Inorganica Chimica Acta 363 (2010) 412–417

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Preparation of cobalt sandwich diphosphine ligand $[(\eta^5\text{-}C_5H_4{}^i\text{Pr})\text{Co}(\eta^4\text{-}C_4(\text{PPh}_2)_2\text{Ph}_2)]$ and its chelated palladium complex: Application of diphosphine ligand in the preparation of mono-substituted ferrocenylarenes

Chin-Pei Chang, Chia-Ming Weng, Fung-E Hong *

Department of Chemistry, National Chung Hsing University, Taichung 40227, Taiwan

ARTICLE INFO

Article history:
Received 29 October 2009
Received in revised form 5 November 2009
Accepted 9 November 2009
Available online 14 November 2009

Keywords:
Suzuki–Miyaura reaction
Ferrocenylboronic acid
dppf
Cobalt-containing phosphine
DFT

ABSTRACT

The reaction of $(\eta^5\text{-}C_5H_4{}^i\text{Pr})\text{Co}(\text{PPh}_3)_2$ with $\text{PhC}{\equiv}\text{CPPh}_2$ furnished two isomeric cyclobutadiene-substituted Cp′CoCb diphosphines, $[(\eta^5\text{-}C_5H_4{}^i\text{Pr})\text{Co}(\eta^4\text{-}1,2\text{-}(\text{PPh}_2)_2C_4\text{Ph}_2)]$ (**5-cis**) and $[(\eta^5\text{-}C_5H_4{}^i\text{Pr})\text{Co}(\eta^4\text{-}1,3\text{-}(\text{PPh}_2)_2C_4\text{Ph}_2)]$ (**5-trans**). Further reaction of **5-cis** with one molar equivalent of Pd(COD)Cl_2 gave palladium complex $[(\eta^5\text{-}C_5H_4{}^i\text{Pr})\text{Co}(\eta^4\text{-}1,2\text{-}(\text{PPh}_2)_2C_4\text{Ph}_2)\text{-PdCl}_2]$ (**6**) in good yield. Both of the molecular structures of **5-cis** and **6** were determined by single-crystal X-ray diffraction methods. Unexpectedly, the palladium complex **6** was found to be more efficient than the combination of the commonly used Buchwald's ligand, biphenyl-2-yl-di-tert-butyl-phosphane, with Pd(OAc)_2 as the catalytic precursor in the Suzuki–Miyaura reaction between ferroceneboronic acid and 4-bromoaldehyde. The X-ray structural analysis and DFT study of several palladium complexes containing sandwich-type diphosphine chelating ligands revealed that the variations in bite angles are much larger than those in bite distances. The more energetically favorable conformation in the Pd(II) complexes is the one with bite angle close to 90°.

1. Introduction

One of the most celebrated achievements of modern synthetic organic chemistry is the rapid development and extensive applications of ligand-assisted palladium-catalyzed cross-coupling methodology. In spite of the emerging employment of *N*-heterocyclic carbenes (NHC) in recent years as potentially effective ligands in transition metal-catalyzed cross-coupling reactions [1–8], organophosphines undoubtedly remain to be the ligands of the most commonly used today [9–11]. Although numerous kinds of organophosphines have been designed, prepared and evaluated as ligands [12], examples of using organometallic phosphines (TM-phosphines) as ligands in cross-coupling reactions are relatively limited in number and scope [13–22]. Bis(diphenylphosphino)ferrocene (**dppf**) [23–27] and its numerous derivatives (Diagram 1) are probably the most widely used organometallic phosphine ligands [28,29]. One of the most admired characteristics of **dppf** is its bite angle flexibility caused by free rotation of two Cp rings [30–32].

For the past few years, we had developed a new category of **dppf**-analogous organocobalt phosphine ligands based on the $(\eta^5$-cyclopentadienyl$)(\eta^4$-cyclobutadiene$)$cobalt framework, **1,2-dppc** (Diagram 1). The efficacy of these ligands in various cross-coupling reactions has been examined [33,34]. These CpCoCb diphosphines carrying the substituents on the same ring, such an arrangement naturally leads to the bulkiness of this type of ligands, which is obviously advantageous for the reductive elimination process, the last step of the catalytic cycle [35–38]. Since the former, **dppc**, contains a Cb ring, the new cobalt system could exhibit a behavior different from that of the **dppf** in terms of the coordinating capacity toward palladium. Comparison between these two systems is expected to provide useful information with respect to the performance of an organometallic ligand upon variation in metal and ring size.

