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Palladium dichloride adduct of *N,N*-bis-(diphenylphosphanylmethyl)-2-aminopyridine: synthesis, structure and catalytic performance in the decarboxylative cross-coupling of 4-picolinic acid with aryl bromide†

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Reaction of $PdCl_2$ with *N,N*-bis-(diphenylphosphanylmethyl)-2-aminopyridine (bdppmapy) afforded a mononuclear complex [(bdppmapy)$PdCl_2$] (**1**). Compound **1** was characterized by elemental analysis, IR, ^1H, ^{13}C and ^{31}P NMR, electrospray ion mass spectra (ESI-MS) and X-ray single crystal crystallography. The Pd(II) center in **1** is chelated by bdppmapy, showing a *cis*-square planar geometry. With the assistance of additive Cu_2O, complex **1** exhibited good catalytic activity toward the decarboxylative cross-coupling reactions between 4-picolinic acid and aryl bromides. In the presence of only 2 mol% catalyst, a family of 4-aryl-pyridines could be isolated in up to 83% yield.

Introduction

In recent years, the palladium-catalyzed C–C coupling reactions have attracted considerable attention because of their application in the formation of a large range of new organic compounds with straightforward procedures.[1] As an expansion of the traditional C–C coupling reactions, efforts to achieve higher yields, better selectivity and more friendly environmental effects have led to exploration of new substrates[2] containing aryl cyanides,[2a] aryl acids,[2b,c] aryl esters,[2d] as well as activated C–H simple[2e,f] or substituted arenes such as anilides,[2g,h] aryl pyridine,[2i,j] fluoroarenes[2k,l] and phenols.[2m] Recently, the decarboxylative coupling reaction has been proved to be effective in refraining from stoichiometric organometallic reagents and to be less polluting as it usually produces CO_2 instead of toxic metal salts.[3] In this area, Myers,[4] Gooßen,[5] Liu,[6] Su,[7] and Larrosa[8] have achieved some exciting breakthroughs. Among them, the most common substrates were benzoic acid and substituted aryl acids, whereas a very limited number of examples were reported to use heteroarylcarboxylic acids such as pyridine-, thiophene- and furan-based carboxylic acids.[9] For instance, Wu developed a novel synthetic route to 2-aryl- and hetero-aryl-pyridines with up to 75% yields by the coupling of 2-picolinic acid with aryl- and heteroarylbromides using 5 mol% $PdCl_2$.[10] Considering that 4-aryl-pyridines are quite popular in some natural products, medicines and organic ligands,[11] it is of importance to investigate the decarboxylative coupling reaction between 4-picolinic acid and aryl halides.

On the other hand, organic ligands can play a crucial role in associating the Pd salts to catalyze the C–C coupling reactions as well as decarboxylative cross-coupling reactions to improve the yields and selectivity.[4b,5c,6b,7b] Up to now, several types of ligands such as N-donor ligands,[5a,e,f] mono-phosphine ligands[7c] and bi-phosphine ligands[12] have been introduced into various decarboxylative reaction systems. A catalytic system with both 1,10-phenanthroline and bi-phosphine ligands was reported by Gooßen to simplify the synthetic methodology of azomethines and ketones *via* one-pot decarboxylative cross-coupling reactions of α-oxo carboxylates, amines and aryl halides with yields up to 85%.[13] However, in the case of hybrid P–N ligands, although they have shown excellent performance in some C–C cross-coupling reactions,[14] their catalytic activity toward the decarboxylative cross-coupling reactions has been rarely reported to date. In addition,

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Cu(I) compounds may exert an important impact on such a decarboxylative reaction because it assists the decarboxylation process *via* the coordination of Cu(I) and the carboxylic group.[5a] Homo-coupling reactions have always occurred, which caused some trouble in optimizing the reaction conditions.[15] Therefore the introduction of a pyridyl group into the phosphine ligands might be helpful in preventing the homo-coupling reactions.

We have been engaged in the synthesis and reactivity of metal complexes derived from multiple phosphine and hybrid P–N ligands.[16] Some hybrid phosphine–pyridyl (P–N) ligands such as *N*-diphenylphosphanylmethyl-4-aminopyridine (dppmapy) and *N*,*N*-bis-(diphenylphosphanylmethyl)-2-aminopyridine (bdppmapy) were used to react with Cu(I) and Ag(I) to produce a family of Cu(I) and Ag(I) coordination polymers with interesting structures.[16c,d,f] The bdppmapy ligand has a pyridyl group in its structure. When $PdCl_2$ reacted with bdppmapy, it simply formed a mononuclear complex [(bdppmapy)$PdCl_2$] (**1**). Could complex **1** show catalytic activity toward decarboxylative cross-coupling reactions? Could bdppmapy prevent the homo-coupling reactions? With these two questions in mind, we performed the decarboxylative cross-coupling reactions of 4-picolinic acid and aryl bromide catalyzed by **1**, Cu_2O, and K_2CO_3. A set of 4-aryl-pyridines were isolated in good yields. The results showed that bdppmapy was effective in preventing the homo-coupling reactions and complex **1** was efficient in catalyzing such a cross-coupling reaction. Herein we report its synthesis, structural characterization and catalytic performance in the decarboxylative cross-coupling reactions of 4-picolinic acid and aryl bromide.

Experimental section

General procedures

The ligand bdppmapy was prepared according to a literature method.[17] Other chemicals were obtained from commercial sources and used as received. All reactions and manipulations were carried out under an oxygen-free nitrogen atmosphere with standard Schlenk techniques. Solvents were dried and degassed before use. The NMR spectra were recorded at room temperature on a Varian UNITY-400 (400 MHz) spectrometer with $CDCl_3$ or DMSO-d_6 as a solvent. Chemical shifts are quoted relative to tetramethylsilane (TMS) and solvent signals. Elemental analyses for C, H, and N were performed on a Carlo-Erbo CHNO-S microanalyzer. The IR spectra (KBr disc) were recorded on a Nicolet MagNa-IR550 FT-IR spectrometer (4000–400 cm^{-1}). Electrospray ion mass spectra (ESI-MS) were recorded on an Agilent 1200/6200 mass spectrometer. GC measurements were recorded on an Agilent 7820A Gas Chromatograph with an Agilent HP-5 chromatographic column and N_2 as the mobile phase. The LC-MS were recorded in a Rapid Resolution HT-3 chromatographic column on an Agilent 1260 Infinity Liquid Chromatograph with a 6120 Quadrupole Mass Spectrometer and MeCN as the mobile phase.

