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Preparation of cobalt-containing bulky monodentate phosphines with electron-withdrawing/donating substituents on bridged arylethynyl and their applications in Suzuki coupling reactions

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1. Introduction

The organic reactions catalyzed by transition metal complexes have been a widely studied subject vital to the modern synthetic chemistry.¹ Among them, the palladium-catalyzed cross-coupling reactions used for the formation of carbon-carbon bonds are probably the most well-known.² Ever since its disclosure, the palladium-catalyzed Suzuki-Miyaura reaction has been a focus of extensive investigation by both experimental and theoretical means.³ To get a clear picture of the reaction mechanism, an insightful discernment on the reaction pathways is essential. In the generally accepted simplified mechanism proposed by Suzuki^{2a} an unsaturated $Pd(0)L_n$ (n=1 and 2 for monodentate and bidentate ligands, respectively) species serves as the catalyst precursor. Three major parts of the mechanism are: (1) oxidative addition; (2) transmetalation; and (3) reductive elimination. Each major part consists of several consecutive elementary steps. The first part involves the addition of an aryl halide to $Pd(0)L_n$. During the second part, the halide is exchanged for another aryl group supplied by an arylboronic acid. In the third part, a biaryl product is released from the Pd(II) complex giving back $Pd(0)L_n$. Oxidative addition and reductive elimination processes are frequently observed in transition metal-catalyzed reactions.⁴ Thereby, the basic components of these two processes have been extensively studied by both

ABSTRACT

Several cobalt-containing bulky monodentate phosphines (μ -PPh₂CH₂PPh₂)Co₂(CO)₄(μ , η -(^tBu)₂PC==C (C₆H₄R)) (**4a**: R=H; **4b**: R=*p*-F; **4cp**: R=*p*-CF₃; **4cm**: R=*m*-CF₃; **4d**: R=*p*-OMe) were prepared from the reactions of (^tBu)₂PC==C(R-C₆H₄) (**2a**: R=H; **2b**: R=*p*-F; **2cp**: R=*p*-CF₃; **2cm**: R=*m*-CF₃; **2d**: R=*p*-OMe) with Co₂(CO)₆(μ -PPh₂CH₂PPh₂) **3**. Further reactions of **4a**, **4b**, **4cp**, **4cm**, and **4d** with Pd(OAc)₂ yielded unique palladium complexes (μ -PPh₂CH₂PPh₂)Co₂(CO)₄(μ , η -(^tBu)₂PC==C(C₆H₃R)- κ C¹)Pd(μ -OAc) (**5a**: R=H; **5b**: R=*p*-F; **5cp**: R=*p*-CF₃; **5cm**: R=*m*-CF₃; **5d**: R=*p*-OMe, respectively). The strong electron-withdrawing substituents, -F and -CF₃, assist the *ortho*-metalation process during the formation of **5b**, **5cp**, and **5cm**. The more positively charged palladium center in **5b** (or **5cp**, **5cm**) enhances the probability for PhB(OH)₃ to attack the metal center and the rate of reduction thereafter. DFT studies on the charges of these palladium centers support this assumption. The enhancement of the reaction rates of the Suzuki–Miyaura cross-coupling reactions using **5b**, **5cp**, and **5cm** is thereby attributed to this effect. © 2008 Elsevier Ltd. All rights reserved.

experimental⁵ and theoretical⁶ methods, and as a result are quite well understood. In contrast, transmetalation is a process that is more complicated and less understood. Obviously, the experimental data for the transmetalation process are difficult to accumulate due to the complexity encountered in characterizing the mechanistically relevant intermediates.⁷

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It has been demonstrated repeatedly that a well-chosen ligand is crucial to the success of a palladium-catalyzed Suzuki reaction.^{3b} Thereby, considerable efforts have been devoted to find more efficient ligands. For many years, organophosphines of various kinds and shapes and their derivatives have been the most frequently employed ligands.^{1a,3b,8} Nevertheless, a limited number of transition metal-containing phosphines have also been reported.^{9,10} Our previous studies had demonstrated that a new category of metalcontaining phosphines (μ -PPh₂CH₂PPh₂)Co₂(CO)₄(μ , η -R¹C \equiv CR²) {R¹,R²: P(^tBu)₂, P(ⁱPr)₂, PCy₂, PPh₂, Ph, py} could be prepared handily according to the processes described elsewhere (Diagram 1).¹¹ This new class of phosphines naturally led to the ligands of bulky character, which is obviously beneficial to the reductive elimination process in catalytic cycle. Their roles as legitimate and



Diagram 1. A generalized structure for cobalt-containing phosphines.



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Scheme 1. Syntheses of cobalt-containing monodentate phosphines 4a–d and palladium complexes 5a–d. Here and throughout the article letters a, b, c, and d in abbreviations correspond to R=H, F, CF₃, and OMe, respectively; while p and m stand for *para*- and *meta*-position, respectively. The phosphine oxides are designated by O.

active ligands in palladium-catalyzed cross-coupling reactions have been carefully evaluated.^{11,12}

