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Note

Synthesis and characterization of new (pyrazolyl)aryl phosphinite PCN pincer palladium(II) complexes

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ABSTRACT

Two unsymmetrical PCN pincer Pd(II) complexes **3a**–**3b** which are based on (pyrazolyl)aryl phosphinite ligands and contain two fused six-membered palladacycles have been synthesized from 3-(3,5-dimethylpyrazol-1-ylmethyl)benzyl alcohol (**2**) by one-pot phosphorylation/palladation reaction via C–H bond activation of the related ligands. The pyrazole-coordinated phosphine-free Pd(II) complex (**4**) was also isolated in the preparation of pincer complex **3a**. The new complexes were characterized by elemental analysis, ^{1}H NMR, ^{13}C NMR, $^{31}P\{^{1}H\}$ NMR (for pincer complexes) and IR spectra. And the molecular structures of **3b** and **4** have been further determined by X-ray single-crystal diffraction. The pincer Pd complexes **3a** and **3b** exhibited rather low activity in the allylation of benzaldehyde.

1. Introduction

Pincer palladium complexes with monoanionic terdentate ligands have found wide applications in organometallic homogeneous catalysis [1]. For example, they have been used as efficient catalysts for a variety of C–C bond forming reactions including allylation of aldehydes and imines with allylic stannanes [2–8], palladium-catalyzed cross-coupling reactions such as the Heck reaction [9–12], Suzuki–Miyaura [13–18] and Sonogashira couplings [14,19] as well as α–arylation of ketones [20]. Palladium pincers have also been successfully applied to the synthesis of organometallic reagents such as allyl [2] or allenyl [21] stannanes, where in most cases they cannot be replaced with simple Pd sources like $Pd(OAc)_2$, $Pd(PPh_3)_4$ and $Pd_2(dba)_3$. Among the pincer Pd catalysts, the most common ones are symmetrical ECE type with two identical donor groups (E = PR_2, OPR_2, NR_2, pyridine, N-containing heterocycles, SR, etc.) in the side arms of the central aryl ring and two equivalent five-membered palladacycles, particularly those of PCP and NCN Pd pincers. The reactivities of the Pd center in these symmetrical complexes can be easily tuned by appropriate choice of substituents on the heteroatom donors or/and heteroatom donors. Nonetheless, introduction of two different donors in the pincer ligand, which gives unsymmetrical pincer Pd complexes, also seems to be an appealing strategy to improve the properties of the ensuing complexes [22–25]. In fact, it has been found that some unsymmetrical pincer Pd complexes do outperform the related symmetrical ones on catalytic activity under certain circumstances. For example, Klein Gebbink and Szabó et al. have demonstrated that the unsymmetrical PCS palladium pincer is the fastest catalyst in aldol condensation reaction between benzaldehyde and methyl isocyanoacetate among the three pincer complexes including symmetrical SCS and PCP complexes [26]. We have also found that in the Suzuki couplings conducted at 40–50 °C, the unsymmetrical (pyrazolyl)aryl phosphinite or (imino)aryl phosphinite PCN Pd complexes exhibit much higher activity than the related symmetrical bis(phosphinite) PCP complexes [27,28]. Despite the facts, reports on the unsymmetrical Pd complexes are relatively few compared to the symmetrical ones and one obvious reason for this is their relatively complicated synthesis. Recently, we have developed a facile, direct method based on one-pot phosphorylation/palladation reaction for the preparation of unsymmetrical PCN pincer palladium complexes containing a phosphinito group (Scheme 1) [27–30]. By using this method, a variety of achiral and chiral Pd pincers which comprise pyrazolyl-, amino-, imino- or chiral imidazolinyl as a N-donor and phosphinito as a P-donor have been conveniently synthesized in good yields (42–72%). Among them, the (pyrazolyl)aryl phosphinite PCN compound **1** (Scheme 2) containing fused five- and six-membered metallacycles was obtained by the reaction of pyrazolyl-containing *m*-phenol derivative, which was derived from *m*-hydroxybenzaldehyde, with diphenylchlorophosphine in the presence of Et_3N, followed by the addition of $PdCl_2$ [27]. In continuation of this investigation, herein we would like to report the synthesis of new (pyrazolyl)aryl phosphinite PCN

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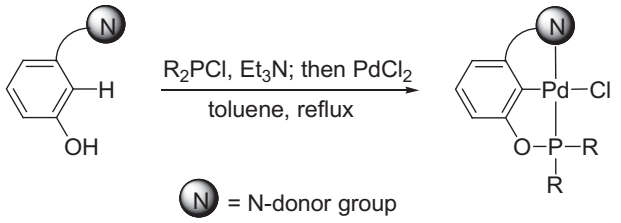
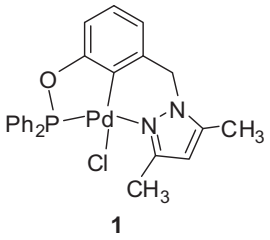


Scheme 1. One-pot phosphorylation/palladation reaction for the synthesis of the unsymmetrical PCN pincer palladium(II) complexes.



