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N-Heterocyclic Carbenes

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Westfälische Wilhelms-Universität, Münster, Germany

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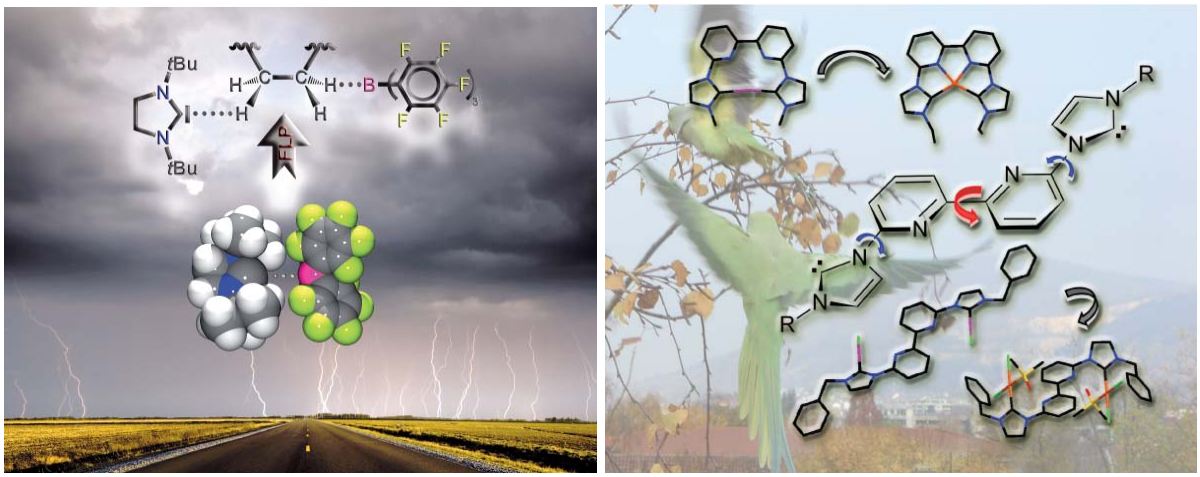

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Aqueous-phase Suzuki–Miyaura cross-coupling reactions catalyzed by Pd-NHC complexes

Hayati Türkmen, Rahime Can and Bekir Çetinkaya*

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Cleavage reactions of $[PdBr_2(NHC)]_2$ with two equiv. of pyridine derivatives (L), having one or two carboxylic acid groups [L = NC_5H_4-2-COOH, NC_5H_4-3-COOH, NC_5H_4-4-COOH, or NC_5H_3-2,6-$(COOH)_2$ in chloroform or DMSO, respectively, afforded the monomeric mixed ligand complexes *trans*-$[PdBr_2(NHC)L]$ (**1–4**) which, due to deprotonation of the carboxylic acid functionality, are water soluble in KOH. The catalytic activity of complexes **1–4** in aqueous Suzuki–Miyaura cross-coupling reactions were evaluated and compared. The dicarboxylic functionality enhances the catalyst reactivity and stability and the carboxylate derived from **4** could be easily recovered and reused for several cycles under the mild reaction conditions.

1. Introduction

The Suzuki–Miyaura reactions, catalyzed by palladium complexes have been commonly employed to generate functionalized biaryls. Since the first report in the early 1980s, a large number of supporting ligands, such as phosphines and N-heterocyclic carbenes (NHCs) have been developed as good catalysts for various C–C cross-coupling reactions.[1,2]

Because they are stable towards air and moisture and tolerant to a variety of functional groups, Pd(NHC) complexes are particularly useful catalysts for this purpose.[3,4] In practice, the steric and electronic properties of the NHC framework composed of two N atoms and a hetero ring, can be tuned by altering the substituents on either portion. Therefore, many reports have since 1995 appeared describing studies of structurally varied complexes.[5]

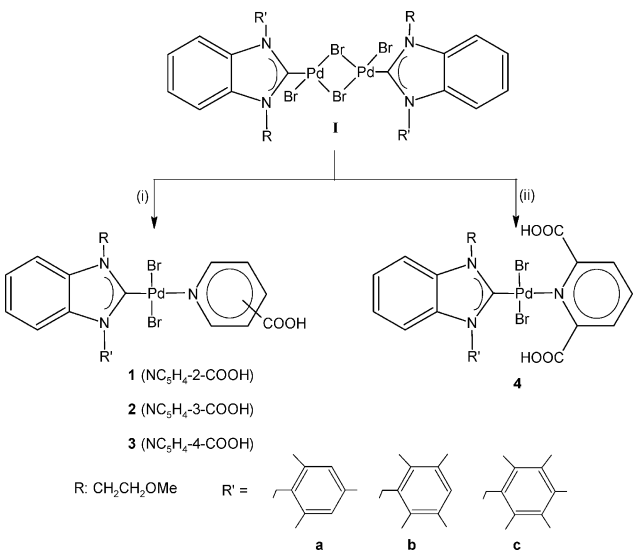
Although the C–C coupling reactions, catalyzed by the Pd(NHC) complexes in organic solvents is well-developed, its potential utility in water is largely limited.[6] Water is an attractive replacement for organic solvents because it is inexpensive, renewable, nontoxic, and nonflammable.[7] Furthermore, the use of water-soluble metal complexes allows an easy separation of the catalyst and the organic reagents, and in principle, combines the virtues of conventional homogeneous and heterogeneous systems. The implementation of aqueous catalysis is due to lack of suitable catalysts. To address this need we synthesized a series of new palladium NHC complexes bearing pyridinecarboxylic acids (**1–4**) and we studied their application in Suzuki–Miyaura cross-coupling reactions. The immediate goals of our studies were to evaluate the effect of new monomeric catalysts on the reactivity and to further determine the extent of their recovery and recycling in water.

