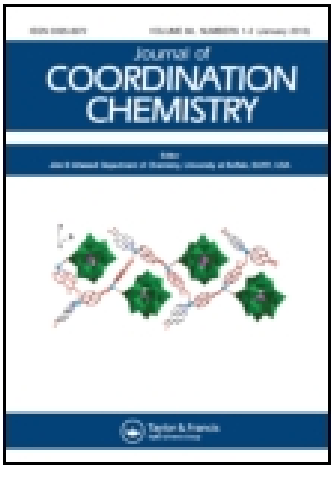




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# Synthesis and characterization of mono- and dinuclear aryl palladium(II) complexes: oxidative additions of 1,4-dihalogenated benzene or 4,4′-dibromobiphenyl to $Pd(PR_3)_4$

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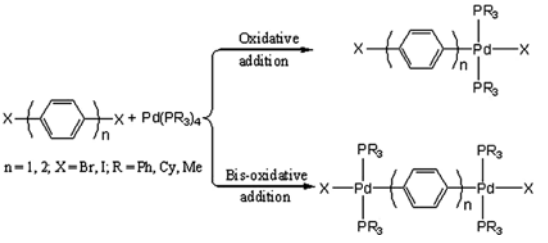


Mononuclear palladium(II) complexes **1–12**, $(C_6H_4X\text{-}4)PdX'(PR_3)_2$ (X = I, Br, or Cl; X′ = I or Br; R = Ph, Cy, Et, or Me), were synthesized by oxidative addition of 1,4-dihalogenated benzene to $Pd(PR_3)_4$; dinuclear palladium(II) complexes **13–15**, $(Me_3P)_2XPd(C_6H_4\text{-}1,4)PdX'(PMe_3)_2$ (X, X′ = I or Br), could be obtained only using trimethylphosphine. Another method to prepare **13–15** is via re-oxidative addition of the corresponding mononuclear palladium(II) complexes and $Pd(PMe_3)_4$. Using 4,4′-dibromobiphenyl as the starting material, the mononuclear palladium(II) complexes $[C_6H_4(C_6H_4Br\text{-}4)\text{-}4]PdBr(PPh_3)_2$ (**16**) and $[C_6H_4(C_6H_4Br\text{-}4)\text{-}4]PdBr(PCy_3)_2$ (**17**) with bulky phosphines could be synthesized at relative low temperature, while dinuclear **18**, $(Cy_3P)_2BrPd(C_6H_4C_6H_4\text{-}4,4')PdBr(PCy_3)_2$, was prepared by bis-oxidative addition at higher temperature. The re-oxidative addition of **16** and $Pd(PMe_3)_4$ gave dinuclear **19**, $(Me_3P)_2BrPd(C_6H_4C_6H_4\text{-}4,4')PdBr(PMe_3)_2$, accompanying phosphine exchange. X-ray diffraction analysis revealed that formation of dinuclear palladium(II) complexes depends on the reaction temperature, phosphine ligands, and bridging groups.

*Keywords*: Aryl palladium(II) complex; Synthesis; Phosphine; Oxidative addition; Crystal structure

## 1. Introduction

Palladium-catalyzed coupling is a powerful tool in the synthesis of organic compounds and polymers [1–9]. As a key intermediate, formation of aryl palladium complex is essential for

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achieving the coupling with oxidative addition generally considered the determining step [1–3]. Thus, design and synthesis of aryl palladium complexes have been an important research topic for understanding the mechanism of coupling [10–12]. These complexes could be used as the initiator in chain-growth polycondensation to afford well-defined conjugated polymers with a narrow-weight distribution and defined end group [13–16], which indicates that the new strategy could prepare functional conjugated polymers by palladium complexes containing functional groups on the aryl ring.

We initially investigated preparation of aryl palladium complexes to obtain stable palladium initiator with catalytic activity in polymerization. The aryl palladium complexes used as the initiator, such as $(Bu^t_3P)Pd(Ph)Br$ [13], are unstable due to unsaturated coordination and have to be handled under inert atmosphere and low temperature, although the bulky phosphine ($Bu^t_3P$) accelerates polymerization. These complexes can be synthesized using the various routes reported earlier [17–20], but a more convenient method is from oxidative addition of aryl halide and palladium(0) precursor $Pd(PR_3)_4$, which is a starting material in the coupling reaction and generated easily *in situ* from $PdCl_2$ and $PR_3$. Therefore, all aryl palladium complexes in this work were prepared by oxidative addition as described [21] but with gradually increasing of the steric bulk of $PR_3$ [R = Me, Et, cyclohexyl (Cy), Ph], especially $P(Cy)_3$ [22]. Herein, we report the synthesis of the aryl palladium complexes and discuss the effect of the reaction conditions, such as aryl–aryl interchange, steric hindrance of the phosphine and the reaction temperature, on formation of mono- and dinuclear palladium complexes.

## 2. Experimental

### 2.1. *Materials and physical measurements*

All manipulations were carried out under an argon atmosphere using standard Schlenk techniques. The solvents were dried and distilled under argon prior to use. All chemicals were purchased from commercial sources such as Aldrich, J&K, and Acros. $^1$H NMR spectra with TMS as internal reference and $^{31}$P NMR spectra with 85% $H_3PO_4$ as external reference were taken on a Bruker AV 400 NMR spectrometer at room temperature. Elemental analyses were performed on a BioRad elemental analysis system.

Synthesis of **1** [23, 24], **3** [25], **4** [26], **13**, and **19** [18] have been reported previously, but most were not fully characterized. In order to obtain complete data and understand the ligand effect of phosphine, these complexes were prepared using modified or similar procedures to the literature and fully characterized, especially their crystal structures. Except for $Pd(PPh_3)_4$ [27], $Pd(PR_3)_4$ were prepared *in situ* by reaction of $PdCl_2$ and hydrazine hydrate in the presence of excess ligand ($PCy_3$, $PEt_3$, or $PMe_3$) in toluene. These complexes were assumed to be the form of $Pd(PR_3)_4$ in discussing their oxidative addition with aryl halide, although they had been confirmed to be easily dissociated to $Pd(PR_3)_3$ or $Pd(PR_3)_2$ in solution [28, 29], and sometimes to be $Pd(PR_3)_2$ in solid state [30, 31], while R is $PPh_3$, $PCy_3$, or $PEt_3$.

