Dalton
www.rsc.org/dalton

Synthesis and structural characterization of novel palladium complexes chelated by bulky cobalt-containing phosphine ligands: unusual palladium–cobalt bond formation

Fung-E Hong,* Chin-Pei Chang and Yu-Chang Chang
Department of Chemistry, National Chung-Hsing University, Taichung 40227, Taiwan. E-mail: fehong@dragon.nchu.edu.tw

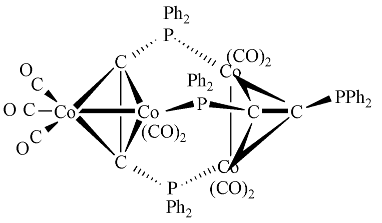
Received 2nd June 2003, Accepted 22nd August 2003
First published as an Advance Article on the web 5th September 2003

The reaction of a bulky phosphine, $[Co_2(CO)_5\{\mu\text{-}P,P\text{-}(\mu\text{-}PPh_2C{\equiv}CPPh_2)\}][Co_2(CO)_4\{\mu\text{-}P\text{-}(\mu\text{-}PPh_2C{\equiv}CPPh_2)\}]$ **1** with $P(OMe)_3$ gave a phosphite substituted tetracobalt-complex, $[Co_2(CO)_4\{P(OMe)_3\}\{\mu\text{-}P,P\text{-}(\mu\text{-}PPh_2C{\equiv}CPPh_2)\}][Co_2(CO)_4\{\mu\text{-}P\text{-}(\mu\text{-}PPh_2C{\equiv}CPPh_2)\}]$ **5**. Further reaction of **5** with $(COD)PdCl_2$ yielded a **5** -coordinated palladium complex, $[Co_2(CO)_4\{P(OMe)_3\}\}\{\mu\text{-}P,P\text{-}(\mu\text{-}PPh_2C{\equiv}CPPh_2)\}][Co_2(CO)_3(\mu\text{-}CO)\{\mu\text{-}P\text{-}(\mu\text{-}PPh_2C{\equiv}CPPh_2)\}]PdCl_2$ **7**. Similar results were obtained for the reaction of **1** with $(COD)PdCl_2$, which yielded $[Co_2(CO)_5\{\mu\text{-}P,P\text{-}(\mu\text{-}PPh_2C{\equiv}CPPh_2)\}][Co_2(CO)_3(\mu\text{-}CO)\{\mu\text{-}P\text{-}(\mu\text{-}PPh_2C{\equiv}CPPh_2)\}]PdCl_2$ **6**. Likewise, reaction of another bulky phosphine $[(\mu\text{-}Ph_2PCH_2PPh_2)Co_2(CO)_4(\mu\text{-}PPh_2C{\equiv}CP({=}O)Ph_2)]$ **3** with $(COD)PdCl_2$ yielded $[\{\mu\text{-}P,P\text{-}PPh_2CH_2PPh_2\}Co_2(CO)_3(\mu\text{-}CO)\{\mu\text{-}PPh_2C{\equiv}CP({=}O)Ph_2\}]PdCl_2$ **8**. The X-ray structural studies of **6**, **7** and **8** reveal that unusual palladium–cobalt bonds were formed. A Suzuki type reaction employing complexes **6**, **7** and **8**, as catalysts in the reaction of 2-bromothiophene with boronic acid did not show encouraging signs.

1 Introduction

Phosphine ligands have played an indispensable role in metal complexes catalyzed organic syntheses.[1] As known, most of the metal complexes catalyze reactions involving both oxidative addition and reductive elimination processes.[2] A phosphine with both electron-rich and bulky nature is believed to be able to facilitate both steps and is regarded as a promising candidate for an effective catalytic performance.[3] Early efforts were mainly focused on preparing phosphine ligands derived from pure organic compounds, which have proved to be competent in most of the designated cases.[4] Recent studies, although reports are few, have involved searching for effective transition-metal-containing phosphine ligands with both electron-rich and bulky characteristics.[5]

Our previous work had demonstrated the preparation of a particularly bulky, monodentate, phosphine ligand, which is an alkyne-bridged, diphosphine-chelated tetracobalt-complex $[Co_2(CO)_5\{\mu\text{-}P,P\text{-}(\mu\text{-}PPh_2C{\equiv}CPPh_2)\}][Co_2(CO)_4\{\mu\text{-}P\text{-}(\mu\text{-}PPh_2\text{-}C{\equiv}CPPh_2)\}]$ **1**, from the reaction of $PPh_2C{\equiv}CPPh_2$ (DPPA) with $Co_2(CO)_8$.[6] (Chart 1). Compound **1** can be regarded as a dimerized product of the bis(diphenylphosphino)acetylene (DPPA) bridged dicobalt complex, $[Co_2(CO)_6(\mu\text{-}PPh_2C{\equiv}CPPh_2)]$.



1

Chart 1 A bulky, monodentate, phosphine ligand **1**.

It is a common observation that a cobalt center with more than three carbonyl ligands is susceptible to the replacement by a strong electron-donating ligand such as a phosphine.[7] Therefore, it was speculated that the only available phosphine site of **1** might attack another molecule of **1** at the designated cobalt center, with three carbonyl ligands, and replace one of them at elevated temperature. Consequently, products with high molecular weights might be formed and insolubility might result. This course of aggregation might be avoided by replacing one of the three carbonyls by a better electron-donating and bulky ligand such as a phosphite, *e.g.* $P(OMe)_3$.

Our previous work also described a new type of metal-containing bidentate phosphine ligand, $[(\mu\text{-}Ph_2PCH_2PPh_2)\text{-}Co_2(CO)_4(\mu\text{-}PPh_2C{\equiv}CPPh_2)]$ **2**, which was prepared from the reaction of DPPA with one equivalent of a bis(diphenylphosphino)methylene (DPPM) bridged dicobalt complex, $Co_2(CO)_6(\mu\text{-}Ph_2PCH_2PPh_2)$.[8] Two oxidized complexes, $[\{\mu\text{-}P,P\text{-}PPh_2CH_2PPh_2\}Co_2(CO)_4\{\mu\text{-}PPh_2C{\equiv}CP({=}O)Ph_2\}]$ **3** and $[\{\mu\text{-}P,P\text{-}PPh_2CH_2PPh_2\}Co_2(CO)_4\{\mu\text{-}P({=}O)Ph_2C{\equiv}CP({=}O)Ph_2\}]$ **4**, were obtained along with **2** during the chromatographic separation process (Chart 2).