2. Results and discussion

Meanwhile, the NHC ligand is widely utilized as an ancillary ligand in coordination and organometallic complexes.[8] Recently, Organ and coworkers reported a combination of Pd(NHC) with PEPPSI (PEPPSI = Pyridine Enhanced Precatalysts Preparation, Stabilization and Initiation) and successfully applied as the cross-coupling catalysts.[9] However, to our knowledge no pyridine derivatives containing carboxyl group, have been utilized as a supporting ligand for the complexation, which will provide a straightforward approach to water-soluble NHC complexes in basic media.

2.1. Synthesis of Pd(II) complexes, 1–4

The dimeric complexes of the type $[PdX_2(NHC)]_2$ can be readily prepared and cleaved by various nucleophiles to give mixed [Pd(NHC)(nuc)] complexes.[10–15] Therefore, we applied this concept to the dimer **I** to obtain *trans*-$[PdBr_2(NHC)L]$ (NHC = 1,3-dialkylbenzimidazol-2-ylidene; L = pyridinecarboxylic acid) complexes of the type. Scheme 1 shows the synthetic routes used to prepare the desired complexes which have carboxylic acid(s) groups on different position of the pyridine ring.



Scheme 1 Reagents and conditions: (i) pyridinecarboxylic acid, $CHCl_3$, 25 °C, 24 h; (ii) pyridine-2,6-dicarboxylic acid, DMSO, 25 °C, 24 h.

Department of Chemistry, Ege University, 35100, Bornova-Izmir, Turkey

Table 1 Comparison of selected spectroscopic data of complexes, **1–4**

Complex	IR($\nu_{C=O}$, ν_{O-H}, cm^{-1})	NMR (^{13}C, C–Pd, ppm)	UV-visible (nm)
1a	1752, 3712	161.1	231, 274, 280, 351
1b	1735, 3650	161.2	233, 270, 284, 350
1c	1739, 3674	161.3	230, 272, 279, 354
2a	1752, 3712	162.4	240, 273, 361
2b	1703, 3433	162.6	243, 246, 271, 361
2c	1731, 3423	162.6	234, 241, 244, 274, 361
3a	1750, 3722	163.5	235, 245, 274, 362
3b	1759, 3712	163.1	233, 242, 271, 362
3c	1705, 3437	163.1	233, 240, 242, 273, 362
4a	1740, 3498	160.5	240, 277, 2.80, 351
4b	1750, 3712	160.6	233, 272, 2.81, 352
4c	1742, 3502	160.9	239, 279, 2.83, 352

All new complexes have been isolated as yellow and air-stable solids. They are insoluble in nonpolar solvents such as diethyl ether, hexane, pentane or toluene, but soluble in DMSO, DMF, C_2H_5OH and H_2O. The complexes were characterized by elemental analysis, by their IR, NMR and UV-visible spectroscopy (Table 1 lists some selected data). The formation of the metal complexes were evident from the distinctive Pd-$C_{carbene}$ peak, appeared at *ca.* 160.5–163.5 ppm for **1–4**. This data suggests that the weakest σ-donor leads to the most upfields ^{13}C chemical shift.[12,15] Furthermore, a comparison of such chemical shift to that of {[$PdBr_2$(1,3-diisopropylbenzimidazolylidene)Py], Py = pyridine, 4,4′-bipyridine, 4,4′-bipridylethane, 4,4′-bipridylethylene}complexes clearly confirm the *trans*-configuration proposed for **1–4**.[12c] The IR spectra of compounds **1–4** displayed absorption bands at 1703–1759 cm^{-1} due to ν(COO), and broad bands between 3423 and 3722 cm^{-1} due to ν(O–H). From the IR data we may infer that the COOH group(s) on the pyridine ring were not involved in metal-bonding, at least under neutral conditions. Whilst, the versatility of 2-pyridinecarboxylic or 2,6-pyridinedicarboxylic acids as multidentate ligands is well known.[16]

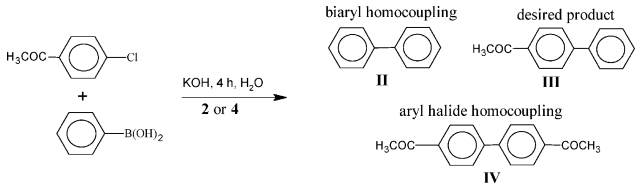
The UV-visible absorption spectral data obtained for complexes, **1–4**, in CH_2Cl_2 are summarized in Table 1. The mixed NHC/pyridinecarboxylic acid complexes, **1–4**, showed weak absorption bands and 350–362 nm corresponding to the metal-to-ligand charge transfer (MLCT).[17] The absorbance maxima spectra of complexes **1–4** exhibited at 240–283 nm, which are assigned to intraligand π → π* transitions.

2.2. Suzuki coupling of aryl halides and phenylboronic acid

We have found that the NHC ligands containing the asymmetric substituents on the N atoms of the ring are more efficient than the symmetrical ones for C–C coupling reactions.[11] Therefore, we have chosen the NHC substituents shown in Scheme 1. First of all, we studied the influence of temperature on the distribution of the possible coupling products (**II–IV**) formed from *p*-chloroacetophenone-phenylboronic acid in the presence of (**2**) and (**4**) and observed that as the temperature increased the yield of desired product (**III**) also increased (Table 2).

At room temperature biphenyl formation from the homocoupling of phenylboronic acid is a dominant reaction which gradually subsides as the temperature rises. Therefore, we set to 100 °C as the standard temperature.

