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Tuning the regioselectivity of (benzimidazolylmethyl)amine palladium(II) complexes in the methoxycarbonylation of hexenes and octenes

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Abstract
Reactions of *N*-(1*H*-benzoimidazol-2-ylmethyl-2-methoxy)aniline (**L1**) and *N*-(1*H*-benzoimidazol-2-ylmethyl-2-bromo) aniline (**L2**) with *p*-TsOH, $Pd(AOc)_2$ and two equivalents of PPh_3 or PCy_3 produced the corresponding palladium complexes, [Pd(**L1**)(OTs)(PPh_3)] (**1**), [Pd(**L2**)(OTs)(PPh_3)] (**2**) and [Pd(**L1**)(OTs)(PCy_3)] (**3**), respectively, in good yields. The new palladium complexes **1**–**3** and the previously reported complexes [Pd(**L1**)ClMe] (**4**) and [Pd(**L2**)ClMe] (**5**) gave active catalysts in the methoxycarbonylation of terminal and internal olefins to produce branched and linear esters. The effects of complex structure, nature of phosphine derivative, acid promoter and alkene substrate on the catalytic activities and selectivity have been studied and are herein reported.

Introduction

Transition metal-catalyzed carbonylation reactions have become an important tool in both laboratory and industrial organic synthesis for the formation of carbonyl compounds such as esters, amides, ketones and aldehydes [1–4]. To date, palladium complexes are the most widely used catalysts in methoxycarbonylation of olefins due to their high catalytic activities, thermal stability and superior selectivities [1–5]. For instance, under low pressures of carbon monoxide and moderate temperatures, some of these catalyst systems show high regioselectivity of up to 90% toward either linear or branched ester [6–11].

Traditionally, phosphine-donor ligands have been used in the preparation of palladium catalysts in the methoxycarbonylation reactions [12]. Another ligand design that is gaining momentum as suitable alternatives to the phosphine systems are the mixed nitrogen-phosphine donors, due to their relative tolerance to impurities, ease of syntheses and affordability. Such examples include palladium complexes of the type [$PdCl_2$(Ph_2PNHpy-k_2-*P,N*)] and [PdCl(Ph_2PNHpy-k_2-*P,N*)(PPh_3)]Cl which give active and stable catalysts in the methoxycarbonylation of styrene [5].

From literature reports, it has been established that regioselectivity toward either the branched or linear esters can also be fine-tuned by variation of the steric properties of the auxiliary phosphine ligands [13–15]. In addition, the use of chelating or monodentate phosphine derivatives is known to significantly influence the activity and regioselectivity of the resultant catalysts [10, 11]. In our recent contribution, we reported the use of palladium complexes of *N*-(benzoimidazol-2-ylmethyl)amine ligands as catalysts in the methoxycarbonylation of terminal olefins [16]. These complexes show moderate catalytic activities but with rather low regioselectivity, giving almost equal proportions of branched and linear esters. In attempts to improve the regioselectivity of these catalysts, we have now modified the complex structure by fine-tuning the basicity of the phosphine ligands in the metal coordination sphere. In addition, internal olefin substrates have been employed to probe the effect of the position of the double bond on regioselectivity of the ester products. Thus, in this contribution, the effect of complex structure, different phosphine derivatives, acid promoter, solvent system and olefin substrates on the methoxycarbonylation reactions have been investigated. In addition,

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studies of the nature of active species have been performed and are discussed.

Experimental section

Materials and methods

All moisture- and air-sensitive reactions were performed using standard Schlenk line techniques. All solvents were purchased from Merck and distilled under nitrogen in the presence of suitable drying agents: diethyl ether, hexane and toluene were dried over sodium wire and benzophenone, methanol and absolute ethanol over calcium oxide, while dichloromethane was dried and distilled over phosphorus pentoxide. The chemicals, potassium iodide, sodium hydroxide and potassium hydroxide, were purchased from Merck, while deuterated chloroform, styrene, 1-hexene, *trans*-2-hexene, *trans*-2-octene, *p*-TsOH, hydrochloric acid, $Pd(OAc)_2$ (98%), PPh_3, 2-methoxyaniline (≥ 99.5%) and 2-bromoaniline (98%) were purchased from Sigma-Aldrich and used without further purification. The proligands *N*-(1*H*-benzoimidazol-2-ylmethyl-2-methoxy)aniline (**L1**) and *N*-(1*H*-benzoimidazol-2-ylmethyl-2-bromo)aniline (**L2**) were synthesized following the published literature method [17]. The palladium complexes [Pd(**L1**)ClMe] (**4**) and [Pd(**L2**)ClMe] (**5**) were prepared following our recently published procedure [16]. 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 a Bruker magnet (9.395 T). All coupling constants are reported in Hz. Elemental analyses were carried out using a CHNS-O Flash 2000 thermoscientific analyzer. GC–MS analyses were conducted on a micromass LCT premier mass spectrometer.