One of the most frequently used methods of preparation of arylferrocenes, ArFc, involves the direct reaction of ferrocene with aryldiazonium salts [39–46]. However, the yields of desired products obtained by this method rarely exceed 50%, and in many cases they are disappointedly low [40,47]. Due to the poor yields and lack of characteristic generality of this method, a more feasible route to arylferrocenes is obvious in need. The employment of the renowned Suzuki–Miyaura reaction might provide a promising alternative. The most commonly used organometallic compounds in the Suzuki–Miyaura reaction are arylboronic acids. The arene aromaticity of boronic acids is considered to be favoring the formation of the transition state during the oxidative addition process. The cyclopentadienyl rings of the ferrocene are also regarded to

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* Corresponding author. Fax: +886 4 22862547.
E-mail address: fehong@dragon.nchu.edu.tw (F.-E Hong).

doi:10.1016/j.ica.2009.11.010

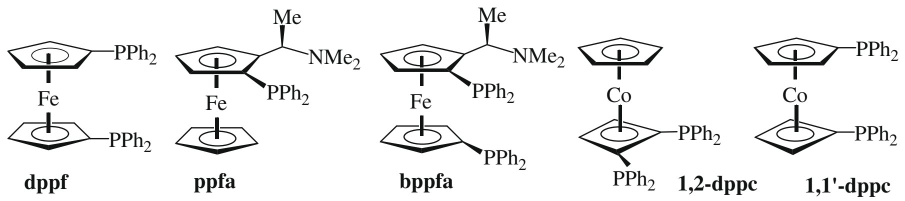
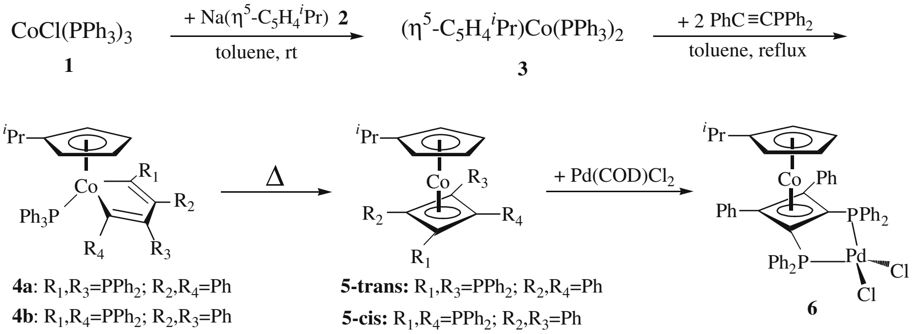


Diagram 1.



Scheme 1. Preparations of **5-trans** and **5-cis** and reaction of **5-cis** with Pd(COD)Cl_2

be aromatic. In principle, the Suzuki–Miyaura reaction between ferroceneboronic acid, $FcB(OH)_2$, and aryl halide, ArX, would yield the desired product, ArFc. Unexpectedly, only a few articles concerning this subject have been found in literature [48]. A systematic investigation of the synthesis of arylferrocenes using the Suzuki–Miyaura reaction is highly desirable for improving the efficiency of the method. In this report the preparation of **1,2-dppc** as well as its application in palladium-catalyzed Suzuki–Miyaura reactions is presented.

2. Results and discussion

2.1. Syntheses of organocobalt diphosphine ligands **5-trans** and **5-cis**

Two isomeric forms of cobalt sandwich diphosphine ligands, **5-trans** and **5-cis**, were prepared as processes described in Section 3 (Scheme 1). As shown, the reaction of $CoCl(PPh_3)_3$ (**1**) with Na(η^5-$C_5H_4{}^iPr$) (**2**) at room temperature yielded an air-sensitive compound (η^5-$C_5H_4{}^iPr$)$Co(PPh_3)_2$ (**3**). Further reaction of **3** with two molar equivalent of alkyne $PhC{\equiv}CPPh_2$ at refluxed toluene presumably gave two isomeric forms of cobaltacycle (η^5-$C_5H_4{}^iPr$)-$Co(C_4Ph_2(PPh_3)_2)$, **4a** and **4b**. Finally, a mixture of trans- and **5-cis** in the ratio of 56:44 was observed from the ^1H NMR. Previously we have reported that only a Cp-unsubstituted analog of **5-trans** was isolated from a similar reaction of (η^5-C_5H_5)$Co(PPh_3)_2$ (**3**) with $PhC{\equiv}CPPh_2$ at refluxed toluene. In contrast, only a cobaltacycle analogous to **4a** was isolated while **3** was reacted with $HC{\equiv}CPPh_2$ at the same reaction condition [33]. Apparently, it is the introduction of a bulky group, –^{i}Pr, on the Cp ring that caused a significant change in the stereochemical outcome of reaction by exerting severe steric hindrance on top of the molecule.