Synthesis

[(bdppmapy)$PdCl_2$] (1). To a solution of bdppmapy (491 mg, 1.0 mmol) in CH_2Cl_2–CH_3CN (5 mL/5 mL) was added $PdCl_2$ (178 mg, 1.0 mmol). The mixture was stirred for 5 min. The resulting pale yellow solution was then covered by acetonitrile (2 mL) and diethyl ether (20 mL). Yellow rhombic crystals of **1**·MeCN were afforded after one hour. The crystals were further dried *in vacuo* to give pure **1**. Yield: 630 mg (94%). Anal. calcd for $C_{33}H_{31}Cl_2N_3P_2Pd$: C, 55.91; H, 4.41; N, 5.93. Found: C, 55.76; H, 4.44; N, 5.44%. IR (KBr disk): 3421 (m), 3049 (s), 2967 (s), 2891 (s), 1593 (w), 1566 (m), 1471 (w), 1435 (w), 1309 (s), 1296 (m), 1224 (w), 1162 (s), 1099 (w), 998 (s), 864 (w), 782 (s), 770 (s), 751 (m), 729 (m), 705 (m), 692 (w), 669 (m), 626 (s), 533 (m) cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6, ppm): δ 7.98 (t, J = 8.8 Hz, 8H), 7.81 (d, J = 4.8 Hz, 1H), 7.57 (t, J = 7.2 Hz, 4H), 7.50 (t, J = 7.2 Hz, 8H), 7.20 (t, J = 7.2 Hz, 1H), 6.50 (m, 2H), 5.04 (s, 4H). ^{13}C NMR (400 MHz, DMSO-d_6, ppm): δ 155.9, 146.4, 137.3, 134.3, 131.4, 128.2, 114.0, 106.8, 54.8. ^{31}P NMR (400 MHz, DMSO-d_6, ppm): δ 9.37 (m).

X-ray structure determination

The measurements were made on a Agilent Xcalibur CCD X-ray diffractometer using graphite monochromated Mo-K_α (λ = 0.71073 Å) radiation. A single crystal of **1**·MeCN was obtained directly from the above preparation and mounted in a capillary and measured at room temperature. The program CrysAlisPro (Agilent Technologies, Ver. 1.171.35.21, 2012) was used for the refinement of cell parameters and the reduction of collected data, while absorption corrections (multi-scan) were applied. The reflection data were also corrected for Lorentz and polarization effects.

The crystal structure of **1**·MeCN was solved by direct methods and refined on F^2 by full-matrix least-squares methods with the SHELX-97 program package.[18] All non-H atoms were refined anisotropically. All H atoms were placed in geometrically idealized positions (C–H = 0.97 Å for methyl groups, C–H = 0.98 Å for methylene groups and C–H = 0.94 Å for pyrazolyl groups) and constrained to ride on their parent atoms with $U_{iso}(H) = 1.2U_{eq}(C)$. A summary of key crystallographic information is given in Table 1.

Typical procedure for the decarboxylative cross-coupling reactions

A solution containing $PdCl_2$ (178 mg) and bdppmapy (491 mg) in *N*,*N*-dimethylacetamide (DMA) (10 mL) was prepared as the catalyst. The decarboxylative cross-coupling reactions were carried out in a 25 mL tube equipped with a stirring bar. The catalyst solution (0.08 mL, 2%) was loaded into the tube with 4-picolinic acid (**2**, 0.4 mmol), aryl bromides (**5**, 0.6 mmol), Cu_2O (0.6 mmol), K_2CO_3 (1.2 mmol) and 1,2-dimethoxyethane (DME) (1.4 mL)–DMA (0.32 mL)–DMSO (0.2 mL). The tube was sealed and stirred at 130 °C for 24 h. After cooling to room temperature, the resulting mixture was diluted with 10 mL ethyl ether and then filtered. The filtrate was washed with saturated NaCl solution (30 mL). The organic phase was dried over

Table 1 Crystal data and structure refinement parameters for **1**·MeCN

Formula	$C_{31}H_{28}C_{l2}N_2P_2Pd$
Formula weight	708.05
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	9.5873(19)
b/Å	27.125(5)
c/Å	13.096(3)
β/°	110.38(3)
V/Å^3	3192.6(11)
D_c/g cm^{-3}	1.475
Z	4
μ (Mo-K$_\alpha$)/mm^{-1}	0.876
F(000)	1440
Total reflections	13 814
Unique reflections	5625
No. of observations	4647
No. of parameters	371
R_{int}	0.0310
R^a	0.0337
wR^b	0.0682
GOF^c	1.036

^{a} $R = ||F_o| - |F_c||/|F_o|$. ^{b} $wR = \{w(F_o^2 - F_c^2)^2/w(F_o^2)^2\}^{1/2}$. ^{c} GOF = $\{w((F_o^2 - F_c^2)^2)/(n-p)\}^{1/2}$, where n = number of reflections and p = total number of parameters refined.

Mg_2SO_4 and concentrated *in vacuo*. The residue was then purified by chromatography on silica gel to provide the corresponding product.

4-(2,4-Dimethoxyphenyl)-pyridine (4a).[19] The typical procedure using 4-pyridinyl acid (0.4 mmol) and 2,4-dimethoxy bromobenzene (0.6 mmol) was performed. After extraction and concentration, the reaction mixture was purified by column chromatography on silica gel (5% diethyl ether–petroleum ether) to afford **4a** as a white solid (67 mg, 78% yield).

2-(2,4-Dimethoxyphenyl)-pyridine (4b).[20] The typical procedure using 2-pyridinyl acid (0.4 mmol) and 2,4-dimethoxy bromobenzene (0.6 mmol) was performed. After extraction and concentration, the reaction mixture was purified by column chromatography on silica gel (50% diethyl ether–petroleum ether) to afford **4b** as a white solid (21 mg, 25% yield).

4-(4-Methoxylphenyl)-pyridine (6a).[21] The typical procedure using 4-pyridinyl acid (0.4 mmol) and 4-methoxy bromobenzene (0.6 mmol) was preformed. After extraction and concentration, the reaction mixture was purified by column chromatography on silica gel (20% diethyl ether–petroleum ether) to afford **6a** as a white solid (61 mg, 83% yield).

4-(3-Methoxylphenyl)-pyridine (6b).[21] The typical procedure using 4-pyridinyl acid (0.4 mmol) and 3-methoxy bromobenzene (0.6 mmol) was performed. After extraction and concentration, the reaction mixture was purified by column chromatography on silica gel (20% diethyl ether–petroleum ether) to afford **6b** as a white solid (40 mg, 54% yield).

4-(2-Methoxylphenyl)-pyridine (6c).[22] The typical procedure using 4-pyridinyl acid (0.4 mmol) and 2-methoxy bromobenzene (0.6 mmol) was performed. After extraction and concentration, the reaction mixture was purified by column chromatography on silica gel (20% diethyl ether–petroleum ether) to afford **6c** as a colorless oil (53 mg, 71% yield).

4-(2-Methylphenyl)-pyridine (6d).[23] The typical procedure using 4-pyridinyl acid (0.4 mmol) and 1-bromo-2-methylbenzene (0.6 mmol) was performed. After extraction and concentration, the reaction mixture was purified by column chromatography on silica gel (30% diethyl ether–petroleum ether) to afford **6d** as a colorless oil (43 mg, 63% yield).

4-(3-Methylphenyl)-pyridine (6e).[24] The typical procedure using 4-pyridinyl acid (0.4 mmol) and 1-bromo-3-methylbenzene (0.6 mmol) was performed. After extraction and concentration, the reaction mixture was purified by column chromatography on silica gel (30% diethyl ether–petroleum ether) to afford **6e** as a white solid (29 mg, 42% yield).