Scheme 2. Structure of the (pyrazolyl)aryl phosphinite PCN pincer Pd(II) complex **1** containing fused five- and six-membered palladacycles.

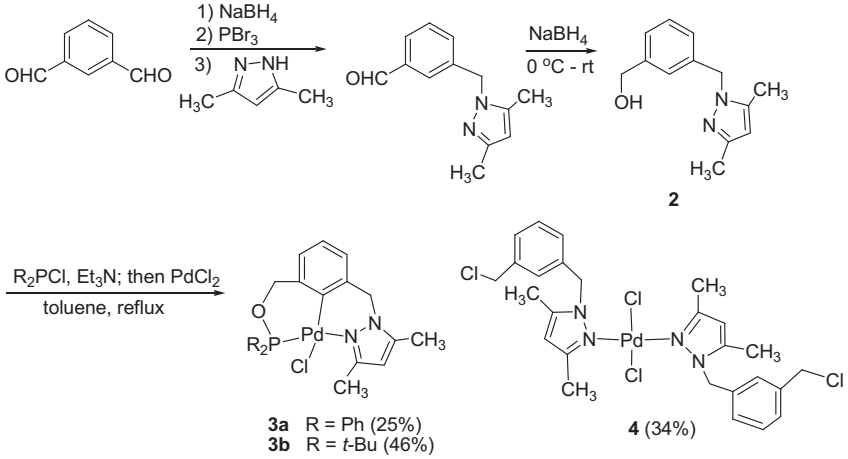
Pd(II) complexes **3a**–**3b** containing two six-membered metallacycles by one-pot phosphorylation/palladation reaction of pyrazolyl-containing *m*-benzyl alcohol derivative **2** (Scheme 3). The pincer Pd complexes were applied to the allylation of aldehydes. The results are shown as below.

2. Results and discussion

2.1. Synthesis and characterization

Starting from inexpensive, commercially available isophthalaldehyde, the 3-(3,5-dimethylpyrazol-1-ylmethyl)benzaldehyde could be prepared after selective reduction of one aldehyde to hydroxymethyl, bromination and nucleophilic substitution with 3,5-dimethylpyrazole according to the published procedure [31] (Scheme 3). Then reduction of the remaining aldehyde group by $NaBH_4$ easily gave the required 3-(3,5-dimethylpyrazol-1-ylmethyl)benzyl alcohol **2**. The following "one-pot phosphorylation/palladation reaction" was carried out in a way similar to that of 3-(3,5-dimethylpyrazol-1-ylmethyl)phenol. Thus, **2** reacted with diphenylchlorophosphine or di-tertbutylchlorophosphine in the presence of triethylamine in toluene at reflux for 8 h, followed by the addition of palladium chloride and reflux for another 18 h. The expected new PCN pincer palladium complexes **3a** and **3b** with two six-membered palladacycles were successfully obtained as white solids after chromatography on silica gel in 25% and 46% yields, respectively. Interestingly, the hydroxymethyl-chlorinated and pyrazole-coordinated phosphine-free Pd(II) complex **4** was also isolated in the preparation of pincer complex **3a**, which led to the lower yield of **3a**. Prolonging the reaction time of **2** with Ph_2PCl for phosphorylation could not inhibit effectively the formation of compound **4**, although it was not observed in the synthesis of complex **3b**. The results indicated that phosphorylation of hydroxymethyl with dialkylchlorophosphine was relatively difficult compared to that of phenolic-hydroxy group under similar conditions.