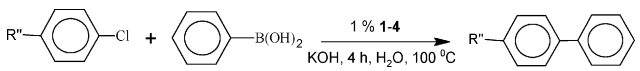
Table 2 Effect of temperature on the Suzuki coupling reaction catalyzed by **2** or **4**[a]



Complex	Temperature (°C)	Conversion (%)	**II** (%)	**III** (%)	**IV** (%)
2a (**4a**)	25	80(83)	60(61)	14(11)	5(9)
2b (**4b**)	25	77(78)	57(59)	13(12)	4(5)
2c (**4c**)	25	82(81)	58 (63)	13(14)	8(3)
2a (**4a**)	50	87(88)	51(52)	27(30)	3(4)
2b (**4b**)	50	80(85)	55(58)	20(22)	5(3)
2c (**4c**)	50	83(88)	42(48)	32(34)	4(4)
2a (**4a**)	80	88(89)	20(21)	62(64)	4(2)
2b (**4b**)	80	90(91)	20(20)	67(66)	2(3)
2c (**4c**)	80	93(94)	13(12)	76(78)	3(3)
2a (**4a**)	100	100(100)	04(05)	89(93)	—
2b (**4b**)	100	100(100)	05(03)	81(91)	—
2c (**4c**)	100	100(100)	03(01)	94(96)	—

[a] Yields were determined by gas chromatography for an average of two runs.

Table 3 The Suzuki coupling reaction of aryl chlorides with phenylboronic acid[a]



Yield (%)

Entry	R″	**1a**	**1b**	**1c**	**2a**	**2b**	**2c**	**3a**	**3b**	**3c**	**4a**	**4b**	**4c**
1	CH_3CO	92	90	93	89	81	94	87	85	88	93	91	96
3	CHO	89	87	92	82	81	84	83	83	87	91	88	92
2	CH_3	86	83	88	83	83	88	84	82	86	89	85	89
4	CH_3O	81	80	89	75	74	77	70	71	75	87	85	88

[a] Yields was determined by gas chromatography for an average of two runs.

In order to determine the influence of the ligands *i.e.* NHC and pyridinecarboxylic acids (L) on the Suzuki reaction in neat water, the coupling reaction of *p*-chloroacetophenone and phenylboronic acid was selected as a model reaction and KOH was used as the base. The yield of unsymmetrical biaryls (**III**) ranged from 81% to 96% (Table 3, Entry 1). The activated and unactivated aryl chloride substrates also were treated under identical conditions (Table 3, Entries 2–4), to give good to excellent yields of the biaryls. The similar reactivity trends with our previous report[11] is in agreement with the stronger donating ability of alkyl substituents, making the donor atoms more electron-rich. Among the complexes tested, **1** and **4** gave the highest yield while complexes **2** and **3**, with 3- and 4-pyridinecarboxylic acids gave moderate or good yields. This result implies that the COOH(K) functionality *ortho* to the N atom of the pyridine has some influence on the stability of active species.

2.3 Catalyst recycling

The potential recyclability of the catalysts derived from the **4c** system was explored in the model cross-coupling of 4-chloroacetophenone and phenylboronic acid (Fig. 1). The reaction

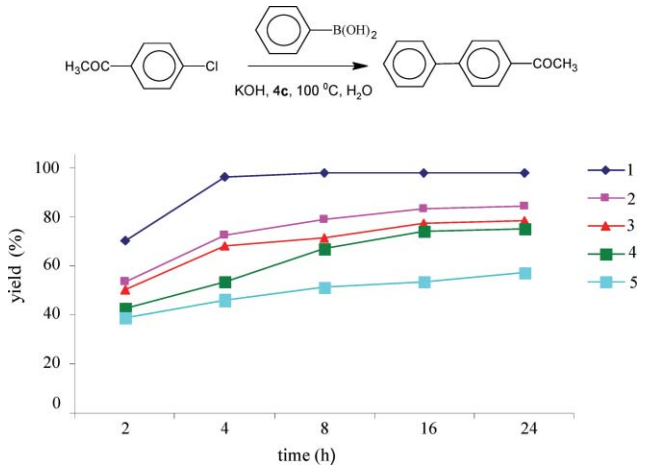


Fig. 1 Recycling of catalyst **4c**.

was carried out in water at 100 °C without any additive. After cooling to room temperature, the organic products were extracted by dichloromethane and the yields were determined by GC. The aqueous phase was then transferred to a new reaction flask for the next cycle. It was shown that the coupling reaction using 1 mol% catalyst could be reused by two cycles and the yield significantly dropped to *ca.* 52% for the fourth cycle. On the other hand, the experiments with the substrate 4-bromoacetophenone can be recycled three times with 90% yield.

Precipitation of palladium black was observed during the heating of reaction mixtures which may be the main reason for the short cut in the recycling attempts. Therefore, efforts are underway to use similar palladium complexes with increased steric bulk around the metal center, which should increase the thermal stability of the active species and activity of the precatalyst by facilitating the reductive elimination step of the catalytic cycle.

3. Conclusion

To render bromo bridged dimeric palladium-NHC complexes (**I**) water soluble, they were cleaved with pyridinecarboxylic acids, since such catalysts have potential applications in industry. The resulting monomeric complexes have been studied for their catalytic properties in the Suzuki coupling reaction of aryl chlorides and phenylboronic acid in neat water under ambient atmosphere with low catalyst loading (1 mol%). The coupling of 4-bromoacetophenone with $PhB(OH)_2$ gave yield and recyclibility. In the case of aryl chlorides, higher temperatures were required. A temperature of 100 °C decreased the formation of homo coupling by-products to a negligible amount in neat water.

4. Experimental

General procedures

All reactions for the preparation of salts were carried out under Ar in flame-dried glass-ware using standard Schlenk-type flasks. Anhydrous solvents were either distilled from appropriate drying agents or purchased from Merck and degassed prior to use by purging with dry argon and kept over molecular sieves. NMR spectra were recorded at 297 K on a Varian Mercury AS 400 NMR spectrometer at 400 MHz (^{1}H), 100.56 MHz (^{13}C). Elemental analyses were carried out by the analytical service of TUBITAK with a Carlo Erba Strumentazione Model 1106 apparatus. The yields of C–C coupling products were determined by using Trace GC Ultra Thermo Al 3000.