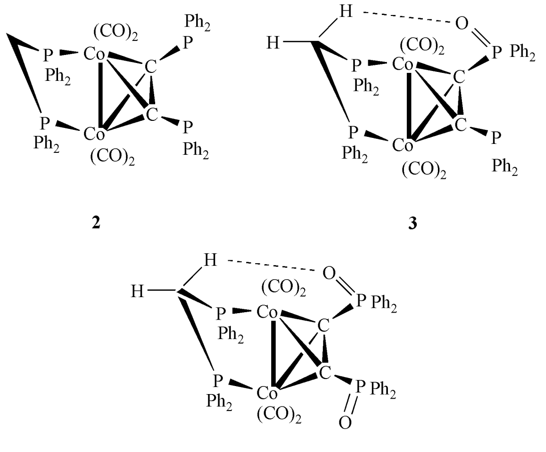


Chart 2 Bulky phosphine ligands **2**, **3** and **4**.

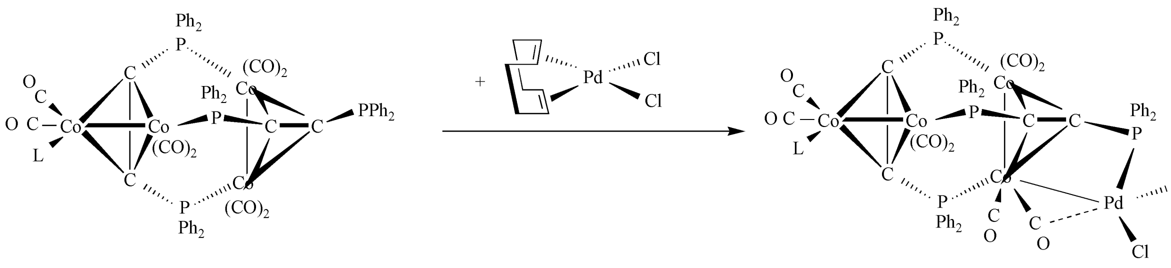
In this paper, the synthesis and structural characterization of some novel palladium complexes coordinated by the above mentioned bulky cobalt-containing phosphine ligands are reported.

2 Results and discussion

2.1 Reaction of 1 with trimethoxylphosphine

Direct treatment of **1** with 1.2 molar equivalent of $P(OMe)_3$ and trimethylamine oxide (TMNO) in mixed solvent (CH_2Cl_2–

DOI: 10.1039/b306228g



1: L=CO

5: L=P(OMe)$_3$

6: L=CO

7: L=P(OMe)$_3$

Scheme 1

THF) at 25 °C for 3 h gave the phosphite coordinated bulky tetracobalt complex, [Co$_2$(CO)$_4${P(OMe)$_3$}{μ-*P*,*P*-(μ-PPh$_2$C≡CPPh$_2$)}][Co$_2$(CO)$_4${μ-*P*-(μ-PPh$_2$C≡CPPh$_2$)}] **5**. Compound **5** was characterized by spectroscopic means, as well as by X-ray diffraction studies. The X-ray study reveals that the structure of **5** is almost the same as its unsubstituted precursor, **1**, with the exception of the replacement of one of the carbonyls by a phosphite ligand (Fig. 1). Interestingly, the phosphite ligand adopts an equatorial position at the cobalt center, which is in contrast to the common observation where the phosphine ligand adopts an axial position (Chart 3). A search for phosphine substituted alkyne-bridged dicobalt complexes from the Cambridge Crystallographic Database shows that all the 26 reported crystal structures have the substituted phosphine ligands located at the axial position.[9] Out of these 26 compounds, a total of 34 P–Co(2)–Co(1) bond angles, ranged from 147.50 to 159.85°, were measured. In the case of **5**, the bond angle of P–Co(2)–Co(1) is 96.95(8)°, which is much sharper than all the reported instances. To the best of our knowledge, this is the first case in which the P(OMe)$_3$ is located at the equatorial position of the alkyne-bridged dicobalt complex. It is believed that the location of the phosphite ligand in the molecule results from the compromise of the steric hindrance between the phosphite ligand and the bulky alkyne substituent phenyl groups. The existence of the substituted P(OMe)$_3$ in **5** is also evidenced from the ^{1}H, ^{13}C, ^{31}P NMR spectra of this dark-brown compound which show doublet, singlet and singlet signals at δ 3.57, 52.05, and 159.1 ppm, respectively. Judging from its structure, **5** is a promising, bulky, monodentate phosphine ligand.

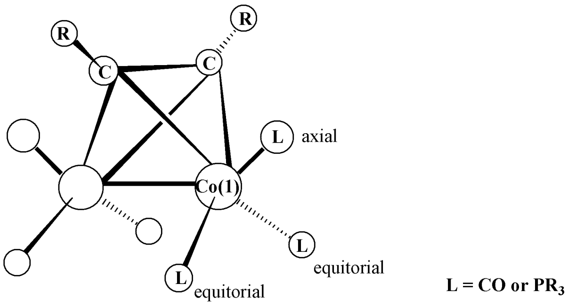


Chart 3 A generalized structure of a phosphine substituted alkyne-bridged dicobalt complex.

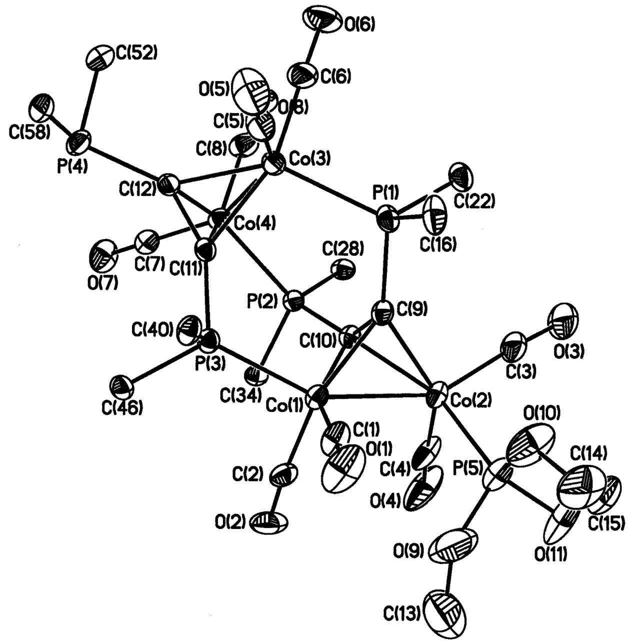
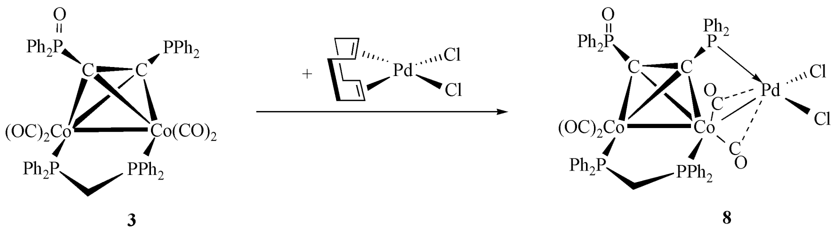


