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Synthesis, Crystal Structures, and Catalytic Application of Two Triphenylphosphine-Cyclopalladated Ferrocenylpyrazine Complexes Containing Chlorine/Iodine Anion Chen Xu^{1,*}, Hong-Mei Li², Zhi-Qiang Wang¹, and Wei-Jun Fu¹

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Two new triphenylphosphine-cyclopalladated ferrocenylpyrazine complexes containing chlorine/iodine anion 2–3 have been easily prepared from the bridge-splitting reaction of the palladacyclic dimer 1 and anion exchange reaction, respectively. They were characterized by elemental analysis, IR, ¹H NMR. Additionally, the structures of these two complexes were determined by single-crystal X-ray analysis and C–H…N hydrogen bonds and π – π interactions were found in the their crystal structures. These complexes displayed good activity in the coupling of terminal alkynes with arylboronic acids under atmospheric conditions. This method provided the corresponding arylalkynes with good to excellent yields.

Keywords

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cyclopalladated ferrocenylpyrazine complex, crystal structure, coupling reaction, alkyne,

arylboronic acid

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INTRODUCTION

Palladium-catalyzed coupling reactions such as Sonogashira reaction have become an extremely powerful method in organic synthesis for the formation of carbon-carbon bonds.^[1-2] Among various Pd catalysts, palladacycles are one of the most developed and studied classes of catalyst precursors because of their structural versatility and easy synthetic accessibility.^[3] Although great progress has been obtained for the coupling reactions, some drawbacks still remained.^[4] For example, the reaction generally does not work well for electron-deficient alkynes. To overcome this limitation, palladium-catalyzed coupling of terminal alkynes with arylboronic acids have been developed.^[5–8] We have also reported *N*-heterocyclic carbene adducts of cyclopalladated ferrocenylpyridine complexes catalyzed coupling of terminal alkynes with arylboronic acids.^[9] As a continuation of our interest in the synthesis and application of cyclometalated complexes,^[10–12] we prepared two new triphenylphosphine-cyclopalladated ferrocenylpyrazine complexes containing chlorine/ iodine anion and examined their catalytic activity in the coupling of terminal alkynes with arylboronic acids need the progress containing chlorine/ iodine anion and examined their catalytic activity in the coupling of terminal alkynes with arylboronic acids need to be a solution of the coupling and the progress containing chlorine/ iodine anion and examined their catalytic activity in the coupling of terminal alkynes with arylboronic acids under atmospheric conditions.

EXPERIMENTAL

Materials and General Methods

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Solvents were dried and freshly distilled prior to use. All other chemicals were commercially available except for palladacyclic dimer **1** which was prepared according to the published procedure.^[12] Elemental analyses were determined with a Carlo Erba 1160 Elemental Analyzer. IR spectra were collected on a Bruker VECTOR22 spectrophotometer in KBr pellets. ¹H NMR spectra were recorded on a Bruker DPX-400 spectrometer in CDCl₃ with TMS as an internal standard.

Synthesis of Complex 2

A solution of palladacyclic dimer **1** (0.1 mmol) and triphenylphosphine (0.21 mmol) in CH_2Cl_2 (10 mL) was stirred at room temperature for 30 min. The product was separated by passing through a short silica gel column with dichloromethane as eluent. The second band was collected to afford complex **2** after the evaporation of the solvent. Red solid, yield: 92%. Anal. Calcd. for $C_{32}H_{26}ClFeN_2PPd$: C, 57.60; H, 3.93; N, 4.20; found: C, 57.89; H, 3.67; N, 4.34%. IR (KBr, cm⁻¹): 3079, 2968, 1610, 1528, 1502, 1434, 1327, 1302, 1250, 1163, 1142, 1096, 1026, 993, 823, 735, 695. ¹H NMR (400 MHz, CDCl₃): δ 9.24(s, 1H, Ar–H), 8.60(s, 1H, Ar–H), 8.39 (s, 1H, Ar–H), 7.78–7.82 (m, 6H, Ar–H), 7.36–7.46 (m, 9H, Ar–H), 4.71 (s, 1H, C₅H₃), 4.20 (s, 1H, C₅H₃), 3.71 (s, 5H, C₅H₅), 3.42 (s, 1H, C₅H₃).