4-(4-Methylphenyl)-pyridine (6f).[21] The typical procedure using 4-pyridinyl acid (0.4 mmol) and 1-bormo-4-methylbenzene (0.6 mmol) was performed. After extraction and concentration, the reaction mixture was purified by column chromatography on silica gel (15% diethyl ether–petroleum ether) to afford **6f** as a white solid (51 mg, 75% yield).

4-(2,4,6-Trimethyl-phenyl)-pyridine (6g).[25] The typical procedure using 4-pyridinyl acid (0.4 mmol) and 1-bromo-2,4,6-trimethylbenzene (0.6 mmol) was performed. After extraction and concentration, the reaction mixture was purified by column chromatography on silica gel (25% diethyl ether–petroleum ether) to afford **6g** as a white solid (32 mg, 40% yield).

4-(3,5-Dimethylphenyl)-pyridine (6h).[26] The typical procedure using 4-pyridinyl acid (0.4 mmol) and 1-bormo-3,5-dimethylbenzene (0.6 mmol) was performed. After extraction and concentration, the reaction mixture was purified by column chromatography on silica gel (25% diethyl ether–petroleum ether) to afford **6h** as a white solid (32 mg, 44% yield).

4-(4-Fluoro-phenyl)-pyridine (6i).[27] The typical procedure using 4-pyridinyl acid (0.4 mmol) and 1-bromo-4-fluorobenzene (0.6 mmol) was performed. After extraction and concentration, the reaction mixture was purified by column chromatography on silica gel (10% diethyl ether–petroleum ether) to afford **6i** as a white solid (34 mg, 48% yield).

4-(Pyridin-4-yl)-benzonitrile (6j).[28] The typical procedure using 4-pyridinyl acid (0.4 mmol) and 4-bromobenzonitrile (0.6 mmol) was performed. After extraction and concentration, the reaction mixture was purified by column chromatography on silica gel (25% diethyl ether–petroleum ether) to afford **6j** as a white solid (42 mg, 58% yield).

4-(4-Trifluoromethylphenyl)-pyridine (6k).[29] The typical procedure using 4-pyridinyl acid (0.4 mmol) and 1-bromo-4-(trifluoromethyl)benzene (0.6 mmol) was performed. After extraction and concentration, the reaction mixture was purified by column chromatography on silica gel (20% diethyl ether–petroleum ether) to afford **6k** as a white solid (39 mg, 44% yield).

4-Biphenyl-4-yl-pyridine (6l).[30] The typical procedure using 4-pyridinyl acid (0.4 mmol) and 4-bromobiphenyl (0.6 mmol) was performed. After cooling down, a white solid was precipitated in the bottom of the tube. The solid was filtrated and washed with water and then dissolved in diethyl ether (20 mL). After concentration, the reaction mixture was purified by column chromatography on silica gel (pure diethyl ether) to afford **6l** as a white solid (57 mg, 62% yield).

4-(Naphthalen-1-yl)-pyridine (6m).[31] The typical procedure using 4-pyridinyl acid (0.4 mmol) and 1-bromonaphthalene (0.6 mmol) was performed. After extraction and concentration, the reaction mixture was purified by column chromatography on silica gel (30% diethyl ether–petroleum ether) to afford **6m** as a white solid (56 mg, 68% yield).

4-(Naphthalen-2-yl)-pyridine (6n).[32] The typical procedure using 4-pyridinyl acid (0.4 mmol) and 2-bromonaphthalene (0.6 mmol) was performed. After extraction and concentration, the reaction mixture was purified by column chromatography on silica gel (45% diethyl ether–petroleum ether) to afford **6n** as a white solid (44 mg, 54% yield).

Results and discussion

Synthetic and spectral aspects

Treatment of $PdCl_2$ with equimolar bdppmapy in CH_2Cl_2–MeCN followed by a standard workup produced yellow crystals of **1** in 94% yield (Scheme 1). Compound **1** is relatively stable towards air and moisture, and soluble in common solvents such as CH_2Cl_2, CH_3CN, *N*,*N*-dimethylformamide (DMF) and DME. The elemental analysis was consistent with its formula. In the IR spectra, the stretching vibrations at 1435 and 998 cm^{-1} are assignable to the coordinated P–C groups[33] of **1** and the stretching vibrations of phenyl groups and the pyridine group of ligands are located at 1592, 1566 and 1471 cm^{-1}. The ^1H NMR spectra of **1** (Fig. S1a, ESI†) in DMSO-d_6 at room temperature showed signals of diphenylphosphine groups including three triplets at 7.98, 7.57 and 7.51 ppm. The pyridine group could be recognized by the signals including a doublet at 7.81 ppm, a triplet at 7.20 ppm and a multiplet at 6.49 ppm. The signals of methylene groups were located at 5.04 ppm as a singlet. The ^{13}C NMR spectra of **1** (Fig. S1b, ESI†) showed three signals at 128–135 ppm for the diphenylphosphine groups, five resonances at 106.8, 114.0, 137.3, 146.4 and 155.9 ppm for the pyridine group and one signal at 54.8 ppm for the methylene groups. In the ^{31}P NMR spectra of **1** (Fig. S1c, ESI†), one signal at 9.37 ppm was clearly observed.

Compound **1**·MeCN crystallizes in the monoclinic space group $P2_1/c$, and its asymmetric unit has one discrete [(bdppmapy)$PdCl_2$] molecule and one MeCN solvent molecule. The Pd(II) atom is coordinated by the two P atoms from a bdppmapy molecule and two chlorides, thereby forming a *cis* square-planar coordination geometry (Fig. 1). The mean Pd–Cl bond length (2.3519(10) Å *vs.* 2.2514(10) Å) is close to those found in [(dppp)$PdCl_2$] (2.355(2) Å *vs.* 2.247(3) Å, dppp = 1,3-bis(diphenylphosphino)-propane)[34] and [(dppf)$PdCl_2$] (2.348(2) Å *vs.* 2.291(3) Å, dppf = 1,1′-bis(diphenylphosphino)-ferrocene).[35] The bite angle P(1)–Pd(1)–P(2) (93.57(3)°) of **1** is in between that of [(dppp)$PdCl_2$] (90.58(3)°) and that of [(dppf)-$PdCl_2$] (99.10(4)°). The pyridyl group of the bdppmapy molecule remains intact.