Synthesis of palladium(II) complexes

[Pd(L1)(OTs)(PPh_3)] (1)

To a solution of **L1** (0.11 g, 0.44 mmol) in chloroform (5 mL) was added dropwise a solution of $Pd(AcO)_2$ (0.10 g, 0.44 mmol) in chloroform (10 mL) followed by a solution of PPh_3 (0.23 g, 0.89 mmol) and *p*-TsOH (0.07 g, 0.44 mmol) in chloroform (10 mL). The mixture was then stirred at room temperature for 24 h. The organic volatiles were removed in vacuo followed by recrystallization of the crude product from CH_2Cl_2-hexane solvent system to give a light yellow solid. Yield = 0.28 g (79%). ^{1}H NMR ($CDCl_3$): δ_H (ppm): 2.10 (s, 3H, OCH_3); 2.32 (s, 3H, CH_3-OTs); 5.33 (s, 2H, CH_2); 7.02–7.16 (m, 8H, Ph-Aniline); 7.30–7.42 (m, 2H, Ph-OTs); 7.44–752 (m, 8H, Ph-PPh_3); 7.60–7.69 (m, 7H, Ph-PPh_3); 7.74–7.82 (m, 2H, Ph-OTs). ^{13}C NMR ($CDCl_3$): δ (ppm): 24.30; 39.00; 55.92; 114.56; 115.10; 118.23; 121.95; 123.00; 128.03; 128.88; 128.91; 129.11; 130.46; 137.37; 137.45; 137.92; 138.95; 141.52; 142.22; 144.70; 146.81. ^{31}P NMR ($CDCl_3$): δ (ppm): 29.42; 23.27. MS (ESI) *m*/*z* (%) 791 (M^+, 78%). Anal. Calc. for $C_{39}H_{34}N_3O_4PPdS.CHCl_3$: C, 53.53; H, 3.93; N, 4.68. Found: C, 53.75; H, 3.92; N, 4.91.

[Pd(L2)(OTs)(PPh_3)] (2)

Complex **2** was synthesized following the procedure described for **1** using $Pd(AcO)_2$ (0.1 g, 0.44 mmol), **L2** (0.13 g, 0.44 mmol), *p*-TsOH (0.07 g, 0.44 mmol), PPh_3 (0.23 g, 0.89 mmol). Yield = 0.35 (93%). ^{1}H NMR ($CDCl_3$): δ_H (ppm): 2.29 (s, 3H, CH_3-OTs); 5.42 (s, 2H, CH_2); 6.92–7.09 (m, 4H, Ph-Aniline); 7.34–7.41 (m, 4H, Ph-Benz); 7.46–7.50 (m, 2H, Ph-OTs); 7.54–7.62 (m, 6H, PPh_3); 7.64–7.70 (m, 9H, PPh_3); 7.72–7.84 (m, 2H, Ph-OTs). ^{13}C NMR ($CDCl_3$): 24.3; 52.61; 114.30; 114.55; 115.72; 118.10; 119.44; 127.38; 128.00; 128.63; 128.80; 128.91; 130.43; 132.55; 137.30; 137.46; 146.81. ^{31}P NMR ($CDCl_3$): δ (ppm): 29.55; 23.23. MS (ESI) *m*/*z* (%) 841 (M^+, 69%). Anal. Calc. for $C_{38}H_{31}BrN_3O_4PPdS.0.5CHCl_3$: C, 52.15; H, 3.58; N, 4.74. Found: C, 52.59; H, 3.30; N, 4.80.

