



Amination and Suzuki coupling reactions catalyzed by palladium complexes coordinated by cobalt-containing monodentate phosphine ligands with bis-trifluoromethyl substituents on bridged arylolethynyl: Observation of some unusual metal-containing compounds

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ARTICLE INFO

Article history:

Received 23 July 2008

Received in revised form 30 September 2008

Accepted 7 October 2008

Available online 14 October 2008

Keywords:

Suzuki–Miyaura cross-coupling reaction

Amination reaction

Phosphine ligand

Electron-withdrawing substituent

Palladium–cobalt bond

Palladium cluster

ABSTRACT

Two cobalt-containing bulky monodentate phosphines $\{[(\mu\text{-PPh}_2\text{CH}_2\text{PPh}_2)\text{Co}_2(\text{CO})_4][(\mu,\eta\text{-}^t\text{Bu})_2\text{PC}\equiv\text{C}Ar]\}$ (**4cm**: Ar = 3-CF₃C₆H₄; **4cmm**: Ar = 3,5-(CF₃)₂C₆H₃) were prepared from the reaction of Co₂(CO)₆(μ-PPh₂CH₂PPh₂) (**3**) with each corresponding alkynes (^tBu)₂PC≡CAr. Both compounds were converted to their oxidized forms $\{[(\mu\text{-PPh}_2\text{CH}_2\text{PPh}_2)\text{Co}_2(\text{CO})_4][(\mu,\eta\text{-}^t\text{Bu})_2\text{P}(=\text{O})\text{C}\equiv\text{C}Ar]\}$ (**4cmO**: Ar = 3-CF₃C₆H₃; **4cmmO**: Ar = 3,5-(CF₃)₂C₆H₃) in the presence of oxide. Further reactions of **4cm** and **4cmm** with Pd(OAc)₂ gave palladium complexes $\{[(\mu\text{-PPh}_2\text{CH}_2\text{PPh}_2)\text{Co}_2(\text{CO})_4][(\mu,\eta\text{-}^t\text{Bu})_2\text{PC}\equiv\text{C}(Ar)\text{-}\kappa\text{C}^1)]\text{Pd}(\mu\text{-OAc})\}$ **5cm** (Ar = 3-CF₃C₆H₃) and **5cmm** (Ar = 3,5-(CF₃)₂C₆H₃), respectively. By contrast, reactions of **4cm** and **4cmm** with Pd(COD)Cl₂ gave products, $[(\mu\text{-P,P-PPh}_2\text{CH}_2\text{PPh}_2)\text{Co}_2(\text{CO})_3\text{-}(\mu\text{-CO})\{\mu,\eta\text{-}^t\text{Bu})_2\text{PC}\equiv\text{C}Ar\}]\text{-PdCl}_2$ **8cm** and **8cmm**, respectively, with unique bonding modes. Several crystallines of $[(\text{4cm})_2\text{Pd}_3(\mu\text{-Cl})(\mu\text{-CO})_2(\mu\text{-Cl})_2]$ (**9**) were obtained along with crystallines of **8cm** during the crystallization process. The crystal structures of all three compounds, **4cmmO**, **8cmm** and **9** were determined by single-crystal X-ray diffraction methods. Fair to excellent efficiencies were observed for employing **4cmm**/palladium salt as catalytic precursor in amination as well as in Suzuki coupling reactions.

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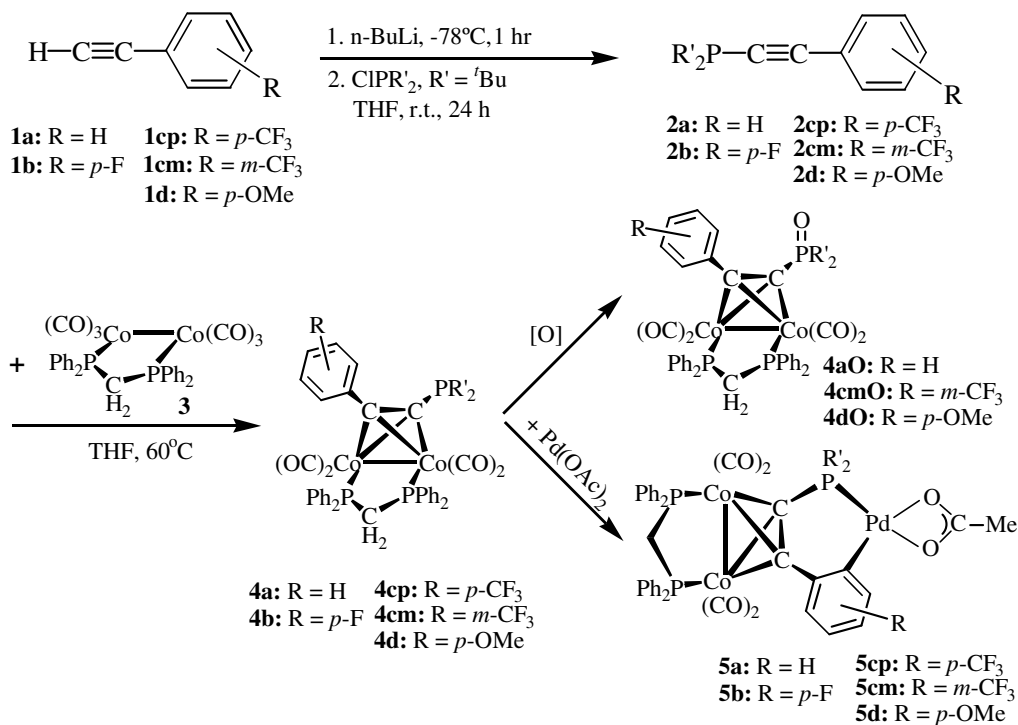
1. Introduction

For the past thirty years, the transition metal-catalyzed coupling reactions have experienced the renaissance since the first discovery of the Ullmann reaction one century ago [1]. The study on the scope of the ligand assisted transition metal-catalyzed cross-coupling reaction is prevailing not only in academic research but also industrial interests [2]. With various metals being employed in coupling reactions, palladium probably is the most frequently chosen transition metal due mostly to its excellent catalytic efficiency in this type of reactions. Among all the factors which might affect the catalytic performance of the reaction, a well-chosen ligand, beyond doubt, is indispensable to the success of a palladium-catalyzed cross-coupling reaction [3]. As a result, numerous efforts have been dedicated to search for more efficient and versatile ligands which might be adaptable to various styles of coupling reactions. For a long while, organic phosphines and their derivatives have been the most favorite ligands mainly due to the readiness of tuning the

ligands' electronic and steric character by simply varying their substituents [4–15]. Yet, only a few types of transition metal-containing phosphine ligands had been prepared and their roles as ligands had been examined [11–18]. We had reported the ready preparation of a new class of metal-containing phosphines $\{[(\mu\text{-PPh}_2\text{CH}_2\text{PPh}_2)\text{Co}_2(\text{CO})_4][(\mu,\eta\text{-}^t\text{Bu})_2\text{PC}\equiv\text{C}(R\text{-C}_6\text{H}_4)]\}$ (**4b**: R = *p*-F; **4cp**: R = *p*-CF₃; **4cm**: R = *m*-CF₃; **4d**: R = *p*-OMe) by the procedures as shown in Scheme 1. Firstly, alkynyl phosphines, $[(^t\text{Bu})_2\text{PC}\equiv\text{C}(\text{C}_6\text{H}_4\text{R})]$ (**2b**: R = *p*-F; **2cp**: R = *p*-CF₃; **2cm**: R = *m*-CF₃; **2d**: R = *p*-OMe) were prepared by the procedures modified from literature [19]. Then, the newly prepared **2a–d** were allowed to react with (μ-PPh₂CH₂PPh₂)Co₂(CO)₆ (**3**) to form the corresponding **4a–d**. The rules of abbreviation for the reaction involved species throughout the article are **a**, **b**, **c**, **d** for substituent R = H, F, CF₃, OMe, respectively; **p**, **m**, **o** for substituent located on *para*, *meta*, *ortho*-position etc. This arrangement naturally leads this type of phosphines to bulkiness, which is a character obviously advantageous to the last step of the catalytic cycle – the reductive elimination process. Their roles as legitimate and active ligands in palladium-catalyzed cross-coupling reactions have been evaluated and proven to be effective [20–28]. Fair to excellent performances of these ligands were shown in various kinds of reactions.