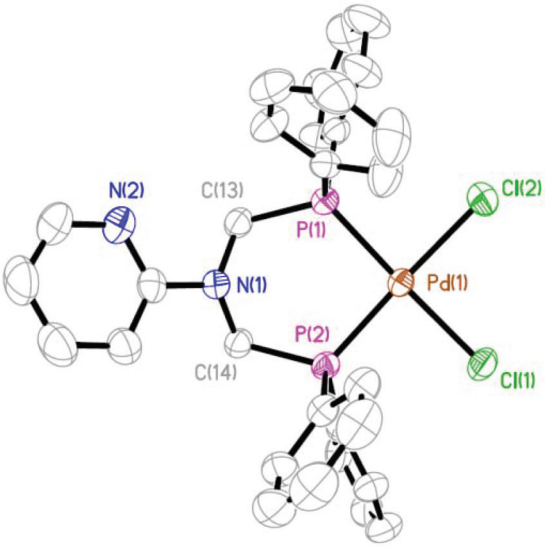
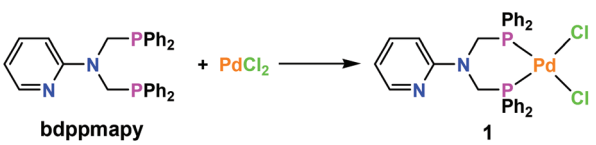


Fig. 1 View of the molecular structure of **1** with a labelling scheme and 50% thermal ellipsoids. All H atoms and the MeCN solvent molecule were omitted for clarity. Selected bond lengths (Å) and angles (°): Pd(1)–Cl(1) 2.3583(8), Pd(1)–Cl(2) 2.3455(10), Pd(1)–P(1) 2.2512(8), Pd(1)–P(2) 2.2516(10), Cl(1)–Pd(1)–Cl(2) 89.72(3), Cl(1)–Pd(1)–Cl(2) 89.72(3), Cl(1)–Pd(1)–P(2) 88.22(3), Cl(2)–Pd(1)–P(1) 88.46(3), P(1)–Pd(1)–P(2) 93.57(3).

As we know, in the many catalytic systems, the catalysts are usually added as the mixture of $PdCl_2$ and phosphine ligands, whereas the exact structures are often left unexplored. Thus at the beginning, we employed a solution of $PdCl_2$ and bdppmapy (molar ratio 1 : 1) in DMA as the catalyst. Parallel experiments proved that similar catalytic activities could be achieved by using this solution or a solution of the powder of complex **1** in DMA. In order to confirm the existence of the same species in both DMA solutions, we measured their positive-ion ESI mass spectra (Fig. S2, ESI†). In both cases, strong signals at m/z = 631.05 for $[(bdppmapy)PdCl]^+$ and m/z = 718.11 for $[(bdppmapy)PdCl + DMA]^+$ (Fig. S3, ESI†) were observed, indicating that the two cations might be the major species in the catalyst solutions. Thus complex **1** may not be necessarily isolated before catalysis reactions and a mixture of $PdCl_2$ and bdppmapy (molar ratio = 1 : 1) could be used directly in the catalysis reactions.

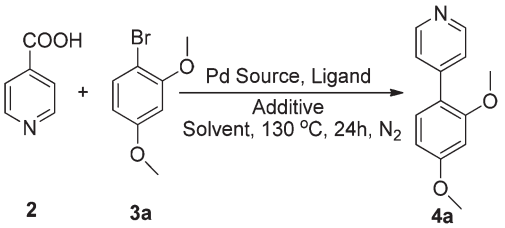
Decarboxylative cross-coupling reaction

Considering the electronic effects, a model decarboxylative cross-coupling reaction between 2,4-dimethoxy bromobenzene (**3a**) and 4-picolinic acid (**2**) was performed to produce 1-(4-pyridyl)-2,4-dimethoxybenzene (**4a**). Eight phosphine ligands including tricyclohexylphosphine (PCy_3), triphenylphosphine (PPh_3), bis(diphenylphosphino)methane (dppm), 1,2-bis-(diphenylphosphino)ethane (dppe), dppp, 2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl (Xphos), 2,2′-bis(diphenyl-



Scheme 1 Synthesis of **1**.

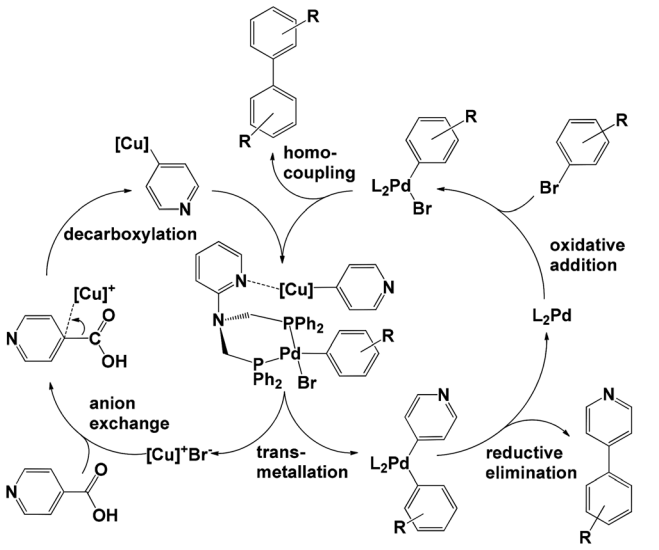
Table 2 Screening of Pd sources, ligands and additives for the cross-coupling of 4-picolinic acid and 2,4-dimethoxy bromobenzene[a]



Entry	Pd source	Ligand	Additive	Yield[b] (%)
1	$PdCl_2$	PCy_3	Cu_2O	20
2	$PdCl_2$	PPh_3	Cu_2O	24
3	$PdCl_2$	dppm	Cu_2O	35
4	$PdCl_2$	dppe	Cu_2O	38
5	$PdCl_2$	dppp	Cu_2O	48
6	$PdCl_2$	XPhos	Cu_2O	15
7	$PdCl_2$	BINAP	Cu_2O	32
8	$PdCl_2$	bdppmapy	Cu_2O	78
9	$Pd(OAc)_2$	bdppmapy	Cu_2O	Trace
10	$Pd(TFA)_2$	bdppmapy	Cu_2O	44
11	$Pd(acac)_2$	bdppmapy	Cu_2O	12
12	$PdCl_2$	bdppmapy	Ag_2O	Trace
13	$PdCl_2$	bdppmapy	Ag_2CO_3	Trace
14	$PdCl_2$	bdppmapy	CuI	36
15	$PdCl_2$	bdppmapy	CuBr	20
16	$PdCl_2$	bdppmapy	CuCl	Trace
17	$PdCl_2$	bdppmapy	$CuCO_3$	Trace

[a] Reaction conditions: **2** (0.4 mmol), **3a** (0.6 mmol), Pd salts (5 mol%), ligand (10 mol% for entries 1–2 and 6 mol% for entries 3–17), K_2CO_3 (1.2 mmol), DME (1.4 mL), DMA (0.4 mL) and DMSO (0.2 mL), additive (0.6 mmol), 130 °C, 24 h, a nitrogen atmosphere, 150 mg 3 Å MS. [b] Isolated yields based on **2**.

