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Research paper

Methoxycarbonylation of olefins catalysed by homogeneous palladium(II) complexes of (phenoxy)imine ligands bearing alkoxy silane groups

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ABSTRACT

The Schiff base compounds 2-phenyl-2-((3(triethoxysilyl)propyl)imino)ethanol (**HL1**) and 4-methyl-2-((3(triethoxysilyl)propyl)imino)methyl)phenol (**HL2**) were synthesized *via* condensation reactions of a suitable ketone or aldehyde and (3-aminopropyl) triethoxy silane (APTES). Whereas the reactions of **HL1** and **HL2** with [Pd(OAc)$_2$] afforded the bis(chelated) palladium compounds [Pd(**L1**)$_2$] (**1**) and [Pd(**L2**)$_2$] (**2**), treatments of **HL1** and **HL2** with [Pd(NCMe)$_2$Cl$_2$] gave the mono(chelated) complexes [Pd(**HL1**)$_2$Cl$_2$] (**3**) and [Pd(**HL2**)$_2$Cl$_2$] (**4**) respectively. Structural characterization of the compounds was achieved using NMR and FT-IR spectroscopies, mass spectrometry and micro-analyses. Complexes **1**–**4** gave active catalysts in the methoxycarbonylation of higher olefins producing linear esters as the major products. The coordination environment around the palladium center of the complexes dictated the relative catalytic activity, where the bis(chelated) analogues **1** and **2** were more active than the mono(chelated) analogues **3** and **4**. The nature of the acid promoter, phosphine groups, solvent system, olefin substrate and reactions conditions influenced the catalytic behaviour of the complexes.

1. Introduction

Transition metal catalysts have been employed in various olefin transformation reactions for the production of a number of industrial and domestic products [1,2]. Notable reactions include olefin polymerization [3–5], epoxidation [6,7], Suzuki cross-coupling [8] and oxidation [9] reactions. Another important olefin transformation that is currently receiving appreciable attention is methoxycarbonylation reaction, catalysed mainly by palladium based catalysts [10]. The significance of this process emanates from its versatility in the syntheses of a wide spectrum of useful commodities such as surfactants, detergents, cosmetics, solvents, food flavours and pharmaceuticals [11,12]

For several years, palladium(II) complexes anchored on various ligand motifs have been used in the methoxycarbonylation of olefins under homogeneous conditions. From the results obtained so far, it is evident that the ligand structure contributes significantly in controlling the catalytic behaviour of the complexes [13–23]. Some outstanding examples of the palladium(II) catalysts include, P^P donor complexes discovered by De La Fuente *et al* [14]. In other findings, Bianchini and co-workers [17] demonstrated that palladium(II) complexes bearing 1,1-bis(diphenylphosphino) metallocenes display moderate catalytic viability in the methoxycarbonylation of styrene to form predominantly linear products (77%), while Zolezzi *et al.* [22] found that the catalytic activity of naphthyl(diphenyl) phosphine palladium(II) catalysts is largely determined by the type of olefin substrate; affording 93% and 47% conversions for styrene and cyclohexene respectively. Separately, palladium(II) complexes of 2-diphenylphosphinoaniline and (2-diphenylphosphino)amine have been shown to exhibit high conversions of 99% within 6 h and excellent regioselectivity of 97% towards branched product in the methoxycarbonylation of styrene [19].

Despite the promising results and successes of these palladium(II) catalysts in the methoxycarbonylation reactions, most of these systems are applied under homogeneous conditions. The import being that separation of the catalysts from the products in addition to recycling have been limited. To date, there are very few palladium catalysts supported on polymer materials [24], clay [25], silica [26] and magnetic nanoparticles [27] for the methoxycarbonylation of olefins. For instance, palladium(II) catalysts supported on 2-vinyl-functional diphenyl-2 pyridylphosphine porous polymer display high TOF of 2983 h^{-1} and can be recycled up to three times [24] in the methoxycarbonylation of acetylene. Another approach has seen the use of silica supported palladium catalyst which give complete conversion of aryl iodides within 2 h and chemoselectivity of 97% towards the ester product. These catalysts exhibit appreciable stability and can be reused five times with minimal drop in catalytic activity [26]. The promising results demonstrated by these supported catalysts in the methoxycarbonylation of

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olefins thus calls for a need to explore more immobilized catalysts, which are amenable to separation and recycling.