### 2.2. *General procedure for the synthesis of 1–4*

A mixture of $Pd(PPh_3)_4$ (1.16 g, 1 mM), 1,4-dihalogenated benzene (7 mM), and $PPh_3$ (0.53 g, 2 mM) in toluene (35 mL) was heated to 30 or 85 °C and stirred for 24 h. The

solvent was removed and the white precipitate was washed with $Et_2O$ (3 × 10 mL) and dried under vacuum. For further purification, the product was recrystallized from $CH_2Cl_2/Et_2O$ to afford colorless crystals.

($C_6H_4$I-4)PdI($PPh_3$)$_2$ (**1**): Crystal yield: 0.82 g (85.8%). $^1$H NMR (400 MHz, $CDCl_3$, ppm): $\delta$ 7.54–7.49(m, 12H, $C_6H_5$P), 7.37–7.44(m, 6H, $C_6H_5$P), 7.28–7.24(m, 12H, $C_6H_5$P), 6.48(d, 2H, 4-I$C_6H_4$Pd, $J$ = 7.9 Hz), 6.29(d, 2H, 4-I$C_6H_4$Pd, $J$ = 8.2 Hz). $^{31}$P{$^1$H} NMR (162 MHz, $CDCl_3$, ppm): $\delta$ 22.6. Anal. Calcd for $C_{42}H_{34}I_2P_2Pd$: C, 52.50; H, 3.57. Found: C, 52.65; H, 3.52.

($C_6H_4$Br-4)PdBr($PPh_3$)$_2$ (**2**): Crystal yield: 0.713 g (82.2%). $^1$H NMR (400 MHz, $CDCl_3$, ppm): $\delta$ 7.54–7.49(m, 12H, $C_6H_5$P), 7.35–7.33(m, 6H, $C_6H_5$P), 7.28–7.24(m, 12H, $C_6H_5$P), 6.44(d, 2H, 4-Br$C_6H_4$Pd, $J$ = 7.8 Hz), 6.33(d, 2H, 4-Br$C_6H_4$Pd, $J$ = 8.2 Hz). $^{31}$P{$^1$H} NMR (162 MHz, $CDCl_3$, ppm): $\delta$ 23.1. Anal. Calcd for $C_{42}H_{34}Br_2P_2Pd$: C, 58.19; H: 3.95. Found: C, 58.34; H, 3.78.

($C_6H_4$Br-4)PdI($PPh_3$)$_2$ (**3**): Crystal yield: 0.770 g (84.3%). $^1$H NMR (400 MHz, $CDCl_3$, ppm): $\delta$ 7.52–7.49(m, 12H, $C_6H_5$P), 7.36–7.33(m, 6H, $C_6H_5$P), 7.26–7.24(m, 12H, $C_6H_5$P), 6.42(d, 2H, 4-Br$C_6H_4$Pd, $J$ = 8.4 Hz), 6.33(d, 2H, 4-Br$C_6H_4$Pd, $J$ = 8.4 Hz). $^{31}$P{$^1$H} NMR (162 MHz, $CDCl_3$, ppm): $\delta$ 22.4. Anal. Calcd for $C_{42}H_{34}BrIP_2Pd$: C, 55.20; H, 3.75. Found: C, 54.37; H, 3.76.

($C_6H_4$Cl-4)PdBr($PPh_3$)$_2$ (**4**): Crystal yield: 0.688 g (83.7%). $^1$H NMR (400 MHz, $CDCl_3$, ppm): $\delta$ 7.52–7.49(m, 12H, $C_6H_5$P), 7.35–7.32(m, 6H, $C_6H_5$P), 7.27–7.24(m, 12H, $C_6H_5$P), 6.50(d, 2H, 4-Cl$C_6H_4$Pd, $J$ = 8.0 Hz), 6.21(d, 2H, 4-Cl$C_6H_4$Pd, $J$ = 8.0 Hz). $^{31}$P{$^1$H} NMR (162 MHz, $CDCl_3$, ppm): $\delta$ 23.1. Anal. Calcd for $C_{42}H_{34}BrClP_2Pd$: C, 61.34; H, 4.17. Found: C, 61.36; H, 4.00.

### 2.3. *General procedure for the synthesis of 5–12*

Hydrazine hydrate (20 mL) was added dropwise to a mixture of $PdCl_2$ (0.44 g, 2.5 mM), ligand ($PCy_3$, $PEt_3$, or $PMe_3$) (12.5 mM) in toluene (35 mL) at 120 °C. The light yellow mixture was stirred for 30 min at 120 °C and then cooled to room temperature. The yellow toluene supernatant was transferred to a solution of 1,4-dihalogenated benzene (1 mM) in toluene (35 mL). The resulting solution was heated to 30, 85, or 120 °C for 24 h, the solvent was removed, white precipitate was washed with $Et_2O$ (3 × 10 mL) and dried under vacuum. The crude product was recrystallized from $CH_2Cl_2/Et_2O$ to afford colorless crystals.

($C_6H_4$I-4)PdI($PCy_3$)$_2$ (**5**): Crystal yield: 0.72 g (72.4%). $^1$H NMR (400 MHz, $CDCl_3$, ppm): $\delta$ 7.25(d, 2H, 4-I$C_6H_4$Pd, $J$ = 8.0 Hz), 7.13(d, 2H, 4-I$C_6H_4$Pd, $J$ = 8.0 Hz), 2.05–1.06 (m, 66H, $C_6H_{11}$P). $^{31}$P{$^1$H} NMR (162 MHz, $CDCl_3$, ppm): $\delta$ 19.2. Anal. Calcd for $C_{42}H_{70}I_2P_2Pd$: C, 50.59; H, 7.08. Found: C, 50.54; H, 7.14.

