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Palladium catalyzed Suzuki coupling reactions using cobalt-containing bulky phosphine ligands

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Abstract—Three bulky mono-dentate alkyne-bridged dicobalt-phosphine complexes $[(\mu\text{-}PPh_2CH_2PPh_2)Co_2(CO)_4](\mu,\eta\text{-}PhC{\equiv}CPPh_2)$ **4a**, $[(\mu\text{-}PPh_2CH_2PPh_2)Co_2(CO)_4](\mu,\eta\text{-}Me_3CC{\equiv}CPPh_2)$ **5a** and $[(\mu\text{-}PPh_2CH_2PPh_2)Co_2(CO)_4](\mu,\eta\text{-}Me_3SiC{\equiv}CPPh_2)$ **6a** were prepared from the reactions of the bis(diphenylphosphino)methylene (dppm) bridged dicobalt complex $Co_2(CO)_6(\mu\text{-}Ph_2PCH_2PPh_2)$ with $PhC{\equiv}CPPh_2$ **1**, $Me_3CC{\equiv}CPPh_2$ **2**, and $Me_3SiC{\equiv}CPPh_2$ **3**, respectively. These three metal-containing compounds **4a**, **5a** and **6a** were employed as ligands, replacing conventional organic phosphines, in the Suzuki cross-coupling reactions and have been proved to be effective, authentic mono-dentate phosphine ligands.

1. Introduction

Many studies have been focused on Suzuki's palladium-catalyzed cross-coupling reaction in recent years because of its exceptional competence in making sp^2–sp^2 carbon–carbon bond.[1] After several successful methodologies, still a great deal of efforts have been made on promoting the catalytic efficiency with the diversity by the ways of the modification of phosphine ligands,[2] the development of recyclable catalyst[3] and the application to aliphatic electrophiles.[4] It is well known that phosphine ligands play an important role in metal complexes catalyzed organic syntheses. Suitable phosphine ligands are always indispensable for their effective catalytic performance.[5] As established, the mechanism of the palladium-catalyzed cross-coupling reaction involves both oxidative addition and reductive elimination processes.[6] A phosphine with either electron-rich or bulky character is presumed to be able to accelerate the reaction rate and perceived as a potential candidate for an effectively catalytic performance.[7] Although a variety of organic phosphines have already been proved to be efficient in palladium-catalyzed processes, to our best knowledge, only few communications over metal-containing phosphine ligand were published lately.[8]

In our efforts in searching effective ligands for transition metal-catalyzed reactions, we are interested in developing a system that will allow us to straightforward access of a family of bulky phosphines, i.e., cobalt-containing phosphine ligands. The electron-donating capacities of the ligands are expected to be varied after adding cobalt fragment onto the organic moieties. These mono/bi-dentate phosphine ligands can be prepared starting from $Co_2(CO)_8$ with alkynyl phosphines, having the formula of $RC{\equiv}CPPh_2$ or $Ph_2PC{\equiv}CPPh_2$.[9]

Palladium-catalyzed Suzuki cross-coupling reactions of aryl halides with arylboronic acids represent one of the most powerful transformations in organic synthesis.[1b,c,10] In this work, we report some remarkable results of using new type of cobalt-containing mono-dentate phosphine ligands in Suzuki type catalytic coupling reactions. The efficiencies of these ligands are compared and discussed subsequently.

2. Results and discussion

2.1. Preparations of cobalt-containing phosphine ligands

Treatment of a dppm-bridged dicobalt compound $[Co_2(CO)_6(\mu\text{-}P,P{-}PPh_2CH_2PPh_2)]$ with one molar equivalent of alkynyl phosphines $R_1C{\equiv}CPPh_2$ (**1**: $R_1{=}Ph$; **2**: $R_1{=}CMe_3$; **3**: $R_1{=}SiMe_3$) in THF at 45 °C afforded alkyne-bridged dicobalt compounds $[(\mu\text{-}PPh_2CH_2PPh_2)\text{-}Co_2(CO)_4][\mu,\eta\text{-}R_1C{\equiv}CPPh_2]$ (**4a**: $R_1{=}Ph$; **5a**: $R_1{=}CMe_3$; **6a**: $R_1{=}SiMe_3$).[11] (Scheme 1). In addition, two oxidized complexes, $[(\mu\text{-}PPh_2CH_2PPh_2)Co_2(CO)_4](\mu,\eta\text{-}PhC{\equiv}CP({=}O)Ph_2)$ **4b** and $[(\mu\text{-}PPh_2CH_2PPh_2)Co_2(CO)_4]\text{-}(\mu,\eta\text{-}Me_3CC{\equiv}CP({=}O)Ph_2)$ **5b**, were also obtained along with **4a** and **5a** during the chromatographic processes. Compounds **4a**, **4b**, **5a** and **5b** were characterized by

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Keywords: Bulky phosphine; Cobalt-complex; Homogeneous catalysis; Palladium; Suzuki reaction.