In attempts to bridge this gap, we herein design palladium(II) complexes supported on (phenoxy)imine ligands bearing silane alkoxy groups. We envisage that by incorporating the alkoxy groups on the ligand backbone, immobilization of the systems on for instance silica support, would be made possible [28]. In this paper, we therefore present the synthesis and characterisation of (phenoxy)imine palladium (II) complexes and their applications in the methoxycarbonylation of higher olefins under homogeneous conditions. The effect of catalyst structure, solvent, nature of acid promoter, type of phosphine additive, olefin substrate and reaction conditions on the catalytic activity and regioselectivity would be discussed.

2. Experimental section and methods

2.1. General instrumentation and material

All air sensitive manipulations were performed under inert atmosphere and moisture free conditions using standard Schlenk techniques. All solvents purchased from Merck were of analytical grade and were dried before use. Toluene solvent was dried over sodium wire and benzophenone while methanol was dried and distilled by heating over magnesium metal activated with iodine. Dichloromethane was distilled using phosphorus pentoxide and stored in molecular sieves, DMF was dried over calcium oxide and chlorobenzene was dried over phosphorus pentoxide [29]. The reagents; (3-aminopropyl) triethoxy silane (99%), 2-hydroxyacetophenone (98%), 2-hydroxy-5-methylbenzaldehyde (98%), palladium(II) dichloride (59%), palladium (II) acetate (98%), olefins, hydrochloric acid, p-TsOH (≥98.5%), PPh_3 (99%), dppe (98%), $P(Cy)_3$ (98%) were obtained from Sigma-Aldrich. NMR spectra were recorded on a Bruker Ultrashield 400 (^{1}H NMR 400 MHz, ^{13}C NMR 100 MHz) spectrometer in $CDCl_3$ solution at room temperature. The chemical shift values (δ) were referenced to the residual proton and carbon signals at 7.24 and 77.0 ppm respectively of the $CDCl_3$ NMR solvent. The infrared spectra were recorded on a Perkin-Elmer Spectrum 100 in the 4000–400 cm^{-1} range. Mass spectral analyses were carried out using LC premier micromass, Elemental analyses were performed on a Thermal Scientific Flash 2000 whereas GC and GC–MS analyses was performed on a Varian CP-3800 and QP2010 respectively.