phosphino)-1,1′-binaphthalene (BINAP) and bdppmapy were selected to form the key Pd intermediate during the transmetallation and reductive elimination steps of the decarboxylative coupling reaction. The results (Table 2, entries 1–8) revealed that the bi-phosphine ligands (dppm, dppe, BINAP and dppp) were more efficient than the monophosphine ligands (PCy_3, XPhos and PPh_3) in this system, whereas the P–N hybrid ligand bdppmapy achieved the best yield of 78% (entry 8). Such a difference between phosphine ligands may depend on the reaction mechanism. Due to the widely established decarboxylative cross-coupling mechanism[5a] which may contain a decarboxylation cycle and a cross-coupling cycle, the transmetallation step connecting the two cycles may require the [Cu] intermediate to approach the [Pd] intermediate. For the decarboxylation cycle, its reaction rate is well known to be affected by the choice of solvents.[7b,8g,i] As a homo-coupling reaction (Ullmann type reaction) is likely to occur on the [Pd] intermediate,[15] it has been proved to be a competitive reaction in such a cross-coupling reaction. The acceleration of decarboxylative coupling should be more apparent. In the case of bdppmapy, as shown in Scheme 2, it is supposed that the uncoordinated pyridyl group of bdppmapy in the [Pd] intermediate may coordinate at the [Cu] intermediate to form a Cu–Pd heterometallic complex. The transmetallation step is more easy to accomplish as the Cu and the Pd centers are drawn



Scheme 2 The proposed reaction mechanism.

closer. Thus the cross-coupling reaction could be achieved. In contrast, when other phosphine ligands were introduced into such a system (entries 1–5), more homo-coupling products such as 1,1′-biphenyl and 2,2′,4,4′-tetramethoxy-biphenyl were isolated (yield 20–50%).

Larrosa[2k] and Liu[6a] once reported that the Density Functional Theory (DFT) calculation could be used to study the mechanism of coupling reactions. Thus we employed a simple DFT method[36] to calculate the energy level between the [Cu] or [Pd] intermediate and the supposed Cu–Pd heterometallic complex (ESI†). As shown in Fig. S4 (ESI†), the binding of the pyridyl group in bdppmapy to the [Cu] intermediate may lead to a decrease of 20.8 kcal mol^{-1} in Gibbs free energy. The 4-pyridyl group in the [Cu] intermediate may be rotated to form the supposed Cu–Pd heterometallic complex with a subsequent increase of 12.3 kcal mol^{-1} in Gibbs free energy, which is quite low and may be easily achieved by the heating of the reaction system. The potential energy surface obtained herein suggested that the closer approaching of the [Cu] intermediate and the [Pd] intermediate would be energy profitable for the transmetallation step, which may finally lead to the acceleration of the decarboxylative cross-coupling reaction.

The Pd salts and the Cu(I)/Ag(I) additives were also optimized to achieve better yields. Four Pd(II) salts including $PdCl_2$, $Pd(OAc)_2$, $Pd(TFA)_2$ (TFA = trifluoroacetate) and $Pd(acac)_2$ (acac = 2,4-acetylacetonate) were investigated (Table 2, entries 6–9). It seems that all O-containing anions are less efficient in this catalytic reaction. The reason is that, relative to the Pd–Cl bond, the Pd–O bond is stronger and is not easily broken to form the oxidative addition [Pd] intermediate, which is one of the key steps of the cross-coupling cycle. Thus $PdCl_2$ exhibited the best catalytic performance among the four Pd(II) salts. In addition, Cu(I) or Ag(I) salts are essential during the decarboxylation cycle as they assist the carboxylic acid to eliminate the carboxyl group.[5c] These salts could be tuned to affect both homo- and cross-coupling reactions. In this work, seven

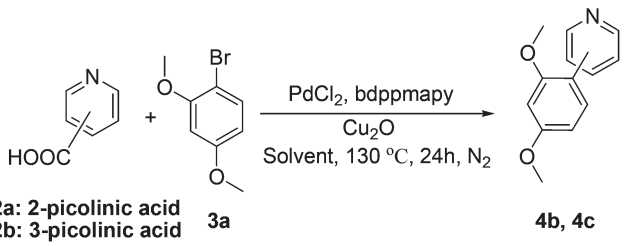
Table 3 Screening of the solvent, base and temperature for the cross-coupling of 4-picolinic acid and 2,4-dimethoxy bromobenzene[a]

Entry	Base	Solvent	Temp. (°C)	Catalyst loading (mol%)	Yield[b] (%)
1	K_2CO_3	DMA	130	5	48
2	K_2CO_3	NMP	130	5	34
3	K_2CO_3	DMSO	130	5	Trace
4[c]	K_2CO_3	DME	120	5	22
5	K_2CO_3	DMF	130	5	29
6	K_2CO_3	DMA–DMSO (3 : 1)	130	5	36
7	K_2CO_3	DMA–DME (7 : 3)	130	5	40
8	K_2CO_3	DMA–DME–DMSO (3 : 3 : 1)	130	5	55
9	K_2CO_3	DMA–DME–DMSO (7 : 2 : 1)	130	5	78
10	$CeCO_3$	DMA–DME–DMSO (7 : 2 : 1)	130	5	Trace
11	Na_2CO_3	DMA–DME–DMSO (7 : 2 : 1)	130	5	30
12	NEt_3	DMA–DME–DMSO (7 : 2 : 1)	130	5	N.R.
13	K_3PO_4	DMA–DME–DMSO (7 : 2 : 1)	130	5	58
14	K_2CO_3	DMA–DME–DMSO (7 : 2 : 1)	120	5	46
15	K_2CO_3	DMA–DME–DMSO (7 : 2 : 1)	110	5	15
16	K_2CO_3	DMA–DME–DMSO (7 : 2 : 1)	140	5	Trace
17	K_2CO_3	DMA–DME–DMSO (7 : 2 : 1)	140	1	54
18	K_2CO_3	DMA–DME–DMSO (7 : 2 : 1)	140	2	78
19	K_2CO_3	DMA–DME–DMSO (7 : 2 : 1)	140	1	75

[a] Reaction conditions: **2** (0.4 mmol), **3a** (0.6 mmol), a solution of $PdCl_2$ (178 mg) and bdppmapy (492 mg) in DMA (10 mL) as the catalyst, base (1.2 mmol), solvent (2 mL), Cu_2O (0.6 mmol), 24 h, a nitrogen atmosphere, 150 mg 3 Å MS. [b] Isolated yields based on **2**. [c] Pure DME could not reach 130 °C.

Cu(I) or Ag(I) salts including Ag_2O, Ag_2CO_3, Cu_2O, CuI, CuBr, CuCl and $CuCO_3$ (Table 2, entries 6 and 10–15) as additives were introduced into the reaction system. With the optimized Pd source ($PdCl_2$) and the phosphine ligand (bdppmapy), Cu_2O clearly exhibited the best activity. Ag(I) salts were not suitable in this reaction due to the trace yields of the expected products, though some Pd/Ag co-catalyzed decarboxylative cross-coupling reactions were also reported.[7b–d]