The mixture of **5-trans** and **5-cis** was characterized by ^1H, ^{13}C, ^{31}P NMR, EA and MS. The ^1H NMR spectrum of **5-cis** shows two sets of triplets at 4.60 ppm (t, J_{H-H} = 2.4 Hz, 2H) and 4.63 ppm (t, J_{H-H} = 2.4 Hz, 2H) corresponding to four cyclopentadienyl protons in two different environments. The isopropyl group signals are observed at 1.82 ppm (m, 1H, ^{i}Pr) and 0.77 ppm (d, J_{H-H} = 7.2 Hz, 6H, ^{i}Pr). A single signal at −17.7 ppm in the ^{31}P NMR spectrum indicates the equivalence of two phosphorous atoms. As far as the *trans*-isomer is concerned, its four cyclopentadienyl protons are observed as two sets of triplets at 4.25 ppm (t, J_{H-H} = 2.0 Hz, 2H, Cp) and 4.75 ppm (t, J_{H-H} = 2.0 Hz, 2H, Cp) in the ^1H NMR spectrum. The isopropyl group signals are at 2.08 (m, 1H, ^{i}Pr) ppm and 0.87 ppm (d, J_{H-H} = 6.8 Hz, 6H, ^{i}Pr). The equivalence of two phosphorous atoms is also evidenced by a single signal at −15.8 ppm in the ^{31}P NMR. The molecular structure of **5-cis** was determined by X-ray diffraction methods, an ORTEP diagram being depicted in Fig. 1. The two rings, cyclopentadienyl and cyclobutadiene, are almost coplanar. The presence of two –PPh_2 groups next to each other makes it potentially a bidentate ligand.

2.2. Synthesis of palladium complex **6**

Compound **5-cis** was expected to act as an authentic diphosphine ligand towards the chelation of transition metals. Indeed, further reaction of **5-cis** with one molar equivalent of Pd(COD)Cl_2 in toluene at 25 °C furnished palladium complex [(η^5-$C_5H_4(CHMe_2)$)Co(η^4-1,2-$(PPh_2)_2C_4Ph_2$)-$PdCl_2$] (**6**) in good yield (Scheme 1). The binding mode of **5-cis** is much more similar to 1,2-bis(diphenylphosphino)ethane (**dppe**) than of 1,1′-**dppf**. Compound **6** was characterized by spectroscopic methods. The spectroscopic data of **6** are not much different from that of **5-cis** except for the observed downfield shift in the ^{31}P NMR (63 ppm) characteristic of coordination. In ^1H NMR, two sets of multiplets observed at 4.38 ppm (t, J_{H-H} = 2.40) and 3.84 ppm (t, J_{H-H} = 2.30) correspond to four protons of the substituted cyclopentadienyl ring of **6**. The isopropyl group appears as a multiplet and a doublet at 1.52 ppm (m, 1H, ^{i}Pr) and 0.31 ppm (d, J_{H-H} = 9.20, 6H, ^{i}Pr), respectively. The molecular structure of **6** was determined by X-ray diffraction methods, the corresponding ORTEP diagram being depicted in Fig. 2. It clearly shows a chelated palladium metal center and an isopropyl group tilted away from it to prevent severe steric hindrance.

2.3. Application of **6** in palladium-catalyzed Suzuki–Miyaura reaction

As is known, the catalytic performance of the palladium-catalyzed Suzuki–Miyaura reaction is subjected to a variety of factors

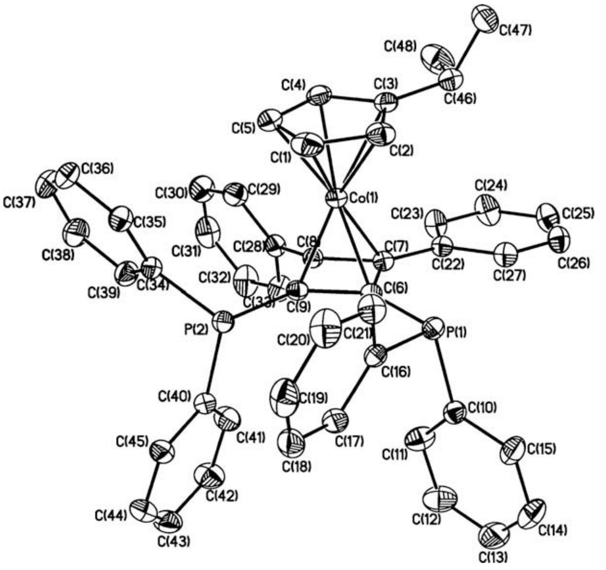


Fig. 1. ORTEP drawing of **5-cis**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): P1–C6 1.804(4). P2–C9 1.816(4). C3–C46 1.507(5). C7–C22 1.467(4). C8–C28 1.484(4). C7–C6–C9 89.9(2). C7–C8–C9 90.4(2). C6–C9–C8 89.2(2). C8–C7–C6 90.5(2). C34–P2–C40 100.82(17). C16–P1–C10 101.89(16).