An organometallic version of 2-(di-tert-butylphosphino)biphenyl,¹³ {[(μ -PPh₂CH₂PPh₂)Co₂(CO)₄][(μ , η -(^tBu)₂PC=C(C₆H₅))]} 4a, was synthesized according to Scheme 1. Firstly, alkynyl phosphine, $[({}^{t}Bu)_{2}PC \equiv C(C_{6}H_{5})]$ **2a**, was prepared by a modified literature procedure.¹⁴ Then, treatment of a dppm-bridged dicobalt compound $[Co_2(CO)_6(\mu-P,P-PPh_2CH_2PPh_2)]$ **3** with 1 molar equivalent of **2a** in THF at 60 °C afforded 4a. A unique palladium complex, {[(µ- $PPh_2CH_2PPh_2)Co_2(CO)_4][(\mu,\eta-({}^tBu)_2PC\equiv C(C_6H_4R)-\kappa C^1)]Pd(\mu-OAc)]$ 5a, was prepared from the reaction of the cobalt-containing bulky phosphine 4a with Pd(OAc)₂ (Scheme 1). As disclosed by its crystal structure, 5a is a result of an ortho-metalation process accompanied by the release of 1 equiv of acetic acid.^{12g,13,15} The Suzuki–Miyaura cross-coupling reactions between an aryl halide and phenylboronic acid were carried out with either isolated and purified 5a or 5a prepared in situ from **4a** and Pd(OAc)₂.¹⁵ In any case, the Pd(II) catalyst precursor is probably reduced to an active Pd(0) catalyst first by PhB(OH)₃ generated from phenylboronic acid in basic medium.¹⁶ In addition to the Suzuki reaction, complex 5a was also employed as a catalyst precursor^{12g} for the amination of bromobenzene by morpholine demonstrating acceptable results.

It was speculated that the positive charge of the palladium center could be increased by introduction of a proper electronwithdrawing substituent into the arylethyne unit of **5**. Thereby, the reaction rate between the anionic PhB(OH)₃ and the more positively charged palladium center shall be significantly increased as well as the rate of reduction process followed. It shall lead to the increase of the whole reaction rate thereafter. We were interested in examining the validity of this assumption. In this study, the preparation of several substituted analogs of phosphine **4a** bearing electron-withdrawing/donating groups such as -F, $-CF_3$, and -OMe at the designated positions of the phenyl group as well as their applications in palladium-catalyzed Suzuki cross-coupling reactions are presented.

2. Results and discussion

2.1. Preparation of cobalt-containing phosphines {[(μ -PPh₂. CH₂PPh₂)Co₂(CO)₄][(μ , η -(${}^{t}Bu$)₂PC \equiv C(C₆H₄R))]} (4b: R=*p*-F; 4cp: R=*p*-CF₃; 4cm: R=*m*-CF₃; 4d: R=*p*-OMe)

A number of cobalt-containing phosphines {[(μ -PPh₂CH₂PPh₂)-Co₂(CO)₄]](μ , η -(${}^{t}Bu$)₂PC \equiv C(C₆H₄R))] (**4b**: R=p-F; **4cp**: R=p-CF₃;

4cm: R=*m*-CF₃; **4d**: R=*p*-OMe) were synthesized according to the procedures shown in Scheme 1. Firstly, the alkynyl phosphines $[({}^{t}Bu)_{2}PC \equiv C(C_{6}H_{4}R)]$ (2b: R=p-F; 2cp: R=p-CF₃; 2cm: R=m-CF₃; **2d**: R=p-OMe) were prepared from the corresponding terminal alkynes HC=C(C₆H₄R) (**1b**: R=*p*-F; **1cp**: R=*p*-CF₃; **1cm**: R=*m*-CF₃; **1d**: R=p-OMe), respectively, via deprotonation at $-78 \degree C$ for 1 h followed by guenching with $CIP(^{t}Bu)_{2}$ at 25 °C for 24 h. Then, **2b**. **2cp**, **2cm**, and **2d** were allowed to react with $Co_2(CO)_6(\mu$ -PPh₂CH₂PPh₂) **3** at 60 °C for 48 h to yield **4b**, **4cp**, **4cm**, and **4d**, respectively, as reddish-brown solids. Either during the crystallization or during the chromatographic separation, compounds 4cm and **4d** have been partially oxidized to pink solids $\{[(\mu PPh_2CH_2PPh_2)Co_2(CO)_4][(\mu,\eta-({}^tBu)_2(O=)PC\equiv C(C_6H_4R))]$ (**4cmO**: R=m-CF₃; 4dO: R=p-OMe). Compounds 4b, 4cp, 4cmO, 4d, and **4dO** were characterized by spectroscopic methods such as ¹H, ¹³C, and ³¹P NMR as well as elemental analysis and mass spectrometry. In 13 C NMR, the quartet signals of $-CF_3$ are weak for both **4cm** and 4cmO. The assignment of the signal is referred to the more discernible pattern in 5cm. Their molecular structures were determined by single-crystal X-ray diffraction methods (Table 1). The ORTEP diagrams are depicted in Figures 1-5.

2.2. Preparation of palladium complexes {[(μ -PPh₂CH₂PPh₂)-Co₂(CO)₄]](μ , η -(^{t}Bu)₂PC \equiv C(C₆H₃R)- κ C¹)]Pd(μ -OAc)} (5b: R=*p*-F; 5cp: R=*p*-CF₃; 5cm: R=*m*-CF₃; 5d: R=*p*-OMe)

Several palladium complexes {[(µ-PPh₂CH₂PPh₂)Co₂(CO)₄]- $[(\mu,\eta-({}^{t}Bu)_{2}PC \equiv C(C_{6}H_{3}R)-\kappa C^{1})]Pd(\mu-OAc)\}$ (**5b**: R=p-F; **5cp**: R=p-CF₃; **5cm**: R=*m*-CF₃; **5d**: R=*p*-OMe) related to **5a** were prepared from the reactions of their corresponding cobalt-containing bulky phosphines (4b: R=p-F; 4cp: R=p-CF₃; 4cm: R=m-CF₃; 4d: R=p-OMe) with Pd(OAc)₂. The reactions carried out in THF at 25 °C for 1 h furnished reddish-brown solids in about 55% yield. All compounds were characterized by spectroscopic methods. In addition, the molecular structure of 5cm depicted in Figure 6 was determined by a single-crystal X-ray diffraction method (Table 1). The molecular structure of 5cm revealed the formation of a Pd-Carvl bond via the ortho-metalation process. The process occurred on C(8) rather than C(4) due to the latter position being shielded by the nearby CF₃ substituent. The acetate ligand coordinates to the palladium center in a chelating mode. Judging from the similarities of ¹H and ³¹P NMR spectra (Table 2), the rest of complexes are expected to possess the structural features analogous to those of 5cm.

