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Applications of a monomeric orthopalladate complex containing mixed phosphorus–nitrogen donors in the Heck reaction

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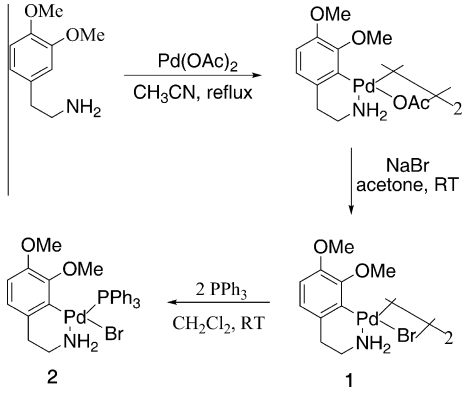
ABSTRACT

The [Pd{$C_6H_2(CH_2CH_2NH_2)$-$(OMe)_2$,3,4}Br(PPh_3)] monomeric orthopalladate complex of homoveratrylamine and triphenylphosphine was synthesized and its application in Heck coupling reactions was investigated. This complex had been demonstrated to be more active than the corresponding dimeric catalyst for Heck reactions of aryl iodides, bromides and even chlorides and also arenesulfonyl chlorides. The cross-coupled products were produced in excellent yields using catalytic amounts of [Pd{C_6H_2-$(CH_2CH_2NH_2)$-$(OMe)_2$,3,4}Br(PPh_3)] as a thermally stable and oxygen insensitive complex in NMP at 130 °C.

The Heck coupling is an important palladium-catalyzed reaction in organic synthesis.[1] Due to the many applications of Heck reactions in the synthesis of monomers, pharmaceuticals and bioactive compounds, natural products, sunscreen agents, herbicides and high performance materials, considerable efforts have been made to find new catalytic systems and methodologies to improve this reaction.[2] A relatively large amount of catalyst (1–5 mol %) is often needed for reasonable conversions in these coupling reactions.[3] Various approaches toward catalyst improvement have been described including the use of highly basic, sterically hindered phosphanes,[4] the use of a large excess of coordinating ligands, for example triphenylphosphine[5] or tris(2,4-di-*tert*-butylphenyl)phosphate (tbp),[6] the use of heterogeneous Pd/C[7] or Pd/MgO,[8] the use of nanostructured palladium clusters,[9] the use of N-heterocyclic carbenes (NHC)[10] and the use of palladacycles.[11,12] Palladacycle-containing catalysts are a very important class of catalyst in organometallic chemistry.[13,14] They have been known for over 30 years[15–20] and have been used as very efficient catalysts in very low concentrations for the synthesis of materials,[21–25] biologically active compounds[26] and macromolecules.[27–29]

In continuation of our investigations on the synthesis and applications of palladacycles in Heck reactions,[30–32] Suzuki[33] and cyanation reactions,[34,35] we report herein the synthesis of the monomeric orthopalladate complex [Pd{$C_6H_2(CH_2CH_2NH_2)$-$(OMe)_2$,3,4}Br(PPh_3)] **2**. The activity of this complex was investigated in the Heck–Mizoroki C–C cross-coupling and compared with a dimeric [Pd{$C_6H_2(CH_2CH_2NH_2)$-$(OMe)_2$,3,4}(μ-Br)]$_2$ palladacycle.



Scheme 1. The synthesis of the monomeric orthopalladate complex **2**.

The palladacycle [Pd{$C_6H_2(CH_2CH_2NH_2)$-$(OMe)_2$,3,4}(μ-Br)]$_2$ **1** was prepared according to our previous work.[30] The acetate-bridged orthopalladate complex was obtained from homoveratrylamine by addition of $Pd(OAc)_2$ in acetonitrile as a binuclear complex. The halogen-bridged orthopalladate complex was prepared by the addition of NaBr to a solution of the acetate-bridged complex in acetone. Addition of triphenylphosphine to this dimeric orthopalladate complex [Pd{$C_6H_2(CH_2CH_2NH_2)$-$(OMe)_2$,3,4}(μ-Br)]$_2$ **1** in dichloromethane gave the monomeric orthopalladate complex **2** [Pd{$C_6H_2(CH_2CH_2NH_2)$-$(OMe)_2$,3,4}Br(PPh_3)] as a yellow powder (Scheme 1).