Fig. 1 ORTEP drawing with the numbering scheme of **5**. Some carbon and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): P(4)–C(12) 1.797(6), Co(4)–C(7) 1.788(8), Co(4)–C(12) 1.970(6), Co(4)–C(11) 1.959(6), Co(3)–C(12) 1.960(6), Co(3)–C(11) 1.979(6), Co(3)–Co(4) 2.5052(13), C(11)–C(12) 1.368(9), P(3)–C(11) 1.781(6); C(7)–Co(4)–C(12) 101.1(3), C(7)–Co(4)–C(8) 94.9(4), C(7)–Co(4)–Co(3) 151.1(2), C(12)–Co(4)–Co(3) 50.22(19), C(8)–Co(4)–Co(3) 92.4(3), C(11)–Co(4)–Co(3) 50.85(18), C(12)–Co(3)–C(11) 40.7(3), C(11)–Co(3)–Co(4) 50.13(17), C(11)–C(12)–Co(4) 69.2(3), P(4)–C(12)–Co(3) 143.0(4).

2.2 Reactions of 1 and 5 with (COD)PdCl$_2$

The reaction of **1** with one molar equivalent of (COD)PdCl$_2$ was carried out in CH$_2$Cl$_2$ at 25 °C for 1 h and gave a yellow–brown colored product, [Co$_2$(CO)$_5${μ-*P*,*P*-(μ-PPh$_2$C≡CPPh$_2$)}]-[Co$_2$(CO)$_3$(μ-CO){μ-*P*-(μ-PPh$_2$C≡CPPh$_2$)}]PdCl$_2$ **6** (Scheme 1). A reaction was also carried out for **5** with (COD)PdCl$_2$ under the same conditions and yielded a yellow–brown colored product, [Co$_2$(CO)$_4${P(OMe)$_3$}{μ-*P*,*P*-(μ-PPh$_2$C≡CPPh$_2$)}]-[Co$_2$(CO)$_3$(μ-CO){μ-*P*-(μ-PPh$_2$C≡CPPh$_2$)}]PdCl$_2$ **7**. Both **6** and **7** were characterized by spectroscopic means, as well as by X-ray diffraction studies. The ^{31}P NMR spectrum of **6** shows singlet, singlet and triplet signals at δ 23.65, 49.70, and 65.69 ppm, respectively, for the phosphorus atoms. The most upfield signal corresponds to the palladium-coordinated phosphorus atom. Similarly, there are signals at δ 24.31, 50.53, and 59.08 ppm, respectively, for the three phosphorus atoms in **7**. Again, the most upfield one corresponds the palladium-coordinated phosphorus atom. For **7**, there is one more highly downfielded signal at δ 158.76 ppm, which corresponds to the substituted P(OMe)$_3$ ligand. The X-ray structural studies of both **6** and **7** reveal that the palladium fragment, PdCl$_2$, is coordinated by bulky phosphine ligands **1** and **5**, respectively (Figs. 2 and 3). Interestingly, an unusual palladium–cobalt bonding was formed accompanied with a semi-bridging carbonyl in both compounds. The axial carbonyls, C(7)–O(7), for both **6** and **7** are slightly bent. The bond angles, Co(4)–C(7)–O(7), for **6** and **7** are 166.51 and 168.59°, respectively, indicating a weak semi-bridging interaction with Pd. The formal oxidation states for the two metal centers are assigned as Pd(II) and Co(0) for both compounds. To the best of our knowledge, this is the first example of forming a direct Pd–Co bond through the reaction



Scheme 2

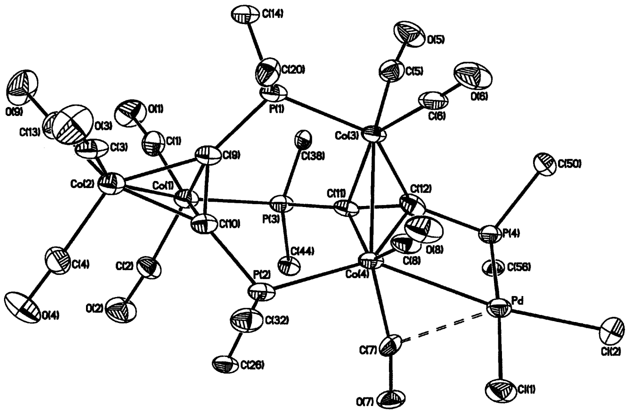


Fig. 2 ORTEP drawing with the numbering scheme of **6**. Some carbon and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Pd–Cl(2) 2.350(4), Pd–Cl(1) 2.382(4), Pd–P(4) 2.202(4), P(4)–C(12) 1.728(16), Co(4)–C(7) 1.780(14), Co(4)–C(11) 2.011(14), Co(4)–C(12) 2.038(15), Co(3)–C(12) 1.941(15), Co(3)–C(11) 1.990(13), Co(3)–Co(4) 2.555(2), C(11)–C(12) 1.372(19), P(3)–C(11) 1.784(16), Pd–C(7) 2.290(14), Pd–Co(4) 2.677(2); C(7)–Co(4)–C(8) 107.8(6), C(7)–Co(4)–C(12) 105.6(6), C(7)–Co(4)–Pd 57.7(4), C(8)–Co(4)–Pd 73.9(5), Co(3)–Co(4)–Pd 109.04(8), Cl(1)–Pd–Co(4) 99.61(12), C(7)–Pd–Cl(1) 84.2(4), P(4)–Pd–Cl(2) 91.18(16), P(4)–Pd–Co(4) 75.31(11), C(7)–Pd–Co(4) 41.1(3).