Synthesis of Complex 3

A solution of complex 2 (0.1 mmol) and NaI (0.2 mmol) in acetone (10 mL) was stirred at room temperature for 3 h. The product was separated by passing through a silica gel column with

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CH₂Cl₂ as eluent. The second band was collected to afford the corresponding complex **3** after evaporation of the solvent. Red solid, yield: 98%. Anal. Calcd. for $C_{32}H_{26}FeIN_2PPd$: C, 50.66; H, 3.45; N, 3.69; found: C, 50.93; H, 3.26; N, 3.87%. IR (KBr, cm⁻¹): 3054, 2922, 1621, 1593, 1507, 1432, 1392, 1317, 1243, 1166, 1091, 1033, 998, 935, 835, 753, 689. ¹H NMR (400 MHz, CDCl₃): δ 9.70 (s, 1H, Ar–H), 8.61 (s, 1H, Ar–H), 8.33 (s, 1H, Ar–H), 7.78–7.83 (m, 6H, Ar–H), 7.40–7.48(m, 9H, Ar–H), 4.70 (s, 1H, C₅H₃), 4.16 (s, 1H, C₅H₃), 3.67 (s, 5H, C₅H₅), 3.55 (s, 1H, C₅H₃).

General Procedure for the Coupling of Terminal Alkynes with Arylboronic Acids

A mixture of arylboronic acids (0.5 mmol), alkynes (0.6 mmol), the prescribed amount of catalysts, Ag_2O (0.5 mmol) and KOAc (0.75 mmol) in 1,2-dichloroethane (DCE) (3 mL) under air was stirred at 80 or 25 °C for 24 h. After being cooled, the mixture was filtered. The solvent was removed under reduced pressure. The resulting residue was purified by flash chromatography on silica gel to afford the desired coupled products, which were characterized by comparing their m.p. and ¹H NMR spectra.

Crystallographic Data Collection and Structure Determination

Crystallographic data for compounds 2–3 were collected on a Bruker SMART APEX-II CCD diffractometer equipped with a graphite monochromator at 296 K using Mo-Ka radiation ($\lambda = 0.071073$ Å). Structures were solved by direct methods and refined by full-matrix least-squares

methods on F^2 with the SHELX-97 program.^[13] All non-hydrogen atoms were refined anisotropically, while hydrogen atoms were placed in geometrically calculated positions. The detailed crystallographic data and structure refinement parameters for **2–3** are summarized in Table 1. **CCDC** reference numbers 969894 and 995704 for **2–3**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www. ccdc. cam. ac.uk/data_request/cif.

RESULTS AND DISCUSSION

Synthesis and Structures of Complexes 2–3

The synthesis route of complexes 2-3 is given in Scheme 1. Bridge-splitting reaction of palladacyclic dimer 1 with triphenylphosphine in CH₂Cl₂ at room temperature readily afforded the corresponding monomer 2 in good yield. The corresponding adduct containing iodine anion 3 has been readily prepared through anion exchange reaction of 2 with NaI in acetone. They are air- and moisture-stable, both in the solid state and in solution. Complexes 2-3 were characterized by elemental analysis, IR, and ¹H NMR. Generally, the spectra of 3 was similar to that of the corresponding 2, they exhibit similar peaks for the Cp ring, with a proton ratio of 1:1:1:5, clearly showing that they are both *ortho*-cyclopalladated complexes. In order to further investigate the structures of these complexes, their crystal structures have been determined by X-ray diffraction.

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The two crystals were obtained by recrystallization from CH₂Cl₂-petroleum ether solution at room temperature. The single-crystal X-ray analysis indicates that the palladacycles 2-3 are trans complexes in the solid state. The molecules are shown in Figs. 1 and 2. They crystallize in triclinic P-1 space group with two mononuclear molecules in each asymmetric unit. The Pd atom in each complex is in a slightly distorted square-planar environment bonded to the phosphorus atom, the chlorine (iodine) atom, the nitrogen atom and the C atom of the ferrocenyl moiety. The bicyclic system formed by the palladacycle and the C_5H_3 moiety is approximately coplanar (dihedral angles of $3.2^{\circ}(0.7^{\circ})$ and $4.9^{\circ}(4.2^{\circ})$ for complexes 2 and 3). The Pd–N and Pd–P bond lengths of 2 are similar to those of the corresponding 3, while Pd-Cl [2.3640(19)-2.3747(19) Å] bond lengths of 2 are obviously shorter than Pd-I [2.6600(14)-2.6561(14) Å] bond lengths of 3. Basically, the crystal structure of **3** is quite similar to that of **2**. Fig.3 shows that **2** exists as a dimer in the crystal due to intermolecular CH···N (H···N = 2.782 Å) hydrogen bonds^[14] and $\pi - \pi$ stacking interactions involving the neighboring pyrazinyl and cyclopentadienyl rings (the interplane distance is 3.727 Å).^[15]