All of the new Pd complexes are air- and moisture- stable both in the solid state and in solution. They were well characterized by elemental analysis, ^1H NMR, ^{13}C NMR, $^{31}P\{^1H\}$ NMR (for pincer complexes) and IR spectra. The formation of the pincer complexes was confirmed by the single resonance at δ about 117 ppm (for Ph_2PO) or 160 ppm (for *t*-Bu_2PO) in the $^{31}P\{^1H\}$ NMR spectra and the absence of the singlet corresponding to the central aryl proton located ortho to both $-CH_2OR$ and $-CH_2Pz$ in the ^1H NMR spectra. In addition, the $-CH_2Pz$ protons appeared as a singlet at δ 5.13 ppm and the $-CH_2OH$ protons appeared as a doublet at 4.60 ppm in the PCN ligand precursor **2**. While in the Pd complexes **3a** and **3b**, the two protons of $-CH_2Pz$ appeared in two different positions including the doublet at δ 5.49 and the multiplet at δ 4.96–4.85 ppm (5.59 and 4.95–4.83 ppm, respectively for **3b**), and the $-CH_2OPR_2$ protons were observed as one doublet of doublets at δ 5.10 ppm and one multiplet at δ 4.96–4.85 ppm (only one multiplet at δ 4.95–4.83 ppm for **3b**). The ^{13}C NMR spectra of the pincer complexes exhibited intensive ^{31}P-^{13}C couplings. On the other hand, although X-ray analysis clearly indicates that the non-cyclometallated compound **4** adopts a *trans*-geometry in the solid state with the two chloride ligands being in a *trans*-position (vide infra), its ^1H NMR and ^{13}C NMR spectra demonstrated more signals than expected, suggesting the presence of isomers in solution. For example, the ^1H NMR spectrum of **4** showed two singlets at δ 6.16 and 5.74 ppm, respectively for $-CH_2Pz$ protons as well as two singlets at δ 4.59 and 4.46 ppm, respectively for $-CH_2Cl$ protons. The signals for the pyrazole proton were observed at δ 5.90 and 5.94 ppm, respectively as two singlets and the four singlets at δ 2.51,



Scheme 3. Synthesis of the new (pyrazolyl)aryl phosphinite PCN pincer Pd(II) complexes **3a-b** with two fused six-membered palladacycles.

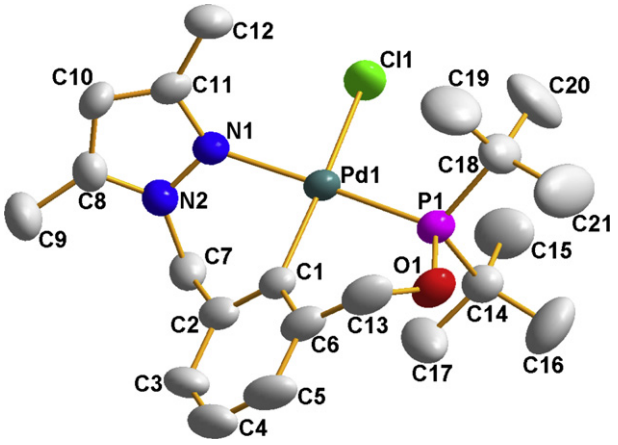


Fig. 1. Molecular structure of pincer Pd complex **3b**. Hydrogen atoms are omitted for clarity.

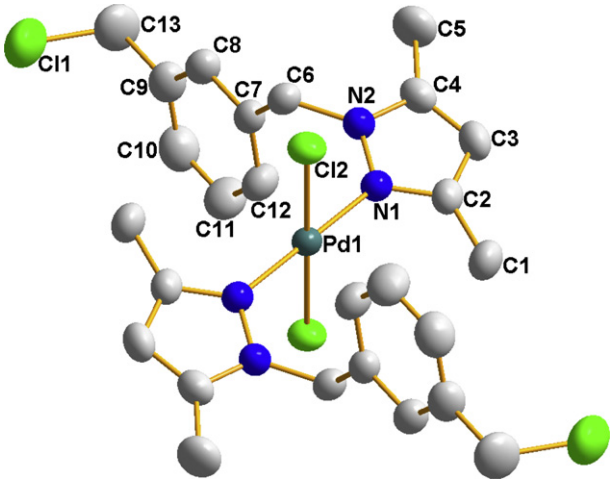


Fig. 3. Molecular structure of non-cyclometallated complex **4**. Hydrogen atoms are omitted for clarity.

2.11, 2.90 and 2.04 ppm, respectively were assigned to the two CH_3-groups in the pyrazole ring. A ratio of about 1.6:1 for the two isomers could be calculated from the above corresponding signals. The complicated NMR spectra of **4** are most likely due to the existence of both *trans*- and *cis*- structures in solution. Another possibility is that all species are *trans*- concerning the two chloride ligands, whereas the two *N*-benzyl groups may be in a *syn*- and *anti*-configuration.

2.2. Crystal structure

The molecular structures of Pd complexes **3b** and **4** were confirmed by X-ray single-crystal analysis. The molecules are illustrated in Figs. 1 and 3, respectively. Selected bond lengths (Å) and angles (°) are given in Table 1.