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Scheme 1. Preparations of cobalt-containing monodentate phosphines **4a–d** and palladium complexes **5a–d**.

Our previous work also reported the preparation of 4-chelated palladium complex, **5**. An unusual palladium complex $\{[(\mu\text{-PPh}_2\text{CH}_2\text{PPh}_2)\text{Co}_2(\text{CO})_4][(\mu, \eta\text{-}(\text{tBu})_2\text{PC}\equiv\text{C}(\text{p-R-C}_6\text{H}_3)\text{-}\kappa\text{C}^1)]\text{Pd}(\mu\text{-OAc})\}$ (**5a**: R = H) was prepared from the reaction of the cobalt-containing bulky phosphine **4a** with Pd(OAc)₂. As disclosed by its crystal structure, during the formation of **5a** a process of orthometallation occurred accompanied by the release of one equivalent of acetic acid [28–30]. The acetate chelates to the palladium metal in a η^2 -mode. By the same token, several **5a**-related palladium complexes $\{[(\mu\text{-PPh}_2\text{CH}_2\text{PPh}_2)\text{Co}_2(\text{CO})_4][(\mu, \eta\text{-}(\text{tBu})_2\text{PC}\equiv\text{C}(\text{R-C}_6\text{H}_3)\text{-}\kappa\text{C}^1)]\text{Pd}(\mu\text{-OAc})\}$ (**5b**: R = *p*-F; **5cp**: R = *p*-CF₃; **5cm**: R = *m*-CF₃; **5d**: R = *p*-OMe) were prepared from the reactions of their corresponding cobalt-containing phosphines (**4b**: R = *p*-F; **4cp**: R = *p*-CF₃; **4cm**: R = *m*-CF₃; **4d**: R = *p*-OMe) with Pd(OAc)₂. The charge of the palladium metal remains +2 in **5**. It is generally accepted that the Pd(II) complex shall be reduced to Pd(0) complex before the oxidative addition process taking place. It was proposed that in Suzuki–Miyaura reaction the reduction might be proceeded via the attack of borate, PhB(OH)₃[−], on the palladium center in basic medium [31]. Our previous works had demonstrated that the Suzuki–Miyaura cross-coupling reaction of aryl halide and organoboronic acid could be carried out catalytically either by *in vitro* **4**/Pd(OAc)₂ or by isolated and purified **5** [29]. In addition, the latter had also been employed in the amination reactions of substituted bromobenzenes and morpholine. Fair to excellent results were obtained [28].

As revealed in crystal structure of **5cm**, orthometallation took place between palladium and arylolefinyl and formed the Pd–C_{aryl} bond. The bulky substituent, –CF₃, stays away from the palladium metal center thus to prevent the severe steric hindrance [32]. It is believed that by deliberately placing two –CF₃ groups on the two *meta*-positions of the arylolefinyl group the orthometallation process shall be prevented due to its severe steric hindrance. The bonding mode of the newly-made ligand to palladium moiety shall be quite different from that in **5** and so as its catalytic performance. Thereby, we were interested in examining the validity of this assumption. In this study, the preparation of double –CF₃ groups

substituted **4cmmm** and its application in **4cmmm**-assisted palladium-catalyzed amination and Suzuki cross-coupling reactions are presented.

2. Results and discussion

2.1. Preparation of cobalt-containing phosphine $\{[(\mu\text{-PPh}_2\text{CH}_2\text{PPh}_2)\text{Co}_2(\text{CO})_4][(\mu, \eta\text{-}(\text{tBu})_2\text{PC}\equiv\text{C}(3,5\text{-}(\text{CF}_3)_2\text{C}_6\text{H}_3))]\}$ (**4cmmm**)

A cobalt-containing phosphine **4cmmm** was prepared from the reaction of Co₂(CO)₆(dppm) (**3**) with (tBu)₂PC≡C(3,5-(CF₃)₂C₆H₃) by similar procedures as the preparation of **4cm**. The reaction was carried out in THF at 60 °C for 48 h and reddish-brown solid was yielded in about 40%. Compound **4cmmm** was characterized by spectroscopic methods such as ¹H and ³¹P NMR and mass spectrum. In the ¹H NMR spectrum of **4cmmm**, one set of multiplets appears around 3.24 ppm which is corresponding to the methylenic protons of the coordinated dppm ligand. Two sets of doublets observed at 1.26 and 1.23 ppm are assigned to the two tBu groups. The ³¹P NMR spectrum displays two singlets at 35.98 and 44.62 ppm. The former signal is assigned to the two equivalent phosphorus atoms of the coordinated dppm ligand; while the latter peak is assigned to the free phosphorus site. During the crystallization process, the **4cmmm** was converted to its oxidized form $\{[(\mu\text{-PPh}_2\text{CH}_2\text{PPh}_2)\text{Co}_2(\text{CO})_4][(\mu, \eta\text{-}(\text{tBu})_2\text{P}(=\text{O})\text{C}\equiv\text{C}\text{Ar})]\}$ (**4cmmmO**: Ar = 3,5-(CF₃)₂C₆H₃). The molecular structure of **4cmmmO** was determined by single-crystal X-ray diffraction methods (Table 1). As revealed in the ORTEP diagram as depicted in Fig. 1, a pseudo-tetrahedral core Co₂C₂ was maintained. The phosphorus atom is oxidized and located in a tetrahedral environment. This substituent, –P(=O)(tBu)₂, is kept away from the dppm thus to prevent serve steric hindrance. Two –CF₃ groups are situated in *meta*-position of the benzene ring. Compound **4cmmmO** might be prepared separately by the oxidation of **4cmmm**. Its ¹H and ³¹P NMR spectra shows similar patterns as that of **4cmmm**. One set of multiplets at 3.33 ppm is assigned to the methylenic protons of the coordinated

Table 1
Crystal data of **4cmmO**, **8cmm** and **9**.

