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Reaction of $CpCo(PPh_3)_2$ with diphenylphosphinoalkynes: Syntheses and X-ray structures of 1,3-cyclobutadiene-substituted CpCoCb diphosphine and 2,5-cobaltacyclopentadiene diphosphine dioxide

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Abstract

A potentially bidentate cobalt-containing phosphine ligand, $[(\eta^5\text{-}C_5H_5)Co(\eta^4\text{-}1,3\text{-}(PPh_2)_2C_4Ph_2)]$ (*trans*-**1**), was prepared from the reaction between $PhC{\equiv}CPPh_2$ and $CpCo(PPh_3)_2$ obtained in situ from $CoCl(PPh_3)_3$ and NaCp. The cobaltacycle $[(\eta^5\text{-}C_5H_5)(PPh_3)Co(2,5\text{-}(PPh_2)_2C_4H_2)]$ (**2**) was prepared from the reaction of $CpCo(PPh_3)_2$ with $HC{\equiv}CPPh_2$. An oxidized product $[(\eta^5\text{-}C_5H_5)(PPh_3)Co(2,5\text{-}(P(O)Ph_2)_2C_4H_2)]$ (**4**), was obtained upon the attempted isolation of **2** using CTLC. Both **2** and **4** failed to produce $[(\eta^5\text{-}C_5H_5)Co(\eta^4\text{-}1,2\text{-}(PPh_2)_2C_4H_2)]$ or its oxidized analog, respectively, upon thermal activation. The performance of phosphine **1** in the Suzuki coupling of several aryl chlorides with phenylboronic acid in the presence of $Pd(OAc)_2$ was evaluated.

Keywords: Dppf; Cobalt-containing phosphine; Suzuki coupling reaction; Diphenylphosphinoalkynes; Cobaltacyclopentadiene; (η^5-Cyclopentadienyl)-(η^4-cyclobutadiene)cobalt

1. Introduction

Phosphine-assisted, palladium complexes catalyzed Suzuki–Miyaura reaction [1] is one of the most popular cross-coupling reactions that leads to C–C bond formation [2]. As known, a well performed phosphine ligand in the Suzuki–Miyaura reaction is typically with either electron-rich and/or bulky character [3]. The former accelerates the rate of oxidative addition of arylhalide to Pd(0), the latter speeds up the process of the reductive elimination of diaryl from Pd(II) [4]. Bulky monodentate phosphine ligands, such as tri-*t*-butylphosphine [5], biphenyl-2-yl-di-*t*-butylphosphine, biphenyl-2-yl-dicyclohexylphosphine [6], have been widely applied in Suzuki's palladium-catalyzed reaction. Although, numerous organic phosphine ligands have been explored [7], to the best of our knowledge, the subject of employing transition metal-containing phosphines (TM-phosphines) as ligands in Suzuki–Miyaura reaction remains relatively untouched [8]. Their usefulness in catalytic enantioselective reactions has been reviewed recently [9].

Bis(diphenylphosphino)ferrocene (dppf) and its derivatives are probably the most wildly used metal-containing bidentate phosphine ligands known so far [10]. The dppf-ligated palladium complexes have been employed in various cross-coupling reactions [11]. One of the most admired advantages of using dppf is the flexibility of the bite angle caused by free rotation of two rings [12]. Recently, excellent results have been obtained in the amination reaction using the dppf derivatives shown below (Diagram 1) [13].

On the one hand, it is of interest to us to develop a series of cobalt-containing analogs of dppf ligands and to

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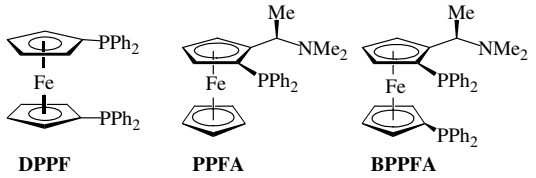