As shown in Fig. 1, in the pincer Pd complex **3b** the ligand coordinates to the Pd(II) center via the phosphinito-P atom, the carbon atom of central aryl ring and the pyrazolyl-N atom in a tridentate manner and the metal atom adopts a slightly distorted square-planar geometry with chloride occupying the fourth coordination site. The formed two palladacycles are both six-membered rings. In comparison with the related (pyrazolyl)aryl phosphinite PCN pincer Pd complexes such as **1**, which has a five-membered P-containing palladacycle, the Pd complex **3b** shows slightly longer Pd–C (2.034 vs 2.005–2.012 Å) and Pd–P bond lengths (2.2416 vs 2.1823–2.1966 Å) [27]. The bond angles around Pd(II) center in **3b** are quite different from those found in complex **1**. For example, the C–Pd–P (89.05°) and N–Pd–P (173.42°) angles in **3b** are significantly bigger than those in complex **1** (79.59 and 166.62°, respectively). The values are also markedly bigger than those in the PCN Pd pincers containing two five-membered-ring metallacycles (around 80 and 160°, respectively) [28,29,32]. The biggest N–Pd–P angle in complex **3b** with two six-membered palladacycles among the three types of PCN Pd pincers suggests that introduction of larger metallacycles can effectively decrease the steric strain of the resultant complexes. In the crystal of complex **3b**, chlorine atom forms hydrogen bond with the adjacent CH_3 group of pyrazole (Cl(1)···H(9A) 2.927 Å, Cl(1)···C(9) 3.765 Å, C(9)–H(9A)···Cl(1) 146°), which constructs the one-dimensional chain structure of **3b** (Fig. 2).

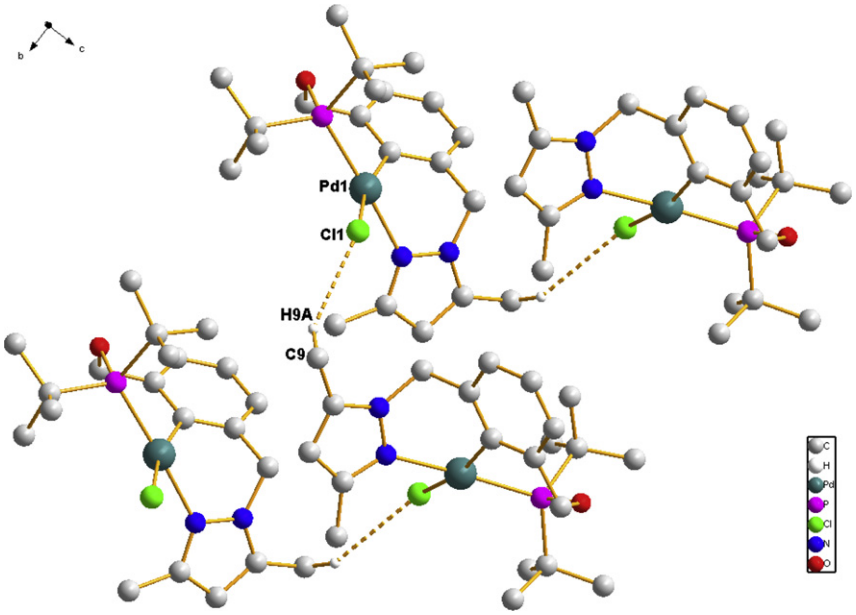


Fig. 2. 1-D chain structure of complex **3b**. Non-hydrogen bonding H atoms are omitted for clarity.

Table 1
Selected bond lengths (Å) and angles (°) for Pd complexes **3b** and **4**

	3b		**4**
Pd(1)–C(1)	2.034(5)	Pd(1)–N(1)	2.012(2)
Pd(1)–N(1)	2.114(4)	Pd(1)–N(1A)	2.012(2)
Pd(1)–P(1)	2.2416(15)	Pd(1)-Cl(2)	2.3012(7)
Pd(1)–Cl(1)	2.4035(14)	Pd(1)-Cl(2A)	2.3012(7)
C(1)-Pd(1)–N(1)	87.17(18)	N(1A)-Pd(1)–N(1)	180.0
C(1)-Pd(1)-P(1)	89.05(15)	N(1A)-Pd(1)-Cl(2A)	89.84(6)
N(1)-Pd(1)-P(1)	173.42(10)	N(1)-Pd(1)-Cl(2A)	90.16(6)
C(1)-Pd(1)-Cl(1)	166.71(14)	N(1A)-Pd(1)-Cl(2)	90.16(6)
N(1)-Pd(1)-Cl(1)	88.49(11)	N(1)-Pd(1)-Cl(2)	89.84(6)
P(1)-Pd(1)-Cl(1)	96.36(6)	Cl(2A)-Pd(1)-Cl(2)	180.0

