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New Pd(II) Binuclear Complexes as Effective Catalysts in Oxidative-Heck Reaction Using Arylboronic Acid Derivatives

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New Pd(II) Binuclear Complexes as Effective Catalysts in Oxidative-Heck Reaction Using Arylboronic Acid Derivatives

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A series of new binuclear Pd(II) complexes based on chelating diimines and bridging diphosphine or diimine ligands have been synthesized and characterized successfully. The formula of the new complexes are $[Pd_2(mbyp)_2(DPA)_2](PF_6)_4$ (1), $[Pd_2(mbyp)_2(DPE)_2]$ (PF₆)_4 (2), $[Pd_2(mbyp)_2(4,4-byp)_2]$ (PF₆)_4 (3), $[Pd_2(mbyp)_2(t-pye)_2]$ (PF₆)_4 (4) [mbyp = 4,4'-dimethyl-2,2'bipyridine, DPA = 1,2-bis(diphenylphosphino)acetylene, DPE =1,2-bis(diphenylphosphino)ethylene, 4,4-byp = 4,4'-bipyridine,and t-ype = trans 1,2-bis(4-pyridyl)ethylene)]. The catalytic activities of the new complexes have been investigated in the couplingof arylboronic acid derivatives to various olefins. Results obtainedshowed interesting catalytic activities and chemoselectivities for thenew complexes in the coupling reactions to produce the conjugateaddition and heck coupling products under free base or oxidantconditions.

Keywords arylboronic acid, binuclear palladium, bipyridines, chemoselectivity, coupling, olefins, phosphines

INTRODUCTION

Palladium complexes based on pyridine-containing ligands have been used effectively as catalysts in different organic and polymeric reactions for the last years. For example, PdCl₂(bpy) complex shows high efficiency as a catalyst for Heck reaction in glycerol-organic biphasic medium.^[1] Pd(II)-catalyzed intramolecular addition of vinylpalladium species to the nitrile groups was achieved in the presence of 2,2'-bipyridine (bpy) as a ligand.^[2] Pd-2,2'-bipyridyl complex also catalyzed the oxidative carbonylation of phenol to diphenyl carbonate.^[3] Palladium complexes containing bulky dinitrogen ligands have been

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used in the olefin-methyl acrylate copolymerization.^[4] Polynuclear palladium-dinitrogen complexes are receiving more interest nowadays. One of the shortcomings in this research is the lack of versatile and general precursors that allow di- and polynuclear complexes to be constructed from mononuclear sources. Square planar Pd(II) complexes have been used in conjugation with a range pyridine-containing ligands to generate two- or three-dimensional arrays via self-assembly.^[5] Palladium dinitrogen-diphosphine complexes showed high catalytic activity in CO-ethylene polymerization.^[6] However, reports on palladium dinitrogen-diphosphine bridged complexes are limited in the literature.^[7]

In this article, we wish to report our results of the synthesis, characterization, and catalytic application of new Pd(II) bimetallic mixed ligand complexes based on chelating diimines and having bridging diphosphines or dimine ligands (Figure 1).

Experimental

Materials and Methods

Pd(OAc)₂, diimine ligands, diphosphine ligands, trifluroacetic acid (TFA), ammonium hexafluorophospate (NH₄PF₆), trans-cinnamate esters, and phenylboronic acid [PhB(OH)2] are highly pure commercially available materials and were used without any purification. Dry solvents have been used in all experiments. ¹H and ¹³C NMR spectra were recorded on 500 MHz Joel NMR machine. IR spectra were recorded on Perkin-Elmer 16F PC FT-IR spectrometer. Melting points were determined using Büchi melting point apparatus. Elemental analysis was carried out using Perkin-Elmer CHNS-O series 2 2400 analyzer. UV-Vis spectra were recorded in dichloromethane using Perkin-Elmer Lambda EZ 210 spectrometer. The screening of the reactants and products of the catalytic application part was carried out using Agilent GC 6890 Series gas chromatograph equipped with a split-splitless injector (split ratios of 20:1). The temperature of the injector was 250°C, with 10 psi constant pressure. The column was an HP-5 column (30 m \times 0.25 mm i.d.,

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1,2-bis(diphenylphosphino)acetylene-(DPA) trans-1,2-bis(diphenylphosphino)ethylene-(DPE)



Diimine ligands 4,4'-dimethyl-2,2'-byridine

FIG. 1. Pd(II) bimetallic mixed ligand complexes.