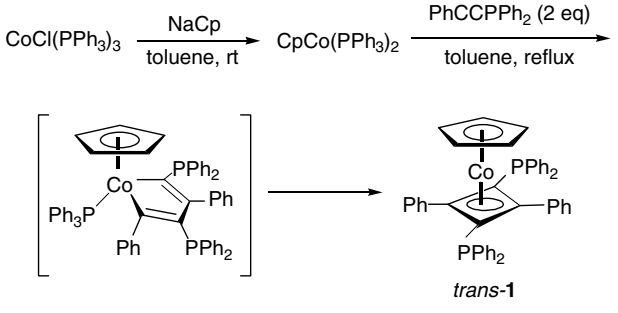
Diagram 1.

examine their catalytic capacities in the above mentioned cross-coupling reactions. Such analogs could be built using a robust (η^5-cyclopentadienyl)(η^4-cyclobutadiene)cobalt framework. When each ring system has a phosphino-substituent attached, the electron-donating abilities of the latter are expected to be slightly different. Thus, such a system could exhibit a behavior different from that of dppf. On the other hand, we are also interested in compounds having both phosphino-substituents attached to the same ring system, either Cp or Cb. Herein, we report our findings in the course of pursuing the synthesis of (η^5-cyclopentadienyl)(η^4-*bis*-(diphenylphosphino)cyclobutadiene)cobalt.

2. Results and discussion

The common approach to the synthesis of cyclobutadiene-substituted CpCoCb complexes is the reaction of $CpCoL_2$ ($L = CO$, PPh_3, $L_2 = COD$) [14] with alkyne(s) bearing the appropriate substituents. (η^5-Cyclopentadienyl)-(η^4-*trans*-diphenylphosphinodiphenylcyclobutadiene)-cobalt, [(η^5-C_5H_5)Co(1,3-(PPh_2)$_2$$C_4Ph_2$)] (*trans*-**1**), was prepared according to Scheme 1. This procedure employing $CoCl(PPh_3)_3$ as a starting material does not require isolation of air-sensitive $CpCo(PPh_3)_2$. In principle, the reaction of the latter with phenyl diphenylphosphinoacetylene could produce a potentially chelating and therefore more interesting *cis*-isomer as well. Unfortunately, not even a trace of *cis*-**1** has been observed. It is believed that the severe steric hindrance of the two bulky diphenylphosphine substituents causes the absence of the desired *cis*-**1**.

In the ^{1}H NMR spectrum of *trans*-**1** there is a sharp singlet at 4.62 ppm corresponding to its 5 equiv. cyclopentadienyl protons. A single signal at −16.2 ppm present in the ^{31}P NMR spectrum indicates the equivalence of two phosphorous atoms, which would also be the case for *cis*-



Scheme 1. One-pot synthesis of *trans*-**1**.

Table 1
Crystal data of **1** and **4** · 2HCl · CH_2Cl_2

Compound	**1**	**4** · 2HCl · CH_2Cl_2
Formula	$C_{45}H_{35}P_2Co$	$C_{52}H_{46}O_2Cl_4P_3Co$
Formula weight	696.60	996.61
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2(1)/c$
a (Å)	9.9405(12)	24.036(3)
b (Å)	13.2536(15)	10.9309(12)
c (Å)	13.9349(17)	20.034(2)
α (°)	92.225(2)	–
β (°)	98.666(2)	110.351(2)
γ (°)	100.838(3)	
V (Å^3)	1778.3(4)	4935.1(9)
Z	2	4
D_c (Mg/m^3)	1.301	1.339
λ (Mo Kα) (Å)	0.71073	0.71073
μ (mm^{-1})	0.604	0.700
θ Range (°)	2.23–26.02	1.81–26.06
Observed reflections ($F > 4\sigma(F)$)	6889	9719
No. of refined parameters	433	595
R_1[a] for significant reflections	0.0417	0.0582
wR_2[b] for significant reflections	0.1204	0.1595
GoF[c]	0.774	1.038

[a] $R_1 = |\sum(|F_o| - |F_c|)/|\sum F_o||$.
[b] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2/\sum[w(F_o^2)^2\}\}^{1/2}$; $w = 0.1276$ and 0.1081 for **1** and **4**, respectively.
[c] $\mathrm{GoF} = [\sum w(F_o^2 - F_c^2)^2/(N_{\mathrm{rflns}} - N_{\mathrm{params}})]^{1/2}$.