($C_6H_4$Br-4)PdI($PCy_3$)$_2$ (**6**): Crystal yield: 0.65 g (68.6%). $^1$H NMR (400 MHz, $CDCl_3$, ppm): $\delta$ 7.25(d, 2H, 4-Br$C_6H_4$Pd, $J$ = 7.8 Hz), 7.09(d, 2H, 4-Br$C_6H_4$Pd, $J$ = 8.0 Hz), 2.15–1.06(m, 66H, $C_6H_{11}$P). $^{31}$P{$^1$H} NMR (162 MHz, $CDCl_3$, ppm): $\delta$ 19.0. Anal. Calcd for $C_{42}H_{70}BrIP_2Pd$: C, 53.09; H, 7.43. Found: C, 52.71; H, 7.26.

($C_6H_4$Br-4)PdBr($PEt_3$)$_2$ (**7**): Crystal yield: 0.43 g (73.6%). $^1$H NMR (400 MHz, $CDCl_3$, ppm): $\delta$ 7.13(d, 2H, 4-Br$C_6H_4$Pd, $J$ = 8.8 Hz), 7.10(d, 2H, 4-Br$C_6H_4$Pd, $J$ = 8.8 Hz), 1.62–1.54(m, 12H, $CH_3CH_2$P), 1.07(qt, 18H, $CH_3CH_2$P, $J$ = 8.0 Hz). $^{31}$P{$^1$H} NMR (162 MHz, $CDCl_3$, ppm): $\delta$ 11.6. Anal. Calcd for $C_{18}H_{34}Br_2P_2Pd$: C, 37.36; H, 5.92. found: C, 37.53; H, 5.98.

($C_6H_4$Br-4)PdI($PEt_3$)$_2$ (**8**): Crystal yield: 0.47 g (74.8%). $^1$H NMR (400 MHz, $CDCl_3$, ppm): $\delta$ 7.15(d, 2H, 4-Br$C_6H_4$Pd, $J$ = 8.0 Hz), 7.08(d, 2H, 4-Br$C_6H_4$Pd, $J$ = 8.0 Hz), 1.70–1.63(m, 12H, $CH_3CH_2$P), 1.05(qt, 18H, $CH_3CH_2$P, $J$ = 8.0 Hz). $^{31}$P{$^1$H} NMR (162 MHz, $CDCl_3$, ppm): $\delta$ 10.3. Anal. Calcd for $C_{18}H_{34}BrIP_2Pd$: C, 34.56; H, 5.48. Found: C, 34.57; H, 5.38.

($C_6H_4$I-4)PdI($PMe_3$)$_2$ (**9**): Crystal yield: 0.42 g (70.5%). $^1$H NMR (400 MHz, $CDCl_3$, ppm): $\delta$ 7.34(d, 2H, 4-I$C_6H_4$Pd, $J$ = 7.8 Hz), 6.97(d, 2H, 4-I$C_6H_4$Pd, $J$ = 7.8 Hz), 1.27(t, 18H, $CH_3$P, $J$ = 3.6 Hz). $^{31}$P{$^1$H} NMR (162 MHz, $CDCl_3$, ppm): $\delta$ −20.7. Anal. Calcd for $C_{12}H_{22}I_2P_2Pd$: C, 24.49; H, 3.77. Found: C, 24.45; H, 3.61.

($C_6H_4$Br-4)PdBr($PMe_3$)$_2$ (**10**): Crystal yield: 0.34 g (68.6%). $^1$H NMR (400 MHz, $CDCl_3$, ppm): $\delta$ 7.17(d, 2H, 4-Br$C_6H_4$Pd, $J$ = 8.0 Hz), 7.13(d, 2H, 4-Br$C_6H_4$Pd, $J$ = 7.8 Hz), 1.22(t, 18H, $CH_3$P, $J$ = 3.2 Hz). $^{31}$P{$^1$H} NMR (162 MHz, $CDCl_3$, ppm): $\delta$ −18.8. Anal. Calcd for $C_{12}H_{22}Br_2P_2Pd$: C, 29.15; H, 4.48. Found: C, 28.34; H, 4.39.

($C_6H_4$Br-4)PdI($PMe_3$)$_2$ (**11**): Crystal yield: 0.36 g (66.9%). $^1$H NMR (400 MHz, $CDCl_3$, ppm): $\delta$ 7.12(d, 2H, 4-Br$C_6H_4$Pd, $J$ = 7.9 Hz), 7.03(d, 2H, 4-Br$C_6H_4$Pd, $J$ = 8.2 Hz), 1.21(t, 18H, $CH_3$P, $J$ = 3.6 Hz). $^{31}$P{$^1$H} NMR (162 MHz, $CDCl_3$, ppm): $\delta$ −20.7. Anal. Calcd for $C_{12}H_{22}IBrP_2Pd$: C, 26.62; H, 4.10. Found: C, 27.60; H, 3.89.

($C_6H_4$Cl-4)PdBr($PMe_3$)$_2$ (**12**): Crystal yield: 0.30 g (66.4%). $^1$H NMR (400 MHz, $CDCl_3$, ppm): $\delta$ 7.18(d, 2H, 4-Cl$C_6H_4$Pd, $J$ = 7.7 Hz), 7.03(d, 2H, 4-Cl$C_6H_4$Pd, $J$ = 7.9 Hz), 1.22(t, 18H, $CH_3$P, $J$ = 3.5 Hz). $^{31}$P{$^1$H} NMR (162 MHz, $CDCl_3$, ppm): $\delta$ −18.8.

### 2.4. *General procedure for the synthesis of 13–15*

The solution of $Pd(PMe_3)_4$, prepared *in situ* by same procedure above, was transferred to a solution of 1,4-dihalogenated benzene (1 mM) in toluene (35 mL). The resulting solution was heated to 60 or 120 °C for 24 h. The solvent was removed and the white precipitate was washed with $Et_2O$ (3 × 10 mL) and dried under vacuum. The crude product was recrystallized from $CH_2Cl_2$/$Et_2O$ to afford colorless crystals.

($Me_3P$)$_2$IPd($C_6H_4$-1,4)PdI($PMe_3$)$_2$ (**13**): Crystal yield: 0.65 g (76.5%). $^1$H NMR (400 MHz, $CDCl_3$, ppm): $\delta$ 6.90(s, 4H, Pd$C_6H_4$Pd), 1.30(t, 36H, $CH_3$P, $J$ = 3.6 Hz). $^{31}$P{$^1$H} NMR (162 MHz, $CDCl_3$, ppm): $\delta$ −21.5. Anal. Calcd for $C_{18}H_{40}I_2P_4Pd_2$: C, 25.52; H, 4.76. Found: C, 26.42; H, 4.79.