[Pd(L1)(OTs)(PCy_3)] (3)

Complex **3** was synthesized following the procedure described for **1** using $Pd(AcO)_2$ (0.1 g, 0.44 mmol), **L1** (0.11 g, 0.44 mmol), *p*-TsOH (0.15 g, 0.44 mmol), PCy_3 (0.24 g, 0.89 mmol). Yield = 0.38 (91%). ^{1}H NMR ($CDCl_3$): δ_H (ppm): 1.24–1.28 (m, 13H, PCy_3); 1.64–1.70 (m, 17H, PCy_3); 1.76–1.86 (s, 3H, OCH_3); 1.93 (s, 3H, CH_3-OTs); 4.84 (s, 2H, CH_2); 6.88–7.02 (m, 4H, Ph-Aniline); 7.10–7.22 (m, 4H, Ph-Benz); 7.48–7.56 (m, 4H, Ph-OTs). ^{13}C NMR ($CDCl_3$): 4.00; 27.20; 28.30; 30.90; 39.10; 55.90; 114.50; 115.30; 118.30; 121.90; 123.00; 128.10; 129.10; 130.10; 132.60; 137.90; 138.90; 141.50; 144.70; 149.80. ^{31}P NMR ($CDCl_3$): δ (ppm): 48.53; 53.83. MS (ESI) *m*/*z* (%) 810 (M^+, 51%). Anal. Calc. for $C_{39}H_{52}N_3O_4PPdS.CHCl_3$: C, 52.97; H, 5.96; N, 4.52. Found: C, 53.12; H, 5.57; N, 4.37.

General procedure for the methoxycarbonylation reactions

The catalytic methoxycarbonylation reactions were performed in a stainless steel autoclave equipped with a temperature control unit and a sample valve. In a typical experiment, complex **1** (22.49 mg, 0.08 mmol), PPh_3 (0.04 g, 0.16 mmol), HCl (0.02 mL, 0.80 mmol) and 1-hexene (2 mL, 15.90 mmol) were dissolved in a mixture of methanol (20 mL) and toluene (40 mL). The reactor was evacuated and the catalytic solution was introduced to the reactor via a cannula. The reactor was purged three times with CO,

and then set at the required pressure, heated to the desired temperature and the reaction stirred at 500 rpm. At the end of the reaction time, the reaction was cooled, excess CO was vented off and samples drawn for GC analysis to determine the percentage conversion of the alkene substrate to esters. GC–MS analyses were run under the following standard chromatography conditions: – 25 m CPSil 19 capillary column, 1.2 mm film thickness, helium carrier column gas 5 psi, injector temperature 250 °C, oven program 50 °C for 4 min rising to 200 °C at 20 °C/min and holding at 200 °C. The identities of the ester products were assigned using standard authentic samples and mass spectral data.

Results and discussion

Synthesis and characterization of the palladium complexes

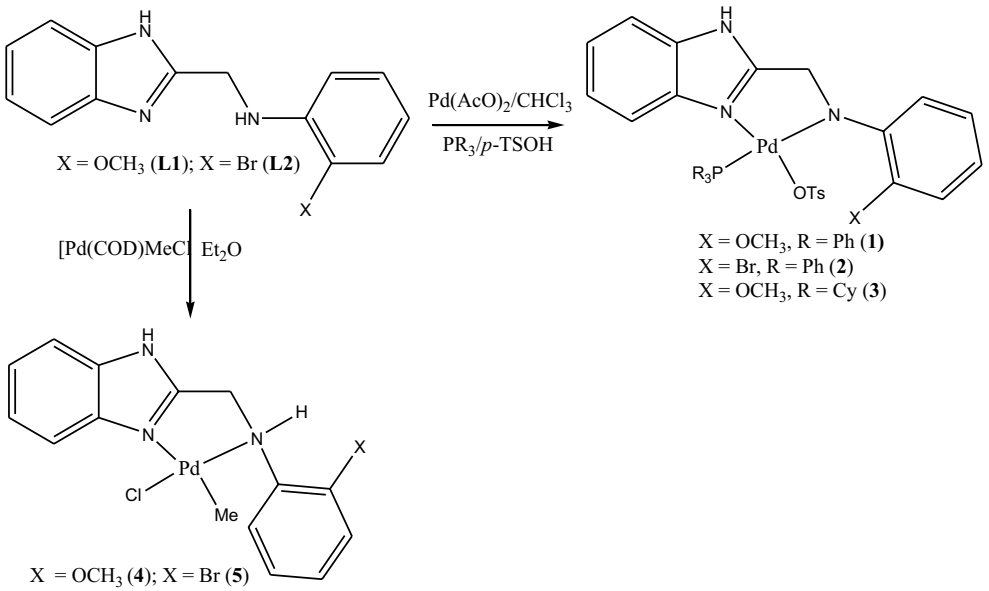
Proligands **L1** and **L2** were prepared by reactions of 2-(chloromethyl)benzoimidazole with the appropriate aniline derivatives, according to a previously reported literature method [17]. Subsequent treatments of **L1** and **L2** with *p*-TsOH, $Pd(AcO)_2$ and two equivalent of PPh_3 or PCy_3 according to the procedure described by Jaysree et al. [18] afforded the palladium(II) compounds **1–3,** respectively, in good yields (Scheme 1). Complexes **4** and **5** were prepared following our recently published procedure [16].