Table 1			
Crystal data of 4b. 4cp.	4cm0.4	4d. 4dO.	and 5cm

Compound	4b	4ср	4cm0	4d	4d0	5cm
Formula	$C_{45}H_{44}Co_2FO_4P_3 \cdot 1/5CH_2Cl_2$	C46H44Co2F3O4P3	C46H44Co2F3O5P3	C46H47C02O2P3	C46H47C02O6P3	C48H46C02F3O6P3Pd·3/2Cd
Formula weight	895.56	928.58	944.58	890.61	906.605	1111.03
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	P21	P-1	P21/n	P21/c	P-1	P-1
a(Å)	12.0836(10)	11.997(5)	11.3617(13)	11.7610(8)	12.0443(13)	12.6101(9)
b(Å)	19.4019(16)	17.865(7)	21.439(2)	18.4205(12)	17.8356(18)	13.5008(9)
c(Å)	19.3272(15)	22.706(9)	19.242(2)	21.2621(14)	22.293(2)	16.6265(11)
$\alpha(^{\circ})$	_	66.915(8)		_	67.346(2)	79.4820(10)
β(°)	101.345(2)	81.074(7)	106.724(2)	104.8740(10)	82.616(2)	86.810(2)
γ(°)	_	87.751(8)	_ ``	_ ``	89.279(2)	69.2030(10)
$V(Å^3)$	4442.6(6)	4422(3)	4488.7(9)	4452.0(5)	4379.3(8)	2601.6(3)
Ζ	4	2	4	4	2	2
$D_{\rm c} ({\rm Mg/m^3})$	1.339	1.395	1.398	1.329	1.375	1.418
λ (Mo Kα) (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
$\mu ({\rm mm}^{-1})$	0.923	0.913	0.902	0.896	0.914	1.119
θ Range(°)	2.01-26.02	1.85-26.45	1.46-26.07	1.48-26.03	1.86-26.06	1.64-26.06
Observed reflections($F > 4\sigma(F)$)	16,431	16,928	8836	8726	17,076	10,140
No. of refined parameters	1027	1099	532	505	1027	573
R ₁ for significant reflections ^a	0.0398	0.0689	0.0367	0.0303	0.0597	0.0558
wR ₂ for significant reflections ^b	0.0705	0.1688	0.0857	0.1053	0.1370	0.1652
GoF ^c	1.061	0.980	0.999	0.999	0.945	0.813

 $R_1 = |\Sigma(|F_0| - |F_c|)/\Sigma|F_0||.$

b wR₂={ $[\Sigma w(F_0^2 - F_c^2)^2/\Sigma w(F_0^2)^2]^{1/2}$; w=0.0250, 0.1100, 0.0500, 0.0900, 0.0750, and 0.1638 for crystal data of **4b**, **4cp**, **4cm**0, **4d**, **4dO**, and **5cm**, respectively.

^c GoF= $[\Sigma w (F_0^2 - F_c^2)^2 / (N_{rflns} - N_{params})]^{1/2}$.

^d 1/4 *n*-Hexane was added without hydrogen.

2.3. Structural comparison of 4b, 4cp, and 4d

The structures of 4b, 4cp, and 4d reveal that each molecule contains a pseudo-tetrahedral Co₂C₂ core, which is typical for an alkyne-bridged dicobalt complex. In addition, the dppm acts as a bridging ligand toward both cobalt atoms. Both substituents of the alkyne are bent away from the dicobalt moiety, as predicted by Dewar-Chatt-Duncanson model, and reside on the same side.¹⁷ In this regard, 4b, 4cp, and 4d can be considered as authentic metalcontaining monodentate phosphine ligands. The variations of structural parameters for all compounds are small, except for the -F, -CF₃, and -OMe substituents on phenyl ring. Selected structural

parameters of **4b**, **4cp**, and **4d** are given in Table 3 for comparison (Diagram 2). As shown in Table 2, these frameworks are rather similar. Again, it shows that the alkyne-bridging dicobalt framework Co₂C₂ core is a rigid entity.

2.4. Application of 4/Pd(OAc)₂ in Suzuki reactions

As known, the performance of a palladium-catalyzed carboncarbon cross-coupling reaction is governed by a number of factors such as the palladium source employed, ligand, base, solvent, reaction temperature, etc.¹⁸ Furthermore, the ratio of ligand to palladium is also crucial since various bonding modes are possible for different types of ligands. Here, Suzuki coupling reactions were

C12

🔊 C10

C15

C13



Figure 1. ORTEP drawing of 4b.



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Figure 2. ORTEP drawing of 4cp.



Figure 3. ORTEP drawing of 4cmO.

carried out by employing the newly made cobalt-containing phosphine ligands **4a**, **4b**, **4cp**, **4cm**, and **4d**-modified palladium complexes (Tables 4–6). In most cases, the reactions were carried out with 1.0 mmol of 2-bromothiophene, 1.5-fold excess of phenylboronic acid, 3-fold excess of a base in 1.0 mL solvent, and 1.0 mol % of **4**/Pd(OAc)₂ at 60 °C (Scheme 2). Initially, KF was chosen as the base due to its good performance in most of the Suzuki reactions.