The Pd atom in the complex **4** has a square-planar coordination geometry, which is bonded to two chloride ligands and two pyrazole ligands (Fig. 3). Both the two chlorides and two pyrazole ligands are *trans*- to each other, with bond angles of N(1A)-Pd(1)–N(1) and Cl(2A)-Pd(1)-Cl(2) being 180.0°. The two *N*-benzyl groups are on the either side of the Pd coordination plane showing an *anti*-configuration. All of the bond distances and angles around Pd(II) centre are very close to those observed in the related pyrazole-coordinated bis[3-(3,5-dimethylpyrazol-1-ylmethyl)phenol]palladium (II) dichloride [33] and also compare well to those of monodentate N-coordinated palladium-benzimidazole [34,35] or pyrazole complexes [36]. Similar to the pincer complex **3b**, the complex **4** also has a one-dimensional chain structure in the crystal formed by intermolecular hydrogen bonds between chlorine atom and the adjacent CH_2 group of *N*-benzyl (Cl(2)···H(6A) 2.740 Å, Cl(2)···C(6) 3.701 Å, C(6)–H(6A)···Cl(2) 171°) (Fig. 4).

2.3. Catalytic studies

Szabó and co-workers first reported that the symmetrical bis(phosphine) and particularly, the bis(phosphinite) PCP pincer Pd(II) complexes were efficient catalysts for allylation of aldehydes and sulfonimines with allylic stannanes. And it was demonstrated that the NCN Pd pincers with bis(amine) or bis(oxazoline) ligands exhibited low catalytic activity in these transformations [2–5]. Subsequent to their findings, the SeCSe [6] and SCS [7] pincer Pd complexes have also been successfully applied to the allylation of aldehydes, which can proceed smoothly at room temperature to 60 °C in the presence of only 0.005–1 mol% of the SeCSe catalyst. Recently, Klein Gebbink and van Koten [32] have investigated the catalytic activity of the unsymmetrical (amino)phosphinite and (imino)phosphinite PCN as well as the (phenylthio)phosphinite PCS complexes in the allylation. With a catalyst loading of 5 mol%, the allylation of benzaldehyde with allyltributyltin was carried out in DMF at 60 °C for 16 h to produce the desired homoallylic alcohol in 68, 21 and 84% yields, respectively. In the case of the activated 4-nitrobenzaldehyde, better product yields (90, 85 and 93% yields, respectively) were obtained. However, for the slightly less electrophilic 4-methylbenzaldehyde the yield dramatically decreased to 33% using the relatively more active PCS pincer as the catalyst. Based on the literature results, the activity of the new obtained PCN pincer Pd complexes **3a** and **3b** in the allylation of benzaldehyde, which is a non-activated aldehyde, was evaluated (Scheme 4). The reaction was performed in DMF at 50 °C for 24 h. It was disappointing to find that the new pincers **3a** and **3b** gave the expected alcohol product in rather low yields with a catalyst loading of 5 mol % (29 and 24%, respectively). In contrast, the related PCN Pd complex **1**, which has been found to be effective catalyst for Suzuki couplings [27], could afford a 67% yield (75% at 60 °C) with a catalyst loading of 2.5 mol%. It was reported in the literatures that the allylation involved the transmetalation of allylstannane with pincer Pd complex to generate an η^1-allyl Pd intermediate, which further underwent an electrophilic attack from the aldehyde [2–5]. The lower activity of the complexes **3a** and **3b** compared to complex **1** may be caused by both steric and electronic effects. On the one hand, the larger metallacycles in the complexes **3** (6,6-membered vs 5,6-membered in **1**) give rise to a steric effect, which may hinder the approach of the allylstannane and/or the aldehyde to the Pd catalyst. On the other hand, the $ArCH_2OPR_2$ group in the complexes **3** makes them electronically different from the complex **1** with $ArOPR_2$ group. And the complex **1** seems to have relatively balanced electronic properties since in the allylation the transmetalation requires an electron-deficient Pd metal-center while the electrophilic attack is enhanced by an electron-rich metal-center [2–5,32]. The effectiveness of the complex **1** in the allylation of other representative aldehydes with allyltributyltin was also investigated (Scheme 4). It was found that the complex **1** displayed comparable or higher activity (in most cases) in the allylation of the related aldehydes in comparison with the (amino)phosphinite and (imino) phosphinite PCN pincer Pd complexes reported by Klein Gebbink and van Koten [32]. Details of this catalytic study are given in the Supporting Information.