($Me_3P$)$_2$BrPd($C_6H_4$-1,4)PdBr($PMe_3$)$_2$ (**14**): Crystal yield: 0.55 g (73.2%). $^1$H NMR (400 MHz, $CDCl_3$, ppm): $\delta$ 6.89(s, 4H, Pd$C_6H_4$Pd), 1.23(t, 36H, $CH_3$P, $J$ = 4.0 Hz). $^{31}$P{$^1$H} NMR (162 MHz, $CDCl_3$, ppm): $\delta$ −19.6. Anal. Calcd for $C_{18}H_{40}Br_2P_4Pd_2 \cdot 0.2C_7H_8$: C, 30.20; H, 5.44. Found: C, 30.63; H, 4.63.

($Me_3P$)$_2$BrPd($C_6H_4$-1,4)PdI($PMe_3$)$_2$ (**15**): Crystal yield: 0.57 g (71.5%). $^1$H NMR (400 MHz, $CDCl_3$, ppm): $\delta$ 6.89(s, 4H, Pd$C_6H_4$Pd), 1.27(s, 36H, $CH_3$P). $^{31}$P{$^1$H} NMR (162 MHz, $CDCl_3$, ppm): $\delta$ −21.4, −19.7. Anal. Calcd for $C_{18}H_{40}BrIP_4Pd_2$: C, 27.02; H, 5.04. Found: C, 27.18; H, 4.93.

### 2.5. *Synthesis of 13–15 using 1, 7, or 3 as the starting material*

The solution of $Pd(PMe_3)_4$, prepared *in situ* by same procedure above, was transferred to a solution of **1**, **7**, or **3** (1 mM) in toluene (35 mL). The resulting solution was heated to 60 or 120 °C for 24 h. The solvent was removed and the white precipitate was washed with $Et_2O$ (3 × 10 mL) and dried under vacuum. The crude product was recrystallized from $CH_2Cl_2$/$Et_2O$ to afford colorless crystals.

### 2.6. *Synthesis of 16*

Similar procedure to the preparation of **1–4** was used with 4,4′-dibromobiphenyl at 85 or 120 °C.

$[C_6H_4(C_6H_4Br\text{-}4)\text{-}4]PdBr(PPh_3)_2$ (**16**): Crystal yield: 0.79 g (83.7%). $^1H$ NMR (400 MHz, $CDCl_3$, ppm): $\delta$ 7.57–7.54(m, 12H, $PC_6H_5$), 7.42(d, 2H, $BrC_6H_4$, $J = 8.0$ Hz), 7.35–7.23(m, 18H, $PC_6H_5$), 7.09(d, 2H, $BrC_6H_4$, $J = 8.2$ Hz), 6.66(d, 2H, $PdC_6H_4$, $J = 8.2$ Hz), 6.39(d, 2H, $PdC_6H_4$, $J = 8.0$ Hz). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, ppm): $\delta$ 23.1. Anal. Calcd for $C_{48}H_{38}Br_2P_2Pd$: C, 61.14; H, 4.06. Found: C, 61.09; H, 3.91.

### 2.7. *Synthesis of 17 and 18*

Solution of $Pd(PCy_3)_4$, prepared *in situ* by same procedure above, was transferred to a solution of 4,4′-dibromobiphenyl (0.312 g, 1 mM) in toluene (35 mL). The resulting solution was heated to 85 or 120 °C for 24 h. The solvent was removed and the white precipitate was washed with $Et_2O$ (3 × 10 mL) and dried under vacuum. The crude product was recrystallized from $CH_2Cl_2/Et_2O$ to afford light yellow or colorless crystals.

$[C_6H_4(C_6H_4Br\text{-}4)\text{-}4]PdBr(PCy_3)_2$ (**17**): Crystal yield: 0.81 g (81.4%). $^1H$ NMR (400 MHz, $CDCl_3$, ppm): $\delta$ 7.52(d, 2H, $J = 7.8$ Hz), 7.46(d, 2H, $J = 8.0$ Hz), 7.39(d, 2H, $J = 8.2$ Hz), 7.13(d, 2H, $J = 8.0$ Hz), 2.09–1.03(m, 66H, $C_6H_{11}P$). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, ppm): $\delta$ 19.3. Anal. Calcd for $C_{48}H_{74}Br_2P_2Pd{\cdot}C_7H_8$: C, 61.66; H, 7.71. found: C, 62.90; H, 8.39.

$(Cy_3P)_2BrPd(C_6H_4C_6H_4\text{-}4,4')PdBr(PCy_3)_2$ (**18**): Crystal yield: 1.55 g (93.3%). $^1H$ NMR (400 MHz, $CDCl_3$, ppm): $\delta$ 7.38(d, 4H, $J = 8.0$ Hz), 7.13(d, 4H, $J = 7.8$ Hz), 2.10–1.04(m, 132H, $C_6H_{11}P$). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, ppm): $\delta$ 19.3. Anal. Calcd for $C_{84}H_{140}Br_2P_4Pd_2{\cdot}2.5CHCl_3$: C, 53.42; H, 7.38. Found: C, 52.90; H, 7.31.

### 2.8. *Synthesis of 19*

Solution of $Pd(PMe_3)_4$ ($PdCl_2$, 1.5 mM; $P(CH_3)_3$, 7.5 mM), prepared *in situ* by procedure above, was transferred to a solution of **16** (1 mM) in toluene (35 mL). The resulting solution was heated to 120 °C for 24 h, the solvent removed, the white precipitate washed with $Et_2O$ (3 × 10 mL) and dried under vacuum. The crude product was recrystallized from $CH_2Cl_2/Et_2O$ to afford colorless crystals.