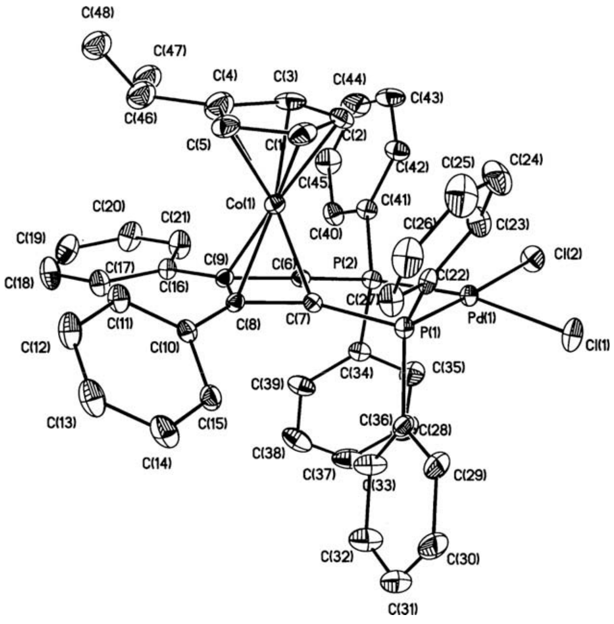


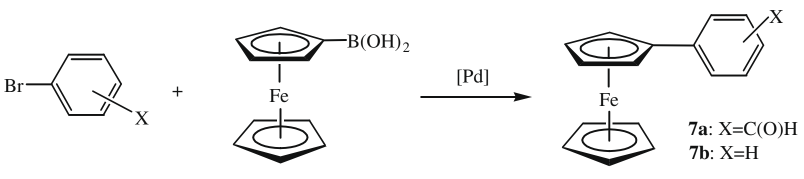
Fig. 2. ORTEP drawing of **6**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): P2–C6 1.799(5). P1–C7 1.804(5). Pd1–P1 2.2418(13). Pd1–P2 2.2628(14). Pd1–Cl2 2.3485(13). Pd1–Cl1 2.3570(15). P1–Pd–P2 101.89(16). Cl1–PdCl$_2$ 93.45(5). C22–P1–C28 108.9(2). C41–P1–C34 106.3(2). C7–P1–Pd1 105.06(14). C6–P2–Pd1 105.60(15).

such as temperature, solvent, base, the palladium salt, the type of ligand, the ratio of ligand/palladium etc. [49,50]. The best catalytic efficiency can be achieved by optimizing all the factors involved. To study the feasibility of employing **6** as the catalytic precursor in Suzuki–Miyaura reaction, ferrocenylboronic acid and 4-bromoaldehyde were chosen (Scheme 2). The general procedure for the catalytic reactions under investigation is as follows. A suitable Schlenk tube was charged with 1.5 mmol of boronic acid, 1.0 mmol of arylhalide, 1.0 mL of solvent, 3.0 mmol of base, 1.0 mol% of palladium source. The mixture was stirred at designated reaction temperature and hours depending on the reactions executed. It was then followed by a work-up. Several commonly bases were surveyed since a well-chosen base is crucial to the success of the reaction. The results are listed in Table 1 [51–53]. As shown, the best result was obtained with K_2CO_3 (Entry 1). Unexpectedly, NaO^tBu, the base of choice in many Suzuki reactions, showed no conversion at all (Entry 4).

The palladium source is one of the most influential factors in the performance of Suzuki–Miyaura reaction. Two more catalytic precursor systems were screened here, the results are shown in Table 2. Unexpectedly, a rather poor yield was observed with a commonly used Buchwald's ligand, biphenyl-2-yl-di-tert-butyl-phosphane **P(^{t}Bu)biPh** and palladium acetate (Entry 2) [54–57]. Furthermore, $Pd(PPh)_4$ was even less efficient (Entry 3). In addition, several arylbromides were examined. The procedures were the same as previously (Table 1) except that K_2CO_3 and complex **6** were chosen as a base and a catalyst precursor, respectively. The arylbromide with an electron-withdrawing group showed a better conversion (Entries 1 versus 4 and 5), confirming the common observation for the palladium-catalyzed Suzuki coupling reaction [15]. No conversion was observed in the case of benzylbromide (Entry 6).