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The structure of this palladacycle was determined by elemental analysis and ^{1}H NMR spectroscopy.

The activity of this complex was investigated in Heck–Mizoroki C–C cross-coupling reactions and compared with the dimeric palladacycle **1**. The monomeric complex contains mixed phosphorus–nitrogen (P–N) donors and was found to be more active in Heck reactions (Scheme 2) than the dimer, which contains only a single nitrogen donor.

In order to optimize the conditions, preliminary experiments were carried out on the vinylation of 4-bromobenzaldehyde with methyl acrylate using palladacycle **2**. With the intention of studying the effects of various parameters on the reaction time and yield, the reaction was carried out in various solvents with organic and inorganic bases and conventional heating at 130 °C, as shown in Table 1.

As demonstrated in Table 1 (entry 4), the use of K_2CO_3 as the base and *N*-methyl-2-pyrrolidone (NMP) as the solvent gave the best results. As the catalyst is thermally stable and not sensitive to oxygen and moisture, the reactions were carried out under air.

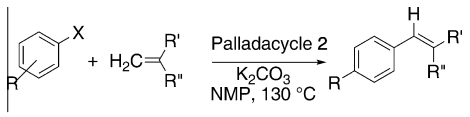
After optimization of the base and solvent, various catalyst concentrations were tested. The results in Table 2 show that 0.4 mol % of the catalyst gave the best results.

We applied the optimized conditions to the Heck cross-coupling reactions of different aryl halides with methyl acrylate, methyl methacrylate, styrene and methylstyrene using conventional heating at 130 °C (Table 3). The results showed that aryl halides with either electron-withdrawing or electron-donating substituents react with olefins and generate the coupled products in excellent yields. Also the results listed in Table 3 clearly show that the coupling reactions with methyl acrylate and methyl methacrylate as the olefin were faster than those of styrene and methylstyrene. In the case of 1-bromo-3-chlorobenzene (Table 3, entries 5, 20 and 27), this procedure activated the C–Cl bond. However, by using a stoichiometric amount of olefin, only the Br was substituted in each case. In all of the reactions, only the *E*-isomers of the products were produced.

Because of the availability of aryl chlorides, they are the best substrates for coupling reactions in comparison with their bromide or iodide analogs. This method can be used for Heck reactions of even less reactive aryl chlorides, albeit with longer reaction times (Table 3, entries 11, 12, 13 and 23).

Arenesulfonyl chlorides could also be used as the electrophilic partners in place of aryl halides under desulfinylation conditions (Table 3, entries 14, 24 and 25). Arenesulfonyl chlorides are inexpensive readily available compounds and are more reactive than the corresponding bromides and chlorides. The reactive Pd(0) catalyst undergoes oxidative addition of the SO_2–Cl bond of the sulfonyl chloride to give a chloro palladium(II) sulfinate (Ar-SO_2-Pd^{II}-Cl). At high temperature (130 °C) desulfinylation occurs rapidly and an Ar–Pd–Cl complex forms, followed by reversible coordination of the olefin. Pd(0) is formed in the main catalytic cycle, after β-hydride and reductive elimination steps.[36]

As demonstrated in Table 4, the monomeric complex **2** was more active than the dimeric complex **1**. In many Heck reactions,



X= Br, I, Cl, SO_2Cl
R= OMe, COMe, COH, Cl, CN, Me
R' =COOMe, COOH, Ph, *p*-$CH_3C_6H_4$
R" = H, Me

Scheme 2. The Heck cross-coupling reaction of aryl halides with olefins using the monomeric orthopalladate complex **2**.

Table 1
Optimization of the reaction conditions for the Heck reaction of 4-bromobenzaldehyde with methyl acrylate

Entry	Solvent	Base	Temp (°C)	Time (min)	Conversion (%)
1	NMP	Et_3N	130	180	0
2	NMP	Na_2CO_3	130	180	30
3	NMP	Cs_2CO_3	130	180	40
4	NMP	K_2CO_3	130	40	100
5	NMP	NaOAc	130	60	90
6	DMF	Et_3N	130	180	0
7	DMF	Cs_2CO_3	130	180	Trace
8	DMF	NaOAc	130	180	60
9	DMF	K_2CO_3	130	180	70
10	CH_3CN	K_2CO_3	80	180	0
11	Toluene	K_2CO_3	110	180	0

