

Palladium complexes bearing the dipyridyl ligand: synthesis, structural studies, and use in the Heck reaction

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Abstract Two new palladium complexes derived from the di(2-pyridinyl)methanone *N*-(2-pyridinyl)hydrazone (DPMNPH) ligand are reported. The compounds were characterized by elemental analysis, spectroscopic studies, and, for the DPMNPH ligand, single-crystal X-ray diffraction analysis. The DPMNPH ligand crystallized as orthorhombic with the space group $P2_12_12_1$. The H1 atom is intramolecularly bonded to the pyridinic N4 with $N1-H1 = 0.92(3)$ Å, $H1 \cdots N4 = 1.87(2)$ Å, $N1 \cdots N4 = 2.615(2)$ Å, and $N1-H1 \cdots N4 = 137(2)^\circ$. Both complexes were excellent catalysts in the Heck reaction in the presence of base.

Keywords Di-2-pyridyl ketone (DPK) · Crystal structure of the DPMNPH ligand · Palladium complexes · Heck reaction

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Introduction

Identification of new metal complexes with interesting properties can be approached from several perspectives; one is study of the chemistry of a specific ligand in combination with different metal ions. Di-2-pyridyl ketone (DPK) has attracted much attention in chemistry since the 1960s when the first work on this ligand was reported [1, 2]. DPK, a versatile ligand of a variety of transition metal ions, forms five and six-membered chelate rings in bidentate coordination; it can thus form mononuclear, binuclear, or polynuclear complexes [3–7]. The most characteristic feature of DPK is that it can occur as a hydrated gem-diol or as an alcoholated hemiketal, via metal-promoted hydration and alcoholate reaction, respectively, at the carbonyl carbon [8]. In recent years, palladium complexes associated with electron-rich phosphine ligands have attracted much attention because of their remarkable properties as homogenous catalysts in variety of coupling reactions in organic synthesis [9, 10]. However, because phosphines have such disadvantages as toxicity, propensity to oxidize in air, high cost, and problems with synthesis, among others [11], catalysis under phosphine-free conditions is an extremely important challenge. In this context, nitrogen-based ligands are advantageous, because they are usually stable in air, inexpensive, and easier to handle than their phosphine counterparts. Recently, Schiff bases and their palladium complexes have been shown to be catalytically active in Mizoroki–Heck and Suzuki–Miyaura cross-coupling reactions, and could become alternatives to phosphine catalysts [12]. The palladium-catalyzed Heck reaction is a versatile tool for formation of C–C bonds in the synthesis of olefins and for preparation of intermediates in the synthesis of natural products and bioactive compounds [13–15]. Herein, we report two novel palladium complexes obtained from the di(2-pyridinyl)methanone *N*-(2-pyridinyl)hydrazone (DPMNPH) ligand [16], and their use as catalysts in the Heck reaction. We report, for the first time, catalytic applications of Pd(II) complexes derived from the DPMNPH ligand; both complexes had good to excellent catalytic activity in KOH. We also report the crystal structure of the DPMNPH ligand.

Experimental

Materials and methods

All reagents and solvents were of AR-grade quality from E. Merck and used as received. All manipulations of complex preparation reactions were conducted under argon by use of Schlenk-line techniques. Elemental analysis was performed with an Elementar Vario EL analyzer. FTIR (4000–400 cm^{-1}) spectra were acquired as KBr pellets by use of a Perkin–Elmer 621 spectrophotometer. ^1H NMR spectra of the DPMNPH ligand and its Pd(II) complexes were recorded in d_6 -DMSO by use of a Jeol 400 spectrometer. The thermal behavior of the synthesized compounds was studied by use of an SDTQ-600 (TA Instrument) in a helium atmosphere (100 ml min^{-1}) at a heating rate of 10 $^\circ\text{C}/\text{min}$ from 0–800 $^\circ\text{C}$. Electronic spectra

of the complexes were obtained in dichloromethane by use of a Pharmacia LKB-Biochem UV-visible spectrophotometer at room temperature.