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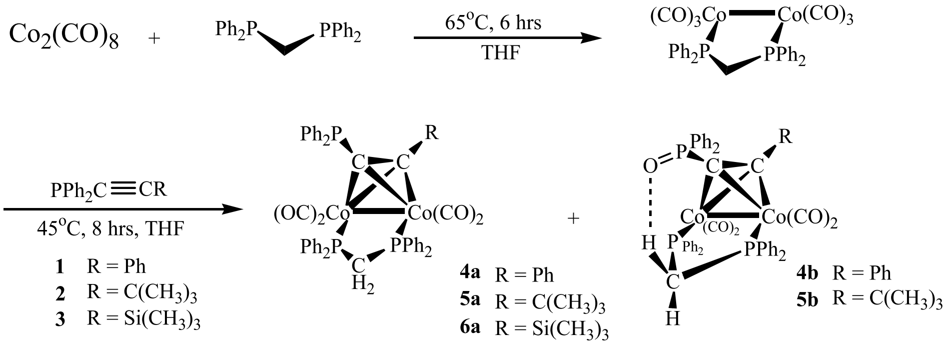


Scheme 1. Synthesis of cobalt-containing phosphine ligands.

spectroscopic means as well as by X-ray diffraction methods (Tables 1 and 2).

The ^{31}P NMR spectrum of **4a** displays two sets of singlet in the ratio of 2:1 at the chemical shifts of 37.5 and 6.8 ppm respectively for three phosphorous atoms. The corresponding signals are 34.7, −6.2 ppm and 34.7, −11.3 ppm for **5a** and **6a**, respectively. The upfield and downfield signals are assigned to the corresponding unbounded and coordinated phosphorous atoms respectively in all cases. The observed large discrepancies in chemical shifts of all three compounds in ^{31}P NMR for the unbounded phosphorous atoms is attributed to the slight difference in electron-donating capacities of these phosphorous atoms. In ^{1}H NMR, there are two distinct chemical shifts 3.32 and 4.25 ppm as well as 3.15 and 4.85 ppm are being observed for the methylene protons of **5a** and **6a**, respectively. Yet, only one set of triplet signal at 3.25 ppm is found for the matching protons in **4a**. It had demonstrated that the signal's outward appearance of the bridged dppm is greatly affected by the degree of its fluxional motion around the dicobalt framework.[9] Based on the ^{1}H NMR spectra, we conclude that the fluxional motion of the bridged dppm is much faster in **4a** than that of **5a** and **6a**.

Similar observations are perceived for the cases of **4b** and **5b**. The ^{31}P NMR spectrum of **4b** shows two singlets in the ratio of 2:1 at 35.7 and 28.4 ppm, respectively, for three phosphorous atoms; while the matching signals are observed at 35.8 and 28.2 ppm, respectively, for **5b**. Large downfield shifts are observed for the oxidized phosphorous atoms. In ^{1}H NMR, a large downfield shift for one of the methylene protons at 5.94 is observed for **4b**, while the matching signal is observed at 6.05 ppm for **5b**.

The selected bond distances and angles for **4a**, **4b**, **5a** and **5b** are displayed in the ORTEP diagrams presented in Figures 1–4. As presented in the figures, the phenyl rings of the bridged alkyne in all cases are pointed away from the center of the molecule to prevent severe steric hindrance. All of the coordinated carbonyl ligands are situated at the terminal positions. Interestingly, the coordinated dppm ligand and the substituent $-PPh_2$ are located on the same side of molecule in **5a**, while they are on the opposite side in **4a**. It can be expected due to the result of minimizing the steric effect among all the bulky groups. In the cases of **4b** and **5b**, the coordinated dppm ligand and the substituent $-P(=O)Ph_2$ are positioned on the same side of molecule. The structures of **4b** and **5b** showed the oxygen atom (of the

Table 1. Crystal data of **4a**, **4b**, **5a** and **5b**

Compound	4a	4b	5a	5b
Formula	$C_{49}H_{37}Co_2O_4P_3{\cdot}CH_2Cl_2$	$C_{49}H_{37}Co_2O_5P_3$	$C_{47}H_{41}Co_2O_4P_3{\cdot}CHCl_3$	$C_{47}H_{41}Co_2O_6P_3$
Formula weight	985.48	916.56	998.93	912.57
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	*P*2(1)/*c*	*P*2(1)/*n*	*P*2(1)/*n*	P-1
a (Å)	13.0444(14)	18.431(3)	23.425(3)	11.2292(10)
b (Å)	19.232(2)	11.5373(17)	9.3966(13)	12.1443(10)
c (Å)	18.983(2)	21.411(3)	23.702(3)	17.4801(16)
α (°)	90(3)	90	90	96.014(2)
β (°)	101.294(2)	111.955(2)	118.080(3)	96.402(2)
γ (°)	90(2)	90	90	112.343(2)
V (Å^3)	4670.0(9)	4222.7(10)	4603.0(11)	2162.8(3)
Z	4	4	4	2
D_c (Mg/m^3)	1.402	1.442	1.441	1.401
λ (Mo Kα), Å	0.71073	0.71073	0.71073	0.71073
μ (mm^{-1})	0.971	0.947	1.402	0.926
θ range (°)	1.52 to 26.05	2.04 to 25.99	1.68 to 26.02	1.84 to 26.02
Observed reflections ($F>4\sigma(F)$)	1437	4760	2984	1753
No. of refined parameters	550	540	541	531
$R1$ for significant reflections[a]	0.0592	0.0319	0.0735	0.0574
$wR2$ significant reflections[b]	0.1149	0.0826	0.2001	0.1081
GoF[c]	0.828	0.518	0.895	0.853