Table 2
Optimization of the catalyst concentration on the Heck reaction of 4-bromobenzaldehyde with methyl acrylate at 130 °C

Entry	Cat. (mol%)	Time (min)	Conversion (%)
1	None	120	0
2	0.02	120	40
3	0.05	120	60
4	0.1	120	85
5	0.2	100	95
6	0.3	60	100
7	0.4	40	100
8	0.5	40	100

tertiary phosphines, usually triphenylphosphine, are required to drive the reaction.[37,38]

$Pd(OAc)_2$ in combination with tertiary phosphine ligands as the catalytic system is generally reduced to the catalytically active palladium(0) species in the presence of a base.[39] The monomeric complexes are easier to reduce to the active Pd(0) species compared with the dimeric catalyst.[37]

In conclusion, the monomeric orthopalladate complex [Pd{$C_6H_2(CH_2CH_2NH_2)$-$(OMe)_2$,3,4}Br(PPh_3)] **2** is an efficient catalyst for Heck reactions of aryl bromides, aryl iodides, aryl chlorides and arenesulfonyl chlorides. This monomeric complex contains mixed phosphorus–nitrogen (P–N) donors and was found to be more reactive than the corresponding dimeric complex which contains only a single nitrogen donor.

Synthesis of the monomeric orthopalladate complex 2

The dimeric palladacycle complex **1** was prepared according to our previous work.[30] A 50 mL round-bottom flask was charged with homoveratrylamine (1.1 mmol), $Pd(OAc)_2$ (1.1 mmol) and acetonitrile (20 mL) and the contents refluxed for 4 h. The resulting suspension was filtered through a plug of $MgSO_4$. The solvent was removed under reduced pressure, and CH_2Cl_2 (2 mL) and *n*-hexane (15 mL) were added to give the acetato-bridged cyclopalladated complex as a yellow precipitate which was filtered, washed with H_2O and air-dried. Yield: 47%. To a solution of this complex (0.2 mmol) in acetone (25 mL) was added NaBr (1.94 mmol) and the suspension was stirred for 8 h. Acetone was evaporated, CH_2Cl_2 (10 mL) was added and the mixture filtered through a plug of $MgSO_4$. The filtrate was concentrated to 2 mL under reduced pressure using a rotary evaporator, and *n*-hexane (15 mL) was added. The suspension produced was filtered and air-dried to afford the dimeric complex **1** as an orange solid. PPh_3 (0.22 mmol) was added to the dimeric complex **1** (0.11 mmol) in CH_2Cl_2 (10 mL). After stirring at room temperature for 2 h the reaction mixture was concentrated. Addition of *n*-hexane afforded the monomeric complex **2** as

Table 3
Heck reactions of aryl halides under conventional heating conditions in an oil bath[a]

