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Palladium complexes of (benzoimidazol-2-ylmethyl)amine ligands as catalysts for methoxycarbonylation of olefins

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ABSTRACT

Reactions of *N*-(1H-benzoimidazol-2-ylmethyl)-2-methoxy aniline (**L1**) and *N*-(1H-benzoimidazol-2-ylmethyl)-2-bromo aniline (**L2**) with either [$PdCl_2$(COD)] or [PdClMe(COD)] afforded the neutral palladium complexes [$PdCl_2$(**L1**)] (**1**), [PdClMe(**L1**)] (**2**) and [PdClMe(**L2**] (**3**), respectively. Treatment of **2** and **3** with one equivalent of PPh_3 in the presence of $NaBAr_4$ (Ar = 3,5-$(CF_3)_2C_6H_3$) produced the corresponding cationic species, [PdMe(**L1**)]BAr_4 (**4**) and [PdMe(**L2**)]BAr_4 (**5**). All the palladium complexes formed active catalysts in the methoxycarbonylation of alkenes to produce linear and branched esters. The catalytic behaviour was dependent on the catalyst structure, presence of PPh_3, acid promoter and alkene chain length.

1. Introduction

The methoxycarbonylation reaction has become one of the most valuable organic reactions in the functionalization of olefins to produce a wide range of industrial and domestic products such as detergents, cosmetics and pharmaceuticals [1–3]. A number of phosphine based transition metal complexes have been applied in methoxycarbonylation reactions over decades [4–9]. To date, palladium-catalysts have attracted much interest in the methoxycarbonylation of olefins due to their superior catalytic activities [10]. Depending on the catalytic system used and reaction conditions employed, high regioselectivity towards branched or linear products can be obtained using Pd(II) catalysts.

In recent years, a number of Pd complexes containing varied ligand architectures have been reported to show high activity as well as selectivity for methoxycarbonylation of olefins such as styrene1, 1-hexene [11] or ethene [12] under mild reaction conditions. For instance, under low partial pressures of carbon monoxide and moderate temperatures, some of these catalyst systems show high regioselectivity (>90%) towards branched esters [13–25]. Currently, one such catalyst design that is attracting significant attention are the mixed nitrogen–phosphine donor Pd complexes. This is presumably due to their perceived stability and tolerance to impurities. For example, Pd catalysts of the type [$PdCl_2$(Ph_2PNHpy-*k*2 *P,N*)] and [PdCl(Ph_2PNHpy-*k*2 *P,N*)(PPh_3)]Cl were reported to be active and stable in the methoxycarbonylation of styrene [11].

In this paper, we report the syntheses of some neutral and cationic Pd(II) complexes anchored on (benzoimidazol-2-ylmethyl) amine ligands and their applications as potential catalysts in the methoxycarbonylation of alkenes. The effects of catalyst structure, identity of alkene substrate, reaction conditions, and nature of acid promoter used have been systematically studied and are herein reported.

2. Experimental

2.1. Material and methods

All moisture and air sensitive reactions were performed using standard Schlenk line techniques. Methanol, acetone, diethyl ether, dichloromethane, absolute ethanol, ethyl acetate, toluene, DMSO-d_6, potassium iodide (KI), sodium hydroxide (NaOH) and potassium hydroxide (KOH) were purchased from Merck. Chloroform ($CDCl_3$), styrene, σ-olefins, *p*-TsOH, hydrochloric acid (HCl), oxalic acid, sulfuric acid (H_2SO_4), HBr and PPh_3 were obtained from Sigma–Aldrich. The chemicals, 2-chloromethylbenzimidazole, aniline (≥99.5%) 2-methoxyaniline (≥99.5%), 2-aminothiophenol (≥99%), and 2-bromoaniline (98%) were purchased from Sigma–Aldrich and were used without further purification. $NaBAr_4$ (Ar_4 = 3,5-$(CF_3)_2C_6H_3$) was obtained from Boulder Scientific and used as received. Starting materials [$PdCl_2$(COD)] [26] and [PdClMe(COD)] [27] were synthesized following literature methods. Ligands **L1–L2** were prepared following