Crystallography data collection and refinement for the DPMNPH ligand

A suitable wedge like section with approximate dimensions $0.45 \times 0.38 \times 0.05$ mm³ was mounted in epoxy resin on a glass fiber, and data were collected at room temperature by use of an Xcalibur/Oxford Diffractometer with enhanced Mo radiation, $\lambda = 0.71073$ Å and equipped with an Eos charge-coupled detector [17]. Analytical absorption corrections were applied with minimum and maximum transmission factors of 0.971 and 0.994, respectively. Cell constants were determined by use of all observed reflections. Data were reduced by use of Olex2 [18]. The structure of the DPMNPH ligand was solved by use of SHELXTL software [19], by direct methods, and refined by least squares on F^2 to $R1 = 0.0391$ [$I \geq 2\sigma(I)$] with $\theta = 3.12$ – 25.01° and diffraction measurement fraction $\theta_{\max} = 0.998$. Goodness-of-fit on $F^2 = 1.042$. All non-hydrogen atoms were refined anisotropically, with all hydrogen atoms except H1 constrained and assigned isotropic thermal values 1.2 times that of the riding atoms. H1, involved in intra molecular hydrogen bonding, was located and refined fully isotropically. The largest diffraction peak and hole were 0.115 and -0.172 e Å⁻³, respectively.

Synthesis of di(2-pyridinyl)methanone *N*-(2-pyridinyl)hydrazine, DPMNPH

An ethanol solution of DPK (0.184 mg, 1 mmol) was added dropwise to an ethanol solution of 2-hydrazinopyridine (0.109 mg, 1 mmol). The reaction mixture was heated under reflux for 3 h then left to cool at room temperature. After cooling, distilled water was added at a volume ratio up to 1:3 ($V_{\text{org}}:V_{\text{aq}}$), followed by addition of few drops of sodium hydroxide solution to neutralize the reaction mixture. The microcrystalline solid product which separated out was washed with ethanol and dried under vacuum over fused CaCl₂. The isolated solid was dissolved in THF–methanol (2:2), and the solution was left to evaporate at room temperature. After a few days, yellow crystals suitable for single crystal X-ray diffraction were obtained.

Yield 88 %, M.P. 107 °C, color, yellow; anal. calc. C, 69.80; H, 4.76; N, 25.43 %, found C, 69.56; H, 4.47; N, 25.25 %; ¹H NMR (CDCl₃, 400 MHz) δ (ppm) 6.5–9.5 (m, 12H, Py, s), 13.9 (s, 1H, HN); IR (KBr, cm⁻¹) 1640 ν (C=N).

Synthesis of Pd(II) complexes 1 and 2

[Pd(PhCN)₂Cl₂] or [Pd(OAc)₂] (1.0 mmol) dissolved in 20 ml dichloromethane was added gradually to a dichloromethane solution of DPMNPH ligand (1 mmol). The resulting reaction mixture was stirred for 30 min to give yellow colored solution which was concentrated to 1 ml followed by addition of 10 ml hexane. The colored product which precipitated was isolated and recrystallized from dichloromethane–hexane to give an analytically pure product. Despite our best efforts we could not obtain a crystal suitable for single-crystal X-ray diffraction.

Complex 1: yield 68 %, M.P. 180 °C; molecular formula $C_{16}H_{13}N_5PdCl$, anal. calc. C 49.0, H 3.14, N 16.78 %; found C 48.68, H 2.99, N 16.52 %; 1H NMR (d_6 -DMSO, 400 MHz) δ (ppm) 7.2–9.0 ppm (m, 12H, Py), 12 (s, 1H, HN); IR (KBr, cm^{-1}) 1620 $\nu(C=N)$.

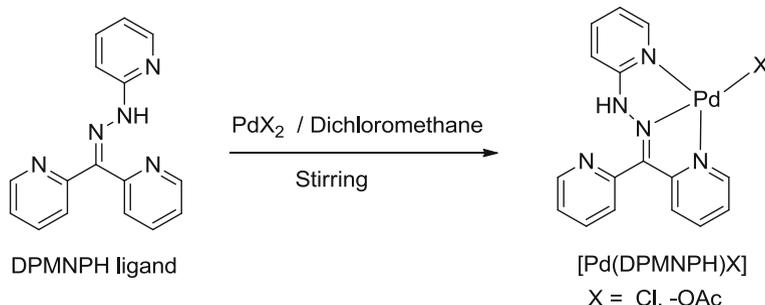
Complex 2: yield 74 %, M.P. 191 °C; molecular formula $C_{18}H_{16}N_5O_2Pd$, anal. calc. C 49.04, H 3.65, N 15.88 %; found C 48.89, H 3.42, N 15.65 %; 1H NMR (d_6 -DMSO, 400 MHz) δ (ppm) 7.3–8.9 ppm (m, 12H, Py), 13.9 (s, 1H, HN); IR (KBr, cm^{-1}) 1630 $\nu(C=N)$.