As shown in Table 4, the best yield was obtained with the **4b**/ $Pd(OAc)_2$ ratio being 1:1 rather than with the 2:1 ratio generally giving the best yield in the case of an organophosphine ligand (entries 1 and 3). Yet, it is consistent with our previous observations for **4a**/ $Pd(OAc)_2$ as a catalyst precursor.^{11b} Therefore, these observations naturally lead to the conclusion that the bonding modes of



Figure 4. ORTEP drawing of 4d.



Figure 5. ORTEP drawing of 4dO.

the active species derived from $4b-d/Pd(OAc)_2$ are similar to that of $4a/Pd(OAc)_2$. As reported, monophosphine-coordinated complexes Pd(0)L (L=phosphine) might be the catalytically active species.^{8d,19} Based on this postulation, the reduction of **5** by $PhB(OH)_3^-$ is proposed (Scheme 3)^{16,20} resulting in a low-coordinated Pd(0) complex, **6**, as an active species. It is followed by the oxidative addition of ArX and the formation of a three-coordinate Pd(II) complex, **7**.²¹ In the presence of excess **4**, the concentration of the active species **6** will be reduced due to the formation of a multi-ligand palladium complex, thereby diminishing the catalytic efficiency (entries 1 and 2). On the contrary, the yield is rather low in the absence of



Figure 6. ORTEP drawing of 5cm.

Table 2 ¹H and ³¹P NMR of **5a**, **5b**, **5cp**, **5cm**, and **5d**^a

-			-			
		5a	5b	5cp	5cm	5d
3	¹ P NMR (δ /ppm)					
[$P(^{t}\mathrm{Bu})_{2}]$	91.6	91.4	91.5	91.4	91.5
[dppm]	38.8	38.6	38.7	38.5	38.5
1	H NMR (δ /ppm)					
[OAc]	2.1	2.0	2.0	2.0	2.0

^a in CD₂Cl₂.

phosphine ligand **4** (entry 6). It implies that the phosphine ligand plays an important role in promoting the catalytic efficiency.

As known, the base selection is essential to the success of a palladium-catalyzed Suzuki reaction.²² Therefore, the effects of the various bases used in the reactions were examined (Table 5). Excellent yields were observed with NaOH and K_2CO_3 (entries 2 and 3). The catalytic efficiency is also good with KF as a base (entry 1). The yields were lower when CsF and Cs₂CO₃ were employed under the same reaction condition (entries 7 and 8).

As shown in Table 5, K_2CO_3 and NaOH are equally efficient in the reaction. To differentiate their activities, a lower reaction temperature and shorter reaction hours were used (Table 6). It is obvious that NaOH is a better choice (entry 1 vs 2). The reaction that stopped after 1 h was still very efficient (entry 4) and even that run at 40 °C for 3 h provided an acceptable result (entry 5).

The influence of the solvent used was evaluated as well (Table 7). The reaction conditions were the same as above. The best yield was observed with toluene as a solvent (entry 5). Unexpectedly, a poor result was observed with 1,4-dioxane (entry 3).

The Suzuki–Miyaura reaction between 2-bromothiophene and phenylboronic acid employing **4b** with various Pd sources in the NaOH/toluene system was carried out at 40 °C for 3 h (Table 8). As shown, excellent yield was obtained with $Pd(OAc)_2$ as a palladium source (entry 1). Interestingly, low yield was obtained with $PdCl_2(CH_3CN)_2$ (entry 5).

The optimized conditions for the **4b**-assisted palladium-catalyzed Suzuki reaction emerged from summing up the above studies, namely, $Pd(OAc)_2$ as a palladium source, NaOH as a base, toluene as a solvent, 40 °C, and 3 h reaction time. For comparison, ligands **4a**,

Table 3

Comparison for selected structural parameters of 4b, 4cp, and 4d

	4b	4cp	4d
Bond length (Å)			
C(1)-C(2)	1.352(5)	1.366(7)	1.357(3)
Co(1)-C(1)	1.986(4)	2.004(5)	2.0188(18)
Co(1)-C(2)	1.967(4)	1.934(4)	1.9549(18)
Co(2)-C(1)	2.007(4)	2.011(5)	1.9860(18)
Co(2)-C(2)	1.942(4)	1.976(5)	1.9752(18)
Co(1)-Co(2)	2.4689(7)	2.4623(12)	2.4907(4)
Co(1)-P(2)	2.2328(12)	2.2276(17)	2.2290(5)
Co(2)-P(3)	2.2268(12)	2.2457(17)	2.2392(5)
P(1) - C(1)	1.816(4)	1.809(5)	1.8155(19)
P(2)-C(45)	1.810(4)	1.840(5)	1.8323(17)
P(3)-C(45)	1.851(4)	1.838(5)	1.8331(18)
F(1) - C(6)	1.358(5)	—	_
C(6)-C(46)	_	1.496(8)	_
C(6)-O(5)	—	—	1.372(2)
Bond angle (°)			
C(2)-Co(1)-C(1)	40.01(14)	40.55(19)	39.89(7)
C(2)-Co(2)-C(1)	40.00(14)	40.07(19)	40.06(7)
C(2)-C(1)-P(1)	132.4(3)	131.8(4)	132.29(15)
C(1)-C(2)-C(3)	136.9(4)	136.0(4)	138.46(17)
Co(1)-C(2)-Co(2)	78.33(15)	78.06(17)	78.65(7)
Co(1)-C(1)-Co(2)	76.38(14)	75.66(16)	76.91(6)
C(13) - P(1) - C(9)	110.1(2)	109.7(3)	109.78(11)
P(2)-C(45)-P(3)	108.79(19)	106.8(3)	109.55(9)
P(2)-Co(1)-Co(2)	98.52(4)	94.05(4)	92.110(16)
P(3)-Co(2)-Co(1)	93.63(4)	97.93(5)	99.563(15)



Diagram 2. Generalized structure for 4b, 4cp, and 4d.