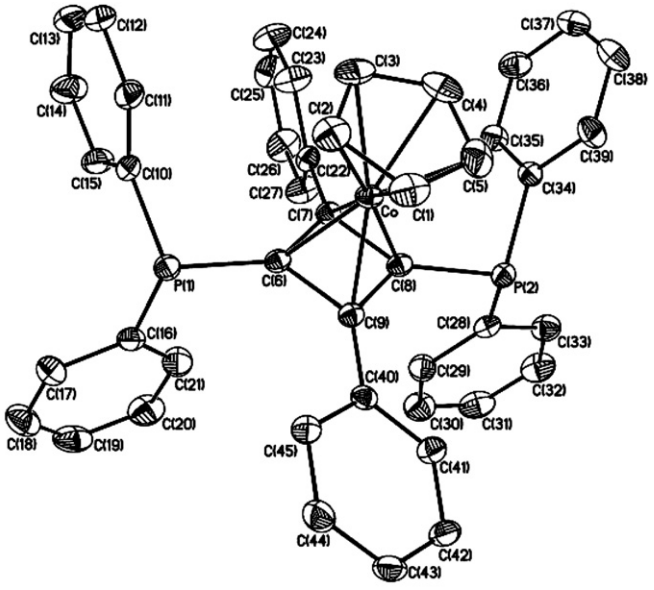
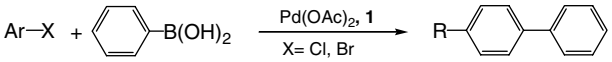


Fig. 1. ORTEP drawing of **1**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°): Co–C(9) 1.980(3); Co–C(7) 1.982(3); Co–C(6) 1.984(3); Co–C(8) 1.989(3); Co–C(4) 2.041(3); Co–C(5) 2.046(3); Co–C(3) 2.057(3); Co–C(1) 2.069(3); Co–C(2) 2.070(3); P(1)–C(6) 1.809(3); P(1)–C(16) 1.831(3); P(1)–C(10) 1.835(3); P(2)–C(8) 1.808(3); P(2)–C(28) 1.844(3); P(2)–C(34) 1.845(3); C(1)–C(5) 1.410(5); C(1)–C(2) 1.411(5); C(2)–C(3) 1.410(5); C(3)–C(4) 1.404(5); C(4)–C(5) 1.405(6); C(6)–C(9) 1.475(4); C(6)–C(7) 1.475(4); C(7)–C(8) 1.473(4); C(8)–C(9) 1.470(4); and C(6)–Co–C(4) 155.71(15); C(6)–P(1)–C(16) 101.28(13); C(6)–P(1)–C(10) 101.44(12); C(16)–P(1)–C(10) 101.25(13); C(8)–P(2)–C(28) 101.76(13); C(8)–P(2)–C(34) 104.20(12); C(28)–P(2)–C(34) 103.09(13); C(5)–C(1)–C(2) 107.2(3); C(3)–C(2)–C(1) 108.3(3); C(4)–C(3)–C(2) 108.0(3); C(3)–C(4)–C(5) 107.9(3); C(4)–C(5)–C(1) 108.6(3); C(9)–C(6)–C(7) 89.7(2); C(9)–C(6)–P(1) 131.8(2); C(7)–C(6)–P(1) 138.2(2); C(8)–C(7)–C(6) 90.1(2); C(9)–C(8)–C(7) 90.0(2); C(9)–C(8)–P(2) 130.19(19); C(7)–C(8)–P(2) 139.8(2); C(8)–C(9)–C(6) 90.2(2).

1. Although the NMR data alone could not provide the unambiguous assignment of the substitution pattern of the isolated product, the molecular structure determined by single-crystal X-ray diffraction method (Table 1, Fig. 1) proved it to be a derivative of a known compound (η^5-cyclopentadienyl)(η^4-cyclobutadiene)-cobalt with two diphenylphosphino-substituents situated on the diagonal of the cyclobutadiene. The four carbon–carbon bond distances of the cyclobutadiene ring of *trans*-**1** are almost the same. The five- and four-membered rings are almost parallel to each other. Although *trans*-**1** cannot act as a chelating ligand, it can certainly behave either as a mono- or bidentate ligand depending on the situation.