$(Me_3P)_2BrPd(C_6H_4C_6H_4\text{-}4,4')PdBr(PMe_3)_2$ (**19**): Crystal yield: 0.554 g (66.8%). $^1H$ NMR (400 MHz, $CDCl_3$, ppm): $\delta$ 7.28(d, 4H, $C_6H_4$, $J = 8.0$ Hz), 7.25(d, 4H, $C_6H_4$, J = 8.2 Hz),1.22(t, 36H, $CH_3P$, $J = 3.6$ Hz). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, ppm): $\delta$ −19.0. Anal. Calcd for $C_{24}H_{44}Br_2P_4Pd_2{\cdot}0.5CH_2Cl_2$: C, 33.76; H, 5.20. Found: C, 34.59; H, 5.43.

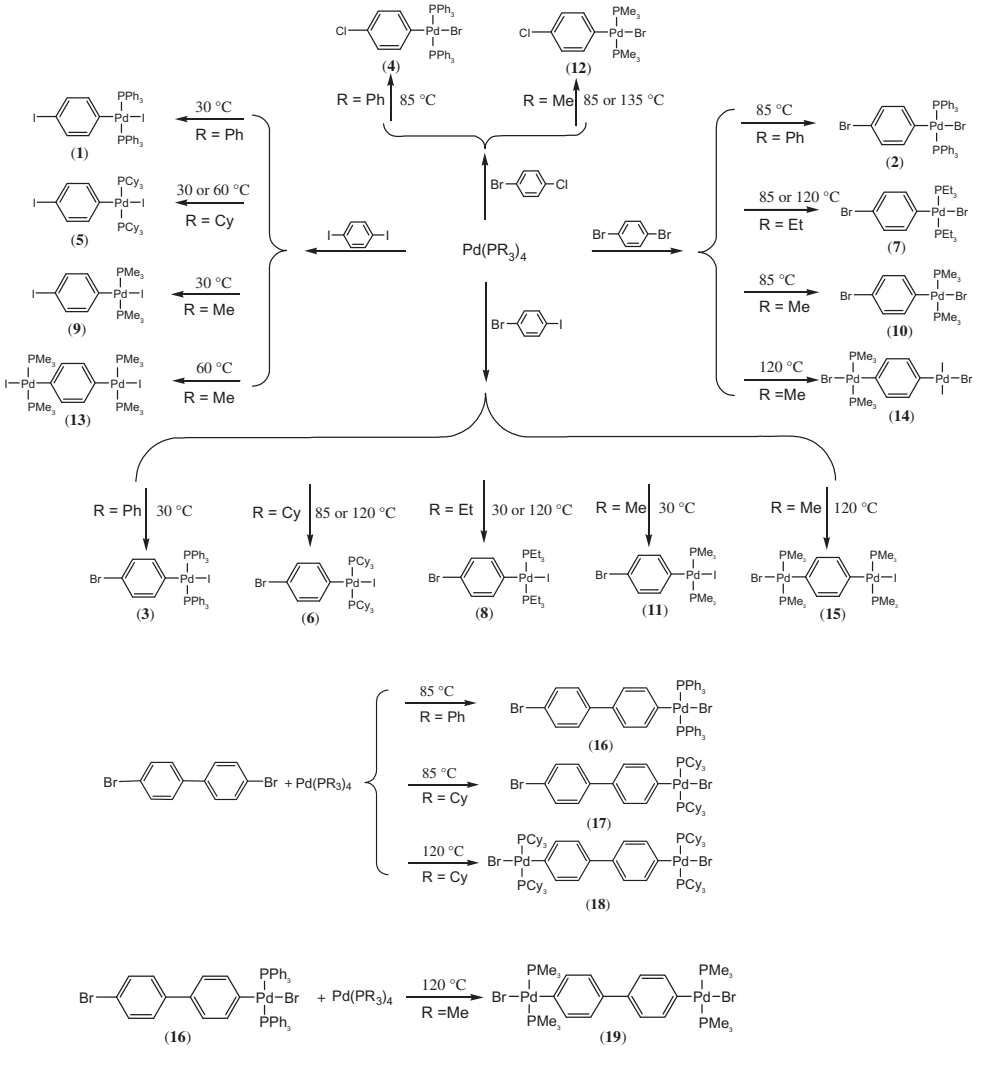
### 2.9. *X-ray crystallographic studies*

Single crystal X-ray measurements were carried out on a Bruker SMART APEX CCD diffractometer equipped with a graphite monochromator using Mo Kα radiation ($\lambda = 0.71073$ Å). Absorption corrections were applied using SADABS [32]. The structures were solved by Patterson or direct methods and refined on $F^2$ using full matrix least-squares (SHELXS97 and SHELXL97 programs) [33]. The non-hydrogen atoms were refined anistropically. Hydrogens attached to carbons were fixed at their ideal positions or found and refined using difference Fourier syntheses.

## 3. Results and discussion

### 3.1. *Synthesis of complexes*

As shown in scheme 1, the mononuclear aryl palladium(II) complexes **1**–**4** were easily synthesized by oxidative addition of excess 1,4-dihalogenated benzene to $Pd(PPh_3)_4$ in the presence of additional $PPh_3$. The oxidative addition reaction starting from aryl iodide is carried out smoothly at lower temperature (30 °C), while higher reaction temperature is required for aryl bromide, similar to previous observations [18, 24, 26]. The excess 1,4-dihalogenated benzene and additional $PPh_3$ inhibit the occurrence of the aryl–aryl exchange side reaction [10, 11]. Only the byproducts, phosphonium salts were isolated, rather than




Scheme 1. Synthesis of the mononuclear aryl palladium(II) complexes.

the expected dinuclear palladium(II) complexes with $Pd(PPh_3)_4$ and 1,4-dihalogenated benzene in a 2.5 : 1 M ratio.

In order to exclude aryl–aryl exchange, tricyclohexylphosphine was used as auxiliary ligand to synthesize the corresponding aryl palladium(II) complexes. Oxidative addition reactions of $Pd(PCy_3)_4$ with 1,4-diiodobenzene or 4-bromo-iodobenzene in 2.5 : 1 M ratio in toluene at 30 or 60 °C, or 85 or 120 °C only gave mono-oxidative addition products **5** and **6** as before. Similarly, only the mononuclear **7** and **8** were isolated even though the smaller phosphine $PEt_3$ was employed as auxiliary ligand and the oxidative additions were carried out at 120 °C.