2.4. Computational studies on various palladium complexes

The bite angle (θ_{P-M-P}) and the bite distance (r_{P-M}) are the two vital factors greatly affecting the catalytic efficiency of a bidentate phosphine ligand-chelated metal complex [58,59]. The bite angles (θ_{P-M-P}) and the bite distances (r_{P-M}) of some complexes related to **6**, namely, **dppf_PdCl$_2$** [60–62], **Fc(P)$_4$^{t}Bu_PdCl$_2$** [63], **Josiphos_PdCl$_2$** (R' = ^{t}Bu. R'' = Cy) [64], **Josiphos_PdCl$_2$** (R' = Cy. R'' = p-$C_6H_4CF_3$) [65], **ppfa_PdCl$_2$** [66], **dppm_PdCl$_2$** [67], **dppe_PdCl$_2$** [68] and **bppfa_PdCl$_2$** [69], obtained from the X-ray data are listed in Table 3. Since the state-of-the-art density functional theory method (DFT) has proven to be a useful tool in the studies of transition metal-mediated catalytic reactions, it was employed to gain information concerning the optimized geometries of these complexes (Diagram 2). This method at the B3LYP level was utilized to examine the effects of the bite angles (θ_{P-M-P}) and the bite distances (r_{P-M}) on the catalytic performance. For comparison, the data obtained from the optimized geometries by DFT methods for several complexes are listed in Table 3. By both methods the bite angles of **dppm_PdCl$_2$** and **dppe_PdCl$_2$** are the smallest ones among all complexes. It is understandable due to the rigidity of the carbon backbone in both **dppm** and **dppe**. The bite angles of **6** and **Fc(P)$_4$^{t}Bu_PdCl$_2$**, which are quite close, are the smallest ones among the sandwich-type ligand complexes by both methods. The bite angles of **dppf_PdCl$_2$** and **bppfa_PdCl$_2$** are relatively large due to the coordination to substituents on both rings. Large bite angles



7a: X=C(O)H
7b: X=H

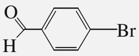
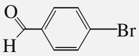
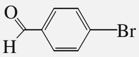
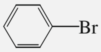
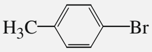
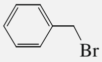
Scheme 2.

Table 1
Suzuki coupling reactions with various bases.[a]

Entry	Base	Yield (%)[b]
1	K_2CO_3	56
2	KF	25 (33[c])
3	K_3PO_4	46 (54[d])
4	NaO^tBu	NR

[a] Reaction conditions: ArX:$FcB(OH)_2$:base = 1:1:3. 1 mol% **6**, 1 mL toluene, 100 °C, 24 h.
[b] Isolated yield.
[c] Dry KF.
[d] Dry K_3PO_4.

Table 2
Suzuki coupling reactions with various catalyst precursors.[a]

Entry	ArBr	Pd complex	Yield (%)[b]
1		**6**	56
2		**BiPh(^{t}Bu)$_2$**/$Pd(OAc)_2$	24
3		$Pd(PPh)_4$	11
4		**6**	33
5		**6**	10.9[c]
6		**6**	NR

[a] Reaction conditions: ArX:$FcB(OH)_2$:K_2CO_3 = 1:1:3. 1 mol% palladium, 1 mL toluene, 100 °C, 24 h.
[b] Isolated yield.
[c] NMR yield.

are also observed for **Josiphos_PdCl$_2$** (R' = ^{t}Bu. R'' = Cy), **Josiphos_PdCl$_2$** (R' = Cy. R'' = p-$C_6H_4CF_3$) and **ppfa_PdCl$_2$** probably due to the formation of six-membered ring after chelation. It shows that the bite angle is greatly affected by the ring size and attributed to the original shape of the bidentate ligand. To contrast it, the bite distances between palladium and phosphorus are similar in all cases suggesting that the bond strengths are of similar scope.

2.5. Summary

A cobalt sandwich diphosphine ligand **5-cis** and its chelated palladium complex **6** were synthesized. The latter was successfully applied in the preparation of ferrocenylarenes via the Suzuki–Miyaura reaction. Compared with the previously reported method, a better efficiency was observed. The DFT study showed that despite of the wide variation of bite angles for different types of bidentate ligands the bite distances between palladium and phosphorus are similar in all cases which suggest that the strength of bonds are of similar scope.