4b, **4cp**, **4cm**, and **4d** were employed in the palladium-catalyzed Suzuki reaction under the above conditions. As shown in Table 9, the catalytic efficiency is better in the case of an electron-with-drawing substituent placed on the arylethyne unit (entries 2 and 3). On the contrary, low catalytic efficiency was observed in the case of the electron-donating substituent (entry 4).

For comparison, the same ligands were employed in the reaction with *p*-bromobenzaldehyde as an aryl halide (Scheme 4). The trend shown in Table 9 was observed here as well. Moreover, the effect of the electron-withdrawing substituent is clearly demonstrated. As shown in Table 10, the catalytic efficiency was the highest in the case

Table 4

Dependence of the yield of the Suzuki–Miyaura reaction on the ${\bf 4b}/{\rm Pd}({\rm OAc})_2$ ratio^a

Entry	Ligand/Pd	Yield ^b (%)
1	2.0/1.0	32
2	1.5/1.0	75
3	1.0/1.0	93
4	0.5/1.0	84
5	0.1/1.0	54
6	0.0/1.0	10

 $^a\,$ Reaction conditions: 1.0 mmol of 2-bromothiophene, 1.5 mmol of phenylboronic acid, 3.0 mmol of KF, 1 mL THF, 60 $^\circ$ C, 24 h.

Average of two runs; isolated yield.

Table 5

Dependence of the yield of the Suzuki-Miyaura reaction on base^a

Entry	Base	Yield ^b (%)
1	KF	93
2	K ₂ CO ₃	>99
3	NaOH	>99
4	K ₃ PO ₄	88
5	КОН	78
6	Na ₂ CO ₃	30
7	Cs ₂ CO ₃	16
8	CsF	0

 $^a\,$ Reaction conditions: 1.0 mmol of 2-bromothiophene, 1.5 mmol of phenylboronic acid, 3.0 mmol of base, L/Pd=1:1 mol %, 1 mL THF, 60 °C, 24 h.

^b Average of two runs; isolated yield.

Table 6

Suzuki-Miyaura reaction with K₂CO₃ versus NaOH^a

Entry	Temp. (°C)	Base	Time (h)	Yield ^b (%)
1	60	K ₂ CO ₃	6	74
2	60	NaOH	6	>99
3	60	NaOH	3	>99
4	60	NaOH	1	>99
5	40	NaOH	3	82

^a Reaction conditions same as in footnote of Table 5.

^b Average of two runs; isolated yield.



Scheme 2. Suzuki–Miyaura cross-coupling reaction of 2-bromothiophene with phenylboronic acid in the presence of 4/Pd(OAc)₂.



Scheme 3. Proposed reduction and oxidative addition steps in 5-assisted Suzuki-Miyaura cross-coupling reaction.

of the strongest electron-withdrawing substituent, $-CF_3$, placed on the arylethyne unit (entry 3). The worst catalytic performance was observed in the case of the electron-donating group, -OMe (entry 4). It shows that the electronic property of the substituent on the arylethyne unit indeed influences the reaction rate and yield.

2.5. DFT studies on the charges of palladium centers in 5

As postulated, the positive charge of the palladium center could be increased by placing an electron-withdrawing substituent on the arylethyne unit of **5a**. Thereby, the rate of the reduction process from Pd(II) to Pd(0) by the anionic PhB(OH)₃ will be enhanced. It could lead to the increase of the overall reaction rate. The positive charge of the palladium center in **5b** or **5cp** is expected to be higher than that in **5a**. It is attributed to the presence of strong electronwithdrawing substituents, -F and $-CF_3$, in the arylethyne units of

Table 7

Dependence of the Suzuki-Miyaura reaction on solvent^a

Entry	Solvent	Yield ^b (%
1	THF	82
2	MeOH	72
3	1,4-Dioxane	15
4	CH₃CN	32
5	Toluene	>99

 $^{\rm a}$ Reaction conditions: NaOH as a base, 40 $^\circ\text{C}$, 3 h, the rest is the same as in footnote of Table 5.

^b Average of two runs; isolated yield.

Table 8

Suzuki-Miyaura reaction with various palladium sources^a

Entry	Palladium source	Yield ^b (%
1	$Pd(OAc)_2$	>99
2	Pd(COD)Cl ₂	83
3	$[(\eta^3 - C_3 H_5)PdCl]_2$	26
4	$Pd_2(dba)_3$	43
5	$Pd(CH_3CN)_2Cl_2$	9

^a Reaction conditions are the same as in footnote of Table 7 except for the palladium sources.

^b Average of two runs; isolated yield.

Table 9

Suzuki-Miyaura reaction with various ligands^a

Entry	Ligand	Yield ^b (%)
1	4a	93
2	4b	>99
3	4cp	>99
4	4cm	95
5	4d	74

^a Reaction conditions are the same as in footnote of Table 7 except for the ligand used.

^b Average of two runs; isolated yield.

5b and **5cp**, respectively. Since the state-of-the-art density functional theory (DFT) method has proven to be a useful tool in providing reliable results in the studies of transition metal-mediated catalytic reactions, it was used to obtain information concerning the charges of the palladium centers in 5^{23} . This method at the B3LYP level was utilized to examine the validity of the postulation. To make the computations feasible, the actual reaction participants **5** were simplified to model compounds, **5**' according to Diagram 3.

The results of Natural Population Analysis (NPA) of the palladium center charges in **5**' are listed in Table 11. The positive charges of the palladium centers decrease in the following order: 5c'>5b'>5d'>5a'>5e'. It is in accordance with the electron-withdrawing/donating capacities of the substituents. Obviously, the analysis of the palladium center charges in **5** validates the assumption that an electron-withdrawing substituent on the arylethyne unit would facilitate the attack of PhB(OH)₃ on metal, thereby enhancing the reaction rate.