The new palladium complexes **1–3** were characterized by ^1H, ^{13}C, ^{31}P NMR spectroscopies (Figs. S1–S9), mass spectrometry and elemental analyses. For example, the ^1H NMR spectra of **L1** and its corresponding complex **1** showed CH_2 proton signals at 4.65 ppm and 5.33 ppm, respectively. In addition, the CH_3 proton signal at 2.32 ppm confirmed the coordination of p-TsO^- anion to the palladium atom. Similar ^1H NMR spectrum was observed for complex **1** (Fig. S1). ^{31}P NMR spectra of complexes **1–3** displayed two singlets in the region 23.23–48.53 ppm, possibly due to the existence of the *cis* and *trans* isomers (Figs. S7–S9). These values fall within the typical ^{31}P NMR signals in the range 23.20–35.70 and 48.53–53.83 ppm reported for related mono-coordinated PPh_3 [16, 18, 19] and PCy_3 compounds, respectively [20]. Mass spectrometry was also used to establish the formation and identity of these complexes. For instance, complex **2** showed an *m*/*z* peak at 841 amu, corresponding to its molecular ion (Fig. S10).

Methoxycarbonylation reactions using palladium complexes 1–5 as catalysts

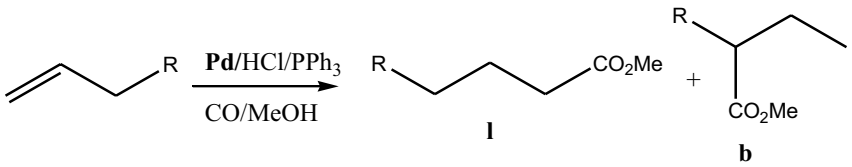
Effect of catalyst structure and phosphine derivatives

In our recent report, we showed that the *N*-(benzimidazolylmethyl)amine palladium complexes **4** and **5** catalyze the methoxycarbonylation of terminal olefins to afford almost equal proportions of linear and branched esters [16]. In this current work, we aimed to improve the catalytic activity and regioselectivity of these palladium systems via modification of the complex design, use of different phosphine derivatives and internal olefin substrates (Table 1). The identities and compositions of the ester products were determined by GC and GC–MS (Figs. S11–S18). Thus



Scheme 1 Synthetic protocol of (benzimidazolylmethyl)amine palladium complexes

Table 1 Effect of the complex structure and phosphine derivatives on the methoxycarbonylation of 1-hexene



Entry	Catalyst	Phosphine	Conv. (%)[a]	*b*/*l* (%)[b]
1	**1**	[c]PPh_3	92	30/70
2	**2**	PPh_3	84	26/74
3	**3**	PPh_3	76	74/26
4	**4**	PPh_3	80	40/60
5	**5**	PPh_3	39	40/60
6	**4**	[d]PCy_3	32	76/24
7	**4**	[e]DPPe	19	88/12
8	**4**	[f]DPEphos	93	31/69
9	**4**	[g]$P(o\text{-}tol)_3$	83	28/72
10	**4**	[h]$P(OMe)_3$	48	84/16