Compound	4cmmO	8cmm	9
Formula	C ₄₇ H ₄₅ Co ₂ F ₆ O ₅ P ₃	C ₄₇ H ₄₂ Cl ₂ Co ₂ F ₆ O ₄ P ₃ Pd · 1/2H ₂ O · CH ₂ Cl ₂	C ₇₂ H ₈₈ Cl ₄ F ₁₂ O ₄ P ₄ Pd ₆ · 0.6CHCl ₃
Formula weight	1014.60	1266.81	2221.12
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>C</i> 2/ <i>c</i>
<i>a</i> (Å)	12.3394(11)	12.8018(8)	35.507(4)
<i>b</i> (Å)	16.1174(15)	25.4586(16)	9.0508(9)
<i>c</i> (Å)	24.095(2)	16.8048(10)	31.599(3)
α (°)	–	–	–
β (°)	99.970(2)	103.1870(10)	112.366(2)
γ (°)	–	–	–
<i>V</i> (Å ³)	4719.6(7)	5332.5(6)	9390.8(16)
<i>Z</i>	4	4	4
<i>D_c</i> (mg/m ³)	1.428	1.578	1.571
λ (Mo K α) (Å)	0.71073	0.71073	0.71073
μ (mm ⁻¹)	0.872	1.302	1.421
θ range (°)	1.53–26.06	1.60–26.02	2.33–26.00
Observed reflections (<i>F</i> > 4 σ (<i>F</i>))	9272	10462	9191
No. of refined parameters	586	640	496
<i>R</i> ₁ for significant reflections ^a	0.0523	0.0459	0.0485
<i>wR</i> ₂ for significant reflections ^b	0.1382	0.1191	0.1481
Goodness-of-fit (GoF) ^c	1.056	1.009	1.029

^a $R_1 = \frac{|\sum(|F_o| - |F_c|)|}{\sum F_o}$.

^b $wR_2 = \frac{\{\sum [w(F_o^2 - F_c^2)]^2\}^{1/2}}{\{\sum w(F_o^2)\}^{1/2}}$; *w* = 0.1000, 0.0690 and 0.1200 for crystal data of **4cmmO**, **8cmm** and **9**, respectively.

^c $GoF = \frac{[\sum w(F_o^2 - F_c^2)^2 / (N_{\text{refl}} - N_{\text{params}})]^{1/2}}{}$.

dppm ligand. Two sets of doublets show up at 1.39 and 1.34 ppm are corresponding to the two ¹Bu groups. In ³¹P NMR spectrum, two singlets at 35.26 and 59.55 ppm are assigned to the two equivalent phosphorus atoms of the coordinated dppm ligand and the

oxidized phosphorus atom. A significant downfield shift of the oxidized phosphine was observed.

2.2. Reactions of **4cm** and **4cmm** with Pd(OAc)₂ and Pd(COD)Cl₂

Attempts to make **4cmm** complexed palladium compounds were pursued by the reaction of **4cmm** with two palladium sources such as Pd(OAc)₂ and Pd(COD)Cl₂ (Scheme 2). Interestingly, this newly-made monodentate phosphine ligand **4cmm** shows quite dissimilar reactivities and reaction types towards different palladium salts.

In the case of reacting with Pd(OAc)₂, **4cmmO** was observed as the major product accompanied with black precipitates within one hour. The composition of the latter is believed as the aggregation of reduced Pd(0). It indicates that **4cmm** is a rather efficient reducing agent toward Pd(II) species. Obviously, the formation of **5cmm** is rather difficult because of the severe steric hindrance between the two –CF₃ groups and the surroundings of the palladium center. Nevertheless, a rather small quantity of presumably **5cmm** was observed, judging from the spectroscopic data of the product, along with large quantity of **4cmmO**. A process of orthometallation occurred during the formation of **5cmm** accompanied by the release of one equivalent of acetic acid. Another probable product might be the **4cmm** chelated palladium dimer, [(**4cmm**)₂Pd(OAc)]₂ **6cmm**. In **6cmm**, the **4cmm** plays the role as a monodentate ligand and the acetate acts as bridging ligand. Nevertheless, the formation of **6cmm** did not observe from the spectroscopic data of the product. In principle, the reaction of **4cmm** with another palladium source Pd(COD)Cl₂ might give a palladium dimer [4cmmPdCl₂]₂ **7cmm**. In **7cmm**, the two chlorides act as the bridging ligands. Compound **8cmm**, with a rather unique conformation, was observed as the major product instead. The identity of **8cmm** was confirmed further by the X-ray diffraction method. The ORTEP diagram of **8cmm** was depicted in Fig. 2. Here, the presumably monodentate phosphine ligand **4cmm**, in fact, acts as a bidentate ligand toward PdCl₂ in a rather unique way. As shown, a direct Pd–Co bond is formed accompanied with the coordination of a P → Pd dative bond (Scheme 2). In ³¹P NMR spectrum, three sets of signals at 25.74, 31.52 and 64.91 ppm, respectively, for two cobalt atoms coordinated phosphines and one palladium coordinated phos-

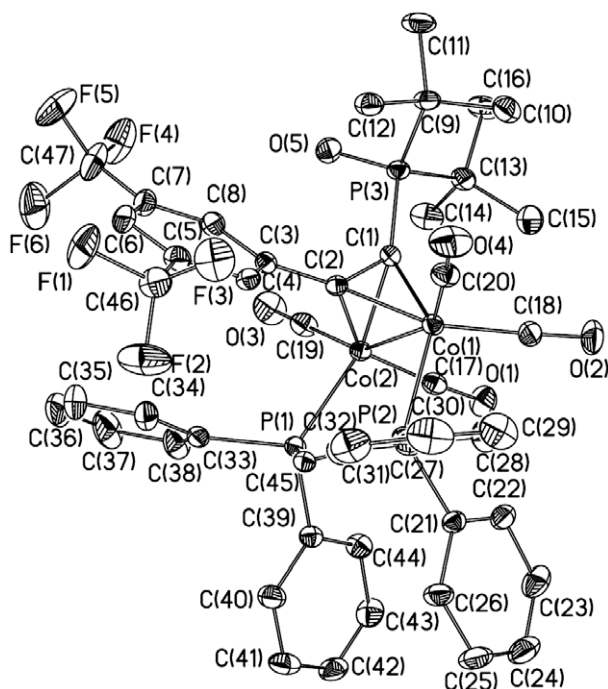
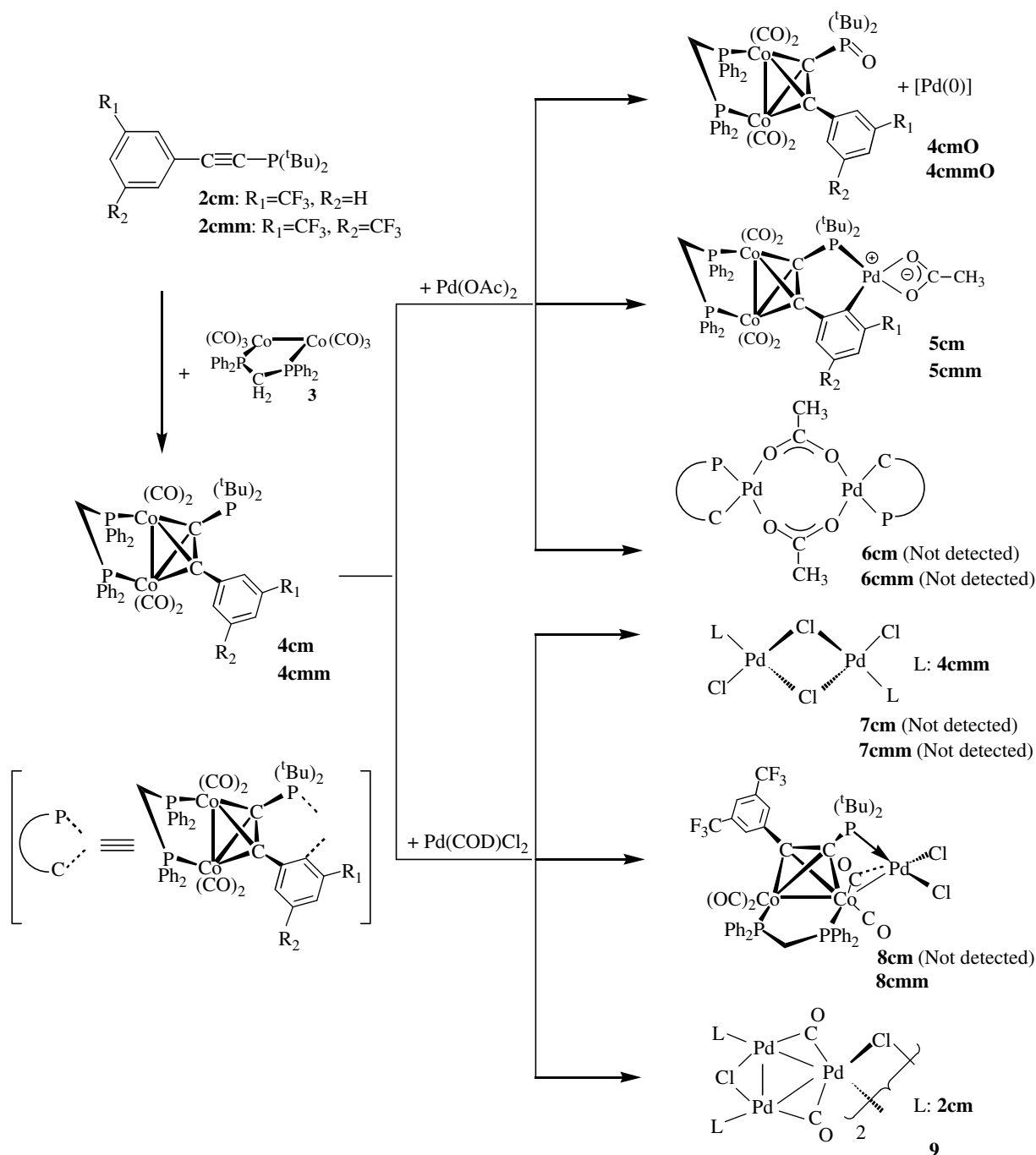