3. Summary

We have demonstrated that placing electron-withdrawing substituents on the arylethyne part of **5** leads to a rate increase in

Table 10

Suzuki–Miyaura coupling reaction between $p\mbox{-}b\mbox{oronbenzaldehyde}$ and phenylboronic acid with various ligands $^{\rm a}$

Entry	Ligand	Yield ^b (%)
1	4a	55
2	4b	75
3	4cp	90
4	4cm	66
5	4d	32

^a Reaction conditions: 1.0 mmol of *p*-bromobenzaldehyde, 1.5 mmol of phenylboronic acid, and 3.0 mmol of NaOH, L/Pd=1:1 mol %, 1 mL of toluene, 40 °C, 3 h. ^b Average of two runs; isolated yield.



Diagram 3. Simplified model compounds of 5'.

Table 11

The Natural Population Analysis (NPA) of the palladium center charges in 5'

Model compound	5a'	5 b ′	5c′	5ď′	5e ′
Charge	0.487	0.493	0.496	0.489	0.486

Scheme 4. Suzuki–Miyaura cross-coupling reaction of *p*-bromobenzaldehyde with phenylboronic acid in the presence of 4/Pd(OAc)₂.

the Suzuki coupling reaction. It is attributed to the enhancement of the Pd(II) to Pd(0) reduction rate. The more and more positively charged palladium centers on **5b**, **5cm**, and **5cp** enhance the probability for the anion PhB(OH)₃⁻ to attack resulting in the acceleration of the reduction rate. The assumption is supported by the Natural Population Analysis (NPA) from DFT calculations.

4. Experimental

4.1. General information

All manipulations were carried out under a dry nitrogen atmosphere. Solvents including deuterated solvents were purified before use. Most separations were performed by Centrifugal Thin Layer Chromatography (CTLC, Chromatotron, Harrison model 8924). The ¹H and ³¹P NMR spectra were recorded on a Varian-400 spectrometer at 400.44 and 162.10 MHz, respectively; ¹³C NMR spectra were recorded on a Varian VXR-300S spectrometer at 75.43 MHz. Chemical shifts are reported in parts per million relative to the residual proton signals of deuterated CHCl₃ or CH₂Cl₂. Mass spectra were recorded on a JOEL JMS-SX/SX 102A GC/MS/MS spectrometer. Elemental analyses were obtained on a Heraeus CHN-O-S-Rapid instrument.

4.2. Synthesis of {[(μ -PPh₂CH₂PPh₂)Co₂(CO)₄(μ , η -(^tBu)₂PC=C-(C₆H₄R))]} (4a: R=H; 4b: R=*p*-F; 4cp: R=*p*-CF₃; 4cm: R=*m*-CF₃; 4d: R=*p*-OMe)

Dicobalt octacarbonyl Co₂(CO)₈ (2.00 mmol, 0.684 g), dppm (2.00 mmol, 0.769 g), and THF (15 mL) were placed in a 100 mL round-bottom flask charged with a magnetic stirrer. The solution was stirred at 60 °C for 6 h giving rise to a yellow compound $[Co_2(CO)_6(\mu-P,P-dppm)]$ **3**. Without further separation, the reaction flask was charged with one equiv of $[({}^{t}Bu)_{2}PC \equiv C(C_{6}H_{4}R)]$ (**2a**: R=H, 0.493 g; **2b**: R=p-F, 0.529 g; **2cp**: R=p-CF₃, 0.629 g; **2cm**: R=m-CF₃, 0.629 g; 2d: R=p-OMe, 0.553 g) in THF (15 mL). Subsequently, the solution was stirred at 60 °C for 48 h before the solvent was removed under reduced pressure. The residue was further separated by CTLC. A reddish-brown band eluted with CH₂Cl₂/ethyl acetate (1:1) was identified as {[(µ-PPh₂CH₂PPh₂)Co₂(CO)₄- $(\mu,\eta-({}^{t}Bu)_{2}PC \equiv C(C_{6}H_{4}R))]$ (2a: R=H; 2b: R=p-F; 2cp: R=p-CF₃; **2cm**: R=p-CF₃; **2d**: R=p-OMe). The yields were 62% (1.24 mmol, 1.067 g) for 4a, 65% (1.30 mmol, 1.141 g) for 4b, 55% (1.10 mmol, 1.021 g) for 4cp, 50% (1.00 mmol, 0.928 g) for 4cm, and 59% (1.18 mmol, 1.050 g) for 4d.

Compound **4b**. ¹H NMR (CD₂Cl₂, δ /ppm): 6.85–7.34 (24H, arene), 3.24–3.16 (m, 1H, dppm), 3.39–3.31 (m, 1H, dppm), 1.26 (d, $J_{P-H}=11.2$ Hz, 18H, ^tBu); ³¹P NMR (CDCl₃, δ /ppm): 36.88 (s, 2P, dppm), 45.20 (s, 1P, P(^tBu)₂); ¹³C NMR (CD₂Cl₂, δ /ppm): 128.01–132.78 (30C, arene), 30.62, 30.49 (d, 6C, -C(CH₃)₃), $J_{P-C}=13.1$ Hz), 34.81 (d, $J_{P-C}=22.2$ Hz, 2C, $-C(CH_3)_3$), 31.96 (t, $J_{P-C}=21.2$ Hz, 1C, $-CH_2$ –). Elemental analysis calculated for C₄₅H₄₄Co₂FO₄P₃: C, 61.52; H, 5.05. Found: C, 61.25; H, 5.31. MS (FAB): m/z=879.0 [M]⁺.