Reaction conditions: Pre-catalysts (0.07 mmol), solvent: toluene 40 mL and methanol 30 mL; Pd/1-hexene ratio 200:1, Pd/HCl ratio; 1:10; Pd/PR_3 ratio; 1:2; $_P$(CO) = 60 bar; temperature: 90 °C; time 24 h

[a]% of 1-hexene converted after 24 h reaction

[b]Branched/linear ester ratio

[c]Triphenylphosphine

[d]Tricyclohexylphosphine

[e]1,2-Bis(diphenylphosphino)ethane

[f](Oxydi-2-1-phenylene)bis-(diphenylphosphine)

[g]Tri(o-tolyl)phosphine

[h]trimethyl phosphite

modification of complex **5** by introducing a tolyl sulfonic group as in complex **2** resulted in a drastic increase in catalytic activity from 39% to 84%, respectively (Table 1, entries 2 and 5). This trend could be attributed to the presence of the PPh_3 and tolyl groups in **2**, which are known to enhance the stability of the resultant palladium catalysts [7, 21]. We also observed a notable shift of regioselectivity toward linear esters for complexes **1** and **2**, in comparison with complexes **4** and **5**. For example, percentage compositions of linear esters of 70 and 74% were reported for complexes **1** and **2**, while 60% was reported for both complexes **4** and **5** (Table 1, entries 1–2 vs. 4–5). This is likely to originate from a hindered isomerization of the coordinated 1-hexene substrate due to the bulkier PPh_3 and OTs groups in complexes **1** and **2** [12].

Encouraged by the results obtained upon modification of the auxiliary phosphine ligands in complexes **1** and **2** in the methoxycarbonylation of 1-hexene, we opted to further investigate the effect of various phosphine derivatives; PPh_3, PCy_3, Dppe, DPEphos, $P(o\text{-}tol)_3$ and $P(OMe)_3$ on the catalytic performance of complex **4** (Table 1, entries 6–10). The results obtained clearly illustrate the influence of the phosphine derivatives; affording conversions ranging from 19% to 80% (Table 1, entries 4, 6–10). For example, the use of PCy_3 afforded conversions of 32% compared to 80% reported for the PPh_3 analogue (Table 1, entries 4 vs. 6). This could be attributed to the inability of the PCy_3 ligand to stabilize the palladium catalyst leading to decomposition to Pd(0), consistent with the observed Pd(0) deposits in the reaction mixture. More discerning was the observed decrease in catalytic activity from 80 to 19% on changing from a non-chelating PPh_3 to the chelating Dppe groups (Table 1, entries 4 and 7). A possible explanation for this behavior could be the competition between the olefin substrate and the chelating Dppe ligand for the vacant coordination site of the palladium catalyst.

Regioselectivity of the ester products was also influenced by the nature of the auxiliary phosphine ligands (Table 1, entries 4–10). For instance DPEphos and $P(OMe)_3$ gave 31 and 84% of the branched esters, respectively (Table 1, entries 8 vs. 10). This high regioselectivity toward the branched esters reported for $P(OMe)_3$ could be largely attributed to

reduced steric hindrance, thus favouring formation of bulkier branched esters via a 2,1 insertion pathway [22]. This was further supported by the lower regioselectivity toward branched esters of 31% reported for DPEphos compared to 88%, obtained when using the chelating Dppe group (Table 1, entries 7–8).

Investigation of the effects of solvent and acid promoter on methoxycarbonylation reactions

We then studied the effect of solvent system and nature of acid promoter on the catalytic performance of complex **1** using 1-hexene substrate (Table 2, entries 1–5). From the results, it was observed that the use of pure methanol solvent system resulted in decreased catalytic activities, achieving conversions of 28%, compared 92% obtained in toluene/methanol system (Table 2, entries 1 vs. 2). On the other hand, the use of higher amounts of toluene solvent did not affect the catalytic activities (Table 2, entry 1 vs. 3). The lower catalytic activities afforded with increase in methanol concentration has been reported by Zollezzi et al. and could be associated with the lower reaction temperature of 65 °C [23]. We also hypothesize that, lower solubility of complex **1** in methanol solvent, may also play a role in the diminished catalytic activities. Indeed, reactions performed in methanol/chlorobenzene solvent system gave higher conversions of 90% (Table 2, entry 4).