General procedure for the Heck reaction

Palladium complex (**1** or **2**) (1.0 mmol), aryl halide (1.0 mmol), methyl acrylate (1.2 mol), base (4 mmol), and DMF (10 mL) were placed in a 100-ml Schlenk tube, and the reaction mixture was subjected to a freeze–thaw cycle before being heated at 80 °C for 10 h. Completion of the reaction was monitored in situ by use of gas chromatography after a specific time. After complete conversion, the reaction mixture was cooled and extracted with ethyl acetate–hexane. The extract was filtered through a pad of silica gel with copious washing, concentrated, and purified by flash chromatography on silica gel. Product purity was checked by NMR spectroscopy.

Results and discussion

Free DPMNPH ligand, obtained by reaction of di-2-pyridyl ketone and 2-hydrazinopyridine in 1:1 molar ratio in ethanol, crystallized as chiral orthorhombic with space group $P2_12_12_1$. The ligand acts as a polydentate chelating ligand when reacted with PdX_2 ($X = Cl, OAc$) in 1:1 molar ratio, and forms mononuclear complexes (Scheme 1). The complexes were characterized by elemental analysis and by spectroscopic studies. The pure complexes were also screened for use in the Heck reaction.



Scheme 1 Schematic representation of synthesis of the Pd(I) complexes

The IR spectrum of DPMNPH contained a band at 1640 cm^{-1} , ascribed to the $\nu(\text{C}=\text{N})$ vibration, which occurred at lower wavenumbers, 1620 and 1630 cm^{-1} , for complexes **1** and **2**, respectively, confirming coordination of the palladium ion with the iminic nitrogen (Fig. 1). The corresponding vibrations for $\nu(\text{Pd}-\text{N})$ were found at 582 and 580 cm^{-1} for complexes **1** and **2**, respectively. All other bands were found at their expected positions [20–22]. The ^1H NMR spectra of the free DPMNPH ligand and its palladium complexes were recorded in d_6 -DMSO at room temperature; the spectral data are given in the “Experimental” section. The ^1H NMR spectrum of free ligand contains a singlet at 13.9 ppm , ascribed to the $-\text{N}-\text{H}$ proton. Pyridine ring proton peaks appeared as multiplets at 6.5 – 9.0 for the free ligand (Supplementary Fig. 1). However, there was little shift of the pyridyl ring protons of the palladium complexes, which appeared at 7.2 – 9.0 ppm . The $-\text{N}-\text{H}$ protons of the palladium complexes were shifted upfield and appeared at ca 12 ppm , indicating the $-\text{N}-\text{H}$ protons remained uncoordinated. An additional resonance signal ascribed to the acetate proton of complex **2** was observed at 2.85 ppm . The electronic spectrum of the free ligand, recorded in dichloromethane, contained an intense band at 290 nm , ascribed to $\pi-\pi^*$ transitions of the aromatic ring; another band at 355 nm was ascribed to $n-\pi^*$ transitions of the $\text{C}=\text{N}$ bond [23, 24]. Both palladium complexes were diamagnetic with square planar geometry, for which three spin-allowed $d-d$ transitions are expected, corresponding to transitions from the three lower-lying d -orbitals [24, 25]. The thermal decomposition behavior of the complexes was studied by TG/DTA at a heating rate of 10° min^{-1} in a nitrogen atmosphere over the temperature range 0 – 800° C . The TG/DTA profiles of both complexes revealed two distinct steps of weight loss with similar thermal decomposition patterns (Supplementary Fig. 2). For complex **2** the first decomposition step occurred at 180° C and was accompanied by weight loss of 18% , which

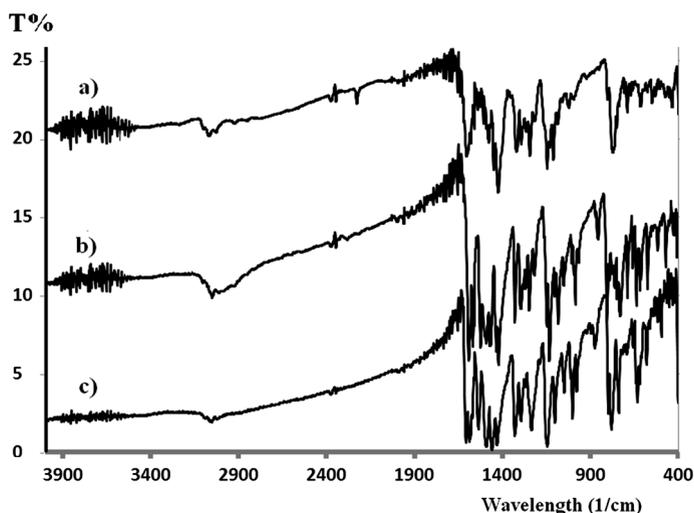


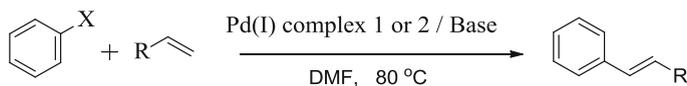
Fig. 1 FTIR spectra; *a* free ligand, *b* complex **2**, *c* complex **1**