2.2. Synthesis of (phenoxy)imine ligands and their palladium(II) complexes

2.2.1. Synthesis of 2-phenyl-2-((3-(triethoxysilyl)propyl)phenoxy)imine (HL1)

A solution of 2-hydroxyacetophenone (1.36 g, 10.00 mmol) in toluene (25 mL) was refluxed in Dean-Stark apparatus for 3 h and a solution of (3-aminopropyl) triethoxy silane, APTES, (2.21 g, 10.00 mmol) in toluene (15 mL) was added and the mixture was further refluxed for 24 h. The organic fraction was then evaporated *in vacuo* to give **HL1** as an analytically pure yellow oil. Yield = 3.20 g (94%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H (ppm) 0.79 (t, 2H, J = 8.4 Hz, Si-CH_2) , 1.26 (t, 9H, $^3J_{HH}$ = 7.2 Hz, OCH_2-CH_3), 1.91 (m, 2H, C-CH_2-C), 2.38 (s, 3H, CH_3) , 3.60 (t, 2H, $^3J_{HH}$ = 7.2 Hz, NCH_2C) , 3.86 (q, 6H, $^3J_{HH}$ = 7.2 Hz, O-CH_2), 6.76 (d, 1H, $^3J_{HH}$ = 7.2 Hz, Ph) 7.02 (d, 2H, $^3J_{HH}$ = 8.4 Hz, Ph), 7.28 (dt, 1H, $^3J_{HH}$ = 7.2 Hz, Ph) 7.52 (d, 1H, $^3J_{HH}$ = 8.0 Hz, Ph). ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 171.5 (CH_3*C*N), 165.2 (Ph-C), 132.6 (Ph-C), 129.0 (Ph-C), 127.9 (Ph-C), 119.2 (Ph-C), 116.5 (Ph-C), 58.5 (O-CH_2), 51.4 (N**C**H_2C), 23.9 (CH_3), 18.3 (OCH_2-*C*H_3), 14.1 (C-*C*H_2-C) 8.2 (Si-CH_2). MS (ESI) *m/z* (%) 255 (M^+, 100). HRMS-ES; Calc: 339.1901; Found: 339.0817. IRν_{max}/cm^{-1}: $\nu_{(OH)}$ = 2973, $\nu_{(C=N)}$ = 1615, $\nu_{(Si\text{-}O)}$ = 1071.

2.2.2. Synthesis of 4-methyl-2-(((3-(triethoxysilyl)propyl)imino)phenoxy) imine (HL2)

To a solution of 2-hydroxy-5-methylbenzaldehyde (0.82 g, 6.00 mmol) in dichloromethane (30 mL), a solution of APTES (1.33 g, 6.00 mmol) in dichloromethane (10 mL) was added dropwise followed by stirring for 12 h. The organic solvent was then evaporated under vacuum to obtain **HL2** as a yellow oil. Yield = 1.54 g (75%). ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 0.71 (t, 2H, $^3J_{HH}$ = 8.0 Hz, Si-CH_2), 1.26 (t, 9H, $^3J_{HH}$ = 4.0 Hz, OCH_2-CH_3), 1.90 (m, 2H, C-CH_2-C), 2.31 (s, 3H, CH_3), 3.61 (t, 2H, $^3J_{HH}$ = 8.0 Hz, NCH_2C), 3.86 (q, 6H, $^3J_{HH}$ = 8.0 Hz, O-CH_2), 6.88 (d, 1H, $^3J_{HH}$ = 8.0 Hz, Ph), 7.05 (s, 1H, H_d), 7.13 (d, 1H, $^3J_{HH}$ = 8.0 Hz, Ph), 8.31 (s, 1H, Ph-CHN). ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 164.8 (Ph-C), 159.1 (Ph-CH-N), 132.7 (Ph-C), 131.2 (Ph-C), 127.4 (Ph-C), 118.5 (Ph-C), 116.7 (Ph-C), 62.1 (N*C*H_2C), 58.4 (O-CH_2), 24.4 (CH_3), 20.3 (C-*C*H_2-C), 18.3 (OCH_2-*C*H_3), 7.9 (Si-CH_2). MS (ESI) *m/z* (%) 454 (M^+, 100). HRMS-ES; Calc: 339.1901; Found: 340.1806. IR ν_{max}/ cm^{-1}: $\nu_{(OH)}$ = 2974, $\nu_{(C=N)}$ = 1634, $\nu_{(Si\text{-}O)}$ = 1073.