General procedure for the Suzuki coupling reactions

A two-necked 25 mL flask fitted with a reflux condenser was charged with aryl chlorides (1.0 mmol), 2 mmol KOH, phenylboronic acid (1.5 mmol), diethyleneglycol-di-*n*-butylether (0.6 mmol, internal standard), then 1.0% **1–4** in 6 mL of H_2O was added. The flask was placed in a preheated oil bath (100 °C) under air atmosphere, temperature 100 °C, 4 h. The conversion was monitored by gas chromatography. Yields were determined by gas chromatography for an average of two runs.

Recycling of catalyst

The flask was charged with catalyst **4c**, 4-bromoacetophenone (4-chloroacetophenone) (1.0 mmol), 2 mmol KOH, phenylboronic acid (1.5 mmol), and diethyleneglycol-di-*n*-butylether (0.6 mmol, internal standard). The reaction was carried out in water at 100 °C. After cooling to room temperature, the organic products were extracted by dichloromethane. The aqueous phase was then transferred to a new reaction flask for the next cycle. Yields were determined by gas chromatography.

General procedure for the preparation of the mixed NHC/pyridine carboxylic acid complexes of palladium(II), 1–4. A sample of dimeric complexes **1** (0.25 mmol) and pyridinecarboxylic acid, C_5H_4NCOOH (0.5 mmol) were dissolved in 15 mL of chloroform; in the case of pyridine-2,6-dicarboxylic acid, DMSO (15 mL) was used as solvent. The mixture was stirred at ambient temperature for 24 h. The solvent was removed in vacuo. The solid residue obtained was dissolved in a few milliliters of ethanol, and the solution was added dropwise to diethyl ether (30 mL). The cream precipitate obtained was collected by filtration, washed with 10 mL of diethyl ether, and dried in vacuo.

{*N*-(2,4,6-trimethylbenzyl)-*N*′-(2-metoxyethyl)benzimidazoline-2-ylidene}(pyridine-2-carboxylic acid) palladium(II) dibromide, 1a. Yield: 0.27 g, 78%. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.78 (d, 1H, J = 4.8 Hz, C_5H_5NCOOH), 8.12 (m, 2H, C_5H_5NCOOH), 7.90 (d, 1H, J = 7.62.0 Hz, Ar-H), 7.73 (m, 1H, C_5H_5NCOOH), 7.50 (t, 1H, J = 7.6 Hz, Ar-H), 7.40 (t, 1H, J = 7.6 Hz, Ar-H), 7.30 (d, 1H, J = 7.6 Hz, Ar-H), 7.02 (s, 2H, $CH_2C_6H_2(CH_3)_3$), 5.93 (s, 2H, $CH_2C_6H_2(CH_3)_3$), 5.00 (t, 2H, J = 5.2 Hz, $NCH_2CH_2OCH_3$), 4.12 (t, 2H, J = 5.2 Hz, $NCH_2CH_2OCH_3$), 3.31 (s, 3H, $NCH_2CH_2OCH_3$), 2.36 (s, 3H, $CH_2C_6H_2(CH_3)_3$), 2.23 (s, 6H, $CH_2C_6H_2(CH_3)_3$). ^{13}C NMR (100 MHz, DMSO-d_6): δ 166.1 (C_5H_5NCOOH), 161.4 (C-Pd), 153.3, 149.2, 140.2, 138.9, 138.6, 135.7, 134.5, 133.0, 130.0, 129.5, 128.4, 125.6, 124.3, 112.4, 111.2 (Ar-C, $C_5H_5NCOONa$, $C_6H_2(CH_3)_3$), 71.2 ($NCH_2CH_2OCH_3$), 59.0 ($NCH_2CH_2OCH_3$), 49.4 ($CH_2C_6H_2(CH_3)_3$), 48.5 ($NCH_2CH_2OCH_3$), 21.5, 21.0 ($CH_2C_6H_2(CH_3)_3$). IR(CH_2Cl_2): $\nu_{C=O}$ 1752 cm^{-1}, ν_{O-H} 3712 cm^{-1}. Anal. Calc. for $C_{26}H_{29}Br_2N_3O_3Pd$ (697.75): C 44.75, H 4.19, N 6.88, Found C 44.71, H 4.11, N 6.97%.

{*N*-(2,3,5,6-tetramethylbenzyl)-*N*′-(2-metoxyethyl)benzimidazoline-2-ylidene}(pyridine-2-carboxylic acid) palladium(II) dibromide, 1b. Yield: 0.27 g, 75%. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.74 (d, 1H, J = 4.8 Hz, C_5H_4NCOOH), 8.11 (m, 2H, C_5H_4NCOOH), 7.77 (d, 1H, J = 4.7 Hz, C_5H_4NCOOH), 7.73 (t, 1H, J = 7.6 Hz, Ar-H), 7.67 (d, 1H, J = 7.6 Hz, Ar-H), 7.22 (t, 1H, J = 7.6 Hz, Ar-H), 7.14 (s, 1H, $CH_2C_6H(CH_3)_4$), 6.85 (d, 1H, J = 7.6 Hz, Ar-H), 5.98 (s, 2H, $CH_2C_6H(CH_3)_4$), 4.95 (t, 2H, J = 5.2 Hz $NCH_2CH_2OCH_3$), 4.14 (t, 2H, J = 5.2 Hz, $NCH_2CH_2OCH_3$), 3.27 (s, 3H, $NCH_2CH_2OCH_3$), 2.22 (s, 6H, $CH_2C_6H(CH_3)_4$), 2.13 (s, 6H, $CH_2C_6H(CH_3)_4$). ^{13}C NMR (100 MHz, DMSO-d_6): δ 166.0 (C_5H_4NCOOH), 161.2 (C-Pd), 153.5, 149.0, 140.7, 139.9, 138.0, 13.1, 133.5, 133.9, 131.0, 128.5, 128.3, 125.2, 124.3, 111.9, 111.0 (Ar-C, C_5H_4NCOOH, $CH_2C_6H(CH_3)_4$), 71.0 ($NCH_2CH_2OCH_3$), 58.9 ($NCH_2CH_2OCH_3$), 49.9 ($CH_2C_6H_2(CH_3)_3$), 48.6 ($NCH_2CH_2OCH_3$), 20.9, 20.0 ($CH_2C_6H(CH_3)_4$). IR(CH_2Cl_2): $\nu_{C=O}$ 1735 cm^{-1}, ν_{O-H} 3650 cm^{-1}. Anal. Calc. for $C_{27}H_{31}Br_2N_3O_3Pd$ (711.78): C 45.56, H 4.39, N 5.90. Found C 45.50, H 4.41, N 5.97%.