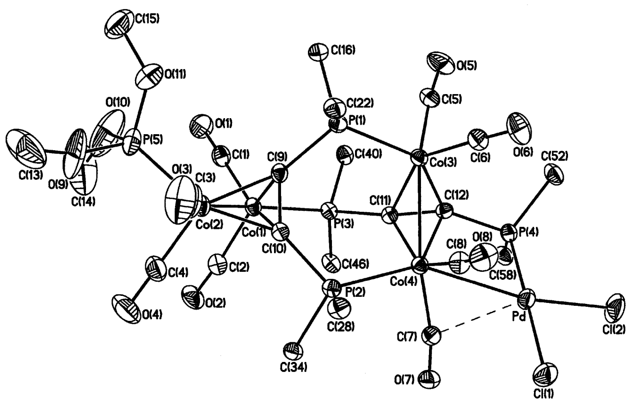


Fig. 3 ORTEP drawing with the numbering scheme of **7**. Some carbon and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Pd–Cl(2) 2.3270(18), Pd–Cl(1) 2.3857(17), P(4)–C(12) 1.757(5), Co(4)–C(7) 1.806(6), Co(4)–C(12) 2.057(5), Co(4)–C(11) 1.995(5), Co(3)–C(12) 1.918(5), Co(3)–C(11) 1.987(5), Co(3)–Co(4) 2.5468(9), C(11)–C(12) 1.341(7), P(3)–C(11) 1.796(5), Pd–P(4) 2.1966(15), Pd–Co(4) 2.6861(8), Pd–C(7) 2.409(6); C(7)–Co(4)–C(8) 105.4(3), C(7)–Co(4)–C(12) 107.7(2), C(7)–Co(4)–Pd 61.20(18), C(8)–Co(4)–Pd 73.36(19), Co(3)–Co(4)–Pd 107.42(3), Cl(1)–Pd–C(7) 85.20(13), Cl(1)–Pd–Co(4) 101.52(5), P(4)–Pd–Co(4) 76.35(4), P(4)–Pd–Cl(2) 89.10(7), C(7)–Pd–Co(4) 41.08(14).

of a cobalt-containing phosphine ligand with a palladium compound.

2.3 Reactions of 3 with (COD)PdCl$_2$

The reaction of **3** with one molar equivalent of (COD)PdCl$_2$ was carried out in CH$_2$Cl$_2$ at 25 °C for 1 h (Scheme 2). The resulting red–brown colored product, $[\{\mu\text{-}P,P\text{-}PPh_2CH_2PPh_2\}\text{-}Co_2(CO)_3(\mu\text{-}CO)\{\mu\text{-}PPh_2C{\equiv}CP({=}O)Ph_2\}]PdCl_2$ **8** was characterized by spectroscopic means, as well as by X-ray diffraction studies. The ^{31}P NMR spectrum of **8** shows three singlet signals in the ratio of 1 : 1 : 2 at δ 24.76, 28.70, and 33.92 ppm, respectively, for all phosphorus atoms. Again, the most upfield signal corresponds to the palladium-coordinated phosphorus atom. The crystal structure of **8** reveals that the bulky phosphine ligand, **3**, coordinates to the palladium fragment, PdCl$_2$, with both phosphorus and cobalt sites (Fig. 4). An unusual palladium–cobalt bonding was formed accompanied with two semi-bridging carbonyls. The structure also reveals that the distance between the oxide (P=O) and the adjacent methylene proton, 2.238 Å, is well within the range of an intramolecular hydrogen bonding.[10] This is also evidenced by the fact that a highly downfield shift of the adjacent methylene proton (6.79 ppm), compared with the remote methylene proton (3.83 ppm), was observed. As known, the 16-electron rule is obeyed for most of second and third row transition metal complexes with d^8 configuration.[11] This rule is observed for **8** (and for **6**, **7**) if the Pd–Co bonding is regarded as a Co to Pd dative bond. Once more, the formal oxidation states for the two metal centers are assigned as Pd(II) and Co(0) for **8**. Interestingly, strikingly similar bonding modes, surrounding the Pd center, were established for **6**, **7** and **8**. As a result, it is safe to state that the formation of a direct Pd–Co bond through this reaction route is not serendipitous, but rather, a general process.

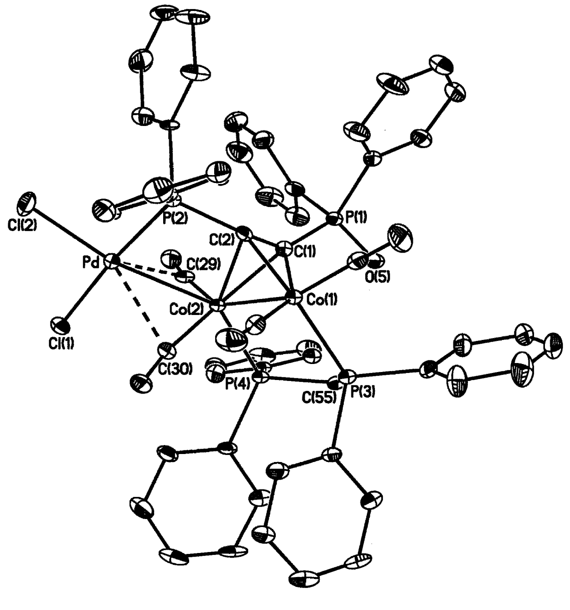


Fig. 4 ORTEP drawing with the numbering scheme of **8**. Some carbon and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Pd–Cl(2) 2.3282(9), Pd–Cl(1) 2.3997(9), P(2)–C(2) 1.766(3), Co(2)–C(30) 1.807(4), Co(2)–C(29) 1.819(4), Co(2)–C(1) 1.991(3), Co(2)–C(2) 2.049(3), Co(1)–Co(2) 2.4999(6), C(1)–C(2) 1.348(4), Pd–P(2) 2.2050(9), Pd–Co(2) 2.6171(5), Pd–C(30) 2.434(3), Pd–C(29) 2.556(3); C(30)–Co(2)–C(29) 114.12(15), C(30)–Co(2)–Pd 63.70(11), C(29)–Co(2)–Pd 67.62(10), P(2)–Pd–Cl(2) 92.04(3), P(2)–Pd–Cl(1) 171.98(3), Cl(2)–Pd–Cl(1) 94.58(4), Cl(1)–Pd–C(30) 83.69(8), P(2)–Pd–C(29) 93.99(8), Cl(2)–Pd–C(29) 140.80(9), Cl(1)–Pd–C(29) 78.02(8), C(30)–Pd–C(29) 75.12(11), P(2)–Pd–Co(2) 75.90(2), Cl(1)–Pd–Co(2) 97.33(3), C(30)–Pd–Co(2) 41.73(8), C(29)–Pd–Co(2) 41.15(8).

Some selected structural data for **6**, **7** and **8** are shown in Chart 4 for comparison. Basically, the variations of the geometrical parameters for all three compounds are small. The four atoms, Co, Pd, P, C, are almost coplanar with the semi-bridging carbonyl(s) off the plane. The measured Pd–P bond lengths for all three compounds are within experimental error. It was also found that the distances between the two metal centers are close to the short side of all reported Pd–Co single bonds.[12] The Pd–Co bond lengths of **6** and **7** are similar and slightly longer than that of **8**.