Fig. 1. ORTEP drawing of **4cmmO**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Co(1)–C(2) 1.943(4); Co(1)–C(1) 1.990(5); Co(1)–P(2) 2.2191(13); P(1)–C(45) 1.840(5); P(1)–Co(2) 2.2419(13); C(1)–C(2) 1.367(6); C(1)–P(3) 1.792(4); C(1)–Co(2) 1.977(4); Co(2)–C(2) 1.962(4); P(2)–C(45) 1.835(4); C(2)–C(3) 1.464(6); P(3)–O(5) 1.483(4); P(3)–C(9) 1.864(5); P(3)–C(13) 1.867(5); C(5)–C(46) 1.511(8); C(7)–C(47) 1.471(9); C(2)–Co(1)–C(1) 40.66(17); C(33)–P(1)–C(39) 101.1(2); C(2)–C(1)–P(3) 132.1(4); Co(2)–C(1)–Co(1) 77.36(16); C(2)–Co(2)–C(1) 40.61(17); C(27)–P(2)–C(21) 103.1(2); C(1)–C(2)–C(3) 138.6(4); O(5)–P(3)–C(1) 109.4(2); O(5)–P(3)–C(9) 109.4(2); C(1)–P(3)–C(9) 106.9(2); O(5)–P(3)–C(13) 109.7(2); C(1)–P(3)–C(13) 109.1(2); P(2)–C(45)–P(1) 107.6(2).



Scheme 2. Reactions of **4cm** and **4cmm** with $\text{Pd}(\text{OAc})_2$ and $\text{Pd}(\text{COD})\text{Cl}_2$.

phine. The significant downfield shift of the last signal indicates that it is a palladium coordinated phosphine. Similar result was obtained from our previous work in which a reaction of $[\{\mu\text{-P},\text{P}-\text{PPh}_2\text{CH}_2\text{PPh}_2\}\text{Co}_2(\text{CO})_4\{\mu\text{-PPh}_2\text{C}\equiv\text{C}(\text{O})\text{Ph}_2\}]$ (**10**) with one molar equivalent of $(\text{COD})\text{PdCl}_2$ gave a red-brown colored product, $[\{\mu\text{-P},\text{P}-\text{PPh}_2\text{CH}_2\text{PPh}_2\}\text{Co}_2(\text{CO})_3(\mu\text{-CO})\{\mu\text{-PPh}_2\text{C}\equiv\text{C}(\text{O})\text{Ph}_2\}]\text{PdCl}_2$ (**11**) [25]. As expected, the orthometallation did not take place between palladium and arylethynyl. The bulky substituents, $-\text{CF}_3$, prevent the approach of the substituted phenyl toward the metal center.

By similar procedures, the reaction of **4cm** with $\text{Pd}(\text{COD})\text{Cl}_2$ give **8cm** by judging from the spectroscopic data. Unfortunately, attempts to grow crystal for **8cm** resulted in failure. Interestingly,

small amount of red crystallines were observed during the crystallization process. The structure of this unusual compound **9** was determined by the X-ray diffraction method and its ORTEP plot was depicted in Fig. 3. As shown from the drawing, the compound can be regarded with a bow tie structure which is consisted of two triangular palladium moieties bridging by two chlorides. There are also four bridging carbonyls as well as two more chlorides are found. The bridging carbonyls shall come from the fragmented dicobalt carbonyls moiety. Unexpectedly, four phosphines, $(\text{tBu})_2\text{PC}\equiv\text{C}(3,5\text{-}(\text{CF}_3)_2\text{C}_6\text{H}_3)$, are observed as terminal ligands. These phosphines most likely are from the unreacted starting material or even the cleavage of alkyne bridging ligand from dicobalt fragment of **4cm**. The structure of a **9**-related compound,