Using $PMe_3$ as auxiliary ligand, mononuclear complexes **9–12** were obtained by oxidative addition of 1,4-dihalogenated benzene and $Pd(PMe_3)_4$ in 1 : 2.5 M ratio at the proper temperature (30 °C for iodide, 85 °C for bromide). With elevation of the reaction temperature, dinuclear palladium(II) complexes could be synthesized. Complex **13** was isolated in good yield by the bis-oxidative addition reaction of 1,4-diiodobenzene with $Pd(PMe_3)_4$ in mole ratio 1 : 2.5 at 60 °C, while **14** and **15** were obtained from 1,4-dibromobenzene or 4-bromo-iodobenzene and $Pd(PMe_3)_4$ at 120 °C. The yield of **13** was improved employing the synthetic route comparable with the previous method [18], in which $PdEt_2(PMe_3)_2$ was used as the starting material. However, an attempted oxidative addition of 4-bromo-chlorobenzene to prepare the dinuclear palladium(II) complex containing chlorine failed even at 135 °C. Complexes **14** and **15** were also prepared *in situ* by two-step oxidative addition, first at 60 °C then 120 °C, indicating that the bis-oxidative addition is a stepwise procedure [18].

Complexes **13**, **14**, and **15** can also be synthesized by oxidative addition of **1**, **7**, or **3** and $Pd(PMe_3)_4$. Likewise, iodine-substituted aryl palladium(II) complex can react with $Pd(PMe_3)_4$ at lower temperature (60 °C), while bromine-substituted ones require higher temperature (120 °C). In the process of the reactions, ligand exchange occurs due to steric hindrance from the larger $PPh_3$ and $PEt_3$.

Oxidative addition of 4,4′-dibromobiphenyl and $Pd(PPh_3)_4$ at 85 or 120 °C only gave the mononuclear palladium(II) complex **16** in the presence of additional $PPh_3$ due to steric hindrance from rigid phenyl rings of $PPh_3$ (see structural analysis). In contrast, the dinuclear **18** containing flexible phosphine $PCy_3$ could be prepared using 4,4′-dibromobiphenyl as the starting material in excellent yield at 120 °C, while mono-oxidative addition was carried out at 85 °C to afford mononuclear **17**. Based on the difference of ligand effect [34], an attempt to synthesize the dinuclear palladium(II) complex containing different phosphines also failed. Instead, the re-oxidative addition of **16** and $Pd(PMe_3)_4$ yielded the dinuclear **19** coordinated only by $PMe_3$.

### 3.2. *Crystal structural description*

X-ray diffraction studies of all palladium complexes, except for **6**, were carried out to further confirm their structures and obtain the structural parameters; the crystal structure of **1** was determined previously [23, 24]. Several structures of **15–19** are shown in figures 1–5 and selected bond distances and angles are given and compared in table 1. Other molecular structures and data are presented in Supplementary material.

All complexes exhibit the expected *trans* configuration, which is consistent with only one $^{31}P$ NMR signal found in solution NMR studies. Palladium is in a nearly square-planar

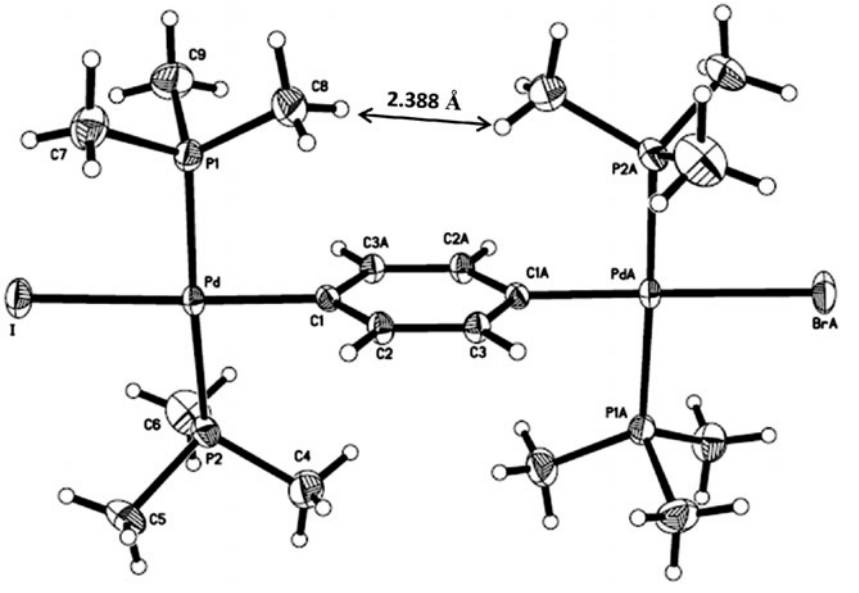



Figure 1. Crystal structure of **15** with thermal ellipoids at 30% probability.

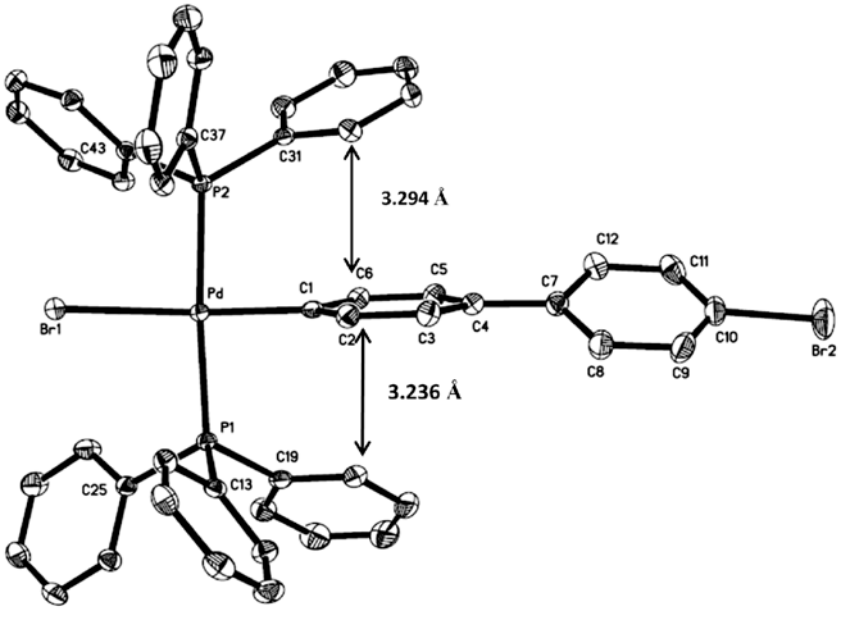



Figure 2. Crystal structure of **16** with thermal ellipsoids at 30% probability. Hydrogens are omitted for clarity.