Interestingly, regioselectivity of the ester products was also influenced by the solvent system employed. For example, the use of pure methanol gave 38% of the branched esters, compared to 51% obtained in a 3:4 mixture of methanol/toluene solvent system (Table 1, entries 2 and 3). Poor selectivity with increase in methanol concentration has been reported by other researchers and has been attributed to the formation of Pd(0) species and increased polarity of the solvent system [11, 23–25].

Table 2 Effect of solvent system on methoxycarbonylation of 1-hexene using complex **1**

Entry	Solvent system	*T* (°C)	Conv (%)[a]	*b/l* (%)[b]
1	MeOH/toluene	90	92	30/70
2	MeOH	65	28	38/62
3	MeOH/toluene (1:4)	90	94	51/49
4	MeOH/chlorobenzene (3:4)	90	90	31/69
5	MeOH/toluene[c]	90	76	41/59

Reaction conditions: Complex (0.07 mmol), solvent system: toluene 40 mL and methanol 30 mL; Pd/1-hexene ratio 200:1, Pd/HCl ratio; 1:10; Pd/PR_3 ratio; 1:2; $_P$(CO) = 60 bar; temperature: 90 °C; time 24 h

[a]% of 1-hexene converted after 24 h reaction

[b]Branched/linear ester ratio

[c]5 drops of mercury using catalyst **4**

The type of acid promoter in palladium catalyzed methoxycarbonylation is known to significantly influence the catalytic performance of the resultant catalysts and possible industrial applications. We thus studied a wide range of Brønsted and Lewis acids using complex **1** and 1-hexene substrate (Fig. 1). Consistent with our previous reports [16], we did not observe any catalytic activities using *p*-TsOH, but conversions of 92 and 81% were achieved using HCl and α-bromo-*p*-toluic acid. This lack of catalytic activity reported for *p*-TsOH acid has been associated with weaker coordination ability of the *p*-TsO^- anion, which may not be sufficient to stabilize the active Pd(II) species [26, 27]. Indeed, extensive decomposition of complex **1** to Pd(0) black was observed in the reactions performed using *p*-TsOH acid promoter. The improved performance of α-bromo-*p*-toluic acid is rather intriguing since it offers more industrial relevance than HCl. The efficacy of Lewis acids; $EtAlCl_2$, $AlCl_3$, $AlMe_3$ was also probed (Fig. 1). The catalytic activities of complex **1** significantly increased with increase in Lewis acidity of the acid promoter. For example, the most acidic $AlCl_3$ recorded the highest conversion of 88%, while the least acidic $AlMe_3$, gave the lowest catalytic activity of 9% conversion.

Regioselectivity in the presence of Lewis acids significantly differed from those obtained using Brønsted-acids. While comparable regioselectivity was observed using protonic acids, HCl and α-Bromo-*p*-toluic acid (54% of the branched esters), Lewis Acids showed marked differences (Fig. 1). For example, $EtAlCl_2$ and $AlMe_3$ gave 24 and 100% of the branched esters, respectively. This trend points to the generation of different active species and that chain isomerization/migration is predominant when $AlMe_3$ was used as the acid promoter [11, 13].

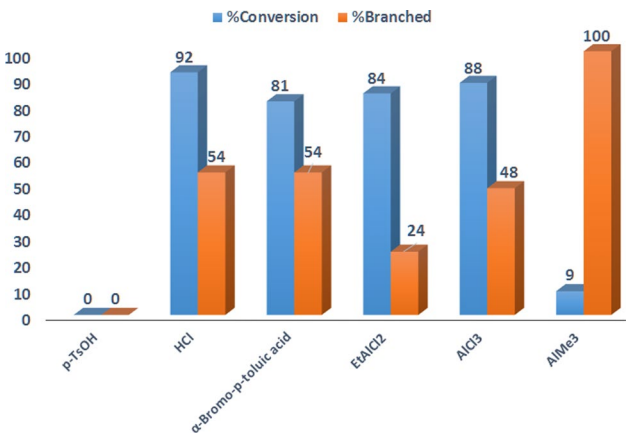


Fig. 1 The effect of acid promoters on percentage conversion and regioselectivity toward branched products using complex **1**. Complex (0.07 mmol), solvent: toluene 40 mL and methanol 30 mL; Pd/1-hexene ratio 200:1, Pd/acid promoter ratio; 1:10; Pd/phosphine ratio; 1:2; $_P$(CO) = 60 bar; temperature: 90 °C; time 24 h