0.25 μ m film thickness). Helium was the carrier gas at a flow rate of 1.5 mL/min and programmed temperature (50°C, hold 2 min, then ramped at 10°C/min to 140°C, then finally ramped at 20°C/min to 250°C, hold time 20 min). The detector was flame ionization detector (FID), with hydrogen and air flow of 40.0 and 450.0 mL/min; respectively. Makeup flow was on with 45.0 mL/min of helium. The products of the reactions were also analyzed on GC-MS Varian Saturn 2000 equipped with 30 m capillary column (HP-5). Helium was the carrier gas at a flow rate of 1.0 mL/min and programmed temperature (50°C, hold 2.0 min, then ramped at 10°C/min to 140°C, then finally ramped at 20°C/min to 250°C, hold time 20 min). The temperatures of injector, transfer line, and ionization source were 250, 225, and 270°C, respectively. NIST MS search was used for compound identification.

4,4'-bipyridine

trans-1,2-bis(4-pyridyl)ethylene

General Procedure for the Conjugate Addition of Phenylboronic Acid to *Trans*-Cinnamate Esters Catalyzed by New Pd(II) Bimetallic Mixed Ligand Complexes

To a 45 mL glass liner tube, phenylboronic acid (0.50 mmol), *trans*-cinnamate ester (0.50 mmol), palladium complex (0.02 mmol), and solvent (10 mL) were added under

nitrogen. The mixture was stirred and heated at 110° C for 24 h. After cooling, the reaction mixture was filtered and a sample of this solution was immediately analyzed by GC and GC-MS. The solvent was then removed and the products were separated by preparative TLC (30% EtOAc/petroleum ether 40–70°C). The products were identified by ¹H and ¹³C NMR, FT-IR, and GC-MS analyses.

Synthesis of the Complexes

Synthesis of Palladium precursor: (4,4'-Dimethyl-2, 2'-bipyridyl) bis(trifluroacetato)palladium(II) [Pd-prec]

The first step in the synthesis of binuclear palladium complexes involves the synthesis of palladium precursor containing chelating 4,4'-dimethyl-2,2'-bipyridine ligand according to Scheme 1. This complex was then allowed to react with bridging ligands in order to produce the new binuclear complexes.

To prepare Pd-prec, a literature method^[8] was modified and used. In 250 mL Erlenmeyer flask, 6.000 mmol (1.347 g) palladium acetate were dissolved in 100 mL of anhydrous methanol. After stirring for 30 min, the orange-red mixture was filtered off to remove undissolved palladium acetate. 7.200 mmol (1.326 g) of 4,4'-dimethyl-2,2'-bipyridine were then added to the filtrate



SCH. 1. Synthesis of [Pd-prec].

under nitrogen with constant stirring. The mixture was then stirred for 30 min. The solution turned intense red. Subsequently, 12.3 mL of 100% trifluroacetic acid were added slowly to the solution to precipitate the trifluroacetate salt (Scheme 1). Immediately after the addition of trifluroacetic acid, a light green creamy suspension was obtained. Stirring was continued for another 30 min. The mixture was thoroughly washed with cold methanol to remove excess of trifluroacetic acid. The yellow precipitate was dried under vacuum (yield: 2.581 g, 83.2%).

Synthesis of the binuclear complexes

All the complexes were prepared using a similar method. A typical example is described below.

$[Pd_2(mbyp)_2(DPA)_2](PF_6)_4(1)$

0.500 mmol (0.257 g) of Pd-prec were dissolved in 50 mL acetonitrile in 125 mL Erlenmeyer flask. Separately, 0.500 mmol (0.197 g) of bis(diphenylphosphino)acetylene (DPA) were dissolved in 10 mL methanol. The two solutions were mixed and stirred for 16 h at room temperature. The color of the mixed solution changed from light orange to dark orange and finally it became light yellow. The volume of the later solution was reduced to 50 mL in vacuum, then a solution of NH_4PF_6 (3.0 mmol, 0.49 g) in 5 mL methanol was added. The resulted solution was stirred at room temperature for 30 min. A light green precipitate was formed. It was then washed with methanol and dried under vacuum.



Light green solid, Yield: 0.514 g (52.7%). M.p (°C): 171–173. Anal. Calcd. for $C_{76}H_{64}N_4P_8F_{24}Pd_2$: C, 46.81; H, 3.31; N, 2.87. Found: C, 46.55; H, 3.45; N, 3.06%. UV-Vis l/nm (e $M^{-1}cm^{-1}$): 253 (1443500), 304 (850000), 306sh (800000). Selected IR bands (cm⁻¹): 3063 w, 2019 w, 1435 m, 833 s, 554 m.