{*N*-(pentamethylbenzyl)-*N*′-(2-metoxyethyl)benzimidazoline-2-ylidene}(pyridine-2-carboxylic acid) palladium(II) dibromide, 1c. Yield: 0.28 g, 78%. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.72 (d, 1H, J = 5.2 Hz, C_5H_4NCOOH), 8.11 (m, 2H, C_5H_4NCOOH), 7.77 (d, 1H, J = 4.8 Hz, C_5H_4NCOOH), 7.66 (d, 1H, J = 7.8 Hz, Ar-H), 7.44 (t, 1 H, J = 7.8 Hz, Ar-H), 7. 28 (t, 1 H, J = 7.8 Hz, Ar-H), 7.17 (d, 1H, J = 7.8 Hz, Ar-H), 5.91 (s, 2 H, $CH_2C_6(CH_3)_5$), 4.98 (t, 2H, J = 5.6 Hz $NCH_2CH_2OH_3$), 4.11 (t, 2H, J = 5.6 Hz, $NCH_2CH_2OCH_3$), 3.33 (s, 3H, $NCH_2CH_2OCH_3$), 2.20, 2.17 (s, 15H, $CH_2C_6(CH_3)_5$). ^{13}C NMR (100 MHz, DMSO-d_6): δ 166.0 (C_5H_4NCOOH), 161.3 (C-Pd), 153.9, 147.9, 139.9, 136.5, 134.9, 133.2, 131.0, 130.3, 128.7, 128.5, 125.5, 123.8, 123.3, 112.0, 111.2 (Ar-C, C_5H_4NCOOH, $CH_2C_6H(CH_3)_4$), 70.9 ($NCH_2CH_2OCH_3$), 59.0 ($NCH_2CH_2OCH_3$), 49.8 ($CH_2C_6H_2(CH_3)_3$), 48.5 ($NCH_2CH_2OCH_3$), 20.1, 19.9, 17.7 ($CH_2C_6(CH_3)_5$). IR(Nujol): $\nu_{C=O}$ 1739 cm^{-1}, ν_{O-H} 3674cm^{-1}. Anal. Calc. for $C_{28}H_{33}Br_2N_3O_3Pd$ (725.81): C 46.33, H 4.58, N 5.79. Found C 46.41, H 4.62, N 5.77%.

{*N*-(2,4,6-trimethylbenzyl)-*N*′-(2-metoxyethyl)benzimidazoline-2-ylidene}(pyridine-3-carboxylic acid) palladium(II) dibromide, 2a. Yield: 0.24 g, 70%. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.21 (s, 1H, C_5H_4NCOOH), 8.95 (s, 1H, C_5H_4NCOOH), 8.41 (d, 1H, J = 6.8 Hz, C_5H_4NCOOH), 7.69 (b, 2H, C_5H_4NCOOH, Ar-H), 7.27 (t, 1H, J = 7.6 Hz, Ar-H), 7.14 (t, 1H, J = 7.6 Hz, Ar-H), 6.99 (d, 1H, J = 8.0 Hz, Ar-H), 6.92 (s, 2H, $CH_2C_6H_2(CH_3)_3$), 5.87 (s, 2H, $CH_2C_6H_2(CH_3)_3$), 5.00 (b, 2H, $NCH_2CH_2OCH_3$), 4.16 (t, 2 H, J = 5.2 Hz, $NCH_2CH_2OCH_3$), 3.26 (s, 3 H, $NCH_2CH_2OCH_3$), 2.26 (s, 3 H, $CH_2C_6H_2(CH_3)_3$), 2.21 (s, 6 H, $CH_2C_6H_2(CH_3)_3$). ^{13}C NMR (100 MHz, DMSO-d_6): 165.5 (C_5H_4NCOOH), 162.4 (C-Pd), 155.9, 153.3, 140.0, 138.7, 135.5, 134.9, 130.1, 128.8, 128.5, 125.6, 124.5, 123.8, 123.6, 112.5, 111.2 (Ar-C, C_5H_4NCOOH, $C_6H_2(CH_3)_3$), 71.4 ($NCH_2CH_2OCH_3$), 59.1 ($NCH_2CH_2OCH_3$), 49.2 ($CH_2C_6H_2(CH_3)_3$), 48.7 ($NCH_2CH_2OCH_3$), 21.4, 21.3 ($CH_2C_6H_2(CH_3)_3$). IR(CH_2Cl_2): $\nu_{C=O}$ 1752 cm^{-1}, ν_{O-H} 3712 cm^{-1}. Anal. Calc. for $C_{26}H_{29}Br_2N_3O_3Pd$ (697.75): C 44.75, H 4.19, N 6.88. Found C 44.81, H 4.12, N 6.77%.