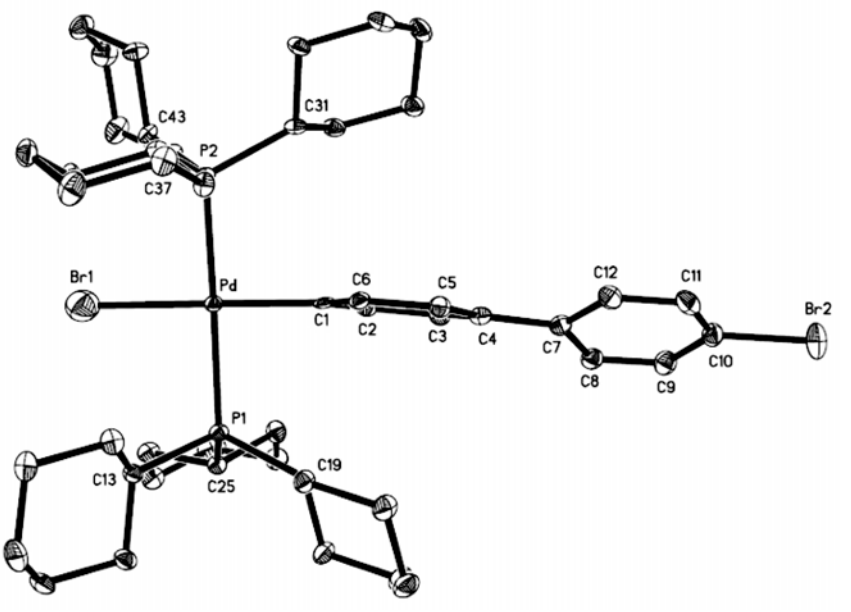



Figure 3. Crystal structure of **17** with thermal ellipsoids at 30% probability. Hydrogens and solvent are omitted for clarity.

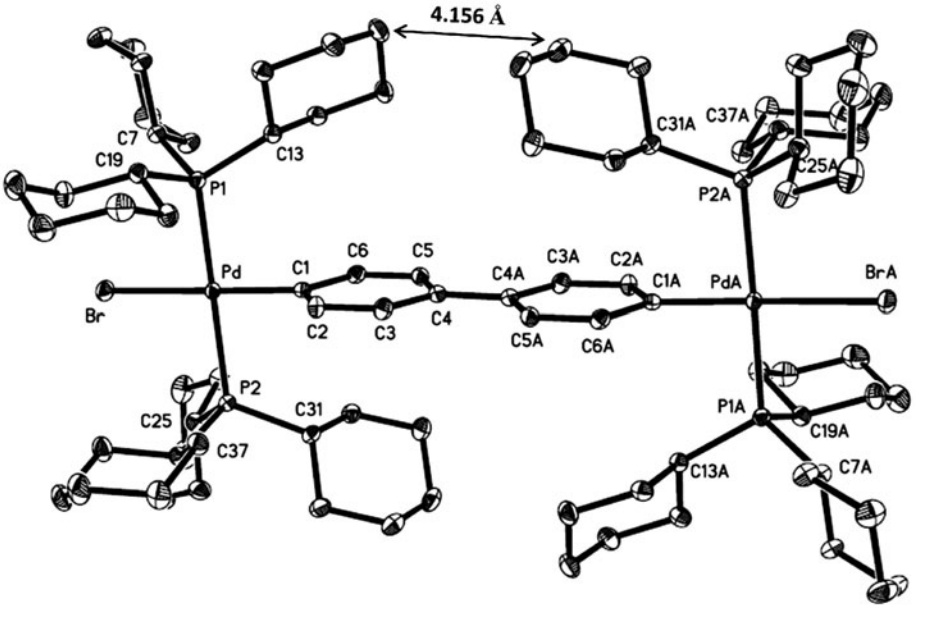



Figure 4. Crystal structure of **18** with thermal ellipsoids at 30% probability. Hydrogens and solvent are omitted for clarity.

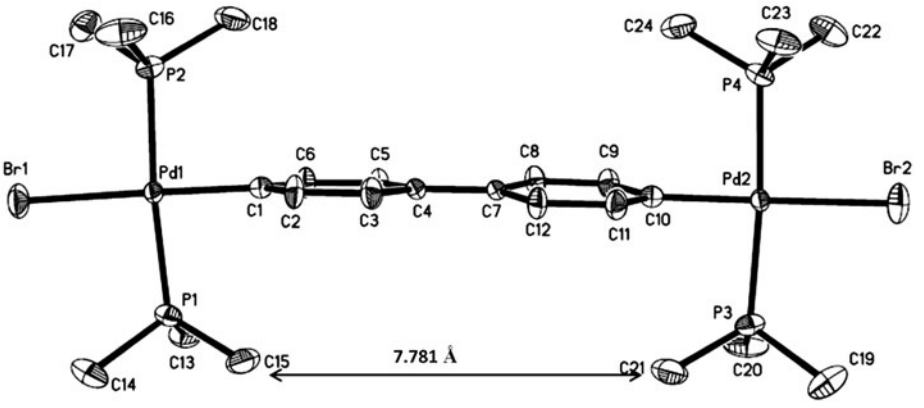



Figure 5. Crystal structure of **19** with thermal ellipsoids at 30% probability. Hydrogens and solvent are omitted for clarity.

coordination environment consisting of the central Pd, two phosphine ligands, and aryl. The aryl is always oriented orthogonal to the plane of PdP1P2X (X = Br, I). The bond lengths and angles around palladium are comparable to those in analogous complexes [18, 19, 21, 35–37].