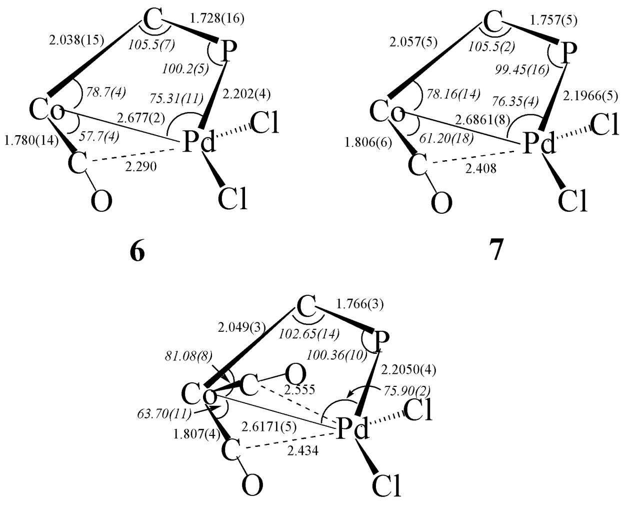


Chart 4 Selected structural parameters for **6**, **7** and **8**.

As revealed from the crystal data, there are two semi-bridging carbonyls between Pd and Co in **8** whilst only one for either **6** or **7**. As known, it is necessary for the metal center to release the strain caused by the excess electron density accumulation, donated from the ligand, a phosphine in this case. In a structurally related compound (dppe)(CH_3)Pd–Co$(CO)_4$, with a direct Pd–Co single bond and two semi-bridging CO groups, a theoretical study has demonstrated that part of the electron density flows from the occupied Pd d orbitals to the Co through the π* orbitals of the bridging CO groups.[13] While electron density is donated to the Pd center, supplementary channels, bridging CO(s) in these cases, are employed in conveying the excess electron density away from Pd. Judging from the number of the semi-bridging CO, it is believed that the coordinated phosphine ligand of **8** donates more electron densities to Pd than in the case of either **6** or **7**. This is also evidenced by the fact that the ^{31}P NMR chemical shifts change is larger for **8** than that of **6** or **7** after coordination.[14]

Many attentions have been focused on the Suzuki cross-coupling reaction in recent years because of its convenience in generating sp^2–sp^2 carbon–carbon bonds. The palladium-catalyzed cross coupling of aryl halides with organoboron reagents has become one of the most widely utilized methods.[15] A Suzuki type coupling reaction employing the above mentioned palladium complexes, **6**, **7** and **8**, as catalysts in the reaction of 2-bromothiophene with boronic acid, was studied.[16] Unfortunately, preliminary results did not show encouraging signs. The yields were below 20% in several trial reaction conditions. A strong bonding between the palladium and halide as well as the bulkiness of the ligand might account for the retardation of the coupling reaction. More systematic investigations of these reactions are currently being undertaken.

Summary. The reactions of some cobalt-containing bulky monodentate phosphine ligands toward palladium complexes have been carried out. These cobalt-containing bulky phosphine ligands have proved to act as authentically monodentate phosphine ligands in coordinating to palladium. In addition, an unusual palladium–cobalt bonding was formed with semi-bridging carbonyl(s) in the products.

3 Experimental

3.1 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). ^{1}H NMR spectra were recorded (Varian VXR-300S spectrometer) at 300.00 MHz; chemical shifts are reported in ppm relative to internal $CHCl_3$ or CH_2Cl_2. ^{31}P and ^{13}C NMR spectra were recorded at 121.44 and 75.46 MHz, respectively. Variable-temperature ^{1}H NMR experiments were recorded by the same instrument. Some other routine ^{1}H NMR spectra were recorded on a Gemini-200 spectrometer at 200.00 MHz or Varian-400 spectrometer at 400.00 MHz. IR spectra of sample powders in KBr were recorded on a Hitachi 270–30 spectrometer. Mass spectra were recorded on a JOEL JMS-SX/SX 102A GC/MS/MS spectrometer. Elemental analyses were recorded on a Heraeus CHN–O–S-Rapid instrument.

3.2 Preparation of 5

Into a 100 cm^3 round flask was placed **1** (0.780 g, 0.611 mmol) in 10 cm^3 of THF and 1.2 molar equivalents of $P(OCH_3)_3$ (0.090 ml, 0.763 mmol). A solution containing TMNO (0.055 g, 0.736 mmol) in 10 cm^3 CH_2Cl_2 was transferred to the 100 cm^3 round flask dropwise. Then, the solution was stirred at 25 °C for 3 h. Subsequently, the mixture was concentrated in a reduced pressure and was subjected to chromatography. Dark brown $[Co_2(CO)_4\{P(OMe)_3\}\{\mu\text{-}P,P\text{-}(\mu\text{-}PPh_2C{\equiv}CPPh_2)\}][Co_2(CO)_4\{\mu\text{-}P\text{-}(\mu\text{-}PPh_2C{\equiv}CPPh_2)\}]$ **5** (0.390 g, 0.284 mmol) was eluted out with mixed solvent (CH_2Cl_2–hexane (1 : 1)); yield 46.5%.

3.2.1 Characterization of 5.

^{1}H NMR ($CDCl_3$, δ/ppm): 3.57 (d, $J_{P\text{–}H}$ = 11.1 Hz, $P(OCH_3)_3$), 6.93–7.65 (m, 40H, arene); ^{13}C NMR ($CDCl_3$, δ/ppm): 52.05(3C, d, $J_{P\text{–}H}$ = 19.5 Hz, $-OCH_3$), 127.28–138.56 (48C, arene), 202.52 (CO), 205.15 (CO), 206.51 (CO); ^{31}P NMR ($CDCl_3$, δ/ppm): 13.0 (s, 1P, dppa), 50.0 (s, 2P dppa), 58.8 (s, 1P, dppa), 159.1 (s, 1P, $P(OCH_3)_3$). Anal. Calc. for **5**: C, 55.12; H, 3.60. Found: C, 54.89; H, 3.52%.