[a] $R1 = |\sum(|F_o| - |F_c|)/|\sum F_o||$.

[b] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2/\sum[w(F_o^2)^2]\}^{1/2}$; $w = 0.0588$, 0.1009, 0.1508 and 0.0509 for **4a**, **4b**, **5a** and **5b**, respectively.

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

Table 2. Comparison of selected structural parameters of **4a**, **4b**, **5a** and **5b**

	Compound	
	4a	**4b**
Bond lengths (Å)		
Co(1)–C(2)	1.945(8)	1.966(2)
Co(1)–C(1)	1.996(8)	1.974(2)
Co(1)–P(2)	2.242(3)	2.2358(8)
Co(1)–Co(2)	2.4711(16)	2.4851(5)
Co(2)–C(1)	1.945(8)	1.952(2)
Co(2)–C(2)	1.961(8)	1.968(2)
Co(2)–P(3)	2.225(2)	2.2524(7)
P(1)–O(1)		1.5022(19)
P(1)–C(1)	1.770(8)	1.774(2)
P(2)–C(49)	1.855(7)	1.843(3)
P(3)–C(49)	1.810(8)	1.841(2)
C(1)–C(2)	1.371(10)	1.361(3)
C(2)–C(3)	1.485(10)	1.474(3)
Bond angles (°)		
C(2)–Co(1)–C(1)	40.7(3)	40.42(10)
P(2)–Co(1)–Co(2)	94.05(7)	96.81(2)
C(1)–Co(2)–C(2)	41.1(3)	40.62(10)
P(3)–Co(2)–Co(1)	100.44(8)	96.79(2)
C(49)–P(2)–Co(1)	111.8(3)	110.00(9)
C(49)–P(3)–Co(2)	109.8(3)	109.86(9)
C(2)–C(1)–P(1)	140.8(6)	139.1(2)
Co(2)–C(1)–Co(1)	77.6(3)	78.54(9)
C(1)–C(2)–C(3)	137.1(7)	142.4(2)
Co(1)–C(2)–Co(2)	78.5(3)	78.36(9)
P(3)–C(49)–P(2)	112.2(4)	109.94(12)
	5a	**5b**
Bond lengths (Å)		
Co(1)–C(2)	1.965(7)	1.984(5)
Co(1)–C(1)	2.006(7)	1.967(5)
Co(1)–P(2)	2.235(2)	2.2533(16)
Co(1)–Co(2)	2.4621(15)	2.4715(11)
Co(2)–C(1)	1.994(8)	1.998(5)
Co(2)–C(2)	1.991(8)	1.966(6)
Co(2)–P(3)	2.240(2)	2.2328(16)
P(1)–O(1)		1.489(4)
P(1)–C(1)	1.780(8)	1.772(5)
P(2)–C(47)	1.815(8)	1.817(6)
P(3)–C(47)	1.831(7)	1.814(5)
C(1)–C(2)	1.340(10)	1.357(7)
C(2)–C(3)	1.534(10)	1.511(7)
Bond angles (°)		
C(2)–Co(1)–C(1)	39.4(3)	40.15(19)
P(2)–Co(1)–Co(2)	95.41(7)	97.68(5)
C(1)–Co(2)–C(2)	39.3(3)	40.0(2)
P(3)–Co(2)–Co(1)	98.65(7)	95.59(5)
C(47)–P(2)–Co(1)	111.8(2)	109.32(19)
C(47)–P(3)–Co(2)	110.1(2)	109.8(2)
C(2)–C(1)–P(1)	154.7(6)	144.6(4)
Co(2)–C(1)–Co(1)	76.0(3)	77.10(18)
C(1)–C(2)–C(3)	146.6(7)	144.0(5)
Co(1)–C(2)–Co(2)	77.0(3)	77.45(19)
P(3)–C(47)–P(2)	111.6(4)	111.4(3)