In conclusion, two new unsymmetrical pincer Pd(II) complexes with (pyrazolyl)aryl phosphinite ligands have been conveniently synthesized starting from commercially available isophthaldehyde with the key step being one-pot phosphorylation/palladation reaction. These new pincers contain two fused six-membered palladacycles and exhibit rather low activity in the allylation of benzaldehyde.

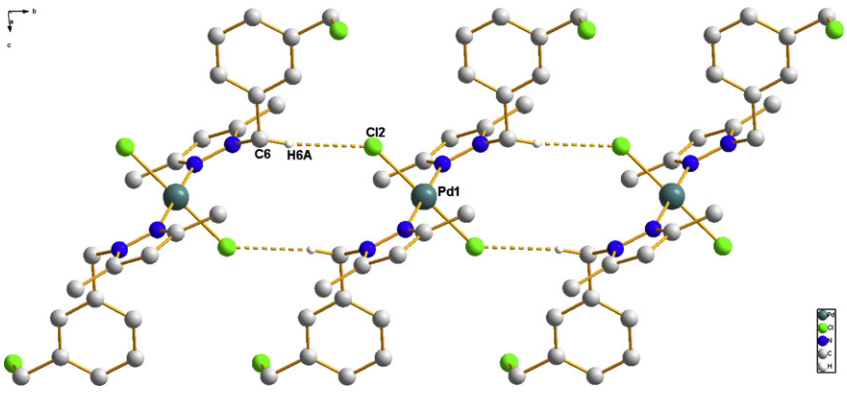
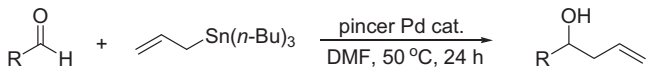


Fig. 4. 1-D chain structure of complex **4**. Non-hydrogen bonding H atoms are omitted for clarity.



R = Ph, with cat. **3a** (5 mol%), 29% yield; cat. **3b** (5 mol%), 24% yield; with cat. **1** (2.5 mol%), 67% yield
Other aldehydes with cat. **1** (2.5 mol%), 15 examples, 33-97% yields

Scheme 4. Allylation of aldehydes with allyltributyltin catalyzed by the pincer Pd complexes **1**, **3a** and **3b**.

3. Experimental

3.1. General

Toluene and triethylamine were distilled over sodium/benzophenone and CaH_2, respectively. *N*,*N*-Dimethylformamide was dried over $CaCl_2$ or molecular sieves and distilled under reduced pressure. The 3-(3,5-dimethylpyrazol-1-ylmethyl)benzaldehyde [31] and 2-(3,5-dimethylpyrazol-1-ylmethyl)-6-(diphenylphosphinoxy)phenylchloropalladium(II) (**1**) [27] were prepared according to the literature methods. All other chemicals were used as purchased. Melting points were measured on an XT4A melting point apparatus and are uncorrected. IR spectra were collected on a Bruker VECTOR22 spectrophotometer in KBr pellets. ^{1}H, ^{13}C and ^{31}P{^{1}H} NMR spectra were recorded on a Bruker DPX-400 or Bruker DPX-300 spectrometer in $CDCl_3$ with TMS as an internal standard for ^{1}H, ^{13}C NMR and 85% H_3PO_4 as the external standard for ^{31}P{^{1}H} NMR. Mass spectra were performed on the Agilent LC/MSD Trap XCT instrument. Elemental analyses were measured on a Thermo Flash EA 1112 elemental analyzer.

3.2. Synthesis of 3-(3,5-dimethylpyrazol-1-ylmethyl)benzyl alcohol **2**

To a stirred solution of 3-(3,5-dimethylpyrazol-1-ylmethyl) benzaldehyde (428 mg, 2 mmol) in methanol (20 mL) was added sodium borohydride (38 mg, 1 mmol) at 0 °C, followed by stirring at room temperature for 5 h. Then the reaction was quenched with water and the PH value of the solution was adjusted to 6-7 by diluted HCl. The aqueous was extracted with dichloromethane and the organic layers were dried over Na_2SO_4, filtered, and evaporated. The residue was purified by preparative TLC on silica gel plates eluting with EtOAc to afford white solids of **2**. 92% yield. m.p. 75–76 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28–7.22 (m, 2H, Ar-H), 7.05 (s, 1H, Ar-H), 6.91 (d, J = 7.1 Hz, 1H, Ar-H), 5.84 (s, 1H, Pz-H), 5.13 (s, 2H, CH_2Pz), 4.60 (d, J = 3.4 Hz, 2H, CH_2OH), 2.94 (br s, 1H, CH_2O*H*), 2.22 (s, 3H, CH_3), 2.13 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.6, 141.8, 139.2, 137.5, 128.8, 125.9, 125.5, 124.9, 105.5, 64.7, 52.3, 13.4, 11.1. IR (KBr, cm^{-1}): υ 3250, 2916, 2850, 1548, 1487, 1462, 1384, 1309, 1214, 1151, 1039, 984, 888, 816, 779, 743, 695. MS (*m*/*z*, ESI$^+$): 217.1 (M + H), 239.1 (M + Na), 255.0 (M + K).