3. Experimental

3.1. General

Most synthetic manipulations were carried out using standard Schlenk techniques or operation in Dry Box under dry nitrogen atmosphere. Moisture-free treated and freshly distilled solvents were used in reaction. Separation was carried out by centrifugal thin-layer chromatography (CTLC) on Chromatotron, Harrison model 8924. The plates were prepared using silica gel 60 PF_{254} containing gypsum (Merck). ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian Mercury-400 spectrometer operating at 400.44 and 162.10 MHz, respectively, and referenced to the residual resonance of $CHCl_3$ and external standard 85% H_3PO_4. $^{13}C\{^1H\}$ NMR spectra were recorded either on a Varian Mercury-400 or 300 spectrometer operating either at 100.70 or 75.43 MHz, respectively, and referenced to the signal of deuterated chloroform. Coupling constants are reported in Hz. Elemental analyses were obtained using a Heraeus CHN–O–S-Rapid instrument. Mass spectra were recorded on JOEL JMS-SX/SX 102A GC/MS/MS spectrometer.

3.2. Syntheses

*3.2.1. Synthesis and characterization of **5-cis** and **5-trans***

A 100 mL round-bottomed flask equipped with a magnetic stir-bar and a rubber septum was charged with $CoCl(PPh_3)_3$ **1** (0.44 g,

Table 3
Bite angles and bite distances of **6**, **dppf**, **Fc(P)$_4$^{t}Bu**, **Josiphos**, **ppfa**, **dppm**, **dppe** and **bppfa** chelated palladium complexes.

Complex	Methods			
	X-ray[a]		DFT[b]	
	Bite angle (°)	Bite distance (Å)	Bite angle (°)	Bite distance (Å)
6	89.87(5)	2.241(13) 2.262(14)	89.12	2.397 2.396
dppf_PdCl$_2$	99.26	2.277 2.277	101.66	2.376 2.362
Fc(P)$_4$^{t}Bu_PdCl$_2$	88.97	2.240 2.246	89.06	2.288 2.284
Josiphos_PdCl$_2$ R' = ^{t}Bu. R'' = Cy	97.46	2.305 2.282	–	–
Josiphos_PdCl$_2$ R' = Cy. R'' = p-$C_6H_4CF_3$	96.02	2.237 2.275	–	–
ppfa_PdCl$_2$	96.06	2.231 (P–Pd) 2.116 (N–Pd)	–	–
Dppm_PdCl$_2$	72.70	2.249 2.235	74.49	2.301 2.301
Dppe_PdCl$_2$	85.77	2.238 2.238	87.46	2.300 2.318
bppfa_PdCl$_2$	98.79	2.298 2.302	–	–

[a] Data from the X-ray crystal structures available.
[b] Data from the optimized geometries obtained by the DFT method.

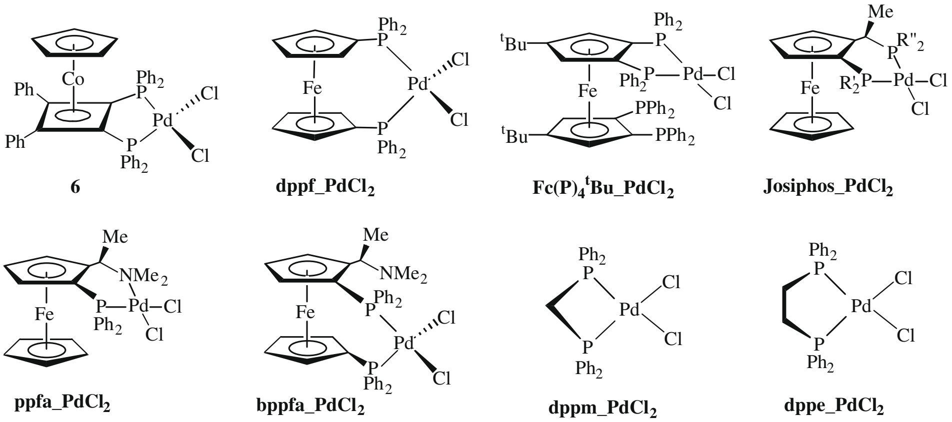


Diagram 2.

0.49 mmol) and sodium isopropylcyclopentadienide **2** (0.65 g, 0.44 mmol) before adding 10 mL toluene. After 0.5 h, a batch of phenylethynyl diphenylphosphine (0.28 g, 1.00 mmol), dissolved in toluene (5 mL), was added, and the solution was refluxed for 12 h. Subsequently, purification was carried out by using CTLC. A yellow band containing both **5-cis** and **5-trans** in the ratio of 56/44 was eluted out by mixed solvent CH_2Cl_2/hexane = 1:1. The total yield of the resulted yellow solid is 34% (0.13 g, 0.17 mmol).