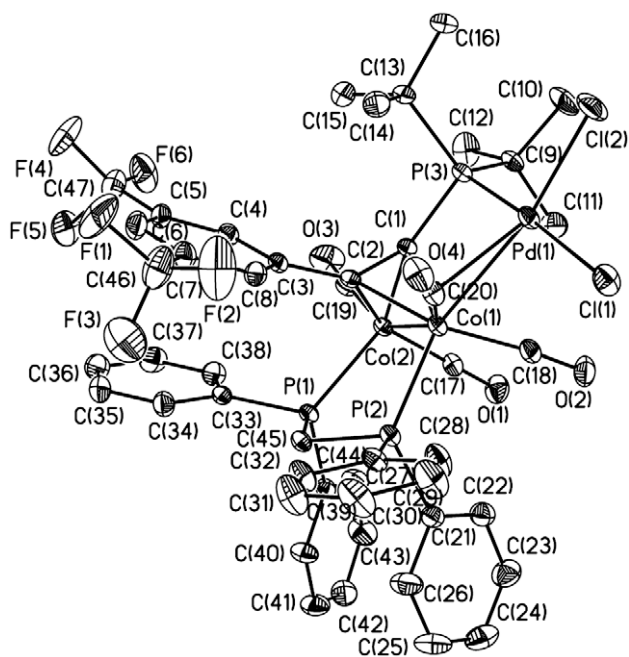


Fig. 2. ORTEP drawing of **8cmm**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Pd(1)–P(3) 2.2236(14); Pd(1)–Cl(2) 2.3209(15); Pd(1)–Cl(1) 2.4022(15); Pd(1)–C(20) 2.466(6); Pd(1)–Co(1) 2.6777(7); C(1)–C(2) 1.354(6); C(1)–P(3) 1.779(5); C(1)–Co(2) 1.924(4); C(1)–Co(1) 2.025(5); P(1)–C(45) 1.832(5); P(1)–Co(2) 2.2443(14); Co(1)–C(2) 1.978(5); Co(1)–P(2) 2.2487(14); P(2)–C(45) 1.825(5); C(2)–C(3) 1.482(7); C(2)–Co(2) 1.955(5); Cl(2)–Pd(1)–Cl(1) 90.72(6); P(3)–Pd(1)–Co(1) 78.64(4); C(20)–Pd(1)–Co(1) 40.44(14); C(2)–C(1)–P(3) 140.3(4); C(20)–Co(1)–Pd(1) 63.39(17); C(2)–Co(1)–Pd(1) 104.92(13); C(1)–Co(1)–Pd(1) 76.46(13); P(2)–Co(1)–Pd(1) 149.48(4); C(1)–C(2)–C(3) 141.1(4); C(9)–P(3)–C(13) 113.7(2); C(1)–P(3)–Pd(1) 94.49(16); P(2)–C(45)–P(1) 109.6(2); P(3)–C(1)–Co(1) 110.3(2).

12, was reported and was prepared from a rather different reaction pathway [33] (see Diagram 1).

2.3. Structural comparison of **8cmm** and **11**

The structures of **8cmm** and **11** reveal that each molecule is consisted of a Pd–Co bond and P → Pd dative bond. The structural comparison of **8cmm** and **11** are listed in Table 2. As shown, the corresponding bond lengths are similar, yet, the bond angles are varied considerably within the tetragon which is consisted of four atoms: Pd, Co(1), C(1) and P. It indicates that the shapes of these two tetragons are not quite the same. The **8cmm** is with two bridging carbonyls; only one bridging carbonyl is observed in **11** (see Diagram 2).

2.4. Applications of **4cmm**/Pd(OAc)₂ in amination reactions

As known, the performance of a successful metal-catalyzed cross-coupling reaction is governed by a number of factors [2]. By finding an optimized condition of the reaction, the effects of various bases, palladium sources, temperatures, solvents and reaction hours on the amination process employing **4cmm**/palladium salt were surveyed. Amination reactions of bromobenzene by morpholine were carried out by employing the cobalt-containing phosphine ligand **4cmm**-chelated palladium complexes as the catalyst precursors (Scheme 3). The general procedures for the catalytic reactions under investigation are shown as the follows. A suitable Schlenk tube was first charged with 1.0 mmol of arylbromide, 1.2 equivalent of morpholine, 1.4 equivalent of base, 1 ml solvent, and 1 mol% of **4cmm**/palladium salt; then, the reaction mixture

was stirred at either 60 °C or 80 °C for 4 h. Normally, an induction period is needed for the reduction of Pd(II) to Pd(0) before the reaction reaches reasonable speed.

First, the reactions using **4cmm** as a ligand, NaO^tBu/toluene and various palladium sources were carried out (Table 3). The ratio of ligand to number of palladium atom is 1:1. As shown, the best performance was obtained while using [(η³-C₃H₅)PdCl]₂ as the palladium source (Entry 1).

The amination reaction which was carried out in toluene in the presence of NaO^tBu under various [(η³-C₃H₅)PdCl]₂/**4cmm** ratios helped to determine the preferred one (Table 4). The optimum yield was achieved with [(η³-C₃H₅)PdCl]₂/**4cmm** = 1/1 (Entry 5). It indicates that **4cmm** most likely acts as a bidentate ligand and the conformation of the active species in this reaction might with a similar geometry as that of **8cmm**. As shown, the yields dropped significantly while the ratio of ligand/palladium salt close to 2. The excess amount of the bulky phosphine **4cmm** might force the formation of the palladium complex in a trans-form, *trans*-Pd(L)₂(Cl)₂. Thereby, the reaction rate was greatly retarded by catalyst in this conformation.

Reaction temperature is another factor critical for amination reaction. In general, amination reaction requires much high reaction temperature than that of Suzuki reaction. As shown in Table 5, a poor performance was observed when the reaction temperature was below 60 °C (Entry 1). However, good efficiency was reached when the reaction temperature was higher than 60 °C (Entries 2 and 3).

As it is well known in the widely accepted reaction mechanism, the deprotonation of the coordinated amine, which requires base, is essential in amination reaction. Thereby, a well-chosen base is crucial to the success of the reaction [34–37]. The influence of the base used in this reaction was examined (Table 6). As shown, the best performance was observed with NaO^tBu (Entry 1). Unexpectedly, the yield was noticeably low when a strong base such as KO^tBu was employed (Entry 2).

The solubility of the reactants and catalyst in the solvent is important to the success of the coupling reaction. The concentration of the reaction is also crucial. Subsequently, the impacts of various solvents on the reactions were evaluated. As shown in Table 7, the reaction is greatly affected by the nature of the solvent used. For instance, the coupling reaction in toluene was rather effective (Entries 4–7). However, the performance was not acceptable for the rest of solvents. The effect of the concentration of the reaction is also demonstrated. The efficiency is better for more concentrated solution (Entry 1).

It has been a common observation that in a palladium-catalyzed Suzuki coupling reaction a better conversion is achieved with aryl halides bearing an electron-withdrawing rather than an electron-donating substituent [11]. In fact, it is valid for the reaction with the oxidative addition process as the rate-determining-step (r.d.s.). Nevertheless, it may not be true for other reactions where the r.d.s. might be anything but the oxidative addition process such as Heck reaction [38–41]. As shown in Table 8, compatible performances were observed for substances with electron-donating groups (Entries 2–3). Nevertheless, steric effect plays the most critical role here (Entries 3–6).

For comparison, the catalytic efficiencies of amination reactions employing *in situ*-prepared or isolated catalytic precursors were examined. As revealed in Table 9, compatible performances were observed for all systems.