2.2.3. Synthesis of [Pd (L1)$_2$] (1)

To a solution of **HL1** (0.34 g, 1.00 mmol) in methanol (20 mL), a solution of [Pd(OAc)$_2$] (0.11 g, 0.50 mmol) in methanol (15 mL) was added and refluxed for 8 h. The resultant mixture was then filtered and washed with methanol. Recrystallization of the crude product from CH_2Cl_2-hexane mixture afforded complex **1** as a yellow powder. Yield = 0.31 g (79%). ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 0.79 (t, 4H, $^3J_{HH}$ = 8.0 Hz, Si-CH_2), 1.22 (t, 18H, $^3J_{HH}$ = 8.0 Hz, OCH_2-CH_3) , 2.02 (m, 4H, C-CH_2-C) , 2.45 (s, 6H, CH_3), 3.80 (q, 16H, $^3J_{HH}$ = 8.0 Hz, NCH_2C, O-CH_2), 6.58 (t, 2H, $^3J_{HH}$ = 8.0 Hz, Ph), 6.87 (d, 2H, $^3J_{HH}$ = 8.0 Hz, Ph), 7.11 (t, 4H, $^3J_{HH}$ = 8.0 Hz, Ph),7.37 (d, 2H, $^3J_{HH}$ = 8.0 Hz, Ph). ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 183.9 (CH_3**C**N), 166.8 (Ph-C), 132.4 (Ph-C), 131.2 (Ph-C), 128.7 (Ph-C), 118.9 (Ph-C), 115.1 (Ph-C), 58.4 (O-CH_2), 54.5 (N**C**H_2C), 26.6 (CH_3), 23.6 (OCH_2-*C*H_3), 18.3 (C-*C*H_2-C) 7.9 (Si-CH_2). IR ν_{max}/ cm^{-1}: $\nu_{(C=N)}$ = 1655, $\nu_{(Si\text{-}O)}$ = 1098. Anal. Calcd for $C_{34}H_{56}N_2O_8PdSi_2$: C, 52.13; H, 7.21; N, 3.58. Found: C, 52.58; H, 6.93; N, 3.36.

2.2.4. Synthesis of [Pd(L2)$_2$] (2)

Complex **2** was synthesised following the procedure employed for complex **1** using [Pd(OAc)$_2$] (0.14 g, 0.64 mmol) and **HL2** (0.43 g, 1.28 mmol). Yield = 0.44 g (87%). ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 0.69 (t, 4H, $^3J_{HH}$ = 8.0 Hz, Si-CH_2), 1.20 (t, 18H, $^3J_{HH}$ = 8.0 Hz, OCH_2-CH_3), 1.90 (m, 4H, C-CH_2-C), 2.24 (s, 6H, CH_3), 3.71 (t, 4H, $^3J_{HH}$ = 8.0 Hz, NCH_2C); 3.80 (q, 12H, $^3J_{HH}$ = 8.0 Hz, O-CH_2), 6.78 (d, 2H, $^3J_{HH}$ = 8.0 Hz, Ph), 6.95 (s, 2H, Ph), 7.05 (d, 2H, $^3J_{HH}$ = 8.4 Hz, Ph),7.60 (s, 2H, Ph-CHN), ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 190.4 (Ph**C**N), 162.8 (Ph-C), 161.7 (Ph-C), 135.8 (Ph-C), 133.2 (Ph-C), 123.5 (Ph-C), 120.0 (Ph-C), 60.7 (N**C**H_2C), 58.4 (O-CH_2), 25.6 (CH_3), 19.9 (C-*C*H_2-C) , 18.3 (OCH_2-*C*H_3), 7.6 (Si-CH_2). IR ν_{max}/ cm^{-1}: $\nu_{(C=N)}$ = 1621, $\nu_{(Si\text{-}O)}$ = 1085. Anal. Calcd. for $C_{34}H_{56}N_2O_8PdSi_2$: C, 52.13; H, 7.21; N, 3.58. Found: C, 52.46; H, 7.11; N, 3.54.