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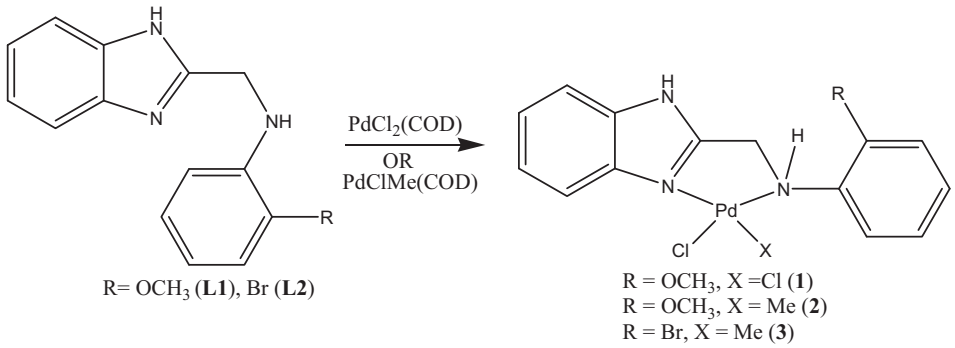


Scheme 1. Syntheses of neutral (benzoimidazol-2-ylmethyl)amine palladium complexes **1**–**3**.

our recently published procedures [28]. Nuclear magnetic resonance spectra were acquired at 400 MHz for ^{1}H, 100 MHz for ^{13}C and 162 MHz for ^{31}P on a Bruker Avance spectrometer equipped with Bruker magnet (9.395 T). All coupling constants are reported in Hertz, Hz. Elemental analyses were carried out using CHNS-O Flash 2000 thermoscientific analyzer. Mass spectral analyses were conducted using micromass LCT premier mass spectrometer.

2.2. Syntheses of palladium complexes

2.2.1. [{N-(1H-benzoimidazol-2-ylmethyl)-2-methoxyaniline}PdCl2] (**1**)

To a solution of **L1** (0.20 g, 0.83 mmol) in CH_2Cl_2 (10 mL) was added a solution of [Pd(COD)Cl_2] (0.22 g, 0.83 mmol) in CH_2Cl_2 (10 mL) and the mixture was stirred for 24 h to give a yellow precipitate. The crude product was filtered and recrystallized from CH_2Cl_2- hexane mixture to afford complex **1** as a light yellow solid. Yield = 0.27 g (77%). ^{1}H NMR (DMSO): δ(ppm): 0.78 (s, 3H, OCH_3); 4.90 (s, 2H, CH_2); 6.48–6.57 (d, 1H, $^{3}J_{HH}$ = 7.60, Ph); 6.59 (t, 1H, $^{3}J_{HH}$ = 5.36, Ph,); 6.61(d, 1H, $^{3}J_{HH}$ = 4.98, Ph,); 6.69 (d, 1H, $^{3}J_{HH}$ = 6.51, Ph); 6.84 (dd, 2H, $^{3}J_{HH}$ = 4.80, Bzim); 6.86–7.27 (dd, 2H, $^{3}J_{HH}$ = 7.66, Bzim). MS (ESI) *m/z* (%) 254 (M^{+}-Cl_2–Pd, 100%). Anal. Calc. for $C_{15}H_{13}N_3PdCl_2.0.75CH_2Cl_2$: C, 38.97; H, 3.06; N, 8.66. Found: C, 39.01; H, 3.66; N, 8.76.

2.2.2. [{N-(1H-benzoimidazol-2-ylmethyl)-2methoxyaniline}PdClMe] (**2**)

Complex **2** was synthesized following the procedure described for **1** using **L1** (0.10 g, 0.41) and PdCl(COD) Me (0.10 g,0.35 mmol) in Et_2O (10 mL). Yield = 0. 09 g (86%) ^{1}H NMR (DMSO-d_6): δ(ppm): 0.78 (s, 3H, OCH_3); 3.84 (s, 3H, CH_3); 4.91 (s, 2H, CH_2); 5.17 (s, 2H, Ph); 6.50 (d, 1H, $^{3}J_{HH}$ = 3.74, Ph); 6.58 (t, 1H, $^{3}J_{HH}$ = 3.21, Ph); 6.69 (d, 1H, $^{3}J_{HH}$ = 3.34, Ph); 6.81 (t, 1H, $^{3}J_{HH}$ = 5.23, Ph); 7.35 (dd, 2H, $^{3}J_{HH}$ = 6.86, Bzim); 7.51 (dd, 2H, $^{3}J_{HH}$ = 7.77, Bzim). Anal. Calc. for $C_{16}H_{18}N_3PdClO$: C, 46.85; H, 4.42; N, 10.24. Found: C, 47.11; H, 4.11; N, 8.58.