5-cis: ^{1}H NMR ($CDCl_3$/ppm): δ 6.96–7.42 (m, 30H, Ph and PPh_2), 4.60 (t, J = 2.0 Hz, 2H, Cp), 4.63 (t, J = 2.0 Hz, 2H, Cp), 1.82 (m, 1H, ^{i}Pr), 0.77 (d, J = 7.2 Hz, 6H, ^{i}Pr). ^{13}C{^{1}H} NMR ($CDCl_3$/ppm): δ 126.0–136.8 (m, Ph and PPh_2), 80.2 (Cp), 24.8 (^{i}Pr), 23.0 (^{i}Pr). ^{31}P{^{1}H} NMR ($CDCl_3$/ppm): δ −17.7. *Anal.* Calc. for $C_{48}H_{41}CoP_2$: C, 78.072; H, 5.59. Found: C, 78.04; H, 5.59. LRMS: m/z = 738 (M^+).

5-trans: ^{1}H NMR ($CDCl_3$/ppm): δ 6.84–7.31 (m, 30H, Ph and PPh_2), 4.25 (t, J = 2.0 Hz, 2H, Cp), 4.75 (t, J = 2.0 Hz, 2H, Cp), 2.08 (m, 1H, ^{i}Pr), 0.87 (d, J = 6.8 Hz, 6H, ^{i}Pr). ^{13}C{^{1}H} NMR ($CDCl_3$/ppm): δ 125.9–136.7 (m, Ph and PPh_2), 87.8 (t, J_{C-P} = 6.1 Hz, C(2) and C(4) of Cb), 80.2 (Cp), 80.5 (Cp), 25.0 (^{i}Pr), 23.1 (^{i}Pr). ^{31}P{^{1}H} NMR ($CDCl_3$/ppm): δ −15.8. LRMS: m/z = 738 (M^+).

3.2.2. Synthesis and characterization of **6**

The same size and set up of 100 mL flask was charged with dichloro(1,5-cyclooctadiene)palladium (0.04 g, 0.15 mmol) and (η^5-C_4H_4-^{i}Pr)Co(η^4-$(PPh_2)_2C_4Ph_2$) **5-cis** (0.11 g, 0.15 mmol), and 10 mL CH_2Cl_2. The solution was stirred at room temperature for 1 h before the solvent was removed in reduced pressure. Subsequently, purification was carried out by using CTLC. A yellow band was eluted out by mixed solvent CH_2Cl_2/EA = 10:1. The yield of the resulted yellow solid is 72% (0.10 g, 0.10 mmol).

6: ^{1}H NMR ($CDCl_3$/ppm): δ 7.14–8.10 (m, 30H, Ph and PPh_2), 4.38 (t, J_{H-H} = 2.4 Hz, 2H, Cp), 3.84 (t, J_{H-H} = 2.3 Hz, 2H, Cp), 1.52 (m, 1H, ^{i}Pr), 0.31 (d, J_{H-H} = 9.2 Hz, 6H, ^{i}Pr). ^{13}C{^{1}H} NMR ($CDCl_3$/ppm): δ 127.5–132.9 (m, Ph), 135.6 (t, J_{C-P} = 6.0, HC=C–PPh_2), 82.0 (2C, Cp), 80.4 (2C, Cp), 24.3 (^{i}Pr), 22.0 (^{i}Pr). ^{31}P{^{1}H} NMR ($CDCl_3$/ppm): δ 63.0. *Anal.* Calc. for $C_{48}H_{41}Cl_2CoP_2Pd$: C, 62.94; H, 4.51. Found: C, 60.93; H, 5.27. LRMS: m/z = 879 $[M-Cl]^+$.

3.3. General procedures for the Suzuki cross-coupling reactions

An oven-dried Schlenk tube was charged with 9.0 mg of **6** (0.01 mmol) and 3.0 mmol of base. The tube was evacuated and backfilled with nitrogen followed by the addition of aryl bromide (1.00 mmol), ferroceneboronic acid (0.229 g, 1.00 mmol) and toluene (2.0 mL). The tube was sealed with a Teflon screw cap, and the mixture was stirred at 100 °C for 24 h then was filtered and concentrated *in vacuo*. The mixture was allowed to cool down to room temperature and then the crude material was purified by CTLC in a CH_2Cl_2/hexane = 1:1 mixed solvent as a mobile phase. A red band was eluted out and characterized latter as **7a** in the yield of 56% (0.164 g, 0.56 mmol) while 4-bromoaldehyde was used as the arylhalide source. A lower yield, 33% (0.087 g, 0.33 mmol), was calculated and identified latter as **7b** for the case where bromobenzene was used as the starting bromide.