{*N*-(2,3,5,6-tetramethylbenzyl)-*N*′-(2-metoxyethyl)benzimidazoline-2-ylidene}(pyridine-3-carboxylic acid) palladium(II) dibromide, 2b. Yield: 0.28 g, 80%. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.19 (s, 1H, C_5H_4NCOOH), 8.91 (b, 1H, C_5H_4NCOOH), 8.34 (d, 1H, J = 6.4 Hz, C_5H_4NCOOH), 7.72 (b, 2H, C_5H_4NCOOH, Ar-H), 7.30 (t, 1H, J = 7.6 Hz, Ar-H), 7.18 (t, 1H, J = 7.6 Hz, Ar-H), 7.11 (s, 1H, $CH_2C_6H(CH_3)_4$), 7.04 (d, 1H, J = 7.6 Hz, Ar-H), 5.93 (s, 2 H, $CH_2C_6H(CH_3)_4$), 5.02 (t, 2H, J = 5.2 Hz $NCH_2CH_2OCH_3$), 4.18 (t, 2H, J = 5.6 Hz, $NCH_2CH_2OCH_3$), 3.28 (s, 3H, $NCH_2CH_2OCH_3$), 2.17 (s, 6 H, $CH_2C_6H(CH_3)_4$), 2.12 (s, 6H, $CH_2C_6H(CH_3)_4$). ^{13}C NMR (100 MHz, DMSO-d_6): δ 165.5 (C_5H_4NCOOH), 162.6 (C-Pd), 155.8, 153.3, 139.9, 135.4, 135.1, 135.0, 134.4, 132.7, 131.6, 128.4, 125.5, 123.8, 123.6, 112.4, 111.2 (Ar-C, C_5H_4NCOOH, $CH_2C_6H(CH_3)_4$), 71.3 ($NCH_2CH_2OCH_3$), 59.1 ($NCH_2CH_2OCH_3$), 49.7 ($CH_2C_6H_2(CH_3)_3$), 48.8 ($NCH_2CH_2OCH_3$), 20.9, 17.1 ($CH_2C_6H(CH_3)_4$). IR(CH_2Cl_2): $\nu_{C=O}$ 1703 cm^{-1}, ν_{O-H} 3433 cm^{-1}. Anal. Calc. for $C_{27}H_{31}Br_2N_3O_3Pd$ (711.78): C 45.56, H 4.39, N 5.90. Found C 45.48, H 5.83, N 5.97%.

{*N*-(pentamethylbenzyl)-*N*′-(2-metoxyethyl)benzimidazoline-2-ylidene}(pyridine-3-carboxylic acid) palladium(II) dibromide, 2c. Yield: 0.31 g, 85%. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.25 (s, 1H, C_5H_4NCOOH), 8.94 (b, 1H, C_5H_4NCOOH), 8.44 (d, 1H, J = 6 Hz, C_5H_4NCOOH), 7.70 (d, 2H, J = 8.4 Hz, C_5H_4NCOOH, Ar-H), 7.27 (t, 1H, J = 7.8 Hz, Ar-H), 7.12 (t, 1H, J = 7.8 Hz, Ar-H), 6.83 (d, 1H, J = 6.4 Hz, Ar-H), 5.97 (s, 2 H, $CH_2C_6(CH_3)_5$), 5.01 (t, 2H, J = 5.4 Hz $NCH_2CH_2OCH_3$), 4.18 (t, 2H, J = 5.6 Hz, $NCH_2CH_2OCH_3$), 3.28 (s, 3H, $NCH_2CH_2OCH_3$), 2.27, 2.17 (s, 15H, $CH_2C_6(CH_3)_5$). ^{13}C NMR (100 MHz, DMSO-d_6): δ 165.6 (C_5H_4NCOOH), 162.6 (C-Pd), 155.9, 153.3, 139.9, 135.9, 135.6, 134.9, 134.6, 133.3, 128.6, 128.5, 125.5, 123.8, 123.5, 112.4, 111.2 (Ar-C, C_5H_4NCOOH, $CH_2C_6H(CH_3)_4$), 71.3 ($NCH_2CH_2OCH_3$), 59.1 ($NCH_2CH_2OCH_3$), 50.8 ($CH_2C_6H_2(CH_3)_3$), 48.7 ($NCH_2CH_2OCH_3$), 18.1, 17.7, 17.4 ($CH_2C_6(CH_3)_5$). IR(CH_2Cl_2): $\nu_{C=O}$ 1731 cm^{-1}, ν_{O-H} 3423 cm^{-1}. Anal. Calc. for $C_{28}H_{33}Br_2N_3O_3Pd$ (725.81): C 46.33, H 4.58, N 5.79. Found C 46.40, H 4.47, N 5.87%.

{*N*-(2,4,6-trimethylbenzyl)-*N*′-(2-metoxyethyl)benzimidazoline-2-ylidene}(pyridine-4-carboxylic acid) palladium(II) dibromide, 3a. Yield: 0.27 g, 79%. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.89 (b, 2H, C_5H_4NCOOH), 7.92 (b, 2H, C_5H_4NCOOH), 7.69 (d, 1H, J = 8.4 Hz, Ar-H), 7.26 (t, 1H, J = 7.8 Hz, Ar-H), 7.12 (t, 1 H, J = 7.8 Hz, Ar-H), 6.94 (s, 2H, $CH_2C_6H_2(CH_3)_3$), 6.83 (d, 1H, J = 7.6 Hz, Ar-H), 5.90 (s, 2 H, $CH_2C_6H(CH_3)_4$), 4.99 (b, 2H, $NCH_2CH_2OCH_3$), 4.17 (b, 2H, $NCH_2CH_2OCH_3$), 3.26 (s, 3H, $NCH_2CH_2OCH_3$), 2.28 (s, 3 H, $CH_2C_6H_2(CH_3)_3$), 2.21 (s, 6H, $CH_2C_6H_2(CH_3)_3$). ^{13}C NMR (100 MHz, DMSO-d_6): δ 165.9 (C_5H_4NCOOH), 163.5 (C-Pd), 153.5, 148.5, 138.9, 138.4, 135.5, 134.7, 130.1, 128.6, 124.5, 123.8, 123.6, 112.5, 111.2 (Ar-C, C_5H_4NCOOH, $CH_2C_6H(CH_3)_4$), 71.4 ($NCH_2CH_2OCH_3$), 59.1 ($NCH_2CH_2OCH_3$), 49.7 ($CH_2C_6H_2(CH_3)_3$), 48.7 ($NCH_2CH_2OCH_3$), 21.4, 21.3 ($CH_2C_6H(CH_3)_4$). IR(CH_2Cl_2): $\nu_{C=O}$ 1750 cm^{-1}, ν_{O-H} 3722 cm^{-1}. Anal. Calc. for $C_{26}H_{29}Br_2N_3O_3Pd$ (697.75): C 44.75, H 4.19, N 6.88. Found C 44.65, H 4.21, N 6.90%.