2.5. Applications of **4cmm**/Pd(OAc)₂ in Suzuki reactions

Suzuki coupling reactions were carried out *in situ* by employing the newly-made cobalt-containing phosphine ligand **4cmm** modified palladium complexes. The reaction was proceeded with

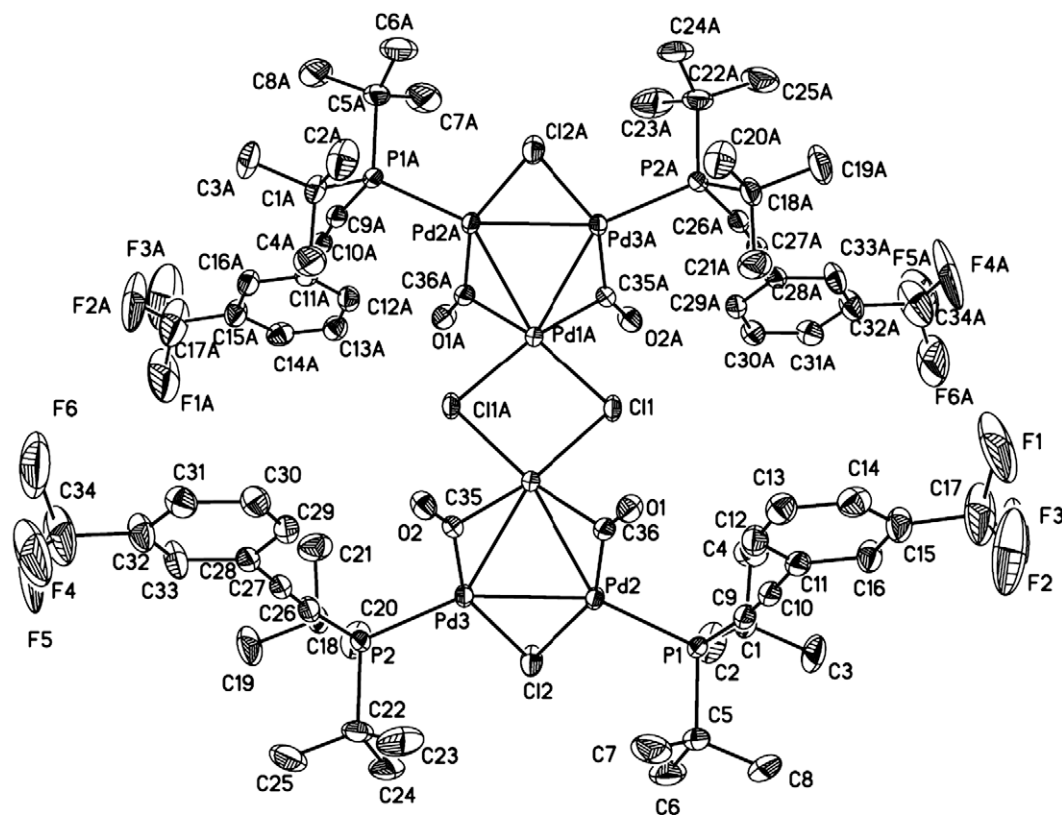


Fig. 3. ORTEP drawing of **9**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Pd(1)–C(36) 2.052(5); Pd(1)–C(36) 2.074(5); Pd(1)–Cl(1) 2.4734(14); Pd(1)–Cl(1)#1 2.4833(14); Pd(1)–Pd(3) 2.7398(6); Pd(1)–Pd(2) 2.7543(6); O(1)–C(36) 1.138(6); P(1)–C(9) 1.766(6); P(1)–C(1) 1.871(6); P(1)–C(5) 1.893(7); P(1)–Pd(2) 2.3242(13); Pd(2)–C(36) 1.916(5); Pd(2)–Cl(2) 2.4122(15); Pd(2)–Pd(3) 2.7115(6); P(2)–Pd(3) 2.3148(13); O(2)–C(35) 1.149(6); Cl(2)–Pd(3) 2.4133(15); Pd(3)–C(35) 1.913(5); C(9)–C(10) 1.199(8); C(35)–Pd(1)–C(36) 96.3(2); Cl(1)–Pd(1)–Cl(1)#1 86.20(4); Pd(3)–Pd(1)–Pd(2) 59.145(14); Pd(1)–Cl(1)–Pd(1)#1 93.80(4); C(9)–P(1)–C(1) 103.7(3); C(9)–P(1)–C(5) 101.7(3); C(1)–P(1)–C(5) 114.2(3); C(9)–P(1)–Pd(2) 111.1(2); C(1)–P(1)–Pd(2) 110.6(2); C(5)–P(1)–Pd(2) 114.5(2); Pd(3)–Pd(2)–Pd(1) 60.161(14); Pd(2)–Cl(2)–Pd(3) 68.38(4); Pd(2)–Pd(3)–Pd(1) 60.693(15); C(10)–C(9)–P(1) 171.0(6); C(9)–C(10)–C(11) 177.2(7); Pd(3)–C(35)–Pd(1) 87.3(2); Pd(2)–C(36)–Pd(1) 87.2(2).

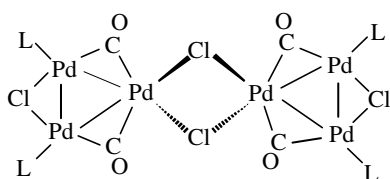


Diagram 1. Generalized structure for **9** (L: **2cm**) and **12** (L: PPh_3).

Table 2
Comparison for selected structural parameters of **8cmm** and **11**.

	8cmm	11
<i>Bond length (Å)</i>		
Pd–Co(1)	2.6777(7)	2.6171(5)
Pd–P	2.2236(14)	2.2050(9)
C(1)–P	1.779(5)	1.766(3)
C(1)–Co(1)	2.025(5)	2.049(3)
Pd–Cl(1)	2.3209(15)	2.3282(9)
Pd–Cl(2)	2.4022(15)	2.3997(9)
<i>Bond angle (°)</i>		
P–Pd–Co(1)	78.64(4)	75.90(2)
Pd–Co(1)–C(1)	76.46(13)	81.07(8)
Co(1)–C(1)–P	110.3(2)	102.65(14)
C(1)–P–Pd	94.49(16)	100.36(10)
Cl(1)–Pd–Cl(2)	90.72(6)	94.58(4)

one molar equivalent of 2-bromothiophene, 1.5-fold phenylboronic acid, and 3-fold of base in 1.0 mL solvent, and with

1.0 mol% of **4cmm**/ $\text{Pd}(\text{OAc})_2$ or **4cmm**/ PdCl_2 under 60 °C for designated times (Scheme 4).

The general procedures for the catalytic reactions under investigation are shown as follows. A suitable Schlenk tube was first charged with 1.0 mmol of bromobenzene, 1.2 equivalent of morpholine, 1.4 equivalent of NaO^tBu , 1.0 ml toluene, and 1 mol% of **4cmm**/ $\text{Pd}(\text{OAc})_2$; then, the reaction mixture was stirred at either 40 °C (or 60 °C) for 3 (or 4) h depending on the reactions executed.

As shown in Table 10, it requires only 40 °C for 3 h to reach excellent efficiency for most of the cases. The reaction condition is milder than that in amination reaction.

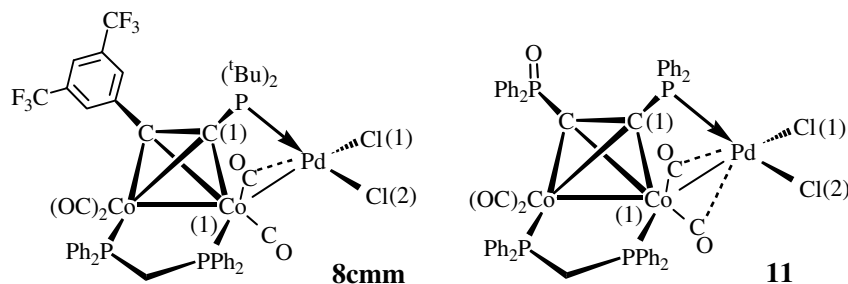
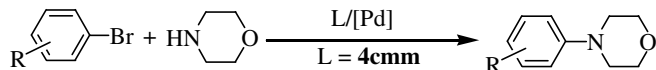
3. Summary

Two cobalt-containing monodentate phosphine ligands, **4cm** and **4cmm**, were prepared. These ligands have been proven to be fairly efficient in the ligands assisted palladium-catalyzed amination and Suzuki reactions. In addition, some palladium complexes with rather unique conformation were observed and characterized while reacting with various palladium sources.