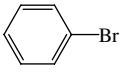
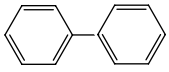
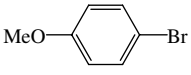
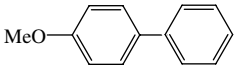
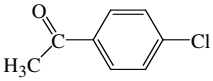
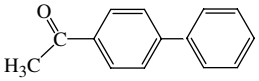
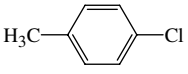
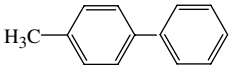
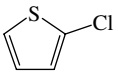
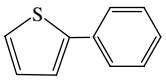
The performance of phosphine **1** in the Suzuki reaction between 4-chloroacetophenone and phenylboronic acid employing various $Pd(OAc)_2$-ligand ratios and bases was briefly surveyed (Table 2). The best yield (63%) was obtained with the metal to ligand ratio of 2:1 and NaOH as a base at 65 °C in aqueous phase (entry 3). Unfortunately, no reaction was observed with 4-chlorotoluene, 2-chlorotoluene or 2-chlorothiophene as substrates. With bromobenzene as a substrate and NaOH as a base the reaction in a mixed solvent (H_2O:THF = 1:5) at room temperature furnished the biaryl product in 88% yield (entry 1). Even a 66% conversion was observed in mild condition when a less reactive 4-methyl-benzyl bromide being used (entry 2) (see Scheme 2).

The catalytic performance of *cis*-**1** or a similar diphosphine capable of chelation could be much better compared with that of the *trans*-isomer. Therefore, we attempted to change the stereochemical outcome of the above reaction (two phosphino-substituents *trans*-to each other) to the desired *cis*-arrangement by using a different alkyne. Presumably, the failure of $PhC{\equiv}CPPh_2$ to produce *cis*-**1** could be attributed to the relatively large size of both phenyl and diphenylphosphino-groups [15], which precludes the formation of the intermediate 3,4-diphenyl- or 3,4-diphenylphosphinocobaltacyclopentadienyl complexes required to yield the *cis*-substituted cyclobutadiene complex. To circumvent this problem, a terminal alkyne, diphenylphosphinoacetylene, was used instead (Scheme 3). Although the analog of *cis*-**1** could not be isolated after reflux, the same reaction carried out at room temperature produced the cobaltacycle $[(\eta^5\text{-}C_5H_5)(PPh_3)Co(2,5\text{-}(PPh_2)_2C_4H_2)]$ (**2**). Interestingly, while **2** of acceptable purity (contaminated only by a small amount of the corresponding monoxide $[(\eta^5\text{-}C_5H_5)(PPh_3)Co(2\text{-}(P(O)Ph_2)\text{-}5\text{-}(PPh_2)C_4H_2)]$ (**3**)) could be isolated by column chromatography, CTLC separation resulted in $[(\eta^5\text{-}C_5H_5)(PPh_3)Co(2,5\text{-}(P(O)Ph_2)_2C_4H_2)]$ (**4**), with both phosphino-substituents oxidized. Since *trans*-**1** does not undergo oxidation upon CTLC separation, this could be an indication that two phosphino-substituents of cobaltacycle **2** are more electron-rich compared with those of *trans*-**1**. Usually **4** isolated after a single CTLC run contains some triphenylphosphine oxide, therefore,

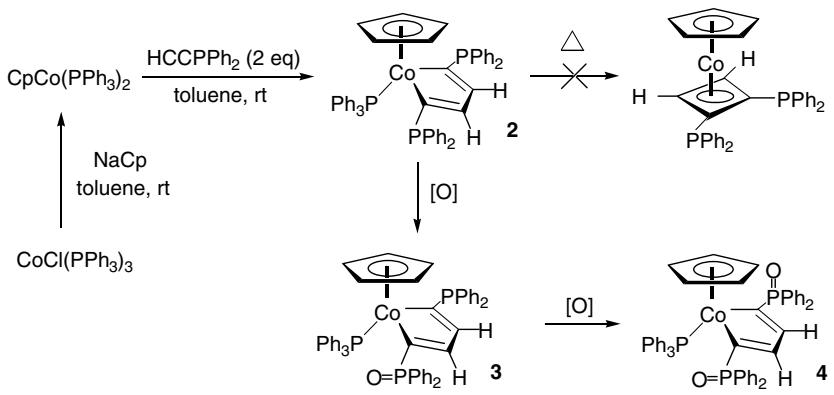


Scheme 2.