Methoxycarbonylation of internal olefins using catalysts 1 and 4

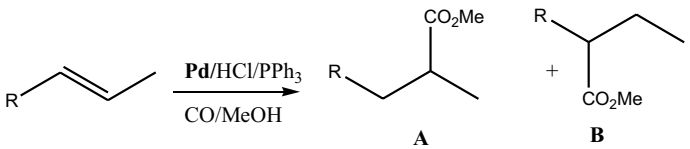
In order to investigate the effect of internal olefins on the catalytic activities and regioselectivities, we used complexes **1** and **4** in the methoxycarbonylation of *trans*-2-hexene and *trans*-2-octene (Table 3). From the results, we observed reduced catalytic activities for the internal olefins compared to the terminal olefins. For example, conversions of 80 and 30% were reported for 1-hexene and *trans*-2-hexene, respectively, using catalyst **4** (Table 1, entry 3, and Table 3, entry 1). In line with our previous reports [16], higher catalytic activity was observed for *trans*-2-hexene (56%) compared to conversions of 12% recorded for *trans*-2-octene (Table 3).

With respect to regioselectivity, only two branched esters, methyl branched isomer **A** and ethyl branched isomer **B**, were obtained (Table 3, Figs. S11–S13); indicating the absence of any isomerization, but rather chain migration/walking as proposed in Scheme 2. Another important observation was the higher composition of ethyl branched isomer **B** using *trans*-2-octene (90%) compared to *trans*-2-hexene (32%), Table 3, entries 1 and 3. This rather contradicts the expected trend, since the ethyl branched isomer **B** is more sterically demanding and is likely to be favoured by the longer chain *trans*-2-octene olefin. The use of complex **1** in the methoxycarbonylation of the *trans*-2-hexene and *trans*-2-octene showed more interesting results, producing only the methyl branched isomer **A** (Table 3, entries 5–8). This could be largely attributed to greater steric restrictions imposed by the more bulky tosylate group, thus hindering the formation of the more bulky ethyl branched isomer **B** [28].

Role of ligand and nature of the active species in methoxycarbonylation reactions

In order to understand the role of the ligand motif in controlling the catalytic activities of complexes **1**–**5** and nature of the active species, NMR spectroscopy was used to study the identity of the active species and possible decomposition of the complex under the catalytic conditions. A quantitative amount of complex **4** (0.050 g, 0.18 mmol) was subjected to 60 bar of CO in the reactor at 90 °C in the presence of HCl. The product obtained (40% yield) was characterized using ^{1}H, ^{13}C and ^{31}P NMR spectroscopy (Figs. S19–S21). From the ^{1}H NMR and ^{13}C NMR spectra of the product, it was clear that the ligand was not displaced, consistent with the observed influence of ligand motif on catalytic activities of complexes **1**–**5**. Rather, a displacement of the chloride ligand was inherent, followed by the migratory insertion of the CO molecule into the Pd-Me bond and coordination of one PPh_3 group (Figs. S19–S21). This is likely to be the active species, where a possible displacement of the PPh_3 group occurs prior to coordination of the alkene substrate via the carbomethoxy mechanism [29]. To further gain more insight into the nature of the active species, a mercury drop test was performed using complex **4** (Table 2, entry 5). No significant reduction on the catalytic activity upon addition of mercury was reported, indicating that the active species

Table 3 Methoxycarbonylation of *trans*-2-hexene and *trans*-2-octene catalyzed by complexes **1** and **4**