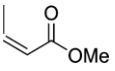
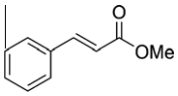
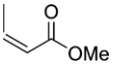
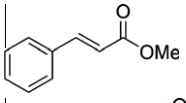
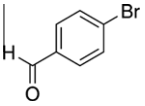
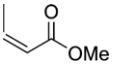
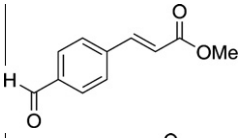
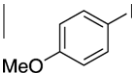
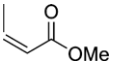
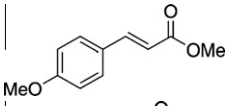
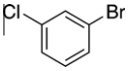
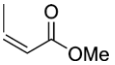
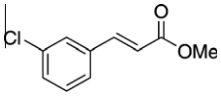
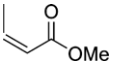
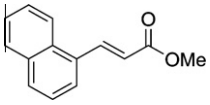
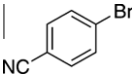
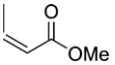
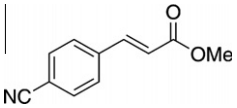
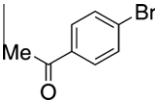
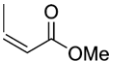
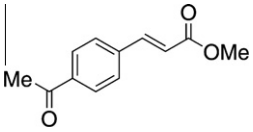
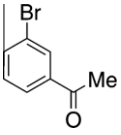
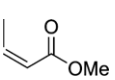
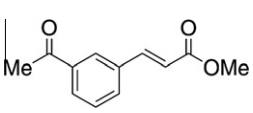
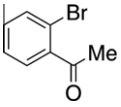
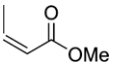
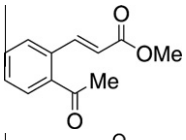
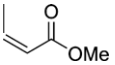
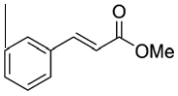
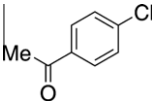
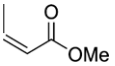
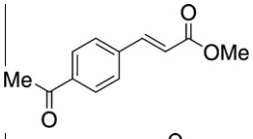
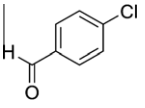
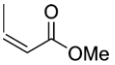
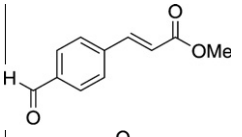
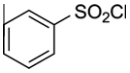
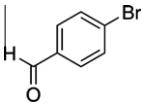
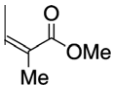
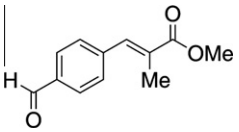
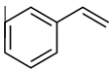
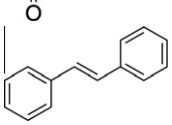
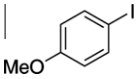
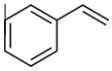
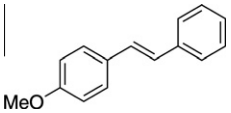
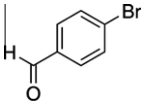
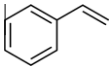
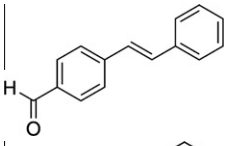
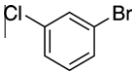
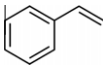
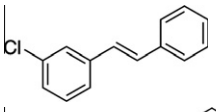
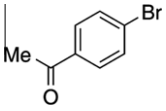
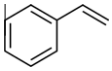
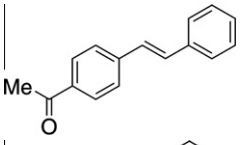
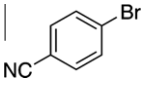
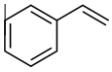
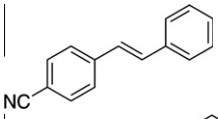
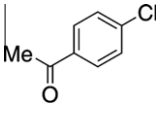
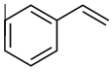
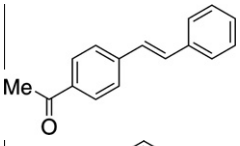
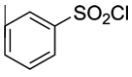
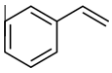
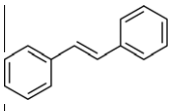
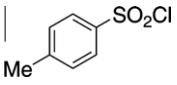
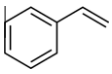
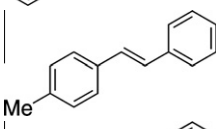
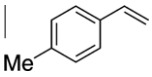
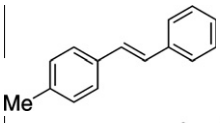
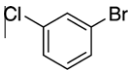
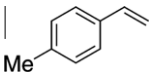
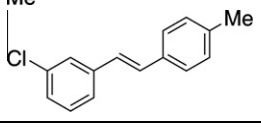
Entry	ArX	R′CH=CH$_2$	Product	Time (min)	Yield[b] (%)
1				20	95
2				30	94
3				40	96
4				25	95
5				30	94
6				150	92
7				20	95
8				35	96
9				50	87
10				120	80
11				70	85
12				60	87
13				50	89
14				50	90
15				20	96

Table 3 (*continued*)

Entry	ArX	R′CH=CH$_2$	Product	Time (min)	Yield[b] (%)
16				20	97
17				60	92
18				80	94
19				120	92
20				20	92
21				150	93
22				100	92
23				180	83
24				80	90
25				130	90
26				80	95
27				100	95