Table 2
Biphasic Suzuki reactions employ $Pd(OAc)_2$/**1** = 2:1 as catalyst precursor[a]

Entry	Halide	Time (h)	Product	Conv. (%)
1		3		88[b]
2		3		66
3[c]		18		79(63[b])
4[c]		18		NR
5[c]		18		NR

[a] Reactions were conducted in mixed solvent (H_2O:THF = 1:5) with 3.0 M NaOH(aq) at 25 °C using 2.0 mol% $Pd(OAc)_2$ plus 1.0 mol% **1** as catalyst precursor. Bromobenzene or bromoanisole (1.0 mmol) and phenylboronic acid (1.0 mmol) were as reaction substrates.
[b] Isolated yield.
[c] The mixed solution was reacted at 65 °C for 18 h.



Scheme 3. One-pot synthesis of cobaltacycle **2**.

additional separation is required to obtain the analytically pure compound. Contrary to the general behavior of cobaltacycles $[(\eta^5\text{-}C_5H_5)(PPh_3)Co(R_4C_4)]$ [16] undergoing transformation to the corresponding η^4-cyclobutadiene complexes upon thermal activation *via* a loss of PPh_3, attempts to convert both **2** and **4** to either $[(\eta^5\text{-}C_5H_5)Co(\eta^4\text{-}1,2\text{-}(PPh_2)_2C_4H_2)]$ or its oxidized analog by reflux in toluene were unsuccessful. Although the starting materials were consumed completely in both cases, the main isolated cobalt-containing products did not display any signals in their ^{31}P NMR spectra.