Compound **4cp**. ¹H NMR (CD₂Cl₂, δ /ppm): 6.97–7.36 (m, 24H, arene), 3.20–3.17 (m, 1H, dppm), 3.33–3.30 (m, 1H, dppm), 1.25 (d, $J_{P-H}=11.2$ Hz, 18H, ^tBu); ³¹P NMR (CDCl₃, δ /ppm): 36.39 (s, 2P, dppm), 44.94 (s, 1P, P(^tBu)₂); ¹³C NMR (CD₂Cl₂, δ /ppm): 150.08 (s, 1C, -CF₃), 128.09–132.82 (30C, arene), 30.59, (d, $J_{P-C}=13.1$ Hz, 6C, -C(CH₃)₃), 34.85 (d, $J_{P-C}=23.1$ Hz, 2C, -C(CH₃)₃), 32.00 (t, 1C, $J_{P-C}=21.2$ Hz, -CH₂–). Elemental analysis calculated for C₄₆H₄₄Co₂F₃O₄P₃: C, 59.60; H, 4.78. Found: C, 60.33; H, 4.90. MS (FAB): m/z=929.0 [M]⁺.

Compound **4cm**. ¹H NMR (CDCl₃, δ /ppm): 6.96–7.45 (m, 24H, arene), 3.15 (q, *J*=12 Hz, 1H, dppm), 3.29 (q, *J*=12 Hz, 1H, dppm), 1.26 (d, *J*_{P-H}=11.2 Hz, 18H, ^tBu); ³¹P NMR (CDCl₃, δ /ppm): 36.41 (s, 2P, dppm), 44.65 (s, 1P, P(^tBu)₂); ¹³C NMR (CD₂Cl₂, δ /ppm): 127.12

(q, 1C, $J_{C-F}=31.7$ Hz, $-CF_3$), 122.16–146.80 (30C, arene), 30.83, (s, 6C, $-C(CH_3)_3$), 35.10 (d, 2C, $J_{P-C}=22.78$ Hz, $-C(CH_3)_3$), 32.31 (t, 1C, $J_{P-C}=21.2$ Hz, $-CH_2-$). Elemental analysis calculated for $C_{46}H_{44}Co_2F_3O_4P_3$: C, 59.48; H, 4.96. Found: C, 58.13; H, 5.19.

Compound **4cm0**. ¹H NMR (CDCl₃, δ /ppm): 7.00–7.78 (m, 24H, arene), 3.44–3.30 (m, J_{P-H} =8.0 Hz, 1H, dppm), 1.35 (d, J_{P-H} =13.2 Hz, 18H, ^tBu); ³¹P NMR (CDCl₃, δ /ppm): 35.52 (s, 2P, dppm), 59.01 (s, 1P, P(^tBu)₂); ¹³C NMR (CD₂Cl₂, δ /ppm): 127.12 (q, 1C, J_{C-F} =31.7 Hz, –CF₃), 122.65–145.31 (30C, arene), 28.34, (s, 6C, –C(CH₃)₃), 38.42 (d, 2C, J_{P-C} =63.15 Hz, –C(CH₃)₃), 33.77 (t, 1C, J_{P-C} =21.2 Hz, –CH₂–). Elemental analysis calculated for C₄₆H₄₄Co₂F₃O₅P₃: C, 58.44; H, 4.87. Found: C, 57.51; H, 4.95. MS (FAB): *m*/*z*=945.0 [M]⁺.

Compound **4d**. ¹H NMR (CD₂Cl₂, δ /ppm): 6.67–7.30 (24H, arene), 3.80 (s, 3H, –OMe), 3.21–3.17 (m, 1H, dppm), 3.42–3.39 (m, 1H, dppm), 1.24 (d, *J*_{P-H}=10.8 Hz, 18H, ^{*t*}Bu); ³¹P NMR (CDCl₃, δ /ppm): 36.65 (s, 2P, dppm), 44.74 (s, 1P, P(^{*t*}Bu)₂); ¹³C NMR (CD₂Cl₂, δ /ppm): 127.94–132.89 (30C, arene), 30.56 (d, *J*_{P-C}=14.1 Hz, 6C, –C(*C*H₃)₃), 34.79 (d, *J*_{P-C}=23.1 Hz, 2C, –*C*(CH₃)₃), 32.04, (t, *J*_{P-C}=21.2 Hz, 1C, –CH₂–). Elemental analysis calculated for C₄₆H₄₇Co₂O₅P₃: C, 62.03; H, 5.32. Found: C, 61.25; H, 4.88. MS (FAB): *m*/*z*=891.0 [M]⁺.

4.3. Synthesis of {[(μ -PPh₂CH₂PPh₂)Co₂(CO)₄]](μ , η -(^{*t*}Bu)₂-PC=C(C₆H₃R)- κ C¹)]Pd(μ -OAc)} (5a: R=H; 5b: R=*p*-F; 5cp: R=*p*-CF₃; 5cm: R=*m*-CF₃; 5d: R=*p*-OMe)

A 100 mL round-bottom flask equipped with a magnetic stirrer was charged with 1.00 mmol of **4a** (0.860 g), 1 molar equiv of Pd(OAc)₂ (1.0 mmol, 0.223 g), and 15 mL THF. The solution was stirred at 25 °C for 1 h before the solvent was removed under reduced pressure. The residue was further separated by CTLC. A reddish-brown band eluted with CH₂Cl₂/ethyl acetate (10:1) was identified as {[(μ -PPh₂CH₂PPh₂)Co₂(CO)₄][(μ , η -(^tBu)₂PC=C-(C₆H₄)- κ C¹)]Pd(μ -OAc)} **5a**. The yield was 50% (1.00 mmol, 1.025 g). Similar procedures were used for preparing **5b**, **5cp**, **5cm**, and **5d**. The yields for **5b**, **5cp**, **5cm**, and **5d** were 45%, 50%, 50%, and 58%, respectively.