4. Experimental

4.1. Synthesis of **4cmm** or **4cmmO**

Into a 100 mL round-bottom flask, charged with a magnetic stirrer, was placed dicobalt octacarbonyl $\text{Co}_2(\text{CO})_8$ (2.00 mmol, 0.684 g), dppm (2.00 mmol, 0.769 g) and 15 mL of THF. The solution was stirred at 60 °C for 6 h and gave a yellow compound

Diagram 2. Generalized structure for **8cmm** and **11**.Scheme 3. **4cmm**-assisted palladium complex catalyzed amination reaction of bromobenzene and morpholine.Table 3
Dependence of the amination reaction yield on the Pd sources.^a

Entry	Palladium source	Yield (%) ^b
1	$[(\eta^3\text{-C}_3\text{H}_5)\text{PdCl}]_2$	82.2
2	$\text{Pd}(\text{COD})\text{Cl}_2$	71.2
3	$\text{Pd}(\text{OAc})_2$	71.0
4	$\text{PdCl}_2(\text{CH}_3\text{CN})_2$	62.0
5	$\text{Pd}_2(\text{dba})_3$	34.8
6	PdCl_2	6.0

^a Reaction conditions: 1.0 mmol of bromobenzene, 1.2 mmol morpholine, 1.4 mmol of NaO^tBu , 2.0 mL toluene, 4 h, 60 °C, and $[\text{Pd}]/[\mathbf{4cmm}] = 1:1$.

^b Determined by ^1H NMR, average of two runs.

Table 4
Dependence of the amination reaction yield on the $[(\eta^3\text{-C}_3\text{H}_5)\text{PdCl}]_2/\mathbf{4cmm}$ ratio.^a

Entry	Pd:L (mol%)	Conversion (%) ^b
1	0.5:1	20.1
2	1:0.5	64.1
3	1:1	82.2
4	1:2	6.8
5	2:1	74.0
6	1:0	2.0

^a Reaction conditions are the same as in footnote of Table 3 except for the palladium source employed.

^b Determined by ^1H NMR, average of two runs.

Table 5
Dependence of the amination reaction yield on temperature.^a

Entry	T (°C)	Yield (%) ^b
1	25	Trace
2	60	82.2
3	80	85.2

^a With the exception of temperature, reaction conditions same as in the footnote of Table 3.

^b Determined by ^1H NMR, Average of two runs.

$[\text{Co}_2(\text{CO})_6(\mu\text{-P,P-dppm})]$ (**3**). Without further separation, the reaction flask was charged again with one equivalent of $[(^t\text{Bu})_2\text{PC}\equiv\text{C}(3,5\text{-}(\text{CF}_3)_2\text{C}_6\text{H}_3)]$ (0.696 g) in THF (15 mL). Subsequently, the solution was stirred at 60 °C for another 48 h before the solvent was removed under reduced pressure. The residue was further separated by CTLC. A reddish-brown band eluted with CH_2Cl_2 /ethyl acetate (1:10) was identified as $\{[(\mu\text{-PPh}_2\text{CH}_2\text{PPh}_2)\text{Co}_2(\text{CO})_4(\mu,\eta\text{-}^t\text{Bu})_2\text{PC}\equiv\text{C}(3,5\text{-}(\text{CF}_3)_2\text{C}_6\text{H}_3)]\}$ (**4cmm**) in 40% yield (0.80 mmol, 0.799 g). Another reddish-brown band eluted

Table 6
Amination reactions employing $[(\eta^3\text{-C}_3\text{H}_5)\text{PdCl}]_2/\mathbf{4cmm}$ and various bases.^a

Entry	Base	Yield (%) ^b
1	NaO^tBu	82.2
2	KO^tBu	1.4
3	NaOH	Trace
4	KF	Trace

^a With the exception of base, reaction conditions same as in the footnote of Table 3.

^b Determined by ^1H NMR, Average of two runs.

Table 7
Dependence of the amination reaction yield on solvent.^a

Entry	Solvent	Yield (%) ^b
1	THF (2.0 mL)	21.1
2	1,4-Dioxene (2.0 mL)	13.6
3	DMF (2.0 mL)	10.4
4	Toluene (1.0 mL)	>99.0
5	Toluene (1.5 mL)	85.1
6	Toluene (2.0 mL)	82.2
7	Toluene (3.0 mL)	76.0

^a With the exception of solvent, reaction conditions same as in the footnote of Table 3.

^b Determined by ^1H NMR, average of two runs.

with CH_2Cl_2 /ethyl acetate (1:1) was identified as $\{[(\mu\text{-PPh}_2\text{CH}_2\text{-PPh}_2)\text{Co}_2(\text{CO})_4(\mu,\eta\text{-}^t\text{Bu})_2\text{P}(\text{=O})\text{C}\equiv\text{C}(3,5\text{-}(\text{CF}_3)_2\text{C}_6\text{H}_3)]\}$ (**4cmmO**) in 10% (0.200 mmol, 0.103 g).

4.1.1. Selected spectroscopic data for **4cmm**

^1H NMR (CD_2Cl_2 , δ/ppm): 7.03–7.60 (23H, arene), 3.24 (m, 2H, dppm), 1.26, 1.23 (d, $J_{\text{P-H}} = 11.2$ Hz, 18H, ^tBu); ^{31}P NMR (CDCl_3 , δ/ppm): 35.98 (s, 2P, dppm), 44.62 (s, 1P, $\text{P}(^t\text{Bu})_2$); elemental analysis: Anal. Calc.: C, 56.64; H, 4.35. Found: C, 56.48; H, 4.68%. MS (FAB): $m/z = 998.0$ [M]⁺.

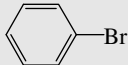
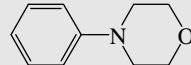
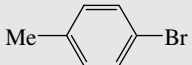
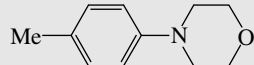
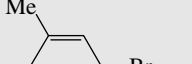
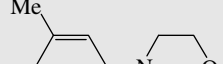
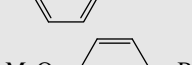
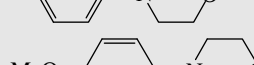
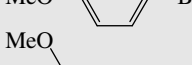
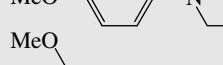
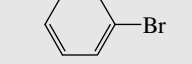
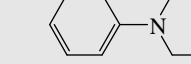
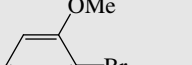
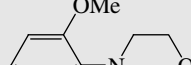
4.1.2. Selected spectroscopic data for **4cmmO**

^1H NMR (CD_2Cl_2 , δ/ppm): 7.02–8.04 (23H, arene), 3.33 (m, 2H, dppm), 1.39, 1.34 (d, $J_{\text{P-H}} = 18.4$ Hz, 18H, ^tBu); ^{31}P NMR (CDCl_3 , δ/ppm): 35.26 (s, 2P, dppm), 59.55 (s, 1P, $\text{P}(^t\text{Bu})_2$); ^{13}C NMR (CD_2Cl_2 , δ/ppm): 122.03–147.75 (30C, arene), 28.31, (d, 6C, $-\text{C}(\text{CH}_3)_3$), 38.40 (d, 2C, $J_{\text{P-C}} = 25.11$ Hz, $-\text{C}(\text{CH}_3)_3$), 33.70 (t, 1C, $J_{\text{P-C}} = 17.0$ Hz, $-\text{CH}_2-$); elemental analysis: Anal. Calc.: C, 56.59; H, 4.51. Found: C, 55.89; H, 4.64%. MS (FAB): $m/z = 1013.0$ [M]⁺.