 $[Pd_2(mbyp)_2(DPE)_2](PF_6)_4(2)$



Light yellow solid, Yield: 0.965 g (98.9%). M.p (°C): 170–173. Anal. Calcd. for $C_{76}H_{70}N_4P_8F_{24}Pd_2$: C, 46.72; H, 3.51; N, 2.87. Found: C, 46.44; H, 3.59; N, 2.98%. UV-Vis l/nm (e $M^{-1}cm^{-1}$): 250 (1698450), 301 (300000), 308sh (250000). Selected IR bands (cm⁻¹): 3057 w, 1617 m, 1436 m, 831 s, 553 m.

 $[Pd_2(mbyp)_2(4,4-byp)_2](PF_6)_4(3)$



Light green solid, Yield: 0.725 g (98.4%). M.p (°C): 180–183. Anal. Calcd. for $C_{44}H_{40}N_8P_4F_{24}Pd_2$: C, 35.86; H, 2.73; N, 7.60. Found: C, 35.67; H, 2.58; N, 8.04%. UV-Vis l/nm (e $M^{-1}cm^{-1}$): 246 (10314539), 319 (437956), 330sh (291970). Selected IR bands (cm⁻¹): 3062 w, 1666 m, 1613 m, 1432 m, 825 s, 552 m.



Light green solid, Yield: 0.758 g (99.4%). M.p (°C): 181–184. Anal. Calcd. for $C_{48}H_{44}N_8P_4F_{24}Pd_2$: C, 37.79; H, 2.91; N, 7.34. Found: C, 37.88; H, 3.06; N, 7.65%. UV-Vis l/nm (e $M^{-1}cm^{-1}$): 250 (27841815), 303 (19618320), 335sh (13078880). Selected IR bands (cm⁻¹): 3018 w, 1612 m, 1436 m, 828 s, 554 m.

TABLE 1 ³¹P chemical shifts (d) (in DMSO- d_6) relative to H₃PO₄ for phosphorus-containing free ligands and their complexes

Compound	³¹ P Chemical ³¹ shift (d) ppm
DPA	-33.58
DPE	-9.13
(1)	32.13
(2)	34.78

RESULTS AND DISCUSSION

Characterization of Complexes

The new Pd(II)-binuclear complexes (1–4) have been prepared in good yields by reacting Pd-prec with diphosphines or diimines bridging ligands in 1:1 ratio at room temperature. The elemental analysis, infrared, UV-Vis, and NMR spectroscopic data are supporting the formation of the new binuclear palladium complexes.

Infrared spectra

The FT-IR spectra were recorded for free ligands and complexes using KBr pellets in the range of 4000–400 cm⁻¹.

All spectra showed a strong absorption range from 820 to 830 cm⁻¹ corresponding to aromatic C–H out of plane bending modes. The spectra showed also a shift in the absorption in the range 1350–1600 cm⁻¹ after complexation. These shifts are attributed to the change in electron density in the pyridine ring when the non-bonding pair of electrons on the nitrogen atom is donated to the metal ion.^[9] The aromatic C=C and C=N stretching absorptions are found in the range of 1400–1650 cm⁻¹.

Electronic spectra of free ligands and complexes

The absorption spectra of all chelating and bridging ligands used were recorded. The chelating 4,4'-dimethyl-2,2'-bipyridine ligand has two specific absorption bands, one at 283 nm with shoulder at 290 nm and the second one at 246 nm. DPA and DPE as bridging ligands showed one absorption band at 246 nm and 244 nm, respectively, while the *trans*-1,2-bis(4-pyridyl)ethylene ligand has three absorption bands at 300, 288, and 246 nm.

cient e. These can be assigned to metal to ligand charge transfer (MLCT) transitions.^[8]

¹H and ³¹P NMR spectroscopy

The 31 P chemical shift variation with respect to the free ligand is consistent with metal phosphorous binding. Down field shifts of 65.71 and 43.91 d ppm have been observed for DPAcontaining complex (1) and DPE bridged complex (2), respectively (Table 1).

For bridging diimine complexes, the change in the ¹H NMR chemical shifts of protons in the chelating and bridging diimine ligands can be used to predict the formation of the new Pd-N bonds in complexes (3) and (4). The complexation process in the previously complexes resulted in an increase in the chemical shifts of ligand protons by the order of 0.10-0.80 d ppm.

It is worth mentioning that our attempts to obtain good crystal growth for the new complexes are in progress.

