** catalysed this reaction at 80 °C to give 85% conversion after 16 h, which is a significant improvement on the corresponding system derived from **1** which required 17 h to reach 88% conversion at 100 °C.[3c] Within this limited study KITPHOS monophosphine **6a** appears to be the ligand of choice for sterically more demanding substrate combinations while **6b** is more efficient for the less hindered substrates.

In conclusion, we have developed a modular and tunable family of biaryl-like monophosphines KITPHOS that are operationally straightforward to prepare, relatively inexpensive and air-stable and which form highly active catalysts for the amination and Suzuki coupling of a range of aryl chlorides. Comparative catalyst testing revealed that for the majority of substrate combinations tested this new system either

Table 4. Palladium-catalysed Suzuki–Miyaura coupling of aryl chlorides using ligands **6a** and **6b**.[a,b]

Entry	L	Aryl chloride	Boronic acid	Time [h]	Temperature [°C]	Conversion [%][c]
1[a]	**6a**			6	80	84
2[a]	**6b**			6	80	98
3[a]	**6a**			6	80	84
4[a]	**6b**			6	80	88
5[b]	**6a**			6	40	61
6[b]	**6b**			6	40	100
7[b]	**6a**			6	40	87
8[b]	**6b**			6	40	>99
9[b]	**6a**			6	50	96
10[b]	**6b**			6	50	100
11[a]	**6a**			6	60	83
12[a]	**6b**			6	60	78
13[b]	**6a**			6	50	>99
14[b]	**6b**			6	50	96
15[b]	**6a**			6	40	>99
16[b]	**6b**			6	40	>99
17[b]	**6a**			6	50	98
18[b]	**6b**			6	50	100
19[a]	**6a**			16	80	85
20[a]	**6b**			16	80	52

[a] *Reaction conditions:* 1.0 equiv. of Ar-Cl, 1.5 equiv. of $ArB(OH)_2$, 2.0 equiv. of K_3PO_4, 1.0 mol% $Pd(OAc)_2$, 2.5 mol% **6a** or **6b**, toluene (2 mL).

[b] 1.0 equiv. of Ar-Cl, 1.5 equiv. of $ArB(OH)_2$, 3.0 equiv. of KF, 1.0 mol% $Pd(OAc)_2$, 2.5 mol% **6a** or **6b**, THF (2 mL).

[c] Conversions determined by GC analysis of the reaction mixture and based on aryl chloride. Average of three runs.

competes with or outperforms its well-established biaryl monophosphine counterpart. Further studies are currently underway to (i) optimise catalyst performance, (ii) explore the substrate scope and applications of this new class of phosphine, particularly with respect to more challenging transformations, (iii) develop a structure-activity relationship by varying the substitution pattern of the biaryl-like aryl ring, the nature of the anthracene fragment and the phosphino group and (iv) develop a chiral version of KITPHOS for use in asymmetric catalysis.

Experimental Section

General Experimental Procedure for the Synthesis of Monophosphine Oxides 5a–c

1-Alkynylphosphine oxide **4a–c** (4.00 mmol) and anthracene (1.07 g, 6.00 mmol) were mixed in a flask which was gradually heated to 220 °C using a Wood's metal bath. The temperature was then lowered to 200 °C and the mixture heated for a further 12 h. The resulting dark solid residue was purified by column chromatography eluting with CH_2Cl_2/ethyl acetate (3:2) to afford **5a–c** as off-white solids in 80% (1.57 g, **5a**), 83% (1.73, **5b**) and 24% (0.51 g, **5c**) yield.

General Experimental Procedure for the Reduction of Monophosphine Oxides 5a–c

A flame-dried Schlenk flask was charged with **5a–c** (1.34 mmol), toluene (25 mL), and triethylamine (7.5 mL, 53.6 mmol). Trichlorosilane (1.35 mL, 13.4 mmol) was added slowly and the mixture heated at 110 °C for 3 days. The reaction mixture was diluted with diethyl ether (20 mL) and added slowly to a mixture of ice (10 g) and 20% aqueous NaOH (20 mL). After stirring vigorously at room temperature for 30 min, the organic layer was removed and the aqueous phase extracted with diethyl ether (3×30 mL). The organic fractions were combined, washed with saturated $NaHCO_3$ (2×20 mL), water (2×20 mL) and brine (2×20 mL), dried over $MgSO_4$, filtered and the solvent removed under vacuum. The product was purified by column chromatography eluting with hexane/ethyl acetate (9:1) to afford **6a–c** as spectroscopically pure white solids in 69% (0.44 g, **6a**), 67% (0.455 g, **6b**) and 65% (0.45 g, **6c**) yield. In each case a spectroscopically and analytically pure sample was obtained by slow diffusion of a chloroform solution layered with methanol at room temperature.

Supporting Information

General comments, synthesis and characterisation data for alkynylphosphine oxides **4a–c**, synthesis and characterisation data for monophosphine oxides **5a–c**, reduction of biaryl diphosphines **5a–c** and characterisation data for **6a–c**, general procedure for the amination of aryl halides, general proce-

dures for the Suzuki–Miyaura coupling of aryl chlorides, and ^{1}H, ^{31}P and ^{13}C NMR spectra for compounds **4a–c**, **5a–c** and **6a–c** are available as Supporting Information.

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