The Catalytic Coupling Reaction of Terminal Alkynes with Arylboronic Acids

Adducts of palladacycles have been successfully used in the coupling reactions.^[3] Usually, cyclopalladated ligands have little effect on the catalytic activity, however, the anionic ligand (Cl, Br, I, etc.) is found to have some effect on the catalytic activity.^[16-17] Here, we investigated the coupling of terminal alkynes with arylboronic acids catalyzed by the palladacycle adducts **2–3**

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since we are interested to see whether the effect of halogen anions (Cl and I) on the catalytic activity. Based on our previous experiments,^[9] the coupling of phenylacetylene with phenylboronic acid using 1 equivalent of Ag₂O as additive was performed under air in 1,2-dichloroethane (DCE) in the presence of KOAc as base at 80 °C for 24 h (Table 2, entries 1-3). The dimer **1** generated the product in low yield (26%), while palladacycles precatalyst **2–3** led to good activity giving the coupled product in good yields (90-93%) and **3** showed slightly more activity. The reactions were performed at room temperature and afforded product in moderate yields (61-63%, entry entries 4-5). Increasing catalyst loading to 1 mol% resulted in excellent yields (94-95%, entries 6-7). In addition, solvent CH_2Cl_2 also afforded excellent yields (95-97%, entries 8-9).

In the following experiments, the coupling reactions between a variety of alkynes and arylboronic acids were investigated by using **3** as catalyst under the reaction conditions (Ag₂O, KOAc, CH₂Cl₂, air, 25 °C, 24 h) (Table 3). Similar to the results of phenylacetylene, excellent yields were obtained in the cases of 4-methylphenylacetylene and arylboronic acids (94-97%, entries 1–3). The hindered 2-methylphenylboronic acid also provided the product in a good yield (88%, entry 4). For aliphatic alkynes oct-1-yne, they could provide the corresponding products in good yields (80–89%, entries 5–8). A noticeable advantage of this reaction is that for electron-deficient such as ethyl propiolate and 3-ethynylpyridine, they still gave the desired product in good yields (81–86%, entries 9–12) since the traditional Sonogashira coupling

procedure leads to low yields for electron-deficient alkynes.

CONCLUSION

Two new triphenylphosphine-cyclopalladated ferrocenylpyrazine complexes containing chlorine/iodine anion 2–3 have been synthesized and characterized. Single-crystal X-ray analysis confirms that there are C–H···N hydrogen bonds and π – π interactions in the their crystal structures. These complexes are efficient catalysts for the coupling of terminal alkynes with arylboronic acids at room temperature under atmospheric conditions.

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Empirical formula	$C_{64}H_{52}Cl_2Fe_2N_4P_2Pd_22$	$C_{64}H_{52}I_2Fe_2N_4P_2Pd_2$ 3
Fw	1334.44	1517.34
Crystal system	Triclinic	Triclinic
Space group	P-1	P-1
a (Å)	11.252(3)	11.611(6)
b (Å)	14.495(3)	14.524(7)
c (Å)	18.089(4)	17.666(9)
α (°)	104.236(3)	101.892(6)
β (°)	99.780(3)	97.748(6)
γ (⁰)	103.529(3)	103.944(6)
Volume ($Å^3$)	2698.2(11)	2775(2)
Z	2	2
$D_c (g/cm^3)$	1.643	1.816
GOF	1.028	1.011
Data / restraints /	9972 / 0 / 685	10258 / 0 / 685
parameters		
Final R indices	R1 = 0.0557, wR2 = 0.1066	R1 = 0.0612, wR2 = 0.1003
[I>2sigma(I)]		
R indices (all data)	R1 = 0.1149, wR2 = 0.1265	R1 = 0.1455, wR2 = 0.1287

TABLE 1 Crystallographic data for complexes 2 and 3

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TABLE 2 The coupling of phenylacetylene with phenyl boronic acid catalysed by palladacycles $1-3^a$