Catalytic Applications of the New Complexes

The use of mononuclear Pd(bpy) complexes as catalysts for the conjugate addition and Heck coupling of arylboronic acid to α,β -unsaturated esters,^[10] encouraged us to investigate the catalytic activity of the new binuclear Pd(II) complexes in the coupling reactions of arylboronic acid derivatives with various olefins. The conjugate addition of organometallic reagents to olefins represents an example of transmetallation between organometallic reagents and transition metals, which represents a powerful tool for the construction of C-C bonds.^[11]

After the first report of $\text{Heck}^{[12]}$ and the further development by Uemura^[13] and Mori,^[14] the transition metal-catalyzed coupling of organoboronic acids and olefins, known as the oxidative Heck reaction, had been extensively investigated,^[15] mainly because boronic acids are stable, nontoxic, and easily available. The methods developed thus far require the presence of an oxidant to reoxidize Pd(0), for example, Cu(OAc)₂, quinone, or O₂, producing stoichiometric amounts of metal waste or being associated with potentially hazardous handling and not suitable for air-sensitive conditions. The development of efficient palladium catalysts for the conjugate addition and Heck coupling of arylboronic acid to olefins without adding any oxidant additives is still a challenging area.



For complexes, the spectra showed absorption bands in the region of 240–250 nm similar to those in free ligands but with slight shift in l_{max} upon complexation. Most of the complexes absorb in the region of 350–300 nm with high absorption coeffi-

With any binuclear-bridged synthetic strategy, a certain amount of rigidity is necessary to generate active catalyst in terms of selectivity and yield, although, in most cases, it is a

Entry	Solvent	Additive (mmol)	Conversion 5a (%) ^b	Products distribution (%) ^c	
				7aa	8aa
1	THF	_	19		100
2	CH_2Cl_2		14	6	94
3	THF/CH ₃ COOH (1:1)	H ₂ O 8.0	41	_	100
4	CH ₃ OH		64	20	80
5	CH ₃ CN		76	28	72
6 ^d	CH ₃ CN		92	36	64
7	CH ₃ CN	<i>p</i> -TsOH 0.50	65	8	92
8	CH ₃ CN	$K_2CO_3 0.50$	20	100	
9 ^e	CH ₃ CN	H ₂ (100 psi)	27	100	_
10	CH ₃ CN/ <i>i</i> -PrOH (1:1)		30	2	98

 TABLE 2

 Coupling of arylboronic acid (6a) to 5a reaction. Effect of varying different solvents^a

^aReaction conditions: (3) (0.02 mmol), 5a (0.50 mmol), 6a (1.0 mmol), Solvent (4 mL), 110°C, 16 h. ^bDetermined by GC. ^cDetermined by GC and ¹H-NMR. ^dCatalyst = 0.04 mmol. ^e93% Hydrogenation product.

mistaken strategy to target only the most rigid structures, since the proceeding of some elementary steps required in the catalytic cycle will not be possible with rigid catalysts.^[16]

The coupling reaction of phenylboronic acid (**6a**) with *trans*cinnamate ester (**5a**), adopted as model substrate, was carried out using complex (**3**) as catalyst precursor (Eq. 1). This reaction gave the conjugate addition (**7aa**) and the heck coupling (**8aa**) as major products.

The effect of varying different types of solvent on the yield and chemoselectivity of the reaction was carefully studied and data are reported in Table 2. Low catalytic activities were obtained with THF and CH_2Cl_2 solvents (Table 2, entries 1,2). The use of glacial acetic acid^[10] mixed with tetrahydrofuran and in the presence of 8.0 mmol water gave a better conversion We examined the catalytic activity of the new binuclear palladium(II)-bridged complexes in the vinylation of arylboronic acid in acetonitrile (4 mL) at 110°C (Eq. 1) (Table 3). The catalytic activity ranges from moderate to excellent with the formation of the heck-coupling product **8aa** as a major product.

Using the optimized conditions, we then examined the reaction of various arylboronic acids (**6a–b**) with different olefins (**5a–h**) (Eq. 2). The results are summarized in Table 4. Cinnamate esters **5a,b** reacted efficiently with **6a** even in the absence of any base or oxidant as additives but with lower chemoselectivity in case of **5b** (Table 4, entries 1,2).^[17] Comparable reaction conversion and chemoselectivity were obtained when **5a** was allowed to react with phenyboronic acid derivative **6b** (Table 4, entry 3).



with complete chemoselectivity toward 8aa (Table 2, entry 3). The use of methanol as a solvent resulted in a good activity (Table 2, entry 4). Changing the reaction solvent to acetonitrile significantly enhanced the activity of the catalyst producing the heck-coupling product 8aa as a predominant product (Table 2, entry 5). The conversion of 5a reached 92% by doubling the amount of palladium catalyst (Table 2, entry 6). The addition of acid as additive enhanced the formation of 8aa, while the addition of base allows the formation of 7aa chemoselectively. which suggests that the formation of 8aa and 7aa takes place via two different catalytic pathways (Table 2, entries 7,8). The attempts to increase the yield of **7aa** by adding H_2 or isopropanol were not successful; the addition of H₂ produced the hydrogenated product of the starting material (Table 2, entry 9), and isopropanol led to the Heck-coupling product 8aa in higher selectivity (Table 2, entry 10).