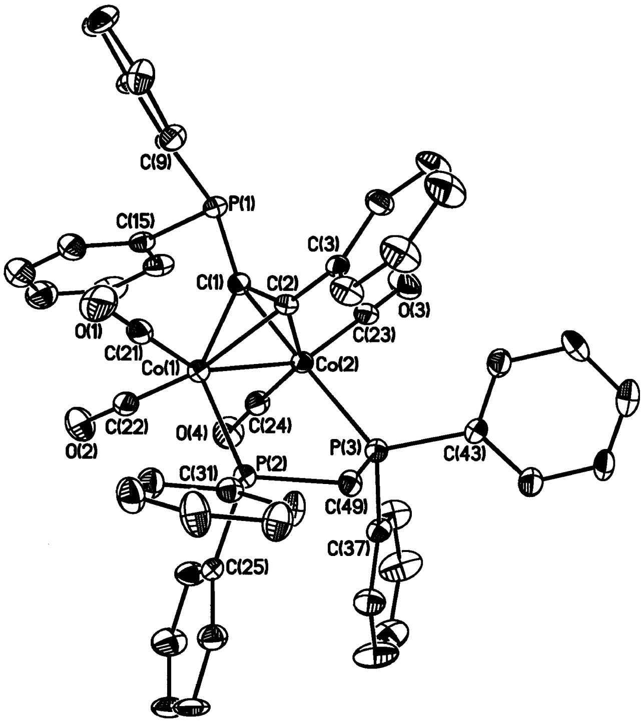


Figure 1. ORTEP drawing of **4a**. Hydrogen atoms are omitted for clarity.

oxidized phosphorus) points down toward the adjacent proton of the methylene. The distances between the oxygen and hydrogen atoms are 2.464 and 2.215 Å for **4b** and **5b**, respectively, which are within the normal range of hydrogen bonding.[12] The shorter bond distance in **5b** than **4b** is caused by the stronger repulsive force arose from the much bulkier –*t*Bu group from the back. The presumption of an intramolecular hydrogen bonding between the oxide and the adjacent methylene proton is also evidenced by the observation of a large downfield shift in ^{1}H NMR at 5.94 and 6.05 ppm for **4b** and **5b**, respectively. Consequently, the effect of the intramolecular hydrogen bonding plays a crucial role in the arrangement of two bulky groups, dppm and –P(=O)Ph$_2$, in **4b** and **5b** ligands. The bond lengths of the bridged alkynes are 1.371(10), 1.361(3), 1.340(10) and 1.357(7) Å for **4a**, **4b**, **5a** and **5b**, respectively, which are close to the regular double bond range. The bond length values between two cobalt atoms are very close in all the ligands. They are 2.4711(16), 2.4851(5), 2.4621(15) and 2.4715(11) Å for **4a**, **4b**, **5a** and **5b**, respectively.

2.2. Suzuki reaction using cobalt-containing phosphine ligands 4a, 5a and 6a with Pd complexes

Suzuki type coupling reactions for arylbromide and phenylboronic acid were carried out by employing the newly made cobalt-containing phosphine ligands **4a**, **5a** and **6a**. The catalytic reaction is performed according to Wolfe's procedures.[7d] Table 3 summarizes the reaction conditions and results.

The cross-coupling reaction of phenylboronic acid with 2-bromothiophene was carried out by employing 1 mol% Pd catalyst (Pd/ligand=1/2) at the reaction temperature of 50 °C for 19 h. The yields are 33 and 42% using **4a** and **5a** as ligands, respectively (entries 1 and 2). These yields are improved to 63 and 75% by raising the temperature to 80 °C and reacting for 16 h (entries 3 and 4). The highest yields 86 and 91% are obtained for **4a** and **5a** ligands, when these reactions were carried out at 100 °C and for 16 h in toluene as solvent (entries 5 and 6). Under similar conditions, the yield is 87% using **6a** as phosphine ligand (entry 7). The results show that these cobalt-containing mono-dentate phosphines are efficient ligands for the Suzuki reactions. Similarly, the cross-coupling reaction was carried out for a less reactive substrate, aryl bromide, under the identical reaction conditions. Initially, the yield was poor (≤29%) in