3.3 Reaction of 1 with (COD)PdCl$_2$

Into a 100 cm^3 flask was placed **1** (0.536 g, 0.420 mmol) and (COD)$PdCl_2$ (0.120 g, 0.420 mmol) with 15 ml of CH_2Cl_2. The solution was stirred at 25 °C for 1 h. Purification with centrifugal thin-layer chromatography (CTLC) was carried out. The first band, yellow–brown in color, $[Co_2(CO)_5\{\mu\text{-}P,P(\mu\text{-}PPh_2\text{-}C{\equiv}CPPh_2)\}][Co_2(CO)_4\{\mu\text{-}P(\mu\text{-}PPh_2C{\equiv}CPPh_2)\}]PdCl_2$ **6** (0.139 g, 0.096 mmol), was eluted out with mixed solvent (ethyl acetate–CH_2Cl_2 (1 : 1)); yield 22.6%.

3.3.1 Characterization of 6.

^{1}H NMR (CD_2Cl_2, δ/ppm): 6.99–7.83 (m, 40H, arene); ^{13}C NMR ($CDCl_3$, δ/ppm): 127.90–137.49 (m, 40C, arene), 199.48–205.45 (m, terminal CO); ^{31}P NMR (CD_2Cl_2, δ/ppm): 23.65 (s, 1P, dppa), 49.70 (d, $J_{P\text{–}P}$ = 37.4 Hz, 2P, dppa), 65.69 (t, $J_{P\text{–}P}$ = 42.3 Hz, 1P, dppa). Anal. Calc. for **6**: C, 48.82; H, 3.19. Found: C, 45.35; H, 3.34%; IR (KBr)/cm^{-1}: ν_{CO} 1980, 2007, 2068; MS: m/z 1416 $(P - Cl)^+$; mp 120 °C (decomp.).

3.4 Reaction of 5 with (COD)PdCl$_2$

Into a 100 cm^3 flask was placed **5** (0.436 g, 0.318 mmol) and (COD)$PdCl_2$ (0.091 g, 0.318 mmol) with 15 ml of CH_2Cl_2. The

Table 1 Crystal data for **5**, **6**, **7** and **8**

Compound	**5**	**6**	**7**	**8**
Formula	$C_{63}H_{49}Co_4O_{11}P_5$	$C_{61}H_{40}Cl_2Co_4O_9P_4Pd$	$C_{63}H_{49}Cl_2Co_4O_{11}P_5Pd\cdot 2CH_2Cl_2\cdot CH_3OH$	$C_{55}H_{42}Cl_2Co_2O_5P_4Pd\cdot CH_2Cl_2$
Formula weight	1372.59	1453.83	1549.98	1286.85
Crystal system	Triclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/c$	$P\bar{1}$
a/Å	13.7890(19)	15.029(4)	16.5696(12)	11.1922(8)
b/Å	13.8536(19)	23.761(7)	19.5107(13)	13.1178(9)
c/Å	18.622(2)	17.180(5)	23.8716(17)	19.4159(14)
α/°	86.151(3)	90	90	94.9880(10)
β/°	85.941(3)	98.846(7)	109.1480(10)	100.917(2)
γ/°	61.916(2)	90	90	101.4100(10)
V/Å^3	3128.3(7)	6062(3)	7290.4(9)	2720.7(3)
Z	2	4	4	2
D_c/Mg m^{-3}	1.457	1.593	1.597	1.571
λ(Mo-Kα)/Å	0.71073	0.71073	0.71073	0.71073
μ/mm^{-1}	1.228	1.611	1.520	1.291
θ Range/°	1.96–26.03	1.68–25.98	1.38–26.00	1.81–26.04
Observed reflections ($F > 4\sigma(F)$)	7388	3819	4570	7517
No. of refined parameters	748	730	865	451
$R1$ [a]	0.0662	0.0889	0.0494	0.0385
$wR2$ [b]	0.1697	0.2158	0.1409	0.0993
GoF [c]	0.959	0.986	0.906	0.983

[a] $R1 = |\Sigma(|F_o| - |F_c|)/|\Sigma F_o||$ for significant reflections. [b] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2/\Sigma[w(F_o^2)^2]\}^{1/2}$ for significant reflections; w = 0.118, 0.1525, 0.1129 and 0.0705 for **5**, **6**, **7** and **8**, respectively. [c] $\mathrm{GoF} = [\Sigma w(F_o^2 - F_c^2)^2/(N_{\mathrm{rflns}} - N_{\mathrm{params}})]^{1/2}$.

solution was stirred at 25 °C for 1 h. Purification with centrifugal thin-layer chromatography (CTLC) was carried out. The first band, yellow-brown in color, $[Co_2(CO)_4\{P(OMe)_3\}\{\mu\text{-}P,P\text{-}(\mu\text{-}PPh_2C{\equiv}CPPh_2)\}][Co_2(CO)_4\{\mu\text{-}P(\mu\text{-}PPh_2C{\equiv}CPPh_2)\}]PdCl_2$ **7** (0.2216 g, 0.1429 mmol), was eluted with mixed solvent (ethyl acetate–CH_2Cl_2 (1 : 1)); yield 45.0%.

3.4.1 Characterization of 7. ^{1}H NMR (CD_2Cl_2, δ/ppm): 3.62 (d, $J_{H\text{–}H}$ = 10.81 Hz, 9H, CH_3), 7.04–7.86 (m, 40H, arene); ^{13}C NMR ($CDCl_3$, δ/ppm): 127.38–134.08 (m, 40C, arene), 201.13–205.80 (m, terminal CO); ^{31}P NMR (CD_2Cl_2, δ/ppm): 24.31 (s, 1P, dppa), 50.53 (s, 1P, dppa), 59.08 (s, 1P, dppa), 158.76 (s, 1P, $POMe_3$). Anal. Calc: C, 48.82; H, 3.19. Found: C, 45.35; H, 3.34%; IR (KBr)/cm^{-1}: ν_{CO} 1980, 2007, 2068; mp 100 °C (decomp.).

3.5 Reaction of 3 with (COD)PdCl$_2$

Into a 100 cm^3 flask was placed **3** (0.673 g, 0.656 mmol) and (COD)$PdCl_2$ (0.187 g, 0.656 mmol) with 15 ml of CH_2Cl_2. The solution was stirred at 25 °C for 1 h. Purification with centrifugal thin-layer chromatography (CTLC) was carried out. The first band, red–brown in color, $[\{\mu\text{-}P,P\text{-}PPh_2CH_2PPh_2\}Co_2(CO)_4\{\mu\text{-}PPh_2C{\equiv}CP(O)Ph_2\}]PdCl_2$ **8** (0.455 g, 0.384 mmol), was eluted with mixed solvent (ethyl acetate–CH_2Cl_2 (1 : 1); yield 57.7%.