3.3. Synthesis of palladium(II) complexes **3**–**4**

To a stirred solution of benzyl alcohol **2** (108 mg, 0.5 mmol) and triethylamine (84 μL, 0.6 mmol) in toluene (20 mL) was added diphenylchlorophosphine or di-tertbutylchlorophosphine (0.6 mmol) under N_2 atmosphere at r.t. The resultant mixture was refluxed for 8 h. Then $PdCl_2$ (90 mg, 0.5 mmol) was added and the reaction mixture was refluxed for another 18 h. After cooling, filtration and evaporation, the residue was purified by preparative TLC on silica gel plates eluting with EtOAc/petroleum ether to afford the corresponding Pd complexes. In the case of diphenylchlorophosphine, the first band gave the Pd complex **4** and the second band was pincer complex **3a**.

Bis[1-chloromethyl-3-(3,5-dimethylpyrazol-1-ylmethyl)benzene] palladium (II) dichloride (4) 34% yield, yellow solids. m.p. 202–203 °C. ^{1}H NMR (400 MHz, $CDCl_3$): The complex exists as a mixture of isomers in $CDCl_3$ solution with a ratio of about 1.6:1. The major isomer: δ 7.39–7.32 (m, 2H, Ar-H), 7.28–7.26 (m, 1H, Ar-H), 7.02 (d, J = 7.5 Hz, 1H, Ar-H), 5.94 (s, 1H, Pz-H), 5.74 (s, 2H, CH_2Pz), 4.46 (s, 2H, CH_2Cl), 2.90 (s, 3H, CH_3), 2.04 (s, 3H, CH_3). The minor isomer: δ 7.48 (s, 1H, Ar-H), 7.23–7.19 (m, 3H, Ar-H), 6.16 (s, 2H, CH_2Pz), 5.90 (s, 1H, Pz-H), 4.59 (s, 2H, CH_2Cl), 2.51 (s, 3H, CH_3), 2.11 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.4, 143.6, 138.2, 138.0, 135.7, 135.6, 129.2, 129.0, 128.1, 127.9, 127.5, 127.1, 127.0, 126.8, 108.1, 53.3, 52.9, 45.9, 15.2, 14.9, 11.9. IR (KBr, cm^{-1}): υ 3122, 3084, 2963, 2921, 1607, 1555, 1467, 1420, 1391, 1354, 1318, 1267, 1216, 1154, 813, 791, 755, 707, 674. Anal. Calcd for $C_{26}H_{30}Cl_4N_4Pd$: C, 48.28; H, 4.68; N, 8.66. Found: C, 48.06; H, 4.67; N 8.46%.

2-(3,5-dimethylpyrazol-1-ylmethyl)-6-(diphenylphosphinoxymethyl)phenylchloropalladium(II) **(3a)** 25% yield, white solids. m.p. 244–246 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00–7.95 (m, 2H, Ph-H), 7.91–7.86 (m, 2H, Ph-H), 7.48–7.35 (m, 6H, Ph-H), 7.07–7.04 (m, 1H, Ar-H), 7.00–6.98 (m, 2H, Ar-H), 5.83 (s, 1H, Pz-H), 5.49 (d, J = 14.0 Hz, 1H, CH_2Pz), 5.10 (dd, J = 8.0, 11.6 Hz, 1H, CH_2OPR_2), 4.96–4.85 (m, 2H, CH_2OPR_2 and CH_2Pz), 2.59 (s, 3H, CH_3), 2.32 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.4 (d, J = 2.8 Hz), 147.0 (d, J = 3.6 Hz), 139.1 (d, J = 2.2 Hz), 138.5, 138.4, 134.8 (d, J = 58.2 Hz), 133.2 (d, J = 12.7 Hz), 132.6, 131.8 (d, J = 13.4 Hz), 131.3 (d, J = 2.1 Hz), 131.1 (d, J = 2.4 Hz), 128.2 (d, J = 11.7 Hz), 128.0 (d, J = 11.2 Hz), 127.2, 126.7, 124.6, 106.6 (d, J = 3.5 Hz), 76.3 (d, J = 4.9 Hz), 55.2, 14.7, 11.2. ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ 116.6. IR (KBr, cm^{-1}): υ 2923, 2854, 1546, 1464, 1439, 1396, 1266, 1107, 1029, 983, 781, 742, 696. Anal. Calcd for $C_{25}H_{24}ClN_2OPPd$: C, 55.47; H, 4.47; N, 5.18. Found: C, 55.31; H, 4.63; N 5.05%. MS (*m*/*z*, ESI$^+$): 505.2 (M − Cl).