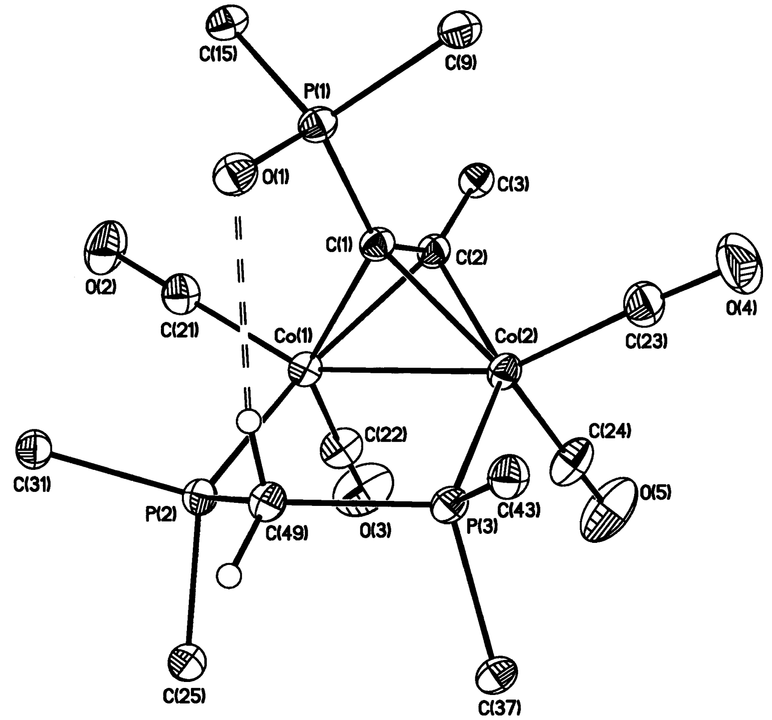


Figure 2. ORTEP drawing of **4b**. Some carbon and hydrogen atoms are omitted for clarity.

the absence of any phosphine ligand (entry 8). On the other hand, much better yields (≥91%) were observed when **4a**, **5a** and **6a** were employed as ligands (entries 9–11). These results are comparable to the data reported by Gladysz et al. using $CpRu(PEt_3)_2PPh_2$ as catalyst.[8c] It clearly shows that all these three compounds are competent phosphine ligands with fairly good activity in Suzuki reaction. Almost complete conversions were obtained using 4-bromobenzaldehyde as substrate, which is in consistence with the common observation for an aryl halide with an electron-withdrawing substituent[8g] (entries 12–14). The results observed in Table 2 echoes the observations of Buchwald and Fu stating that a phosphine ligand with a bulky −*t*Bu as substituent is more efficient than with a less bulky −Ph.[2,7d]

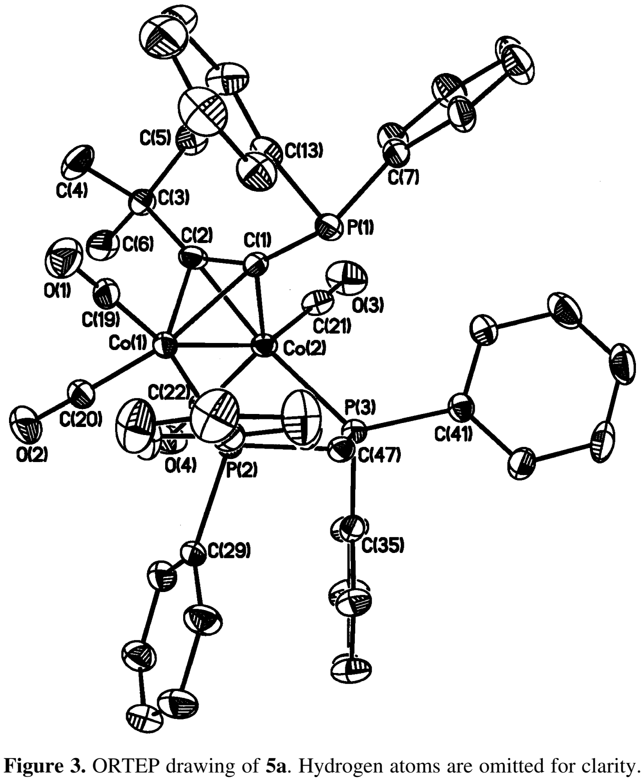


Figure 3. ORTEP drawing of **5a**. Hydrogen atoms are omitted for clarity.

3. Summary

We have demonstrated the preparations and reactivity studies of three new organometallic phosphine ligands **4a**, **5a** and **6a** designed for the palladium-catalyzed Suzuki cross-coupling reaction. Compound **5a** exhibited the highest catalytic efficiency among ligands **4a**, **5a** and **6a** for the cross-coupling reaction of aryl bromides with phenylboronic acid.

4. Experimental

4.1. General

All operations were performed in a nitrogen-flushed glove box or in a vacuum system. Freshly distilled solvents were used. All processes of separations of the products were performed by Centrifugal Thin Layer Chromatography (CTLC, Chromatotron, Harrison model 8924) or column chromatography. ^1H NMR spectra were recorded on 300 MHz Varian VXR-300S spectrometer. The chemical shifts are reported in ppm relative to internal standard $CHCl_3$ or CH_2Cl_2. ^{31}P and ^{13}C NMR spectra were recorded at 121.44 and 75.46 MHz, respectively. Some other routine ^1H NMR spectra were recorded over Gemini-200 spectrometer at 200.00 MHz or Varian-400 spectrometer at 400.00 MHz. IR spectra of samples using KBr were