corresponds to loss of acetate ion and moisture; DTA revealed an endothermic process at 160 °C. The second stage of decomposition starts at 181 °C and ends at 545 °C, with one broad DTA peak corresponding to an exothermic process at 331 °C, with 43 % weight loss, ascribed to loss of the pyridyl units. There was no further weight loss above 545 °C indicating that the final product, Pd–O, corresponding to a calculated mass of 28 %, has been formed (Scheme 2).

Details of data collection and refinement for the ligand are given in Tables 1, 2, 3 and 4. An Ortep drawing of the asymmetric unit (30 % probability), showing the naming scheme, is given in Fig. 2. A packing diagram with projection down the a-axis, and revealing four rather discrete molecular units, C16 H13 N5 per unit cell without π – π contacts, is shown in Fig. 3. The intra molecular N1–H1...N4 hydrogen bond of 2.615(2) Å is shown in Fig. 4. The plane passing through N1, N2, C1 is almost coplanar with the pyridinic ring containing N4, with a dihedral angle of 2.7(1)° between them; it is also not far from coplanar 10.8(1)° with the pyridinic ring containing N3. The dihedral angle N3 pyridine–N4 pyridine is 8.3(1)°. It could be said that the N1, N2, C1 plane is close to coplanar with the pyridinic rings containing N3 and N4, which implies the same π system extends over all of the atoms involved. The plane passing through N1, N2, C1, however, forms a dihedral angle of 43.7(1)° with the pyridinic ring containing N5, indicating that the π system of N5 pyridine is independent of that for the rest of the molecule. The dihedral angles N5 pyridine–N4 pyridine and N5 pyridine–N3 pyridine are 45.9(1)° and 54.1(1)°, respectively. The bond length C1–N2 = 1.305(2) Å is mainly a double bond whereas N1–N2 = 1.346(2) Å and N1–C2 = 1.379(3) Å are mainly single bonds. The sum of the bond angles around N1 is 359.8(2)°, further indicating sp² hybridization and partial double-bond nature for N1–N2 and N1–C2. The H1 atom, located and refined fully, is intramolecular hydrogen bonded to the pyridinic N4 with N1–H1 = 0.92(3) Å, H1...N4 = 1.87(2) Å, N1...N4 = 2.615(2) Å, and N1–H1...N4 = 137(2)° (Fig. 4).

Heck reaction catalyzed by palladium complexes 1 and 2

The catalytic activity of newly synthesized palladium complexes **1** was tested for the Heck coupling reaction of an aryl halide with methyl acrylate. To test the catalytic activity, aryl halide and methyl acrylate were chosen as model substrates. Initially, 10–100 mol % Pd(II) complex **1** was used in the presence of KOH (4.0 eq.) in DMF at 80 °C for 3–10 h (Table 5, entries 1–4). Yields in 10 h improved substantially, from 32 to 99 %, when catalyst loading was increased from 10 to 100 mol % (Table 5, entries 1–4). It is evident from the results that, taking



X = Cl, Br, I, R = -CO₂Me

Scheme 2 Catalytic Heck reaction of aryl halides with olefins

Table 1 Crystal data and structure refinement for di(2-pyridinyl)methanone *N*-(2-pyridinyl)hydrazone