Table 4
Crystal data of **5-cis**, and **6**.

Compound	**5-cis**	**6**
Formula	$C_{48}H_{41}CoP_2$	$C_{48}H_{41}Cl_2CoP_2Pd$
Formula weight	738.68	915.98
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$
a (Å)	14.18(2)	19.142(4)
b (Å)	17.89(2)	10.991(2)
c (Å)	15.17(2)	23.112(5)
α (°)	–	–
β (°)	93.79(3)	110.14(3)
γ (°)	–	–
V (Å^3)	3839(10)	4564.8(16)
Z	4	4
D_{calc} (mg/m^3)	1.278	1.333
λ (Mo Kα), Å	0.71073	0.71073
μ (mm^{-1})	0.563	0.975
θ Range(°)	1.10–24.40	1.83–26.05
Observed reflections ($F > 4\sigma(F)$)	7533	8964
Number of refined parameters	460	484
R_1 for significant reflections[a]	0.0545	0.0516
wR_2 for significant reflections[b]	0.1365	0.0966
Goodness-of-fit[c]	0.981	1.006

[a] $R_1 = |\Sigma(|F_o| - |F_c|)/|\Sigma F_o||$.

[b] $wR_2 = \left\{\Sigma\left[w(F_o^2 - F_c^2)^2\right]/\Sigma\left[w(F_o^2)^2\right]\right\}^{1/2}$, w = 0.0934 and 0.0400 for **5-cis** and **6**, respectively.

[c] $\mathrm{GoF} = \left[\Sigma w(F_o^2 - F_c^2)^2/(N_{\mathrm{rflns}} - N_{\mathrm{params}})\right]^{1/2}$.

3.3.1. Characterization of **7a** and **7b**

7a: ^{1}H NMR ($CDCl_3$/ppm): δ 9.91 (s, 1H, CHO), 7.73 (d, 2H, J_{H-H} = 8.4 Hz, Ph), 7.54 (d, 2H, J_{H-H} = 8.1 Hz, Ph), 4.69 (t, 2H, J_{H-H} = 2.1 Hz, Cp), 4.38 (t, 2H, J_{H-H} = 2.1 Hz, Cp), 3.99 (s, 5H, Cp). ^{13}C{^{1}H} NMR ($CDCl_3$/ppm): δ 191.66, 129.87, 126.01, 70.69, 69.81, 39.98 (m). *Anal.* Calc. for $C_{17}H_{14}FeO$: C, 70.37; H: 4.86. Found: C, 69.83; H: 5.35. LRMS: m/z = 290 (M^+).

7b: ^{1}H NMR ($CDCl_3$/ppm): δ 7.49 (m, 2H, Ph), 7.30 (m, 2H, Ph), 7.17 (m, 1H, Ph), 4.63 (t, 2H, J_{H-H} = 1.6 Hz, Cp), 4.30 (t, 2H, J_{H-H} = 1.6 Hz, Cp), 4.04 (s, 5H, Cp). ^{13}C{^{1}H} NMR ($CDCl_3$/ppm): δ 128.29, 126.13, 125.89, 69.55, 68.84, 66.48. *Anal.* Calc. for $C_{16}H_{14}Fe$: C, 73.31; H: 5.38. Found: C, 72.93; H: 5.20. LRMS: m/z = 262 (M^+).

3.4. X-ray crystallographic studies

Suitable crystals of **5-cis** and **6** 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 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 [70]. 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. Crystallographic data of **5-cis** and **6** are summarized in Table 4.

3.5. Computational methods

All calculations were carried out using the Gaussian 03 package, in which the tight criterion (10^{-8} hartree) is the default for the SCF convergence [71]. The molecular geometries were fully optimized with the hybrid B3LYP-DFT method under C_1 symmetry, in which the Becke three parameter exchange functional [72] and the Lee-Yang-Parr correlation functional [73] were used. The LANL2DZ including the double-ζ basis sets for the valence and outermost core orbitals combined with pseudopotential were used for Pd [74,75], and 6-31G(d) basis sets for the other atoms.

Acknowledgements

We are grateful to the National Science Council of the ROC (Grant NSC 95-2113-M-005-015-MY3) for financial support. The CPU time that was used to complete this project was mostly provided by the National Center for High-Performance Computing (NCHC).

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2009.11.010.

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