2.2.5. Synthesis of [Pd(HL1)(Cl$_2$)] (3)

To a solution of [Pd(NCMe)Cl_2] (0.30 g, 1.20 mmol) in dichloromethane (20 mL), was added ligand **HL1** (0.41 g, 1.20 mmol) dissolved in dichloromethane (10 mL). The resulting orange solution was then stirred for 24 h. The solvent was then reduced to about 10 mL and recrystallization by layering the solution with hexane (5 mL) produced complex **3** as an analytically pure orange solid. Yield = 0.51 g (83%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H (ppm) 0.72 (t, 2H, J = 8.0 Hz, Si-CH_2) , 1.19 (t, 9H, $^3J_{HH}$ = 8.0 Hz, OCH_2-CH_3), 1.91 (m, 2H, C-CH_2-C), 2.23 (s, 3H, CH_3) , 3.74 (t, 2H, $^3J_{HH}$ = 8.0 Hz, NCH_2C) , 3.85 (m, 6H, O-CH_2), 7.02 (d, 1H, $^3J_{HH}$ = 7.2 Hz, Ph) 7.21 (d, 2H, $^3J_{HH}$ = 8.4 Hz, Ph), 7.46 (t, 1H, $^3J_{HH}$ = 7.2 Hz, Ph) 7.55 (d, 1H, $^3J_{HH}$ = 8.0 Hz, Ph). ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 181.6 (CH_3*C*N), 164.4 (Ph-C), 131.2 (Ph-C), 129.4 (Ph-C), 126.6 (Ph-C), 117.5 (Ph-C), 113.2 (Ph-C), 56.9 (O-CH_2), 52.8 (N*C*H_2C), 24.7 (CH_3), 21.8 (OCH_2-*C*H_3), 18.1 (C-*C*H_2-C) 7.7 (Si-CH_2). IR ν_{max}/ cm^{-1}: $\nu_{(OH)}$ = 2993,$\nu_{(C=N)}$ = 1650, $\nu_{(Si\text{-}O)}$ = 1080. Anal. Calcd. for $C_{17}H_{29}Cl_2NO_4PdSi$: C, 39.51; H, 5.66; N, 2.71. Found: C, 39.25; H, 5.34; N, 2.65.

*2.2.6. Synthesis of [Pd(**HL2**)(Cl_2)] (**4**)*

Complex **4** was synthesized according to the procedure described for complex **3** using **HL2** (0.20 g, 0.60 mmol and [Pd(NCMe)Cl_2] (0.15 g, 0.60 mmol). Orange solid. Yield = 0.21 g (65%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H (ppm) 0.70 (t, 2H, J = 8.0 Hz, Si-CH_2) , 1.21 (t, 9H, $^3J_{HH}$ = 8.0 Hz, OCH_2-CH_3), 1.92 (m, 2H, C-CH_2-C), 2.03 (s, 2H, CH_3) , 3.74 (t, 2H, $^3J_{HH}$ = 8.0 Hz, NCH_2C) , 3.82 (m, 6H, O-CH_2), 6.80 (d, 1H, $^3J_{HH}$ = 8.0 Hz, Ph) 6.90 (d, 2H, $^3J_{HH}$ = 8.4 Hz, Ph), 7.05 (t, 1H, $^3J_{HH}$ = 7.2 Hz, Ph) 7.06 (s, H, Ph-CHN). ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 186.4 (PhCHN), 161.7 (Ph-C), 159.6 (Ph-C), 134.8 (Ph-C), 132.3 (Ph-C, 122.5 (Ph-C), 118.3 (Ph-C), 61.6 (NCH_2C), 57.5 (O-CH_2), 22.8 (CH_3), 20.4 (OCH_2-CH_3), 18.9(C-CH_2-C), 7.5 (Si-CH_2). IR ν_{max}/ cm^{-1}: $\nu_{(OH)}$ = 2998, $\nu_{(C=N)}$ = 1651, $\nu_{(Si\text{-}O)}$ = 1083. Anal. Calcd. for $C_{17}H_{29}Cl_2NO_4PdSi$: C, 39.51; H, 5.66; N, 2.71. Found: C, 39.85; H, 5.85; N, 2.58.