Identification code	exp_622	
Empirical formula	C ₁₆ H ₁₃ N ₅	
Formula weight	275.31	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2 ₁ 2 ₁ 2 ₁	
Unit cell dimensions	$a = 7.9169(6)$ Å	$\alpha = 90^\circ$
	$b = 10.6433(13)$ Å	$\beta = 90^\circ$
	$c = 16.5348(14)$ Å	$\gamma = 90^\circ$
Volume	1393.3(2) Å ³	
Z	4	
Density (calculated)	1.313 mg/m ³	
Absorption coefficient	0.083 mm ⁻¹	
F(000)	576	
Crystal size	0.4528 × 0.3770 × 0.0518 mm ³	
Theta range for data collection	3.12–25.01°	
Index ranges	$-6 \leq h \leq 9, -7 \leq k \leq 12, -19 \leq l \leq 12$	
Reflections collected	3615	
Independent reflections	2270 [R(int) = 0.0178]	
Completeness to theta = 25.01°	99.8 %	
Absorption correction	Analytical	
Max. and min. transmission	0.994 and 0.971	
Refinement method	Full-matrix least-squares on F ²	
Data/restraints/variables	2270/0/194	
Goodness-of-fit on F ²	1.042	
Final R indices (I > 2σ(I))	R1 = 0.0391, wR2 = 0.0813	
R indices (all data)	R1 = 0.0519, wR2 = 0.0885	
Absolute structure variable	-1(3)	
Largest diff. peak and hole	0.115 and -0.172 e Å ⁻³	

Table 2 Bond lengths (Å) and angles (°) for di(2-pyridinyl)methanone *N*-(2-pyridinyl)hydrazone

	N(4)–C(8)	1.337(3)
	N(4)–C(7)	1.348(2)
	N(2)–C(1)	1.305(2)
	N(2)–N(1)	1.346(2)
	C(2)–N(3)	1.332(3)
	C(2)–N(1)	1.379(3)
	C(2)–C(3)	1.394(3)
Symmetry transformations were used to generate equivalent atoms	N(5)–C(12)	1.338(3)
	N(5)–C(13)	1.339(3)

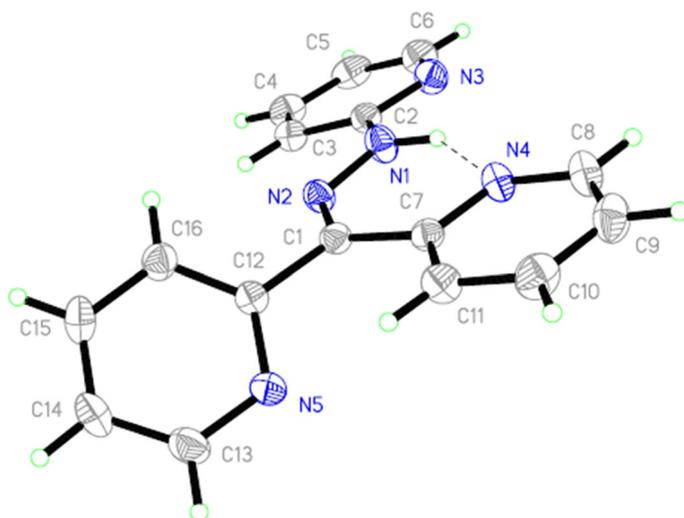
Table 3 Torsion angles (°) for di(2-pyridinyl)methanone *N*-(2-pyridinyl)hydrazone

N(1)-C(2)-N(3)-C(6)	177.3(2)	
C(3)-C(2)-N(3)-C(6)	-1.9(3)	
C(8)-N(4)-C(7)-C(11)	0.2(3)	
C(8)-N(4)-C(7)-C(1)	178.3(2)	
N(3)-C(2)-C(3)-C(4)	1.1(3)	
Symmetry transformations were used to generate equivalent atoms	C(11)-C(7)-C(1)-N(2)	176.52(19)
	N(4)-C(7)-C(1)-C(12)	177.52(17)

Table 4 Hydrogen bonds for di(2-pyridinyl)methanone *N*-(2-pyridinyl)hydrazone (Å and °)

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1)...N(4)	0.92(3)	1.87(2)	2.615(2)	137(2)

Symmetry transformations were used to generate equivalent atoms

**Fig. 2** Ortep drawing of free DPMNPH ligand

into consideration the cost of the catalyst, 50 mol % catalyst is the optimum amount for the 10-h reaction (Table 5, entries 3). To discover the optimum conditions, reactions were performed in different solvents and with several bases. With 50 mol % complex 1 at 80 °C and 10-h reaction (Table 5, entries 5–15) the best result was obtained by use of 4 eq. KOH in DMF (Table 5, entry 3). No product was obtained by use of ACN or toluene (Table 5, entries 13, 14).