{*N*-(2,3,5,6-tetramethylbenzyl)-*N*′-(2-metoxyethyl)benzimidazoline-2-ylidene}(pyridine-4-carboxylic acid) palladium(II) dibromide, 3b. Yield: 0.29 g, 82%. ^{1}H NMR (400 MHz, DMSO-d_6):

δ 8.85 (b, 2H, C_5H_4NCOOH), 7.92 (b, 2H, C_5H_4NCOOH), 7.68 (d, 1H, J = 8.00 Hz, Ar-H), 7.26 (t, 1H, J = 7.4 Hz, Ar-H), 7.13 (t, 1 H, J = 6.00 Hz, Ar-H), 7.09 (s, 1H, $CH_2C_6H(CH_3)_4$), 6.90 (d, 1H, J = 7.6 Hz, Ar-H), 5.93 (s, 2 H, $CH_2C_6H(CH_3)_4$), 4.99 (b, 2H, $NCH_2CH_2OCH_3$), 4.16 (b, 2H, $NCH_2CH_2OCH_3$), 3.26 (s, 3H, $NCH_2CH_2OCH_3$), 2.17 (s, 6H, $CH_2C_6H(CH_3)_4$), 2.10 (s, 6H, $CH_2C_6H(CH_3)_4$). ^{13}C NMR (100 MHz, DMSO-d_6): δ 165.8 (C_5H_4NCOOH), 163.1 (C-Pd), 153.5, 140.8, 135.5, 135.0, 134.9, 134.5, 132.8, 131.5, 124.5, 123.8, 123.6, 112.4, 111.2 (Ar-C, C_5H_4NCOOH, $CH_2C_6H(CH_3)_4$), 71.3 ($NCH_2CH_2OCH_3$), 59.1 ($NCH_2CH_2OCH_3$), 49.9 ($CH_2C_6H_2(CH_3)_3$), 48.7 ($NCH_2CH_2OCH_3$), 20.9, 17.1 ($CH_2C_6H(CH_3)_4$). IR(CH_2Cl_2): $\nu_{C=O}$ 1759 cm^{-1}, ν_{O-H} 3712 cm^{-1}. Anal. Calc. for $C_{27}H_{31}Br_2N_3O_3Pd$ (711.78): C 45.56, H 4.39, N 5.90. Found C 45.40, H 4.49, N 6.00%.

{*N*-(pentamethylbenzyl)-*N*′-(2-metoxyethyl)benzimidazoline-2-ylidene}(pyridine-4-carboxylic acid) palladium(II) dibromide, 3c. Yield: 0.29 g, 80%. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.87 (b, 2H, C_5H_4NCOOH), 7.91 (b, 2H, C_5H_4NCOOH), 7.72 (d, 1H, J = 8.00 Hz, Ar-H), 7.24 (t, 1H, J = 7.6 Hz, Ar-H), 7.13 (t, 1 H, J = 7.2 Hz, Ar-H), 6.72 (d, 1H, J = 8.0 Hz, Ar-H), 5.97 (s, 2H, $CH_2C_6(CH_3)_5$), 4.99 (b, 2H, $NCH_2CH_2OCH_3$), 4.16 (t, 2H, J = 5.0 Hz, $NCH_2CH_2OCH_3$), 3.26 (s, 3H, $NCH_2CH_2OCH_3$), 2.25 (s, 3H, $CH_2C_6(CH_3)_5$), 2.15 (s, 12H, $CH_2C_6(CH_3)_5$). ^{13}C NMR (100 MHz, DMSO-d_6): δ 165.8 (C_5H_4NCOOH), 163.1 (C-Pd), 153.5, 140.8, 135.9, 135.6, 134.6, 133.3, 128.6, 124.5, 123.8, 123.6, 123.6, 112.4, 111.2 (Ar-C, C_5H_4NCOOH, $CH_2C_6(CH_3)_5$), 71.3 ($NCH_2CH_2OCH_3$), 59.1 ($NCH_2CH_2OCH_3$), 51.0 ($CH_2C_6H_2(CH_3)_3$), 48.7 ($NCH_2CH_2OCH_3$), 18.0, 17.7, 17.4 ($CH_2C_6(CH_3)_5$). IR(CH_2Cl_2): ν_{O-H} 1705 cm^{-1}, $\nu_{C=O}$ 3437 cm^{-1}. Anal. Calc. for $C_{28}H_{33}Br_2N_3O_3Pd$ (725.81): C 46.33, H 4.58, N 5.79. Found C 46.33, H 4.70, N 5.65%.

{*N*-(2,4,6-trimethylbenzyl)-*N*′-(2-metoxyethyl)benzimidazoline-2-ylidene}(pyridine-2,6-dicarboxylic acid) palladium(II) dibromide, 4a. Yield: 0.28 g, 82%. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.24 (d, 2H, J = 7.2 Hz, $C_5H_3N(COOH)_2$), 8.18 (t, 1H, J = 6.8 Hz, $C_5H_3N(COOH)_2$), 7.69 (d, 1H, J = 8.4 Hz, Ar-H), 7.25 (t, 1H, J = 8.0 Hz, Ar-H), 7.09 (t, 1H, J = 8.0 Hz, Ar-H), 6.98 (s, 2H, $CH_2C_6H_2(CH_3)_3$), 6.67 (d, 1H, J = 7.2 Hz, Ar-H), 5.86 (s, 2H, $CH_2C_6H_2(CH_3)_3$), 4.94 (b, 2H, $NCH_2CH_2OCH_3$), 4.13 (b, 2H, $NCH_2CH_2OCH_3$), 3.26 (s, 3H, $NCH_2CH_2OCH_3$), 2.28 (s, 3H, $CH_2C_6H_2(CH_3)_3$), 2.21 (s, 6H, $CH_2C_6H_2(CH_3)_3$). ^{13}C NMR (100 MHz, DMSO-d_6): δ 165.8 ($C_5H_3N(COOH)_2$), 160.5 (C-Pd), 148.3, 139.8, 138.7, 138.6, 135.5, 134.5, 129.9, 128.0,127.9, 123.6, 123.4, 112.2, 110.9 (Ar-C, $C_5H_3N(COOH)_2$, $C_6H_2(CH_3)_3$), 71.1 ($NCH_2CH_2OCH_3$), 58.7 ($NCH_2CH_2OCH_3$), 49.9 ($CH_2C_6H_2(CH_3)_3$), 48.7 ($NCH_2CH_2OCH_3$), 20.9, 20.7 ($CH_2C_6H_2(CH_3)_3$). IR(CH_2Cl_2): $\nu_{C=O}$ 1740 cm^{-1}, ν_{O-H} 3498 cm^{-1}. Anal. Calc. for $C_{27}H_{29}Br_2N_3O_5Pd$ (741.76): C 43.72, H 3.94, N 5.66. Found C 43.71, H 4.01, N 5.77%.