4.2. Synthesis of **8cmm**

A 100 mL round-bottom flask equipped with a magnetic stirrer was charged with 1.00 mmol of **4cmm** (0.998 g), one molar equivalent of PdCl_2 (1.0 mmol, 0.285 g) and 15 mL THF. The solu-

Table 8Dependence of the yield of the amination reaction using **4cmm**/[(η^3 -C₃H₅)PdCl]₂ on substrate.^a

Entry	Substrate	Product	Yield (%) ^b
1			>99.0
2			90.1
3			18.4
4			98.9
5			95.2
6			7.4
7			56.7

^a Reaction conditions are the same as in footnote of Table 3 except for the substrate employed.^b Determined by ¹H NMR, average of two runs.**Table 9**Dependence of the yield of the amination reaction using various catalytic precursors^a

Entry	Catalyst	Yield (%) ^b
1	4cm /Pd(OAc) ₂	>99.0
2	5cm	>99.0
3	4cmm /[(η^3 -C ₃ H ₅)PdCl] ₂	>99.0
4	4cmm /Pd(COD)Cl ₂	90.2
5	6cmm	94.2

^a Reaction conditions are the same as in footnote of Table 3 except for the catalytic precursor employed.^b Determined by ¹H NMR, average of two runs.

tion was stirred at 25 °C for 1 h before the solvent was removed under reduced pressure. The residue was further separated by TLC. A reddish-brown band eluted with CH₂Cl₂/ethyl acetate (5:1) was identified as {[$(\mu$ -PPh₂CH₂PPh₂)Co₂(CO)₄][$(\mu$, η -^tBu)₂PC≡C(3,5-(CF₃)₂C₆H₃)]]PdCl₂} (**8cmm**) in the yield of 42% (0.42 mmol, 0.494 g).

4.2.1. Selected spectroscopic data for **8cmm**

¹H NMR (CD₂Cl₂, δ /ppm): 6.71–7.91 (23H, arene), 3.63 (t, J_{P-H} = 22.8 Hz, 2H, CH₂), 1.18 (d, J_{P-H} = 16.4 Hz, 9H, ^tBu), 1.85 (d, J_{P-H} = 16.4 Hz, 9H, ^tBu); ³¹P NMR (CD₂Cl₂, δ /ppm): 25.40–26.07 (d, J_{P-P} = 26.8 Hz, 1P, dppm), 31.18–31.85 (d, J_{P-P} = 26.8 Hz, 1P, dppm), 64.91 (s, 1P, P(^tBu)₂); ¹³C NMR (CD₂Cl₂, δ /ppm): 122.03–143.75 (30C, arene), 27.93, (d, 6C, -C(CH₃)₃), 30.63 (d, 2C, J_{P-C} = 25.11 Hz, -C(CH₃)₃), 31.41 (t, 1C, J_{P-C} = 17.0 Hz, -CH₂-); MS (FAB):

Table 10Dependence of the yield of the Suzuki reaction using various catalytic precursors.^a

Entry	Catalyst	Yield (%) ^b
1	4cm /Pd(OAc) ₂	91.2
2	5cm	>99.0
3	4cmm /[(η^3 -C ₃ H ₅)PdCl] ₂	>99.0
4	4cmm /Pd(COD)Cl ₂	60.0(>99.0 ^c)
5	6cmm	70.0(>99.0 ^c)

^a Reaction conditions: 1.0 mmol of 2-bromothiophene, 1.5 mmol phenylboronic acid, and 3.0 mmol of NaOH, 1.0 ml toluene, 40 °C, 3 h, 1.0 mol% of L/[Pd] = 1:1.^b Average of two runs; isolated yield.^c 60 °C, 4 h.

m/z = 1118 [M–2CO]⁺; elemental analysis: Anal. Calc.: C, 48.09; H, 3.69. Found: C, 46.41; H, 4.63%.

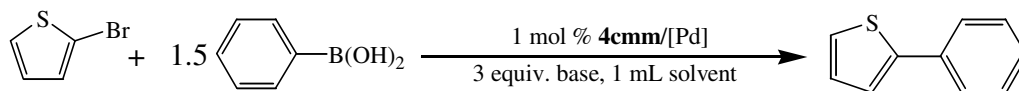
4.3. General procedure for coupling reactions

For amination reaction, the following procedures were followed. An oven-dried Schlenk tube was charged with **4cmm** (0.01 mmol, 0.998 mg), palladium salt (0.01 mmol) and a base (1.4 mmol). The tube was evacuated and backfilled with nitrogen and followed by the addition of aryl bromide (1.0 mmol, 0.156 g), morpholine (1.2 mmol, 0.103 g) and toluene (1.0 mL). The tube was sealed with a Teflon screw cap, and the mixture was stirred at 60 °C for 3 h. After all starting materials had been consumed; the mixture was allowed to cool down to room temperature and then diluted with ether (30 mL). The resulting suspension was transferred into a separatory funnel and washed with water (10 mL). The organic layer was separated, dried with anhydrous MgSO₄ and concentrated under reduced pressure. The crude residue was purified by TLC with hexane/ethyl acetate as a mobile phase. The solvent was removed under reduced pressure, and the yield of the eluted product was determined.

Similar procedures were taken for Suzuki reaction except the reactants and conditions were varied. A Schlenk tube was first charged with 1.0 mmol of bromobenzene, 1.2 equivalent of morpholine, 1.4 equivalent of NaO^tBu, 1.0 ml toluene, and 1 mol% of **4cmm**/Pd(OAc)₂; then, the reaction mixture was stirred at either 40 °C (or 60 °C) for 3 (or 4) h depending on the reactions executed.

4.4. X-ray crystallographic studies

Suitable crystals of **4cmmO**, **8cmm** and **9** were sealed in thin-walled glass capillaries under nitrogen atmosphere and mounted on a Bruker AXS SMART 1000 diffractometer. Intensity data were collected in 1350 frames with increasing ω (width of 0.3° per frame). The absorption correction was based on the symmetry equivalent reflections using SADABS program. The space group determination was based on a check of the Laue symmetry and systematic absences, and was confirmed using the structure solution. The structure was solved by direct methods using a SHELXTL package [42]. All non-H atoms were located from successive Fourier maps and hydrogen atoms were refined using a riding model. Anisotropic thermal parameters were used for all non-H atoms, and fixed isotropic parameters were used for H atoms [43]. Crystallographic data for compounds **4cmmO**, **8cmm** and **9** are summarized in Table 1.

**Scheme 4.** **4cmm**-assisted palladium complex catalyzed Suzuki–Miyaura cross-coupling reaction of 2-bromothiophene and phenylboronic acid.

Acknowledgment

We thank the National Science Council of the ROC (Grant NSC 95-2113-M-005-015-MY3) for financial support.

Appendix A. Supplementary material

CCDC 692970, 692971 and 692972 contain the supplementary crystallographic data for **4cmmO**, **8cmm** and **9**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2008.10.005](https://doi.org/10.1016/j.jorganchem.2008.10.005).

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