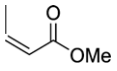
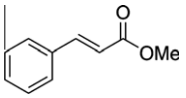
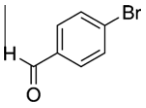
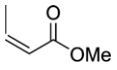
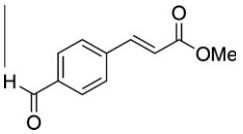
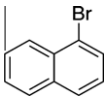
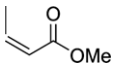
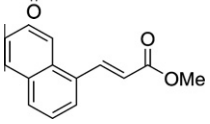
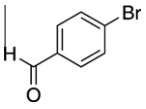
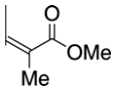
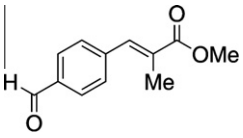
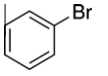
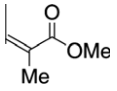
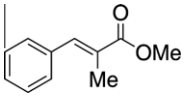
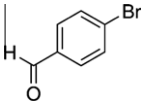
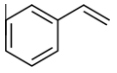
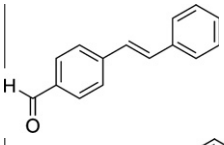
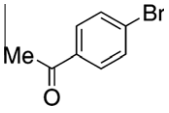
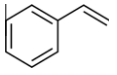
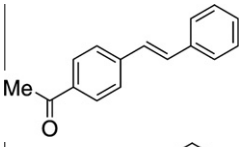
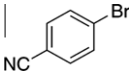
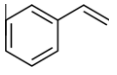
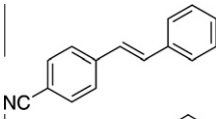
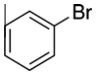
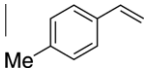
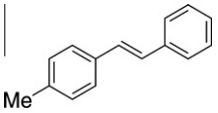
[a] Reaction conditions: aryl halide (1 mmol), olefin (2.2 mmol), K_2CO_3 (1.1 mmol), catalyst **2** (0.4 mol %), NMP; 130 °C.
[b] Isolated yield.

a yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ, 7.77–7.74 (m, 6H, PPh_3), 7.30–7.15 (m, 9H, PPh_3), 6.83 (br d, 1H, J = 7.30 Hz, C_6H_2), 6.81 (br d, 1H, J = 6.85 Hz, C_6H_2), 3.90 (s, 3H, OMe), 3.89 (s, 3H, OMe), 3.17–3.07 (m, 2H, NH_2), 2.93–2.80 (m, 2H, CH_2), 2.65–2.45 (br m, 2H, CH_2) ppm. ^{31}P NMR: 30 ppm. IR (KBr, cm^{-1}): 3298–3152 (N–H). Decomp: 180 °C. Color: yellow. Yield: 66%. Anal. Calcd for $C_{28}H_{29}BrNPO_2Pd$: C, 53.48; H, 4.66; N, 2.23. Found: C, 53.31; H, 4.71; N, 2.45.

General procedure for Heck reactions of aryl halides with olefins

To a round-bottom flask equipped with a magnetic stirring bar were added monomeric palladacycle **2** (0.4 mol %), K_2CO_3 (1.1 mmol), olefin (2.2 mmol) and aryl halide (1 mmol) in NMP (3 mL). The mixture was heated at 130 °C using an oil bath and the progress was monitored by TLC (hexane/EtOAc, 80:20) and

Table 4
Comparison of the efficiencies of the dimeric and monomeric orthopalladated complexes **1** and **2** in Heck reactions[a]

Entry	ArX	R′CH=CH$_2$	Product	Catalyst	Time (min)	Yield[b] (%)
1				**1** **2**	80 20	92 95
2				**1** **2**	240 40	80 96
3				**1** **2**	420 150	90 92
4				**1** **2**	120 20	90 97
5				**1** **2**	120 20	92 96
6				**1** **2**	180 120	87 92
7				**1** **2**	600 150	80 93
8				**1** **2**	480 100	85 92
9				**1** **2**	180 80	96 95

[a] Reaction conditions: aryl halide (1 mmol), olefin (2.2 mmol), K_2CO_3 (1.1 mmol), catalyst (0.4 mol %), NMP; 130 °C.
[b] Isolated yield.

gas chromatography (GC). After completing the reaction, the mixture was diluted with *n*-hexane (30 mL) and H_2O. The organic layer was washed with brine (20 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by recrystallization from EtOH and H_2O. The products were characterized by comparing their mp and IR, ^1H and ^{13}C NMR spectra with those reported in the literature.[30–32]

Acknowledgments

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