The model reaction was further explored to optimize the solvent, base, reaction temperature and catalyst loading. As indicated in entries 1–7 in Table 3, analogous reactions in pure DMA, *N*-methylpyrrolidone (NMP), DMSO, DME and DMF as well as mixed DMA–DMSO could only give low yields. Su *et al.* reported that during the decarboxylative cross-coupling reactions, addition of DME into the polar solvents such as NMP and DMF could improve the yield of **4a** by nearly 30%, and prevent the formation of side-products derived from proto-decarboxylation.[7b,8g] Therefore we introduced DME into our system to make a mixture of DMA–DME–DMSO = 7 : 2 : 1. The best yield (78%) was attained (entry 9) in such a mixed solvent system. In this solvent system, several bases were also examined (entries 9–13), and K_2CO_3 was proved to be most suitable. In addition, the temperature was examined in the range of 110–140 °C (entries 9 and 14–16). Obviously, when the temperature was raised, the yield of **4a** increased from 15% (110 °C) to 78% (130 °C), but decreased to a trace at 140 °C, which may be due to the decomposition of the phosphine ligand at higher temperature.[16e] The influence of the catalyst loading was also explored (entries 9 and 17–19). The yield of **4a** increased to 78% when the catalyst loading was enhanced from 1% to 2%. However, the yield of **4a** could not be improved using 5 mol% and 10 mol% of catalyst loading. To this end, the optimized reaction conditions could be fixed as follows: $PdCl_2$ (2 mol%), bdppmapy (2 mol%) in DMA–DME–DMSO = 7 : 2 : 1 (2 mL) and in the presence of K_2CO_3 (1.2 mmol) and Cu_2O (0.6 mmol) at 130 °C. In order to explore the reactivity of this catalytic system, 2- and 3-picolinic acids (**2a** and **2b**) were introduced into the model system to react with 2,4-dimethoxy bromobenzene under the optimized conditions (Scheme 3). Low yields (25% for **4b** and ~0% for **4c**) were obtained, which implied that bdppmapy in this system was highly selective for 4-picolinic acid. To this end, only 4-picolinic acid was utilized in this work.



Scheme 3 Reactions of 2- and 3-picolinic acids with 2,4-dimethoxy bromobenzene. Reaction conditions: $PdCl_2$ (2 mol%), bdppmapy (2 mol%), K_2CO_3 (1.2 mmol) and Cu_2O (0.6 mmol) in DMA–DME–DMSO = 7 : 2 : 1 (2 mL), a nitrogen atmosphere, 150 mg 3 Å MS, 24 h at 130 °C.

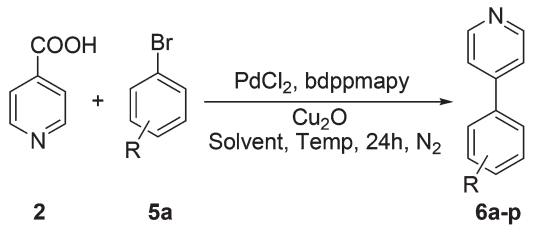
The substituent effects of aryl bromides on this reaction were investigated under the above optimized conditions (Table 4). The *p*-substituted aryl bromides provided the desired products in moderate yields no matter whether the substituted groups were electron-donating groups or electron withdraw groups (**3a**, **5a–5c**, **5j**, **5k**). In the case of strong electron withdrawing groups like CF_3 and F, lower yields were obtained (**5j**, **5k**). Furthermore, the positions of aryl bromides did affect the reactions. Those with *m*-substituted aryl bromides had low yields while those with *o*-mono-substituted aryl bromides offered good yields (**5b–5e**). However reactions with the *o*-di-substituted aryl bromide gave a negative result in the same yield with *m*-disubstituted aryl bromide because the steric effect of bdppmapy was the key factor in this situation (Table 4, **5g**, **5h**). To expand the scope of this reaction, we employed some other substrates (**5l–5n**), which gave medium yields (**6i–6n**).

As an expansion of this work, chlorobenzene was used to replace aryl bromides. It was quite inactive and only a trace product (**6o**) was monitored by LC-MS in the reaction (**5o** in Table 4). In addition, iodobenzene was also employed and the yield of **6o** was found to be only 18% as a large number of by-products were observed which might be due to the homo-coupling of iodobenzene (**5p** in Table 4).

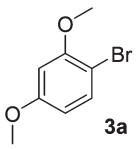
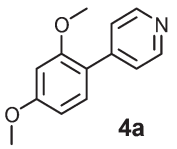
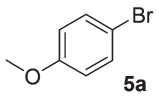
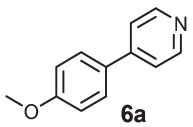
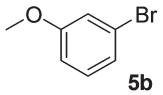
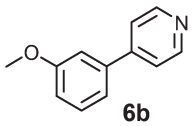
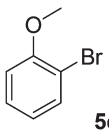
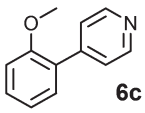
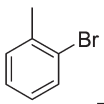
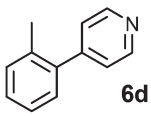
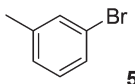
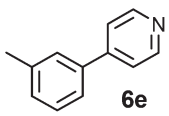
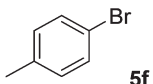
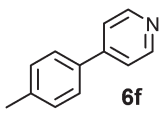
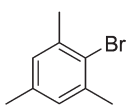
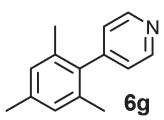
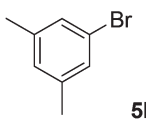
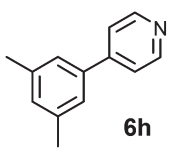
Conclusions

In the work reported here, we demonstrated the design, synthesis and structural characterization of a new mononuclear

Table 4 The palladium-catalyzed decarboxylative cross-coupling reactions of 4-picolinic acid with aryl bromides[a]



2 5a 6a-p

Substrate	Product	Yield[b] (%)
 3a	 4a	78
 5a	 6a	83
 5b	 6b	54
 5c	 6c	71
 5d	 6d	63
 5e	 6e	42
 5f	 6f	75
 5g	 6g	40
 5h	 6h	44

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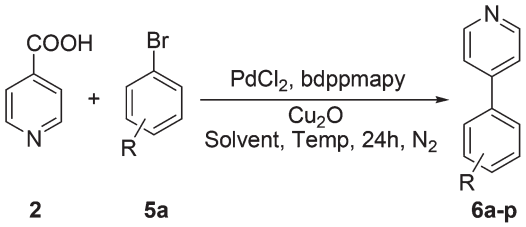
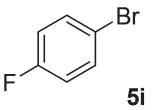
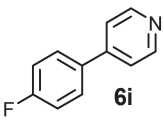
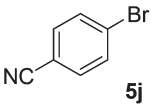
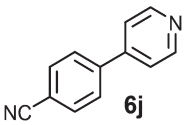
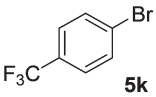
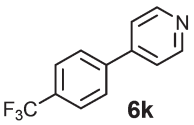
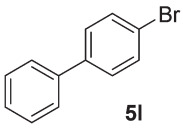
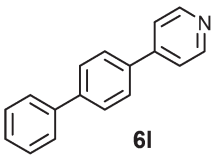
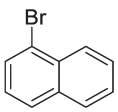
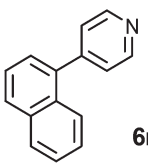
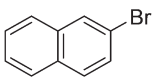
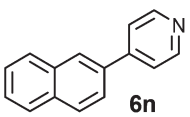
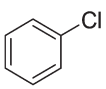
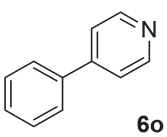
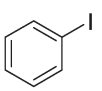
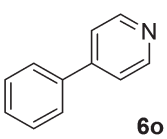


2 5a 6a-p

Substrate	Product	Yield[b] (%)
 5i	 6i	48
 5j	 6j	58
 5k	 6k	44
 5l	 6l	62
 5m	 6m	68
 5n	 6n	54
 5o	 6o	Trace
 5p	 6o	18

[a] Reaction conditions: **2** (0.4 mmol), **5a** (0.6 mmol), a 0.08 mL solution of $PdCl_2$ (178 mg) and bdppmapy (492 mg) in DMA (10 mL), K_2CO_3 (1.2 mmol), DME (1.4 mL), DMA (0.32 mL) and DMSO (0.2 mL), Cu_2O (0.6 mmol), 24 h, a nitrogen atmosphere, 150 mg 3 Å MS. [b] Isolated yields based on **2**.