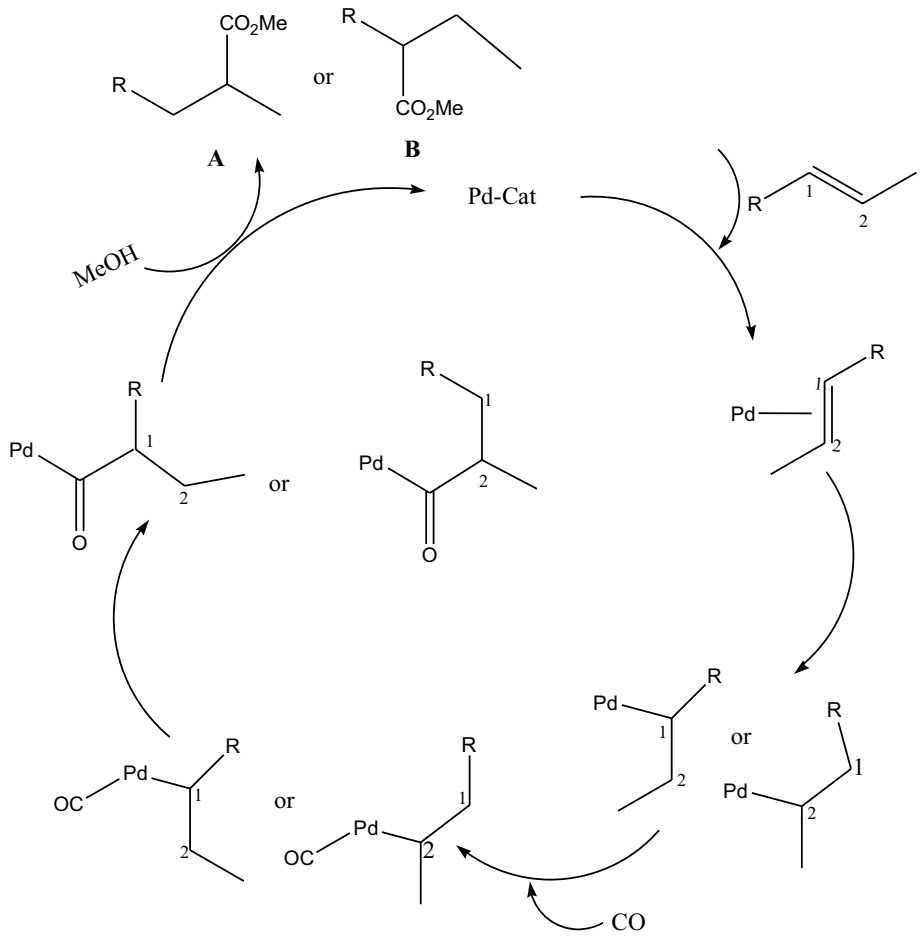


Entry	Substrate	Catalyst	Time	Conv. (%)[a]	*A* (%)[b]	*B* (%)[b]
1	*trans*-2-hexene	**4**	24	30	68	32
2	*trans*-2-hexene	**4**	48	56	66	34
3	*trans*-2-octene	**4**	24	6	10	90
4	*trans*-2-octene	**4**	48	12	24	76
5	*trans*-2-hexene	**1**	24	54	100	–
6	*trans*-2-hexene	**1**	48	73	100	–
7	*trans*-2-octene	**1**	24	21	100	–
8	*trans*-2-octene	**1**	48	61	100	–

Reaction conditions: Complexes (0.07 mmol), solvent: toluene 40 mL and methanol 30 mL; [Pd]:[PPh_3]:[HCl]:[substrate] ratio of 1:2:10:200; p(CO) = 60 bar; temperature: 90 °C

[a]% of substrate converted after a given time as determined by GC

[b]Determined by GC



Scheme 2 Possible mechanistic pathway for the formation of methyl and ethyl branched esters from *trans*-2-hexene and *trans*-2-octene using catalyst **4**

was largely homogeneous in nature [30], which was in good agreement with the NMR studies.

Conclusions

In summary, this work has demonstrated the potential of (benzoimidazol-2-ylmethyl)amine palladium complexes to catalyze the methoxycarbonylation of alkenes to afford 100% chemoselectivity and regioselectivity. The work also showed that by careful design of the complex structure, selection of the phosphine derivative, acidic promoter and olefin substrate, high catalytic activities and regioselectivities could be achieved. The active palladium species were homogeneous in nature, in which the palladium complex is stabilized by the ligands. This work therefore provides a platform to rationally design selective homogeneous palladium catalyst systems for the methoxycarbonylation of both terminal and internal alkenes.

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