 TABLE 3

 Coupling of arylboronic acid (6a) to 5a catalyzed by binuclear palladium complexes (1–4)^a

Entry		Conversion 5a (%) ^b	Products distribution (%) ^c	
	Complex		7aa	8aa
1	(1)	48	20	80
2	(2)	76	33	67
3	(3)	76	28	72
4	(4)	76	33	67

^aReaction conditions: Complex (0.02 mmol), **5a** (0.50 mmol), **6a** (1.0 mmol), CH₃CN (4 ml), 110°C, 16 h. ^bDetermined by GC. ^cDetermined by GC and ¹H-NMR.

				Products distribution (%) ^c	
Entry	Olefin 5	Boronic acid 6	Conversion 5 (%) ^b	7	8
1	R = Ph, R' = COOMe	R'' = Ph	76	28	72
	5a	6a		7aa	8aa
2	R = Ph, R' = COOEt	6a	75	40	60
	5b			7ba	8ba
		Cl B(OH) ₂			
3	5a	Cl	72	32	68
		6b		7ab	8ab
4	Ph_OMe	6 a	60	36	64
	5c			7ca	8ca
5	R = H, R' = COOMe	6a	44	24	76
	5d			7da	8da
6 ^d	$R = H, R' = COCH_2CH_3$	6a	100	91	9
	5e			7ea	8ea
7	R = Ph, R' = CHO	6a	-	-	—
	5f				
8	R = Ph, R' = H	6a	79	28	72
	5g			7ga	8ga
9	$R = H, R' = CH_2OPh$	6a	11	23	77
	5h			7ha	8ha

 TABLE 4

 Reaction of various olefins (5a-h) with arylboronic acids (6a-b)^a

^aReaction conditions: Catalyst (**3**) (0.02 mmol), **5** (0.50 mmol), **6** (1.0 mmol), CH₃CN (4 mL), 110°C, 16 h. ^bDetermined by GC. ^cDetermined by GC and ¹H-NMR. ^d27% double conjugate addition products.

Acrylate esters 5c,d reacted moderately with 6a (Table 4, entries 4,5). Excellent catalytic activity and chemoselectivity of the new palladium complex (3) was observed with alkene bearing ketone group (5e). This is expected since palladium(II) catalysts promote 1,4-additions to unsaturated ketones more efficiently than to unsaturated esters (Table 4, entry 6). This is mainly due to a slow equilibration between C-enolate and water-sensitive O-enolate for ester derivatives.^[18] Surprisingly, aldehyde 5f showed no reactivity with phenylboronic acid 6a using the optimized catalyst system (Table 4, entry 7). For more screening of different electron-rich and deficient olefins, we explored the reactivity of substrates 5g-h with 6a under optimized reaction conditions. The alkene 5g was arylated effectively with higher chemoselectivity (72%) forming the heck-coupling product 8ga (Table 4, entries 8), while low conversion (11%) was obtained with 5h (Table 4, entries 9). This can be explained by the difference in electronic environment of the double bond in the studied olefins.

The catalytic activity of the binuclear palladium complexes reported herein in the absence of any base, water and oxidant additives suggests some modifications on the mechanism already proposed in the literature.^[19,20] Previous studies suggested that the regeneration of Pd(II) after each catalytic cycle is the key step for the Pd-catalyzed oxidative Heck reaction. Following the release of the coupling product from Pd(II), the Ar-Pd-H intermediate might be intercepted by a hydrogen acceptor, such as solvent or substrate, thus regenerating the Pd(II) without forming Pd(0) and so circumventing the need for traditional oxidants or base.^[17]

CONCLUSION

In summary, new binuclear palladium complexes with chelating diimines and bridging diphosphines and diimines have been synthesized and characterized. We have developed an efficient protocol for the conjugate addition and oxidative Heck coupling of arylboronic acids with both electron rich and electron deficient olefins using the new palladium complexes. The method requires neither oxidant nor base to operate, broadening the scope of palladium-catalyzed coupling reactions.

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