Pd(II) complex **1**. Complex **1**, assisted by a Cu_2O additive, was employed as an efficient catalyst for the decarboxylative cross-coupling reactions of 4-picolinic acid with aryl bromides. Under the optimized conditions, the yield of the resulting 4-aryl-pyridines (compound **6a**) was up to 83% with only 2% catalyst loading. The method reported in this work provides an effective route to synthesize 4-aryl-pyridines from commercially economical and stable 4-picolinic acid. It is anticipated that more P–N hybrid ligands could be used to design and synthesize other Pd(II) complexes with new structures and higher catalytic activities. Further studies in this direction are currently underway.

Acknowledgements

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References

1 A. De Meijere and F. Diederich, *Metal-catalyzed Cross-Coupling Reactions*, Wiley-VCH, Weinheim, 2004.

2 (*a*) J. A. Miller, *Tetrahedron Lett.*, 2001, **42**, 6991; (*b*) B. M. Trost, *Catalysis: Unlimited Frontiers – Our Early Personal Journey into the World of Palladium*, Springer, 2013; (*c*) N. Rodríguez and L. J. Gooßen, *Chem. Soc. Rev.*, 2011, **40**, 5030; (*d*) M. Á. Fernández-Ibañez, B. Maciá, D. A. Alonso and I. M. Pastor, *Molecules*, 2013, **18**, 10108; (*e*) R. Li, L. Jiang and W. Lu, *Organometallics*, 2006, **25**, 5973; (*f*) L. Zhou and W. Lu, *Organometallics*, 2012, **31**, 2124; (*g*) G. Song, F. Wang and X. Li, *Chem. Soc. Rev.*, 2012, **41**, 3651; (*h*) C. Liu, H. Zhang, W. Shi and A. W. Lei, *Chem. Rev.*, 2011, **111**, 1780; (*i*) Y. Matsuura, M. Tamura, T. Kochi, M. Sato, N. Chatani and F. Kakiuchi, *J. Am. Chem. Soc.*, 2007, **129**, 9858; (*j*) F. Juliá-Hernández, M. Simonetti and I. Larrosa, *Angew. Chem., Int. Ed.*, 2013, **52**, 11458; (*k*) P. Ricci, K. Kramer, X. C. Cambeiro and I. Larrosa, *J. Am. Chem. Soc.*, 2013, **135**, 13258; (*l*) N. Kuhl, M. N. Hopkinson, J. Wencel-Delord and F. Glorius, *Angew. Chem., Int. Ed.*, 2012, **51**, 10236; (*m*) X. Chen, K. M. Engle, D. H. Wang and J. Q. Yu, *Angew. Chem., Int. Ed.*, 2009, **48**, 5094; (*n*) R. Jana, T. P. Pathak and M. S. Sigman, *Chem. Rev.*, 2011, **111**, 1417.

3 M. Nilsson, *Acta Chem. Scand.*, 1966, **20**, 423.

4 (*a*) A. G. Myers, D. Tanaka and M. R. Mannion, *J. Am. Chem. Soc.*, 2002, **124**, 11250; (*b*) D. Tanaka, S. P. Romeril and A. G. Myers, *J. Am. Chem. Soc.*, 2005, **127**, 10323.

5 (*a*) L. J. Gooßen, G. J. Deng and L. M. Levy, *Science*, 2006, **313**, 662; (*b*) L. J. Gooßen, P. P. Lange, N. Rodríguez and C. Linder, *Chem. – Eur. J.*, 2010, **16**, 3906; (*c*) L. J. Gooßen, N. Rodríguez, P. P. Lange and C. Linder, *Angew. Chem., Int. Ed.*, 2010, **49**, 1111; (*d*) L. J. Gooßen, N. Rodríguez, B. Melzer, C. Linder, G. J. Deng and L. M. Levy, *J. Am. Chem. Soc.*, 2007, **129**, 4824; (*e*) L. J. Gooßen, F. Rudolphi, C. Oppel and N. Rodríguez, *Angew. Chem., Int. Ed.*, 2008, **47**, 3043; (*f*) L. J. Gooßen, B. Zimmermann, C. Linder, N. Rodríguez, P. P. Lange and J. Hartung, *Adv. Synth. Catal.*, 2009, **351**, 2667.

6 (*a*) R. Shang, Y. Fu, J. B. Li, S. L. Zhang, Q. X. Guo and L. Liu, *J. Am. Chem. Soc.*, 2009, **131**, 5738; (*b*) R. Shang, Y. Fu, Y. Wang, Q. Xu, H. Z. Yu and L. Liu, *Angew. Chem., Int. Ed.*, 2009, **48**, 9350.

7 (*a*) Z. J. Fu, S. J. Huang, W. P. Su and M. C. Hong, *Org. Lett.*, 2010, **12**, 4992; (*b*) P. Hu, Y. Shang and W. Su, *Angew. Chem., Int. Ed.*, 2012, **51**, 5945; (*c*) P. Hu, M. Zhang, X. M. Jie and W. P. Su, *Angew. Chem., Int. Ed.*, 2012, **51**, 227; (*d*) H. Q. Zhao, Y. Wei, J. Xu, J. A. Kan, W. P. Su and M. C. Hong, *J. Org. Chem.*, 2011, **76**, 882.

8 (*a*) C. Arroniz, A. Ironmonger, G. Rassias and I. Larrosa, *Org. Lett.*, 2013, **15**, 910; (*b*) J. Cornella, H. Lahlali and I. Larrosa, *Chem. Commun.*, 2010, **46**, 8276; (*c*) J. Cornella and I. Larrosa, *Synthesis*, 2012, **44**, 653; (*d*) J. Cornella, P. F. Lu and I. Larrosa, *Org. Lett.*, 2009, **11**, 5506; (*e*) J. Cornella, M. Righi and I. Larrosa, *Angew. Chem., Int. Ed.*, 2011, **50**, 9429; (*f*) J. Cornella, M. Rosillo-Lopez and I. Larrosa, *Adv. Synth. Catal.*, 2011, **353**, 1359; (*g*) J. Cornella, C. Sanchez, D. Banawa and I. Larrosa, *Chem. Commun.*, 2009, 7176; (*h*) R. Grainger, A. Nikmal, J. Cornella and I. Larrosa, *Org. Biomol. Chem.*, 2012, **10**, 3172; (*i*) P. F. Lu, C. Sanchez, J. Cornella and I. Larrosa, *Org. Lett.*, 2009, **11**, 5710.