3.5.1 Characterization of 8. ^{1}H NMR (CD_2Cl_2, δ/ppm): 3.83 (m, 1H, CH_2), 6.79 (m, 1H, CH_2), 6.71–8.41 (m, 40H, arene); ^{13}C NMR ($CDCl_3$, δ/ppm): 31.57 (s, 1C, CH_2), 116.86–136.66 (m, 40C, arene), 201.13–205.80 (m, terminal CO); ^{31}P NMR (CD_2Cl_2, δ/ppm): 24.76 (s, 1P, dppa), 28.70 (s, 1P, dppa), 33.92 (s, 2P, dppm). Anal. Calc: C, 54.96; H, 3.52. Found: C, 50.62; H, 3.93%; IR(KBr)/cm^{-1}: ν_{CO} 1969, 2019, 2052; MS: m/z 1166 (P^+ − Cl); mp 210 °C (decomp.).

3.6 X-Ray crystallographic studies

Suitable crystals of **5**, **6**, **7** and **8** 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). Absorption corrections were based on symmetry equivalent reflections using the SADABS program. Space group determinations were based on a check of the Laue symmetry and systematic absences, and confirmed using structure solution. The structures were solved by direct methods using the SHELXTL package.[17] 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.[18] Crystallographic data for **5**, **6**, **7**, and **8** are summarized in Table 1.

CCDC reference numbers 209741–209744.

See http://www.rsc.org/suppdata/dt/b3/b306228g/ for crystallographic data in CIF or other electronic format.

Acknowledgements

We thank the National Science Council of the R.O.C. (Grant NSC-91-2113-M-005-017) for support.

References

1 (*a*) *Applied Homogeneous Catalysis with Organometallic Compounds*, ed. B. Cornils and W. A. Herrmann, VCH, New York, 1996, vol. 1, p. 2; (*b*) R. Noyori, *Asymmetric Catalysis In Organic Synthesis*, John Wiley & Sons, Inc., New York, 1994; (*c*) G. W. Parshall and S. D. Ittel, *Homogeneous Catalysis*, John Wiley & Sons, Inc., New York, 2nd edn., 1992, ch. 8; (*d*) H. B. Kagan, *Asymmetric Synthesis Using Organometallic Catalysts*, in *Comprehensive Organometallic Chemistry*, ed. G. Wilkinson, F. G. A. Stone and E. W. Abel, Pergamon Press, Oxford, 1982, vol. 8, ch. 53.

2 R. H. Crabtree, *The Organomatalic Chemistry of the Transition Metals*, John Wiley & Sons, New York, 2nd edn., 1994, ch. 6.

3 (*a*) S. R. Chemler, D. Trauner and S. J. Danishefsky, *Angew. Chem., Int. Ed.*, 2001, **40**, 4544; (*b*) J. P. Wolfe and S. L. Buchwald, *Angew. Chem., Int. Ed.*, 1999, **38**, 2413; (*c*) J. P. Wolfe, H. Tomori, J. P. Sadighi, J. Yin and S. L. Buchwald, *J. Org. Chem.*, 2000, **65**, 1158; (*d*) J. P. Wolfe, R. A. Singer, B. H. Yang and S. L. Buchwald, *J. Am. Chem. Soc.*, 1999, **121**, 9550; (*e*) A. F. Littke and G. C. Fu, *Angew. Chem., Int. Ed.*, 1998, **37**, 3387; (*f*) X. Bei, T. Crevier, A. S. Guran, B. Jandeleit, T. S. Powers, H. W. Turner, T. Uno and W. H. Weinberg, *Tetrahedron Lett.*, 1999, **40**, 3855.

4 Hundreds of organic phosphorus ligands are listed in a Strem booklet: *Phosphorus Ligands and Compounds*, Strem Chemicals, Inc., Newburyport, MA 01950-4098, USA, 2000.

5 (*a*) Q. S. Hu, Y. Lu, Z. Y. Tang and H. B. Yu, *J. Am. Chem. Soc.*, 2003, **125**, 2856; (*b*) O. Delacroix and J. A. Gladysz, *Chem. Commun.*, 2003, 665.

6 F.-E Hong, H. Chang, Y.-C. Chang and B.-T. Ko, *Inorg. Chem. Commun.*, 2001, **4**, 723.

7 For example, the carbonyl of [(μ-alkyne)$Co_2(CO)_6$] is readily replaced by a phosphine ligand under mild conditions.

8 F.-E Hong, Y.-C. Chang, R.-E Chang, S.-C. Chen and B.-T. Ko, *Organometallics*, 2002, **21**, 961.

9 (*a*) J.-J. Bonnet and R. Mathieu, *Inorg. Chem.*, 1978, **17**, 1973; (*b*) A. Meyer, A. Gorgues, Y. Le Floc'h, Y. Pineau, J. Guillevic and J. Y. Le Marouille, *Tetrahedron Lett.*, 1981, **22**, 5181; (*c*) S. J. Doig, R. P. Hughes, R. E. Davis, S. M. Gadol and K. D. Holland, *Organometallics*, 1984, **3**, 1921; (*d*) R. P. Hughes, S. J. Doig, R. C. Hemond, W. L. Smith, R. E. Davis, S. M. Gadol and K. D. Holland, *Organometallics*, 1990, **9**, 2745; (*e*) C. J. McAdam, J. J. Brunton, B. H. Robinson and J. Simpson, *J. Chem. Soc., Dalton Trans.*, 1999, 2487; (*f*) D. H. Bradley, M. A. Khan and K. M. Nicholas, *Organometallics*, 1989, **8**, 554; (*g*) R. H. Cragg, J. C. Jeffery and M. J. Went, *J. Chem. Soc., Chem. Commun.*, 1990, 993; (*h*) R. H. Cragg, J. C. Jeffery and M. J. Went, *J. Chem. Soc., Dalton Trans.*, 1991, 137; (*i*) G. Conole, M. Kessler, M. J. Mays, G. E. Pateman and G. A. Solan, *Polyhedron*, 1998, **17**, 2993; (*j*) J. Castro, A. Moyano, M. A. Pericas, A. Riera, M. A. Maestro and J. Mahia, *Organometallics*, 2000, **19**, 1704; (*k*) B. T. Heaton and J. J. Ko, personal communication, 1996; (*l*) J. Castro, A. Moyano, M. A. Pericas, A. Riera, A. Alvarez-Larena and J. F. Piniella, *J. Am. Chem. Soc.*, 2000, **122**, 7944; (*m*) C. J. McAdam, N. W. Duffy, B. H. Robinson and J. Simpson, *J. Organomet. Chem*, 1997, **527**, 179; (*n*) A. J. Fletcher, R. Fryatt, D. T. Rutherford, M. R. J. Elsegood and S. D. R. Christie, *Synlett*, 2001, 1711; (*o*) A. J. Fletcher, R. Fryatt, D. T. Rutherford, M. R. J. Elsegood and S. D. R. Christie, *Synlett*, 2001, 1711; (*p*) H. Mayr, O. Kuhn, C. Schlierf and A. R. Ofial, *Tetrahedron*, 2000, **56**, 4219; (*q*) R. P. Hughes, S. J. Doig, R. C. Hemond, W. L. Smith, R. E. Davis, S. M. Gadol and K. D. Holland, *Organometallics*, 1990, **9**, 2745; (*r*) D. H. Bradley, M. A. Khan and K. M. Nicholas, *Organometallics*, 1992, **11**, 2598; (*s*) A. A. Pasynskii, Y. V. Torubaev, F. S. Denisov, A. Y. Lyakina, R. I. Valiullina, G. G. Alexandrov and K. A. Lyssenko, *J. Organomet. Chem.*, 2000, **597**, 196; (*t*) A. A. Pasynskii, Yu. A. Torubayev, A. Yu. Lyakina, R. I. Valiullina, G. G. Aleksandrov and K. A. Lyssenko, *Koord. Khim.*, 2000, **26**, 112; (*u*) J. C. Jeffery, R. M. S. Pereira, M. D. Vargas and M. J. Went, *J. Chem. Soc., Dalton Trans.*, 1995, 1805; (*v*) F.-E Hong, F.-C. Lien, Y.-C. Chang and B.-T. Ko, *J. Chin. Chem. Soc*, 2002, **49**, 509.