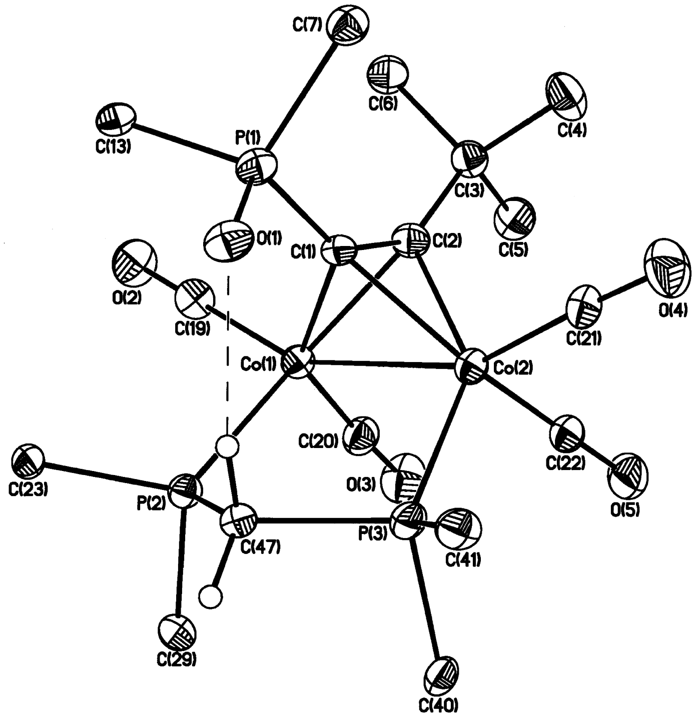
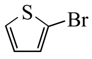
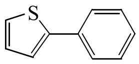
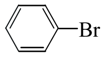
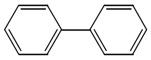
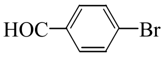
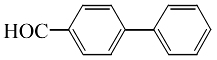


Figure 4. ORTEP drawing of **5b**. Some carbon and hydrogen atoms are omitted for clarity.

Table 3. Suzuki coupling reactions using cobalt-containing phosphine ligands[a]

Entry	Aryl halide	Product	Ligand	Time (h)	Yield (%)
1			**4a**	19	33[b]
2			**5a**	19	42[b]
3			**4a**	16	63[c]
4			**5a**	16	75[c]
5			**4a**	16	86
6			**5a**	16	91
7			**6a**	16	87
8			None	16	29
9			**4a**	16	93
10			**5a**	16	95
11			**6a**	16	91
12			**4a**	16	98
13			**5a**	16	99
14			**6a**	16	97

[a] Reaction conditions: 1.0 equiv. aryl bromide, 1.5 equiv. boronic acid, 2.0 equiv. K_3PO_4, 1 mol% $Pd(OAc)_2$, 2 mol% cat. ligand, toluene (1 mL/mmol aryl bromide), 100 °C; reaction times have not been minimized. Yields in the table are represented in isolated yields (average of two or more experiments) of compounds are estimated to be ≥95% pure as determined by ^{1}H NMR.

[b] The reaction was conducted at 50 °C using THF (1 mL/mmol aryl bromide) and KF (3.0 equiv.) in place of toluene and K_3PO_4.

[c] The reaction was conducted at 80 °C.

recorded on a Hitachi 270-30 spectrometer. Mass spectra were recorded on JOEL JMS-SX/SX 102A GC/MS/MS spectrometer. Elemental analyses were recorded on Heraeus CHN-O-S-Rapid.

4.2. Synthesis of $PhC{\equiv}CPPh_2$ 1 and $Me_3CC{\equiv}CPPh_2$ 2

The preparative procedure for the formation of **1** or **2** was modified to the method reported in literature.[13] Phenylacetylene (1.021 g, 10.000 mmol) and dimethylether (10 mL) were taken in a 100 mL round bottomed flask charged with magnetic stirrer. In a separate round bottomed flask, one molar equivalent of *n*-butyllithium (2.0 M in cyclohexane) dissolved in dimethylether (5 mL). The *n*-butyllithium solution is slowly added to the above mixture under stirring at −78 °C. The resultant mixture is continued to stir at −78 °C for more than 1 h, then one molar equivalent of diphenylchlorophosphine (2.206 g, 10.0 mmol) dissolved in 5 mL dimethylether (5 mL) was slowly added to it. The reaction mixture was then allowed to warm up to room temperature and then stirred for another 1 h. The solvent was removed under reduced pressure and toluene was added to precipitate the lithium chloride. After filtration, the resulted solution was further purified by chromatography. The solid obtained in white needles was identified as **1**.The isolated yield obtained in the reaction is

75.0% (2.147 g, 7.500 mmol). The same procedure was followed for the preparation of **2**.The reaction is started with 3,3-dimethyl-1-butyne (0.822 g, 10.000 mmol) as the alkyne source. The white colored compound obtained was identified as **2**.The isolated yield obtained in the reaction is 78.0% (2.077 g, 7.800 mmol).