9 (*a*) O. Baudoin, *Angew. Chem., Int. Ed.*, 2007, **46**, 1373; (*b*) P. Forgione, M. C. Brochu, M. St-Onge, K. H. Thesen, M. D. Bailey and F. Bilodeau, *J. Am. Chem. Soc.*, 2006, **128**, 11350; (*c*) D. K. Rayabarapu and J. A. Tunge, *J. Am. Chem. Soc.*, 2005, **127**, 13510.

10 X. Li, D. Zou, F. Leng, C. Sun, J. Li, Y. S. Wu and Y. J. Wu, *Chem. Commun.*, 2013, **49**, 312.

11 (*a*) C. G. Arena and G. Aricò, *Curr. Org. Chem.*, 2010, **14**, 546; (*b*) G. D. Henry, *Tetrahedron*, 2004, **60**, 6043; (*c*) M. Schlosser and F. Mongin, *Chem. Soc. Rev.*, 2007, **36**, 1161.

12 S. R. Waetzig and J. A. Tunge, *J. Am. Chem. Soc.*, 2007, **129**, 14860.

13 F. Collet, B. Song, F. Rudolphi and L. J. Gooßen, *Eur. J. Org. Chem.*, 2011, 6486.

14 (*a*) R. Ghosh and A. Sarkar, *J. Org. Chem.*, 2010, **75**, 8283; (*b*) R. Pratap, D. Parrish, P. Gunda, D. Venkataraman and M. K. Lakshman, *J. Am. Chem. Soc.*, 2009, **131**, 12240; (*c*) J. L. Serrano, L. García, J. Pérez, E. Pérez, J. García, G. Sánchez, P. Sehnal, S. De Ornellas, T. J. Williams and I. J. S. Fairlamb, *Organometallics*, 2011, **30**, 5095; (*d*) E. Ullah, J. McNulty, C. Kennedy and A. Robertson, *Org. Biomol. Chem.*, 2011, **9**, 4421.

15 A. Jutand and A. Mosleh, *J. Org. Chem.*, 1997, **62**, 261–274.
16 (*a*) D. X. Li, Z. G. Ren, H. F. Wang and J. P. Lang, *Inorg. Chem. Commun.*, 2011, **14**, 1665; (*b*) N. Y. Li, Z. G. Ren, D. Liu, J. Wang, M. Dai, H. X. Li and J. P. Lang, *Inorg. Chem. Commun.*, 2009, **12**, 1031; (*c*) N. Y. Li, Z. G. Ren, D. Liu, R. X. Yuan, L. P. Wei, L. Zhang, H. X. Li and J. P. Lang, *Dalton Trans.*, 2010, **39**, 4213; (*d*) Z. G. Ren, S. Sun, M. Dai, H. F. Wang, C. N. Lu, J. P. Lang and Z. R. Sun, *Dalton Trans.*, 2011, **40**, 8391; (*e*) X. Y. Wu, Z. G. Ren and J. P. Lang, *Dalton Trans.*, 2014, **43**, 1716; (*f*) J. H. Yang, X. Y. Wu, R. T. He, Z. G. Ren, H. X. Li, H. F. Wang and J. P. Lang, *Cryst. Growth Des.*, 2013, **13**, 2124.
17 E. C. Yang, W. Feng, J. Y. Wang and X. J. Zhao, *Inorg. Chim. Acta*, 2010, **363**, 308.
18 (*a*) G. M. Sheldrick, *SHELXS-97, Program for Solution of Crystal Structures*, University of Göttingen, Göttingen, Germany, 1997; (*b*) G. M. Sheldrick, *SHELXL-97, Program for Refinement of Crystal Structures*, University of Göttingen, Göttingen, Germany, 1997.
19 C. Betschart, K. Hayakawa, O. Irie, J. Sakaki, G. Iwasaki, R. Lattmann, M. Missbach and N. Teno, *PCT Int. Appl.*, WO03020721A1, 2003.
20 G. R. Dick, E. M. Woerly and M. D. Burke, *Angew. Chem., Int. Ed.*, 2012, **51**, 2667.
21 A. R. Katritzky, H. Beltrami and M. P. Sammes, *J. Chem. Soc., Perkin Trans. 1*, 1980, 2480.
22 D. D. Weller and G. R. Luellen, *Tetrahedron Lett.*, 1981, **22**, 4381.
23 J. Srogl, W. S. Liu, D. Marshall and L. S. Liebeskind, *J. Am. Chem. Soc.*, 1999, **121**, 9449.
24 S. P. Gromov and N. A. Kurchavov, *Russ. Chem. Bull.*, 2003, **52**, 1606.
25 G. Häfelinger and G. Ott, *Liebigs Ann. Chem.*, 1984, 1605.
26 S. A. Hauser, V. Korinth, E. Herdtweck, M. Cokoja, W. A. Herrmann and F. E. Kühn, *Eur. J. Inorg. Chem.*, 2010, 4083.
27 O. P. Shkurko, S. G. Baram and V. P. Mamaev, *Chem. Heterocycl. Compd. (N. Y., NY, U. S.)*, 1983, **19**, 60.
28 S. T. Lin, F. M. Yang, D. Liang and M. J. Shiao, *J. Chin. Chem. Soc. (Taipei, Taiwan)*, 1997, **44**, 527.
29 E. Le Gall, C. Gosmini, J. Y. Nédélec and J. Périchon, *Tetrahedron*, 2001, **57**, 1923.
30 I. Yamaguchi, A. Kado, T. Fukuda, H. Fukumoto, T. Yamamoto and M. Sato, *Eur. Polym. J.*, 2010, **46**, 1119.
31 G. A. Molander and F. Beaumard, *Org. Lett.*, 2010, **12**, 4022.
32 A. K. Gupta, H. Ila and H. Junjappa, *Tetrahedron*, 1990, **46**, 2561.
33 D. Dolphin and A. E. Wick, *Tabulation of Infrared Spectral Data*, John Wiley & Sons, New York, 1977.
34 W. L. Steffen and G. J. Palenik, *Inorg. Chem.*, 1976, **15**, 2432.
35 T. Hayashi, M. Konishi, Y. Kobori, M. Kumada, T. Higuchi and K. Hirotsu, *J. Am. Chem. Soc.*, 1984, **106**, 158.
36 (*a*) A. M. Echavarren and D. J. Cárdenas, *Metal-Catalyzed Cross-Coupling Reactions*, Wiley-VCH, Weinheim, Germany, 2004; (*b*) L. Q. Xue and Z. Y. Lin, *Chem. Soc. Rev.*, 2010, **39**, 1692–1705; (*c*) L. Q. Xue, W. P. Su and Z. Y. Lin, *Dalton Trans.*, 2010, **39**, 9815; (*d*) L. Q. Xue, W. P. Su and Z. Y. Lin, *Dalton Trans.*, 2011, **40**, 11926; (*e*) Y. Jiang, Y. Fu and L. Liu, *Sci. China: Chem.*, 2012, **55**, 2057.