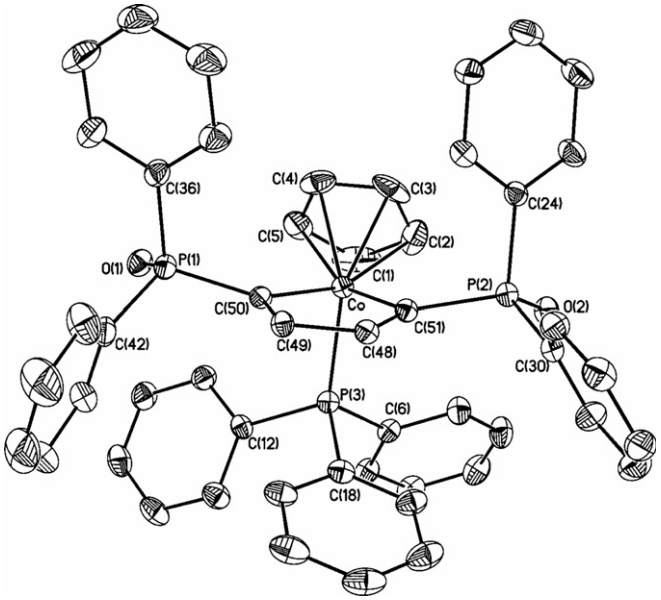


Fig. 2. ORTEP drawing of **4**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°):Co–C(50) 1.956(4); Co–C(51) 1.977(3); Co–C(3) 2.068(5); Co–C(4) 2.081(5); Co–C(1) 2.087(5); Co–C(2) 2.091(5); Co–C(5) 2.095(5); Co–P(3) 2.2192(11); P(1)–O(1) 1.492(3); P(1)–C(50) 1.787(4); P(2)–O(2) 1.487(3); P(2)–C(51) 1.780(4); C(1)–C(2) 1.372(9); C(1)–C(5) 1.379(9); C(2)–C(3) 1.369(9); C(3)–C(4) 1.369(8); C(4)–C(5) 1.317(8); C(48)–C(51) 1.346(5); C(48)–C(49) 1.444(5); C(49)–C(50) 1.355(5); and C(50)–Co–C(51) 82.20(15); C(50)–Co–P(3) 87.81(11); C(51)–Co–P(3) 91.76(11); O(1)–P(1)–C(50) 117.34(17); O(2)–P(2)–C(51) 115.90(16); C(51)–C(48)–C(49) 114.9(3); C(50)–C(49)–C(48) 115.1(3); C(49)–C(50)–P(1) 117.5(3); C(49)–C(50)–Co 113.7(3); P(1)–C(50)–Co 128.2(2); C(48)–C(51)–P(2) 119.5(3); C(48)–C(51)–Co 113.4(3); P(2)–C(51)–Co 126.4(2).

Compounds **2** and **4** were characterized by NMR. In their ^1H NMR spectra cyclopentadienyl protons appear as sharp singlets at 4.52 and 4.94 ppm, respectively. There is also a significant downfield shift for the cobaltacyclopentadienyl protons of **4** compared with the corresponding resonance of **2** (6.34 vs. 6.14 ppm). Two signals in the 2:1 ratio were observed in the ^{31}P NMR spectra of compounds **2** and **4**. The coordinated triphenylphosphine signals appear at 52.7 and 53.5 ppm while the phosphorus atoms directly attached to the cobaltacycle appear at 1.6 and 35.5 ppm, respectively. The ^{31}P NMR spectrum of **2** isolated by column chromatography usually displays additional signals of low intensity at 54.2, 36.2 and −0.4 ppm (1:1:1) due to small amounts of monoxide **3** present. In addition, compound **4** was characterized by X-ray diffraction methods (Table 1, Fig. 2). Suitable crystals were grown by addition of hexane to a solution of **4** in CH_2Cl_2 containing some $CDCl_3$. In crystal packing, each molecule of **4** contains two HCl molecules which might be a contamination of $CDCl_3$. Compound **4** has a typical cobaltacycle structure with both phosphino-substituents attached to the α-carbons of the cycle. This outcome is believed to be a result of the kinetic control of cobalt-mediated coupling of two diphenylphosphinoacetylene moieties at room temperature.

3. Conclusions

A potentially bidentate cobalt-containing phosphine ligand, $[(\eta^5\text{-}C_5H_5)Co(\eta^4\text{-}1,3\text{-}(PPh_2)_2C_4Ph_2)]$ (*trans*-**1**), was prepared using the CpCo-mediated dimerization of (diphenylphosphino)phenylacetylene. Formation of *cis*-**1** was not observed. Attempts to prepare a closely related *cis*-isomer using diphenylphosphinoacetylene instead of (diphenylphosphino)- phenylacetylene resulted in cobaltacycle $[(\eta^5\text{-}C_5H_5)(PPh_3)Co(2,5\text{-}(PPh_2)_2C_4H_2)]$ (**2**), which could not be converted to the corresponding CpCoCb derivative

upon thermal activation. [(η^5-C_5H_5)(PPh_3)Co(2,5-(P(=O)-Ph_2)$_2C_4H_2$)] (**4**), the product of oxidation of both phosphino-substituents in **2**, was obtained in the course of isolation of **2** by CTLC. The performance of **1** as an efficient ligand in Suzuki reactions of bromobenzenes and chlorobenzenes with boronic acid was briefly examined.

4. Experimental

4.1. General information

$CoCl(PPh_3)_3$ was synthesized according to the procedure by Aresta et al. [17] employing zinc as a reducing agent. Phenylethynyl diphenylphosphine [18a] and diphenylphosphinoacetylene [18b] were synthesized according to the published procedures. Most synthetic manipulations were carried out using standard Schlenk techniques under dry nitrogen atmosphere. Freshly distilled solvents were used. Separations were carried out by column chromatography on Silica gel 60 (70–230 mesh, Merck) or 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.