Compound **5a**. ¹H NMR (CD₂Cl₂, δ /ppm): 7.54–6.92 (24H, arene), 3.30 (t, *J*_{P-H}=10.2 Hz, 2H, CH₂), 1.53 (d, *J*_{P-H}=16.0 Hz, 18H, ^{*t*}Bu); ³¹P NMR (CD₂Cl₂, δ /ppm): 38.8 (s, 2P, dppm), 91.6 (s, 1P, P(^{*t*}Bu)₂).

Compound **5b**. ¹H NMR (CD₂Cl₂, δ /ppm): 7.36–6.53 (23H, arene), 3.63 (t, J_{P-H}=10.4 Hz, 2H, CH₂), 1.50 (d, J_{P-H}=14.0 Hz, 18H, ^tBu); ³¹P NMR (CD₂Cl₂, δ /ppm): 38.56 (s, 2P, dppm), 91.37 (s, 1P, P(^tBu)₂).

Compound **5cp**. ¹H NMR (CD₂Cl₂, δ /ppm): 7.36–7.02 (23H, arene), 3.63 (t, J_{P-H} =10.4 Hz, 2H, CH₂), 1.51 (d, J_{P-H} =14.4 Hz, 18H, ^tBu); ³¹P NMR (CD₂Cl₂, δ /ppm): 38.7 (s, 2P, dppm), 91.5 (s, 1P, P(^tBu)₂).

Compound **5cm**. ¹H NMR (CD₂Cl₂, δ /ppm): 7.68 (d, J_{H-H} =7.6 Hz, 1H, arene), 7.36–7.16 (m, 23H, arene), 3.63 (t, J_{P-H} =10.4 Hz, 2H, CH₂), 1.49 (d, J_{P-H} =14.4 Hz, 18H, ^tBu), 2.00 (s, 3H, $CH_3CO_2^-$); ³¹P NMR (CD₂Cl₂, δ /ppm): 38.5 (s, 2P, dppm), 91.4 (s, 1P, P(^tBu)₂); ¹³C NMR (CD₂Cl₂, δ /ppm): 127.12 (q, 1C, J_{C-F} =31.7 Hz, –CF₃), 121.31–158.99 (30C, arene), 30.40, (s, 6C, –C(CH₃)₃), 39.15 (d, 2C, J_{P-C} =21.9 Hz, –C(CH₃)₃), 41.21 (t, 1C, J_{P-C} =20.5 Hz, –CH₂–), 23.87 (s, 1C, CH₃CO₂⁻), 188.42 (s, 1C, CH₃CO₂⁻). Anal. Calcd: C, 52.78; H, 4.21. Found: C, 51.70; H, 4.64. MS (FAB): m/z=980 [M–4CO]⁺.

Compound **5d**. ¹H NMR (CD₂Cl₂, δ /ppm): 7.35–6.41 (24H, arene), 3.65 (t, J_{P-H}=10.0 Hz, 2H, CH₂), 1.51 (d, J_{P-H}=14.0 Hz, 18H, ^tBu); ³¹P NMR (CD₂Cl₂, δ /ppm): 38.5 (s, 2P, dppm), 91.5 (s, 1P, P(^tBu)₂).

4.4. General procedure for the Suzuki cross-coupling reactions

Suzuki cross-coupling reactions using **4a–d** were performed according to the following general procedure. Compounds **4a–d** (0.01 mmol), phenylboronic acid (0.183 g, 1.50 mmol), and NaOH (0.120 g, 3.00 mmol) were placed into a 20 mL Schlenk flask. The flask was evacuated and backfilled with nitrogen before adding

toluene (1 mL) and 2-bromothiophene (0.11 mL, 1.00 mmol). The solution was stirred at 40 °C for 3 h. Subsequently, excess amount of water was added and the product was extracted with ether (3×20 mL). The combined organic extracts were dried over anhydrous MgSO₄ and concentrated under vacuum. The crude residue was purified by flash chromatography on silica gel.

4.5. X-ray crystallographic studies

Suitable crystals of **4b**, **4cp**, **4cmO**, **4d**, **4dO**, and **5cm** 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.²⁴ 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.²⁵ Crystallographic data for compounds **4b**, **4cp**, **4cmO**, **4d**, **4dO**, and **5cm** are summarized in Table 1.

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.²⁶ The molecular geometries were fully optimized with the hybrid B3LYP-DFT method under *C*₁ symmetry, in which the Becke three parameter exchange functional²⁷ and the Lee-Yang-Parr correlation functional²⁸ were used. The LANL2DZ including the double- ζ basis sets for the valence and outermost core orbitals combined with pseudo-potential was used for Pd,^{29,30} and 6-31G(d) basis sets for the other atoms. All the stationary points found were characterized via harmonic vibrational frequency analysis as minima (number of imaginary frequency $N_{imag}=0$). Natural Population Analysis (NPA)³¹ was performed with NBO 5.0 software³² using B3LYP/LANL2DZ as the level. Stability analysis³³ has been performed to determine if the Kohn–Sham (KS) solutions are stable with respect to variations, which break spin and spatial symmetries.

6. Supplementary material

Crystallographic data for the structural analysis have been deposited at the Cambridge Crystallographic Data Center, CCDC nos. 653734, 653735, 666136, 653736, 653737, and 666137 for compound **4b**, **4cp**, **4cmO**, **4d**, **4dO**, and **5cm**, 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 website: http:// www.ccdc.cam.ac.uk).

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