10 The commonly observed hydrogen-bonding range is from 2.05 to 2.40 Å: R. Taylor and O. Kennard, *J. Am. Chem. Soc.*, 1982, **104**, 5063.

11 C. M. Lukehart, *Fundamental Transition Metal Organometallic Chemistry*, Brooks/Cole Publishing Company, Monterey, CA, 1985, ch. 1.

12 The statistics search from the Cambridge Structure Data base by the enquired Pd–Co distance from 16 citations reveals that the distances range from 2.511 to 2.942 Å: (*a*) P. Braunstein, J.-M. Jud, Y. Dusausoy and J. Fischer, *Organometallics*, 1983, **2**, 180; (*b*) P. Braunstein, C. de Meric de Bellefon, M. Ries, J. Fischer, S.-E. Bouaoud and D. Grandjean, *Inorg. Chem.*, 1988, **27**, 1327; (*c*) I. Bachert, P. Braunstein, M. K. McCart, F. F. de Biani, F. Laschi, P. Zanello, G. Kickelbick and U. Schubert, *J. Organomet. Chem.*, 1999, **573**, 47; (*d*) P. Braunstein, C. de Meric de Bellefon, M. Ries, J. Fischer, S.-E. Bouaoud and D. Grandjean, *Inorg. Chem.*, 1988, **27**, 1327; (*e*) U. Thewalt and S. Muller, *Z. Naturforsch., Teil B*, 1989, **44**, 1206; (*f*) N. Komine, H. Hoh, M. Hirano and S. Komiya, *Organometallics*, 2000, **19**, 5251; (*g*) M. Pfeffer, J. Fischer, A. Mitschler and L. Ricard, *J. Am. Chem. Soc.*, 1980, **102**, 6338; (*h*) M. Pfeffer, J. Fischer and A. Mitschler, *Organometallics*, 1984, **3**, 1531; (*i*) R. Vilar, S. E. Lawrence, S. Menzer, D. M. P. Mingos and D. J. Williams, *J. Chem. Soc., Dalton Trans.*, 1997, 3305; (*j*) A. Fukuoka, S. Fukagawa, M. Hirano and S. Komiya, *Chem. Lett.*, 1997, 377; (*k*) A. Fukuoka, S. Fukagawa, M. Hirano, N. Koga and S. Komiya, *Organometallics*, 2001, **20**, 2065; (*l*) G. le Borgne, S. E. Bouaoud, D. Grandjean, P. Braunstein, J. Dehand and M. Pfeffer, *J. Organomet. Chem.*, 1977, **136**, 375; (*m*) Y. Misumi, Y. Ishii and M. Hidai, *Chem. Lett.*, 1994, 695; (*n*) Y. Misumi, Y. Ishii and M. Hidai, *J. Chem. Soc., Dalton Trans.*, 1995, 3489; (*o*) P. Braunstein, C. de Bellefon, Y. Dusausoy and D. Bayeul, *J. Cluster Sci.*, 1995, **6**, 175; (*p*) R. E. Marsh, *Acta Crystallogr., Sect. B*, 2002, **58**, 893; (*q*) F. H. Allen, *Acta Crystallogr., Sect. B*, 2002, **58**, 380–388.

13 A. Fukuoka, S. Fukagawa, M. Hirano, N. Koga and S. Komiya, *Organometallics*, 2001, **20**, 2065.

14 ^{31}P NMR chemical shift (δ/ppm): **1** (12.98) ⟶ **6** (23.65); **5** (13.00) ⟶ **7** (24.31); **3** (0.80) ⟶ **8** (24.76).

15 (*a*) A. Suzuki, in *Metal-Catalyzed Cross-Coupling Reactions*, ed. F. Diederich and P. J. Stang, Wiely-VCH: Weinheim, Germany, 1988, ch. 2; (*b*) N. Miyaura and A. Suzuki, *Chem. Rev.*, 1995, **95**, 2457; (*c*) A. Suzuki, *J. Organomet. Chem.*, 1999, **576**, 147.

16 Suzuki coupling reaction was performed according to Wolfe's procedure. Into a oven-dried Schlenk flask, which was previously evacuated and backfilled with nitrogen, was placed 0.01 mmol of **6** (or **7**, **8**), boronic acid (183 mg, 1.5 mmol), and KF (174 mg, 3.0 mmol). This was then followed by adding 1 mmol of 2-bromothiophene and 1 ml of THF. The solution was stirred at 60 °C for 19 h. Consequently, 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); the aqueous layer was then extracted with ether (20 mL) again. The combined organic layers were washed with saturated NaCl (20 mL), and dried with anhydrous magnesium sulfate, filtered, and concentrated *in vacuo*. The crude material was purified by flash chromatography on silical gel. The reaction yield was calculated based on the isolated product.

17 G. M. Sheldrick, SHELXTL PLUS User's Manual . Revision 4.1 Nicolet XRD Corporation, Madison, WI, USA, 1991.

18 The hydrogen atoms were ride on carbons or oxygens in their idealized positions and held fixed with the C–H distances of 0.96 Å.