{*N*-(2,3,5,6-tetramethylbenzyl)-*N*′-(2-metoxyethyl)benzimidazoline-2-ylidene}(pyridine-2,6-dicarboxylic acid) palladium(II) dibromide, 4b. Yield: 0.28 g, 74%. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.22 (d, 2H, J = 7.2 Hz, $C_5H_3N(COOH)_2$), 8.15 (m, 1H, $C_5H_3N(COOH)_2$), 7.65 (d, 1H, J = 8.4 Hz, Ar-H), 7.21 (t, 1H, J = 7.6 Hz, Ar-H), 7.08 (s, 1H, $CH_2C_6H(CH_3)_4$), 7.02 (t, 1H, J = 7.8 Hz, Ar-H), 6.46 (d, 1 H, J = 6.8 Hz, Ar-H), 5.93 (s, 2 H, $CH_2C_6H(CH_3)_4$), 4.92 (t, 2H, J = 5.4 Hz $NCH_2CH_2OCH_3$), 4.10 (t, 2H, J = 5.8 Hz, $NCH_2CH_2OCH_3$), 3.24 (s, 3H, $NCH_2CH_2OCH_3$), 2.19 (s, 6H, $CH_2C_6H(CH_3)_4$), 2.11 (s, 6H, $CH_2C_6H(CH_3)_4$). ^{13}C NMR (100 MHz, DMSO-d_6): δ 165.1 ($C_5H_3N(COOH)_2$), 160.6 (C-Pd), 148.8, 139.9, 135.6, 135.0, 134.6, 134.5, 132.9, 130.7, 128.1, 123.8, 123.6, 112.4, 111.2 (Ar-C, $C_5H_3N(COOH)_2$, $CH_2C_6H(CH_3)_4$), 71.2 ($NCH_2CH_2OCH_3$), 59.1 ($NCH_2CH_2OCH_3$), 51.4 ($CH_2C_6H_2(CH_3)_3$), 48.6 ($NCH_2CH_2OCH_3$), 20.9, 16.9 ($CH_2C_6H(CH_3)_4$). IR(CH_2Cl_2): $\nu_{C=O}$ 1750 cm^{-1}, ν_{O-H} 3712 cm^{-1}. Anal. Calc. for $C_{28}H_{31}Br_2N_3O_5Pd$ (755.79): C 44.50, H 4.13, N 5.56. Found C 44.51, H 4.21, N 5.62%.

{*N*-(pentamethylbenzyl)-*N*′-(2-metoxyethyl)benzimidazoline-2-ylidene}(pyridine-2,6-dicarboxylic acid) palladium(II) dibromide, 4c. Yield: 0.27 g, 71%. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.23-8.20 (m, 2H, $C_5H_3N(COOH)_2$), 8.17-8.13 (m, 1H, $C_5H_3N(COOH)_2$), 7.64 (d, 1H, J = 8.4 Hz, Ar-H), 7.19 (t, 1H, J = 7.8 Hz, Ar-H), 6.99 (t, 1H, J = 7.8 Hz, Ar-H), 6.37 (d, 1H, J = 7.6 Hz, Ar-H), 5.95 (s, 2H, $CH_2C_6(CH_3)_5$), 4.92 (t, 2H, J = 5.2 Hz, $NCH_2CH_2OCH_3$), 4.11 (t, 2H, J = 5.6 Hz, $NCH_2CH_2OCH_3$), 3.25 (s, 3H, $NCH_2CH_2OCH_3$), 2.24 (s, 3H, $CH_2C_6(CH_3)_5$), 2.17 (s, 6H, $CH_2C_6(CH_3)_5$), 2.14 (s, 6H, $CH_2C_6(CH_3)_5$). ^{13}C NMR (100 MHz, DMSO-d_6): δ 164.3 ($C_5H_3N(COOH)_2$), 160.9 (C-Pd), 138.1, 134.4, 133.8, 132.8, 132.7, 131.5, 126.3, 126.1, 122.0, 121.7, 116.9, 110.5, 109.3 (Ar-C, $C_5H_3N(COOH)_2$, $CH_2C_6(CH_3)_5$), 69.3 ($NCH_2CH_2OCH_3$), 57.2 ($NCH_2CH_2OCH_3$), 50.0 ($CH_2C_6H_2(CH_3)_3$), 46.7 ($NCH_2CH_2OCH_3$), 16.1, 15.9, 15.5 ($CH_2C_6(CH_3)_5$). IR(CH_2Cl_2): $\nu_{C=O}$ 1742 cm^{-1}, ν_{O-H} 3502 cm^{-1}. Anal. Calc. for $C_{29}H_{33}Br_2N_3O_5Pd$ (769.82): C 45.25, H 4.32, N 5.46. Found C 45.18, H 4.33, N 5.37%.

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