To investigate substrate scope, the Heck coupling reaction was performed with bromobenzene and chlorobenzene with methyl acrylate, using the same set of

Fig. 3 Structure of the free ligand, packed along the *a*-axis

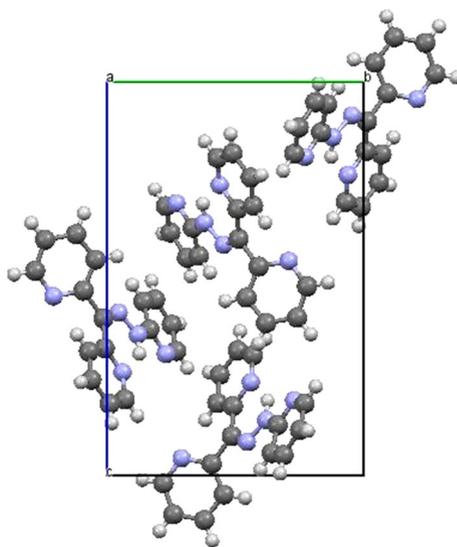
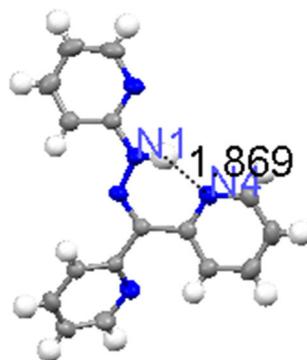


Fig. 4 Structure of the free ligand accompanied by intramolecular N1–H1...N4 hydrogen bonding



conditions (Table 5, entries 16, 17) and the results showed that bromobenzene resulted in excellent yields (93 %), in contrast with chlorobenzene (4 %).

Unfortunately, the catalysts are oxygen-sensitive and must be kept under an inert atmosphere to avoid deactivation and to maintain high activity. In addition, no conversion was observed if non-degassed DMF was used as solvent (Table 5, entry 18). Therefore, DMF was dried and deoxygenated before use, and the reactions were performed under argon. A control experiment revealed that coupling reactions did not occur in the absence of base (Table 5, entry 19). When palladium complex 2 was used for Heck coupling of aryl halides with methyl acrylate the trends were almost the same as for catalyst 1 (Table 5, entries 20–23). These results are similar to those reported elsewhere [26, 27].

Table 5 The Heck coupling reaction of aryl halides with methyl acrylate

No.	PhX	Complex no.	mol %	Base	Solvent (dry)	Yield after 3 h	Yield after 10 h
1	PhI	1	10	KOH	DMF	25	32
2	PhI	1	20	KOH	DMF	36	43
3	PhI	1	50	KOH	DMF	52	97
4	PhI	1	100	KOH	DMF	55	99
5 ^a	PhI	1	50	KOH	DMF	14	41
6 ^b	PhI	1	50	KOH	DMF	21	68
7	PhI	1	50	K ₂ CO ₃	DMF	21	71
8	PhI	1	50	Na ₂ CO ₃	DMF	24	65
9	PhI	1	50	TEA	DMF	7	12
10	PhI	1	50	NaOAc	DMF	15	19
11	PhI	1	50	K ₃ PO ₄	DMF	18	26
12	PhI	1	50	KOH	DMAc	22	53
13	PhI	1	50	KOH	ACN	–	–
14	PhI	1	50	KOH	Toluene	–	–
15	PhI	1	50	KOH	DMSO	31	59
16	PhBr	1	50	KOH	DMF	34	93
17	PhCl	1	50	KOH	DMF	0	4
18 ^c	PhI	1	50	KOH	DMF	0	0
19 ^d	PhI	1	50	–	DMF	0	0
20	PhI	2	10	KOH	DMF	15	29
21	PhI	2	20	KOH	DMF	26	63
22	PhI	2	50	KOH	DMF	55	92
23	PhI	2	50	K ₂ CO ₃	DMF	10	35

Reaction conditions: Pd(II) 10–50 mol %, aryl halide 1 mmol, methyl acrylate 1.2 mmol, base 4 mmol, in 10 mL DMF at 80 °C for 10 h, isolated yields are based on aryl halide, TON = 1000, all reactions were monitored by GC

^a Base KOH 1.5 eq. was used

^b Base KOH 3.0 eq. was used

^c Non-degassed solvent was used

^d No-base was added

Conclusion

In this work we prepared and characterized two new palladium complexes with DPMNPH ligand. The structure of the ligand was determined by single crystal X-ray diffraction analysis, and both the complexes were studied by elemental analysis and by spectroscopic studies. Both the new palladium complexes were tested for catalytic activity, and were found to be highly efficient homogeneous catalysts of the Heck reaction.

Supplementary materials

CCDC 1035466 contains the supplementary crystallographic data for the ligand DPMNPH. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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