4.2.1. Compound 1. ^{1}H NMR ($CDCl_3$, ppm): 7.70–7.22 (15H, arene). ^{31}P NMR ($CDCl_3$, ppm): −32.7 (s, 1P, $C{\equiv}CP$). IR (KBr, cm^{-1}): 2170 (s) ($C{\equiv}C$). MS (FAB): *m/z* 286 (M^+).

4.2.2. Compound 2. ^{1}H NMR ($CDCl_3$, ppm): 7.71–7.36 (10H, arene), 1.42 (s, 9H, CMe_3). ^{31}P NMR ($CDCl_3$, ppm): −33.6 (s, 1P, $C{\equiv}CP$). IR (KBr, cm^{-1}): 2171 (s), 2220 (s) ($C{\equiv}C$). MS (FAB): *m/z* 266 (M^+).

4.3. Synthesis of $[(\mu\text{-}PPh_2CH_2PPh_2)Co_2(CO)_4](\mu,\eta\text{-}PhC{\equiv}CPPh_2)$ 4a, $[(\mu\text{-}PPh_2CH_2PPh_2)Co_2(CO)_4](\mu,\eta\text{-}PhC{\equiv}CP({=}O)Ph_2)$ 4b, $[(\mu\text{-}PPh_2CH_2PPh_2)Co_2(CO)_4]\text{-}(\mu,\eta\text{-}Me_3CC{\equiv}CPPh_2)$ 5a and $[(\mu\text{-}PPh_2CH_2PPh_2)\text{-}Co_2(CO)_4](\mu,\eta\text{-}Me_3CC{\equiv}CP({=}O)Ph_2)$ 5b

1.0 mmol of dicobalt octacarbonyl, $Co_2(CO)_8$ (0.342 g), 1.0 mmol of dppm (0.385 g) and 10 mL of THF were taken in a 100 mL round bottomed flask charged with magnetic stirrer. The solution was stirred at 65 °C for 6 h, a yellow-colored compound, $Co_2(CO)_6(\mu\text{-}P,P{-}PPh_2CH_2PPh_2)$, was yielded. Without separation, the reaction flask was further charged with one molar equivalent of **1** (0.286 g) in 5 mL of THF and then the solution was allowed to stir at 45 °C for 8 h. The solvent was removed under reduced pressure and the resulted dark red-colored residue was separated by CTLC. A purple band was eluted out by mixed solvent (CH_2Cl_2–hexane=1:1) and the compound was identified as **4a** with the yield of 55.0% (0.495 g, 0.550 mmol). A small red band, followed by **4a** during the chromatographic process, was eluted out and the red-colored compound was identified as **4b** with the yield of 9.3% (0.085 g, 0.093 mmol). The similar procedure was followed for the preparations of **5a** and **5b** started with $Co_2(CO)_8$ (0.342 g, 1.000 mmol), dppm (0.385 g, 1.000 mmol) and **2** (0.266 g, 1.000 mmol). The first separated red-colored compound, which was eluted out by mixed solvent (CH_2Cl_2–hexane=1:1), was identified as **5a** with the yield of 60.0% (0.480 g, 0.600 mmol). The second red-colored compound was identified as **5b** with the yield of 6.1% (0.055 g, 0.061 mmol).

4.3.1. Complex 4a. ^{1}H NMR ($CDCl_3$, ppm): 7.54–6.92 (35H, arene), 3.30 (t, J_{P-H}=10.2 Hz, 2H, CH_2). ^{13}C NMR ($CDCl_3$, ppm): 132.3–127.8 (42C, arene), 36.6 (s, 1C, CH_2). ^{31}P NMR ($CDCl_3$, ppm): 37.5 (s, 2P, dppm), 6.8 (s, 1P, PPh_2). IR (KBr, cm^{-1}): 2020 (s), 1994 (s), 1967 (s) ($C{=}O$). MS (ESI): *m/z* 902 (M^++1). Anal. Calcd for $C_{49}H_{37}Co_2O_4P_3$: C, 65.35; H, 4.14. Found: C, 62.56; H, 3.86.

4.3.2. Complex 4b. ^{1}H NMR ($CDCl_3$, ppm): 7.78–7.04 (35H, arene), 6.02–5.94 (m, 1H, CH_2), 3.40–3.33 (m, 1H, CH_2). ^{13}C NMR ($CDCl_3$, ppm): 206.5, 200.8 (s, 2C, CO), 138.2–126.4 (42C, arene), 36.7 (t, J_{P-C}=78.0 Hz, 1C, CH_2). ^{31}P NMR ($CDCl_3$, ppm): 35.7 (s, 2P, dppm), 28.4 (s, 1P, PPh_2). IR (KBr, cm^{-1}): 2021 (s), 1995 (s), 1974 (s) ($C{=}O$). MS (FAB): *m/z* 918 (M^++1). Anal. Calcd for $C_{49}H_{37}Co_2O_5P_3$: C, 64.21; H, 4.07. Found: C, 61.50; H, 3.59.