4.2. Synthesis of [(η^5-C_5H_5)Co(η^4-1,3-(PPh_2)$_2C_4Ph_2$)] (**1**)

A 100 mL round-bottomed flask equipped with a magnetic stirbar and a rubber septum was charged with $CoCl(PPh_3)_3$ (0.440 g, 0.499 mmol) and 10 mL toluene. To the resulting suspension 0.25 ml of 2.0 M solution of NaCp in THF (0.50 mmol) was added dropwise. After 30 min, a solution of phenylethynyl diphenylphosphine (0.210 g, 1.000 mmol) in toluene (5 mL) was added, and the mixture was refluxed for 12 h. Subsequent purification was carried out using CTLC. From the yellow band eluted with CH_2Cl_2–hexane (1:1) 0.123 g of the title compound was isolated (35% yield). ^1H NMR ($CDCl_3$): δ 7.32–6.87 (m, 30H, Ph and PPh_2), 4.62 (s, 5H, Cp). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.43 MHz): δ 136.7 (d, $J_{C-P} = 8.1$), 135.5, 133.6 (d,$J_{C-P} = 18.8$), 129.6, 128.2–127.3 (m), 126.1, 88.7 (t, $^2J_{C-P} = 7.0$, C(2) and C(4) of Cb), 82.7 (Cp), 69.5 (dd, $^1J_{C-P} = 33.6$, $^3J_{C-P} = 6.7$; C(1) and C(3) of Cb). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −16.2. Anal. Calc. for $C_{45}H_{35}P_2Co$: C, 77.58; H, 5.06. Found: C, 78.01; H, 5.06%. LRMS: $m/z = 696.6$ (M^+).

4.3. Synthesis of [(η^5-C_5H_5)(PPh_3)Co(2,5-(PPh_2)$_2C_4H_2$)] (**2**)

A 100 mL round-bottomed Schlenk flask equipped with a magnetic stirbar and a rubber septum was charged with ethynyldiphenylphosphine (1.458 g, 6.94 mmol) and 20 mL toluene. Another 100 mL round-bottomed Schlenk flask equipped with a magnetic stirbar and a rubber septum was charged with $CoCl(PPh_3)_3$ (3.092 g, 3.510 mmol) and 20 mL toluene. To the resulting suspension 1.75 ml of 2.0 M solution of NaCp in THF (3.50 mmol) was added dropwise within 10 min. After 45 min of stirring at room temperature the ethynyldiphenylphosphine solution was added to the dark-red solution of $CpCo(PPh_3)_2$ via a cannula. The ethynyldiphenylphosphine flask was washed with 5 mL toluene, and the wash was added to the reaction mixture. After 26 h of stirring at room temperature toluene was removed in vacuo. The residue was transferred into a 250 mL round-bottomed flask using dichloromethane, and 6.8 g silica gel was added to the mixture followed by solvent evaporation. The crude product on silica gel was added atop of a column and chromatographed. Initially dichloromethane was used as an eluent to wash out triphenylphosphine, followed by dichloromethane-ethyl acetate (3:2). The title compound was obtained as a dark-brown solid (0.480 g, 17%). ^1H NMR ($CDCl_3$): δ 8.00–7.78 (m, 8H, PPh_3, PPh_2), 7.64–7.38 (m, 13H, PPh_3, PPh_2), 7.07–6.96 (m, 10H, PPh_2), 6.42 (t, 4H, $J = 6.6$, PPh_2), 6.16–6.12 (m, 2H, =CH), 4.52 (s, 5H, Cp). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.70 MHz): δ 173.4 (dd, $J_{C-P} = 76.5$, 29.5; HC=*C*-PPh_2), 155.8 (apparent t, $J_{C-P} = 7.4$, H*C*=C–PPh_2), 141.1 (d, $J_{C-P} = 25.7$), 139.9 (d, $J_{C-P} = 17.1$), 135.1 (d, $J_{C-P} = 21.3$), 135.0 (br s), 132.6 (d, $J_{C-P} = 18.0$), 129.9 (br s), 128.6, 128.3 (d, $J_{C-P} = 6.8$), 127.6 (br s), 127.3 (d, $J_{C-P} = 6.0$), 126.7, 87.7 (Cp). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 52.7 (br s, PPh_3), 1.6 (s, PPh_2). Anal. Calc. for $C_{51}H_{42}P_3Co$: C, 75.93; H, 5.25. Found: C, 75.12; H, 4.68%. LRMS: $m/z = 806.5$ (M).