2.2.3. [{N-(1H-benzoimidazol-2-ylmethyl)-2-bromoaniline} [PdClMe] (**3**)

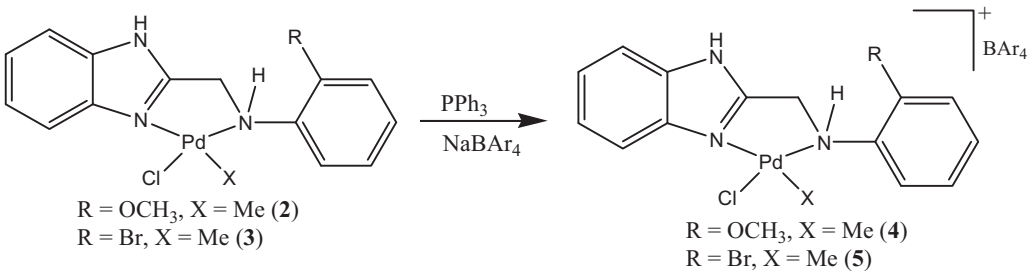
Complex **3** was prepared according to the procedure for **1** using **L2** (0.10 g, 0.34 mmol) and PdCl(COD) Me (0.10 g, 0.34 mmol). Yield = 0.09 (58%) ^{1}H NMR (DMSO-d_6): $_{H}$ (ppm): 0.80 (s, 3H, CH_3); 4.61 (s, 2H, CH_2);5.01 (s, 2H, CH_2); 6.27 (d, 1H, $^{3}J_{HH}$ = 6.67, Ph); 6.56 (t, 1H, $^{3}J_{HH}$ = 5.64, Ph); 7.06 (t, 1H,$^{3}J_{HH}$ = 6.77, Ph); 7.15 (d, 1H, $^{3}J_{HH}$ = 7.89, Ph); 7.31 (dd, 2H, $^{3}J_{HH}$ = 6.78, Bzim); 7.48 (dd, 2H, $^{3}J_{HH}$ = 7.33, Bzim). MS (ESI) *m/z* (%) 482 (M^{+}-Cl, 22%). Anal. Calc. for $C_{15}H_{15}N_3BrPdCl$: C, 39.24; H, 3.29; N, 9.15. Found: C, 38.94; H, 3.87; N, 8.99.

2.2.4. [{N-(1H-benzoimidazol-2-ylmethyl)-2-methoxyaniline} [PdMe(PPh3)] BAr4 (**4**)

To a suspension of **2** (0.02 g, 0.09 mmol), in CH_2Cl_2 (10 mL), PPh_3 (0.01 g, 0.09 mmol) and $NaBAr_4$ (Ar_4 = 3,5-$(CF_3)_2C_6H_3$) (0.037 g, 0.09 mmol) were added and stirred for 24 h. The solution mixture was filtered and the filtrate concentrated to approximately 3 mL and recrystallized from hexane/CH_2Cl_2 solvent mixture to obtain compound **4** as a yellow crystalline solid. Yield = 0.08 g (66%). ^{1}H NMR ($CDCl_3$): δ (ppm):0.95 (s, 3H, CH_3), 3.43 (s, 3H, OCH_3), 5.52 (s, 2H, CH_2), 6.47 (d, 1H, Ph-aniline), 6.69 (t, 1H, $^{3}J_{HH}$ = 6.80, Ph), 6.75 (d, 1H, $^{3}J_{HH}$ = 7.20, Ph), 7.21 (m, 6H, $^{3}J_{HH}$ = 7.60, PPh_3), 7.34 (d, 2H, $^{3}J_{HH}$ = 6.80, Bzim), 7.36 (d, 8H, $^{3}J_{HH}$ = 8.00, BAr_4), 7.50 (m, 9H, $^{3}J_{HH}$ = 8.00, PPh_3), 7.71 (t, 4H, $^{3}J_{HH}$ = 7.60, BAr_4), 7.72 (d, 2H, $^{3}J_{HH}$ = 7.88, Bzim). ^{31}P NMR ($CDCl_3$) δ(ppm): 37.85. Anal. Calc. for $C_{66}H_{45}BF_{24}ON_3PPd$: C, 52.46; H,3.05; N, 2.82. Found: C, 52.94; H, 1.39; N, 3.09.

2.2.5. [{N-(1H-benzoimidazol-2-ylmethyl)-2-bromoaniline} [PdMe(PPh3)] BAr4 (**5**)

Complex **5** was prepared according to the same procedure for **4** using **3** (0.04 g, 0.09 mmol), PPh_3 (0.02 g, 0.09 mmol) and $NaBAr_4$ (Ar_4 = 3,5-$(CF_3)_2C_6H_3$) (0.08 g, 0.09 mmol). Yield = 0.06 (67%). ^{1}H



Scheme 2. Syntheses of cationic (benzoimidazol-2-ylmethyl)amine palladium complexes **4** and **5**.