4.3.3. Complex 5a. ^{1}H NMR ($CDCl_3$, ppm): 7.46–7.00 (30H, arene), 4.33–4.19 (m, 1H, CH_2), 3.39–3.28 (m, 1H, CH_2), 1.29 (s, 9H, $C(CH_3)_3$). ^{13}C NMR ($CDCl_3$, ppm): 207.8, 203.1 (s, 2C, CO), 138.5–127.4 (36C, arene), 37.6 (s, 1C, CH_2), 33.2 (s, 3C, $C(CH_3)_3$). ^{31}P NMR ($CDCl_3$, ppm): 34.7 (s, 2P, dppm), −6.2 (s, 1P, PPh_2). IR (KBr, cm^{-1}): 2009 (s), 1984 (s), 1962 (s) ($C{=}O$). MS (ESI): *m/z* 880 (M^+). Anal. Calcd for $C_{47}H_{41}Co_2O_4P_3$: C, 64.10; H, 4.69. Found: C, 63.92; H, 5.07.

4.3.4. Complex 5b. ^{1}H NMR ($CDCl_3$, ppm): 7.82–7.00 (30H, arene), 6.05 (brd, 1H, CH_2), 3.29 (brd, 1H, CH_2), 1.26 (s, 9H, $C(CH_3)_3$). ^{13}C NMR ($CDCl_3$, ppm): 209.6, 208.0 (s, 2C, CO), 138.5–125.1 (36C, arene), 38.0 (s, 1C, $C(CH_3)_3$), 35.4 (t, J_{P-C}=76.4 Hz, 1C, CH_2), 33.2 (s, 3C, $C(CH_3)_3$). ^{31}P NMR ($CDCl_3$, ppm): 35.8 (s, 2P, dppm), 28.2 (s, 1P, PPh_2). IR (KBr, cm^{-1}): 2016 (s), 1991 (s), 1960 (s) ($C{=}O$). MS (FAB): *m/z* 896 (M^+). Anal. Calcd for $C_{47}H_{41}Co_2O_5P_3$: C, 62.96; H, 4.61. Found: C, 63.83; H, 4.91.

4.4. General procedure for the Suzuki coupling reactions

Suzuki coupling reaction was performed according to Wolfe's procedure.[7d] The four reactants, $Pd(OAc)_2$ (2.200 mg, 0.010 mmol), phosphine ligand **4a** (or **5a**, **6a**) (L/$Pd(OAc)_2$=2/1), the boronic acid (0.183 g, 1.500 mmol) and K_3PO_4 (0.425 g, 2.000 mmol) were taken into a suitable oven-dried Schlenk flask. The flask was evacuated and backfilled with nitrogen before adding toluene (1 mL) and the aryl halide (1.000 mmol) through a rubber septum. The aryl halides being solids at room temperature were added prior to the evacuation/backfill cycle. The flask was sealed with Teflon screw cap and the solution was stirred at the required temperature for designated hours. Then, the reaction mixture was diluted with ether (30 mL) and poured into a separatory funnel. The mixture was washed with aqueous NaOH (1 M, 20 mL) and the aqueous layer was extracted with ether (20 mL). The combined organic layer were washed with brine (20 mL) and dried with anhydrous magnesium sulfate. The dried organic layer was concentrated in vacuo. The crude material was further purified by flash chromatography on silica gel.

4.4.1. 2-Phenylthiophene. ^{1}H NMR ($CDCl_3$, ppm): 7.69 (d, *J*=7.2 Hz, 2H), 7.44 (dd, *J*=7.8, 7.2 Hz, 2H), 7.44 (t, *J*=7.8 Hz, 1H), 7.37 (d, *J*=3.8 Hz, 1H), 7.33 (d, *J*=5.0 Hz, 1H), 7.13 (dd, *J*=5.0, 3.8 Hz, 1H).

4.4.2. Biphenyl. ^{1}H NMR ($CDCl_3$, ppm): 7.59 (t, *J*=11.2 Hz, 2H), 7.44 (m, *J*=46.8 Hz, 4H), 7.35 (d, *J*=8 Hz, 4H).

4.4.3. 4-Biphenylcarbaldehyde. ^{1}H NMR ($CDCl_3$, ppm): 10.01 (s, 1H, COH), 7.73 (d, *J*=8.2 Hz, 2H), 7.52 (d, *J*=8.2 Hz, 2H), 7.40 (d, *J*=8.4 Hz, 2H), 7.30–7.19 (m, *J*=23.4 Hz, 3H).

4.5. X-ray crystallographic studies

Suitable crystals of **4a**, **4b**, **5a**, and **5b** 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.[14] All non-H atoms were located from successive Fourier maps and the 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.[15] Crystallographic data of **4a**, **4b**, **5a**, and **5b** are summarized in Table 1.

5. Supplementary information

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC no. 216404-216407 for compounds **4a**, **4b**, **5a**, and **5b**, respectively. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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