$ \begin{array}{ c c c c }\hline \hline $							
Entry	Solvent	Temperature	Catalyst (mol%)	Yield ^b (%)			
1	DCE	80 °C	1 (0.5)	26			
2	DCE	80 °C	2 (0.5)	90			
3	DCE	80 °C	3 (0.5)	93			
4	DCE	25 °C	2 (0.5)	61			
5	DCE	25 °C	3 (0.5)	63			
6	DCE	25 °C	2 (1)	94			
7	DCE	25 °C	3 (1)	95			
8	CH_2Cl_2	25 °C	2 (1)	95			
9	CH_2Cl_2	25 °C	3 (1)	97			

^a Reaction conditions: phenylacetylene (0.6 mmol), PhB(OH)₂ (0.5 mmol), Ag₂O (0.5 mmol),

KOAc (0.75 mmol), solvent (3 mL), 24 h.

^b Isolated yields.

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	$R \longrightarrow Ar \longrightarrow B(OH)$	$H_{2} \xrightarrow{3, Ag_{2}O} Ar \xrightarrow{3}$	≡R
Entry	R	Ar	Yield ^b (%)
1	<i>p</i> -MeC ₆ H ₄	Ph	94
2	<i>p</i> -MeC ₆ H ₄	<i>p</i> -MeC ₆ H ₄	95
3	<i>p</i> -MeC ₆ H ₄	<i>p</i> -MeOCC ₆ H ₄	97
4	<i>p</i> -MeC ₆ H ₄	o-MeC ₆ H ₄	88
5	Me(CH ₂) ₅	Ph	89
6	Me(CH ₂) ₅	<i>p</i> -MeC ₆ H ₄	85
7	Me(CH ₂) ₅	<i>p</i> -MeOC ₆ H ₄	87
8	Me(CH ₂) ₅	<i>p</i> -EtOOCC ₆ H ₄	80
9	COOEt	Ph	81
10	COOEt	<i>p</i> -MeC ₆ H ₄	83
11	Pyridin-3-yl	Ph	85
12	Pyridin-3-yl	<i>p</i> -MeC ₆ H ₄	86

TABLE 3 The coupling of alkynes with arylboronic acids catalysed by 3^{a}

^a Reaction conditions: catalyst **3** (1 mol%), alkyne (0.6 mmol), arylboronic acid (0.5 mmol), KOAc (0.75 mmol), Ag₂O (0.5 mmol), CH₂Cl₂ (3 mL), 25 °C, 24 h.

^b Isolated yields.

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SCH. 1. Synthesis route of cyclopalladated ferrocenylpyrazine complexes 2–3.

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FIG. 1. ORTEP drawing of **2** at the 30% probability level for thermal displacement ellipsoids, with hydrogen atoms being omitted for clarity (representation of one of the two independent molecules). Selected bond lengths (Å) and angles (°) are as follows (corresponding values for the unshown second structure are given in brackets): Pd(1)-C(10) 1.987(6) [1.990(6)], Pd(1)-N(1) 2.134(5) [2.146(5)], Pd(1)-P(1) 2.2488(18) [2.2486(18)], Pd(1)-Cl(1) 2.3640(19) [2.3747(19)] and C(10)-Pd(1)-N(1) 81.2(2) [80.8(2)], C(10)-Pd(1)-P(1) 93.10(19) [93.6(2)], P(1)-Pd(1)-Cl(1) 95.27(7) [95.69(7)], N(1)-Pd(1)-Cl(1) 90.50(15) [90.12(16)].

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FIG. 2. ORTEP drawing of **3** at the 30% probability level for thermal displacement ellipsoids, with hydrogen atoms being omitted for clarity (representation of one of the two independent molecules). Selected bond lengths (Å) and angles (°) are as follows (corresponding values for the unshown second structure are given in brackets): Pd(1)-C(2) 1.988(9) [2.028(10)], Pd(1)-N(1) 2.155(8) [2.160(5)], Pd(1)-P(1) 2.256(3) [2.258(3)], Pd(1)-I(1) 2.6600(14) [2.6561(14)] and C(2)-Pd(1)-N(1) 79.8(3) [81.0(4)], C(2)-Pd(1)-P(1) 93.1(3) [92.2(3)], P(1)-Pd(1)-I(1) 96.03(7) [95.19(8)], N(1)-Pd(1)-I(1) 91.3(2) [91.7(2)].

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FIG. 3. The dimeric structure of complex 2 showing C–H···N hydrogen bonds and π – π interactions. Non-hydrogen bonding H atoms are omitted for clarity.

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