2-(3,5-dimethylpyrazol-1-ylmethyl)-6-(di-tertbutylphosphinoxymethyl)phenylchloropalladium(II) (**3b**) 46% yield, white solids. m.p. 161–163 °C ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.97 (s, 3H, Ar-H), 5.79 (s, 1H, Pz-H), 5.59 (d, J = 13.9 Hz, 1H, CH_2Pz), 4.95–4.83 (m, 3H, CH_2OPR_2 and CH_2Pz), 2.49 (s, 3H, CH_3), 2.31 (s, 3H, CH_3), 1.69 (d, J = 14.5 Hz, 9H, *t*-Bu), 1.09 (d, J = 14.9 Hz, 9H, *t*-Bu). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.8 (d, J = 2.1 Hz), 147.9 (d, J = 4.8 Hz), 138.7 (d, J = 1.9 Hz), 138.4, 138.1 (d, J = 10.0 Hz), 126.6, 126.3, 124.2, 106.5 (d, J = 3.1 Hz), 78.5, 55.4, 41.6 (d, J = 21.6 Hz), 38.2 (d, J = 26.1 Hz), 29.6 (d, J = 3.9 Hz), 27.9 (d, J = 5.0 Hz), 14.5, 11.2. ^{31}P{^{1}H} NMR (121 Hz, $CDCl_3$): δ 160.2. IR (KBr, cm^{-1}): υ 2958, 2923, 1628, 1549, 1470, 1438, 1398, 1365, 1291, 1188, 1026, 988, 808, 762, 729. Anal.

Table 2
Summary of crystal structure determination for Pd complexes **3b** and **4**

	3b	**4**
Formula	$C_{21}H_{32}ClN_2OPPd$	$C_{26}H_{30}Cl_4N_4Pd$
*M*r	501.31	646.74
crystal size (mm)	0.30 × 0.24 × 0.20	0.37 × 0.21 × 0.04
a (Å)	15.555(3)	7.6818(10)
b (Å)	8.6177(17)	8.0810(10)
c (Å)	17.262(4)	12.7020(16)
α (°)	90	83.3870(10)
β (°)	92.28(3)	80.2630(10)
γ (°)	90	67.0590(10)
V (Å^3)	2312.2(8)	714.62(16)
Z	4	1
space group	*Monoclinic, P2(1)/n*	*Triclinic, P-1*
D_{calcd} (g cm^{-3})	1.440	1.503
μ (mm^{-1})	1.000	1.045
θ range (°)	1.73–24.99	2.74–25.50
Number of data collected	16488	5506
Number of unique data	4055	2645
R (all data)	0.0667	0.0325
*R*w (all data)	0.1401	0.0755
R ($I > 2\sigma(I)$)	0.0536	0.0294
R_w ($I > 2\sigma(I)$)	0.1312	0.0737
F(000)	1032	328
peak/hole (e·Å^{-3})	0.387/−0.504	0.769/−0.575

Calcd for $C_{21}H_{32}ClN_2OPPd$: C, 50.31; H, 6.43; N, 5.59. Found: C, 50.37; H, 6.70; N 5.51%. MS (*m/z*, ESI^+): 465.4 (M − Cl).

3.4. X-ray diffraction studies

Crystals of **3b** were obtained by recrystallization from EtOAc and those of **4** were from CH_2Cl_2–CH_3OH at ambient temperature. The data for **3b** were collected on a Rigaku Saturn 724 CCD diffractometer and those for **4** on a Bruker SMART APEX-II CCD diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The diffraction data were corrected for Lorentz and polarization factors. The structures were solved by direct methods and expanded using Fourier techniques and refined by full-matrix least-squares methods. The non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were included but not refined. Their raw data were corrected and the structures were solved using the SHELXS-97 program. Details of crystal structure determination for complexes **3b** and **4** are listed in Table 2.

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Appendix A. Supplementary material

CCDC 805500 and 804891 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Appendix. Supplementary material

Supplementary data related to this article can be found online at doi:10.1016/j.jorganchem.2011.04.034.

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