4.4. Isolation of [(η^5-C_5H_5)(PPh_3)Co(2,5-(P(=O)Ph_2)$_2C_4H_2$)] (**4**)

A 100 mL round-bottomed flask equipped with a magnetic stirbar and a rubber septum was charged with $CoCl(PPh_3)_3$ (0.440 g, 0.499 mmol) and 10 mL toluene. After addition of NaCp in THF (0.25 ml of 2.0 M solution, 0.499 mmol) and stirring for 30 min at room temperature, ethynyldiphenylphosphine (0.210 g, 1.000 mmol) in 5 mL toluene was added. The reaction mixture was stirred at room temperature for 16 h followed by concentration under reduced pressure and CTLC separation using CH_2Cl_2–ethyl acetate (1:1) as an eluent. After the additional CTLC run 0.094 g of the analytically pure compound was obtained as a yellow-brown solid (22%). ^1H NMR ($CDCl_3$): δ 7.89–6.95 (m, 35H, PPh_3, P(O)Ph_2), 6.35–6.25 (br m, 2H, *H*C=C), 4.94 (s, 5H, Cp). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.43 MHz): δ 170.94 (dd, $J_{C-P} = 59.8$, 29.3; HC=*C*–P(O)Ph_2), 159.2 (dd,

$J_{C-P} = 27.5$, 9.8; H*C*=C–P(O)Ph_2), 136.7 (d, $J_{C-P} = 18.9$), 135.4 (d, $J_{C-P} = 14.0$), 134.8 (br s), 132.0 (d, $J_{C-P} = 9.1$), 131.2 (d, $J_{C-P} = 9.8$), 130.8, 129.9, 128.2 (d, $J_{C-P} = 11.6$), 127.5 (d, $J_{C-P} = 11.5$), 86.9 (Cp). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 53.5 (s, PPh_3), 35.5 (br s, P(=O)). Anal. Calc. for $C_{51}H_{42}O_2P_3Co$: C, 73.03, H: 5.05. Found: C, 73.22; H: 4.63%. LRMS: $m/z = 839.3$ (M^+).

4.5. Suzuki cross-coupling reactions using *1*

4.5.1. Method I (conducted in a THF–H_2O mixed solvent)

Complex **1** (0.069 mg, 0.010 mmol), $Pd(OAc)_2$ (2 mol%) and boronic acid (0.121 g, 1.000 mmol) were charged into a 20 ml Schlenk flask. The flask was evacuated and backfilled with nitrogen before adding THF (5 mL), 3 M NaOH solution (1 mL), aryl halide (1.000 mmol) and, in some cases, tetrabutylammonium bromide (TBAB, 0.65 g, 0.2 mmol). The solution was stirred at 65 °C for 18 h. Aqueous NaOH (1 M, 20 mL) was added followed by extraction with ether (30 mL). The organic layer was washed with brine (20 mL), dried with anhydrous magnesium sulfate, filtered, and concentrated in vacuo. The crude material was purified by flash chromatography on silica gel.

4.5.2. Method II (conducted in H_2O)

Complex **1** (0.069 mg, 0.010 mmol), $Pd(OAc)_2$ (2 mol%) and boronic acid (0.121 g, 1.000 mmol) were charged into a 20 ml Schlenk flask. The flask was evacuated and backfilled with nitrogen before adding 3 M NaOH solution (2 mL), aryl halide (1.000 mmol) and, in some cases, tetrabutylammonium bromide (TBAB, 0.65 g, 0.2 mmol). The solution was stirred at 65 °C for 18 h followed by the work-up described in Method I.

4.6. X-ray crystallographic studies

Suitable crystals of **1** and **4** 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 [19]. 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. Crystallographic data of **1** and **4** are summarized in Table 1.

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Appendix A. Supplementary data

CCDC 292852 and 292853 contain the supplementary crystallographic data for **1** and **4**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.09.043.

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