As shown in figure 1, the phenylene plane is almost perpendicular to the plane consisting of Br, I, two Pd, and four P with the dihedral angles of 93.5° in the centrosymmetric binuclear **15**. The shortest H–H distance between two $PMe_3$ from one side of the phenylene plane is 2.388 Å, which means that the phenylene only has adequate space to arrange two $PMe_3$ ligands for coordination, consistent with these attempts to prepare other dinuclear complexes using $PPh_3$, $PCy_3$, and $PEt_3$ as auxiliary ligands.

The similar structural features containing two perpendicular planes are also observed in molecular structures of **18** and **19**. With increasing space of 4,4′-biphenylene bridging group, the shortest C–C distances are 4.156 and 7.781 Å, while the corresponding H–H distances are 2.691 and 6.740 Å between phosphine ligands (figures 4 and 5). Apparently, there is abundant space allowing coordination of $PCy_3$ with Pd in **18**. Two phenyl rings of 4,4′-biphenylene are in one plane or nearly coplanar with dihedral angles of 0.0° and 5.3° in the dinuclear **18** and **19**, while the relevant angles in mononuclear **16** and **17** are 28.8° and 25.4°, respectively. The difference is attributed to the steric congestion of phosphine around Pd. The same structural feature has also been observed in a similar Pd complex [18], but is glaringly different from the similar Pt complex with dihedral angle of 18.9° [21].

Another structural feature is existence of $\pi$–$\pi$ interactions in palladium(II) complexes with aryl phosphine auxiliary ligands. Intramolecular $\pi$–$\pi$ interactions are observed in the complexes reported here. For example, in **16,** the C6–C20 and C6–C36 distances are 3.294 and 3.236 Å, respectively. The strong $\pi$–$\pi$ interactions and rigidity from phenyl rings of $PPh_3$ gives more crowded coordination, resulting in the formation of **19** rather than the expected $(Ph_3P)_2BrPd(C_6H_4C_6H_4\text{-}4,4')PdBr(PMe_3)_2$.

Table 1. Selected bond lengths [Å] and angles [°] for **15–19**.

| Complex | **15** | | **16** | **17** | **18** | | **19** | | |
|---|---|---|---|---|---|---|---|---|---|
| Pd–C1 | 2.020(4) | Pd–C1 | 2.005(2) | 2.033(7) | 2.005(5) | Pd1–C1 | 1.994(6) | Pd2–C10 | 1.993(6) |
| Pd–P1 | 2.3005(13) | Pd–P1 | 2.3382(6) | 2.3679(18) | 2.3575(12) | Pd1–P1 | 2.3098(14) | Pd2–P3 | 2.3192(14) |
| Pd–P2 | 2.3006(13) | Pd–P2 | 2.3157(6) | 2.3510(17) | 2.3650(12) | Pd1–P2 | 2.3110(14) | Pd2–P4 | 2.3052(15) |
| Pd–Br | 2.608(10) | Pd–Br1 | 2.5276(3) | 2.4930(13) | 2.5618(6) | Pd1–Br1 | 2.5233(7) | Pd2–Br2 | 2.5198(7) |
| Pd–I | 2.651(7) | Pd–Br2 | | | 2.5618(6) | | | | |
| C1–Pd–P1 | 89.24(11) | C1–Pd–P1 | 88.69(7) | 88.60(18) | 89.15(13) | C1–Pd1–P1 | 86.42(14) | C10–Pd2–P3 | 87.84(15) |
| C1–Pd–P2 | 88.19(12) | C1–Pd–P2 | 87.41(7) | 91.22(18) | 88.09(13) | C1–Pd1–P2 | 88.42(15) | C10–Pd2–P4 | 87.29(15) |
| P1–Pd–P2 | 174.63(5) | P1–Pd–P2 | 175.74(2) | 173.29(6) | 173.30(4) | P1–Pd1–P2 | 174.84(6) | P3–Pd2–P4 | 175.10(6) |
| C1–Pd–Br | 172.6(3) | C1–Pd–Br1 | 168.68(7) | 175.1(2) | 176.65(13) | C1–Pd1–Br1 | 178.69(15) | C10–Pd2–Br2 | 178.90(15) |
| C1–Pd–I | 174.9(2) | P1–Pd–Br1 | 94.781(17) | 90.62(5) | 91.30(3) | P1–Pd1–Br1 | 92.36(4) | P3–Pd2–Br2 | 92.77(5) |
| P1–Pd–Br | 93.1(3) | P2–Pd–Br1 | 89.371(17) | 90.12(5) | 91.81(3) | P2–Pd1–Br1 | 92.79(4) | P4–Pd2–Br2 | 92.10(5) |
| P2–Pd–I | 91.1(2) | | | | | | | | |

## 4. Conclusion

By changing the reaction conditions including temperature and auxiliary phosphine, mono- or dinuclear palladium complexes have been synthesized by oxidative addition of 1,4-dihalogenated benzene or 4,4′-dibromobiphenyl with $Pd(PR_3)_4$ (R = Ph, Cy, Et, Me). Formation of the expected complexes depends on the reactivity for oxidative addition of aryl halide to $Pd(PR_3)$, the steric factor of phosphine and the reaction temperature. Mononuclear palladium complexes can be obtained at relative low reaction temperature and with various phosphines including $PPh_3$ and $PCy_3$, while the dinuclear palladium complexes are prepared at higher temperature and using the smaller ($PMe_3$ and $PEt_3$) or flexible ($PCy_3$) phosphines as auxiliary ligands. These results demonstrate that bis-oxidative addition of 1,4-dihalogenated benzene or 4,4′-dibromobiphenyl and $Pd(PR_3)_4$ is a stepwise procedure, in which the second step requires higher reaction temperature. The results are also consistent with previous report using different palladium(0) precursor [17]. Further research using these palladium complexes in the Suzuki polymerization is in progress.

## Supplementary material

Supplementary data contain figures S1–S13 (see online supplemental material at http://dx.doi.org/10.1080/00958972.2014.894993) about crystal structures of **1–5** and **7–14**, tables S1–S3 about crystallographic data for **1–5** and **7–19**, and tables S4 and S5 about selected bond lengths [Å] and angles [°] for **1–5** and **7–14**. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif with CCDC 932941–932958 for **1–5** and **7–19**.

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