2.3. Typical procedure for the methoxycarbonylation reactions

The methoxycarbonylation catalytic reactions were performed in a stainless steel autoclave Parr reactor equipped with a temperature control unit, an internal cooling system and a sampling valve. In a typical experiment, complex **2** (0.06 g, 0.08 mmol), HCl (0.025 mL), 1-hexene (2 mL, 16.00 mmol) and PPh_3 (0.04 g, 0.16 mmol) to give 0.5 mol% were placed in a Schlenk tube. A mixture of toluene (50 mL) and methanol (50 mL) were then added to dissolve them. The mixture was then introduced into the reactor and purged three times with CO, set at the required temperature and pressure and then the reaction stirred at 500 rpm. At the end of the reaction time, the reactor was cooled to room temperature and the excess CO vented off. Samples were drawn and filtered using micro-filter prior to GC analysis to determine the percentage conversion of the substrate to the products, assuming 100% mass balance. GC–MS was used to determine the identity of the ester products, while the linear and branched esters were assigned using standard authentic samples. The GC analyses was carried out under the following conditions of: 25 m (1.2 mm film thickness) CP-Sil 19 capillary column, injector temperature 250 °C, oven program 50 °C for 4 min, rising to 200 °C at 20 °C/min and holding at 200 °C for 30 min, nitrogen carrier column gas 5 psi.

3. Results and discussion

3.1. Synthesis of (phenoxy)imine ligands and their palladium (II) complexes

The (phenoxy)imine ligands **HL1** and **HL2** were synthesized by condensation of 2-hydroxyacetophenone and 2-hydroxy-5-methylbenzaldehyde respectively with (3-aminopropyl) triethoxy silane (Scheme 1) following a modified literature procedure [30]. Treatments of **HL1** and **HL2** with [Pd(OAc)$_2$] gave the corresponding bis(chelated) complexes **1** and **2**, while reactions of **HL1** and **HL2** with [Pd(NCMe)$_2$$Cl_2$] afforded the respective mono(chelated) complexes **3** and **4** (Scheme 1). The formation of the bis(chelated) complexes **1** and **2**, bearing anionic ligands **L1** and **L2**, is likely to be driven by the presence of the acetate ions (conjugate base), which deprotonates the ligands, to give acetic acid as the by-product.

NMR spectroscopy was useful in the elucidation of the synthesized compounds (Figs. S1-S10). For example, a shift of the N-CH_2 signal from 3.59 ppm in **HL1** to 3.80 ppm in the corresponding complex **1** established successful isolation of the palladium complex (Figs. S1 and S5). Similarly, in the ^{13}C NMR spectra, the signature imine carbon peaks were recorded at 159.1 ppm and 190.4 ppm in **HL2** and its corresponding complex **2** respectively (Figs. S4 and S8). These observations were in tandem with those previously reported by Murphy [31] and Singh and co-workers [32].

FT-IR spectra of ligands **HL1** and **HL2** displayed sharp bands in the region 1614–1651 cm^{-1} indicative of the $\nu_{(C=N)}$ functional group, and confirmed the formation of the ligands [33]. General shifts to lower wavenumbers upon coordination to the palladium atom (Table S1), consistent with literature precedence were observed [33]. For instance, the $\nu_{(C=N)}$ signals in **HL2** and complex **2** were recorded at 1634 cm^{-1} and 1621 cm^{-1} respectively. On the same breadth, absorption bands between 1071 cm^{-1} to 1098 cm^{-1} were assigned to the Si-O stretching vibrations [32]. Another important information that was derived from the IR spectra of the compounds was the OH signal. While in **HL1** and **HL2**, the O—H stretching vibrations were observed at 2973 cm^{-1} and 2974 cm^{-1} respectively, these signals were absent in the IR spectra of the corresponding complexes **1** and **2** (Figs. S13 and S14). This is consistent with deprotonation of the O—H proton to form anionic ligands **L1** and **L2** as given Scheme 1. In contrast, complexes **3** and **4** showed downfield shifts of OH signals at 2993 cm^{-1} and 2998 cm^{-1} (Figs. S15 and S16), in line with the presence of the neutral ligands in complexes **3** and **4**.

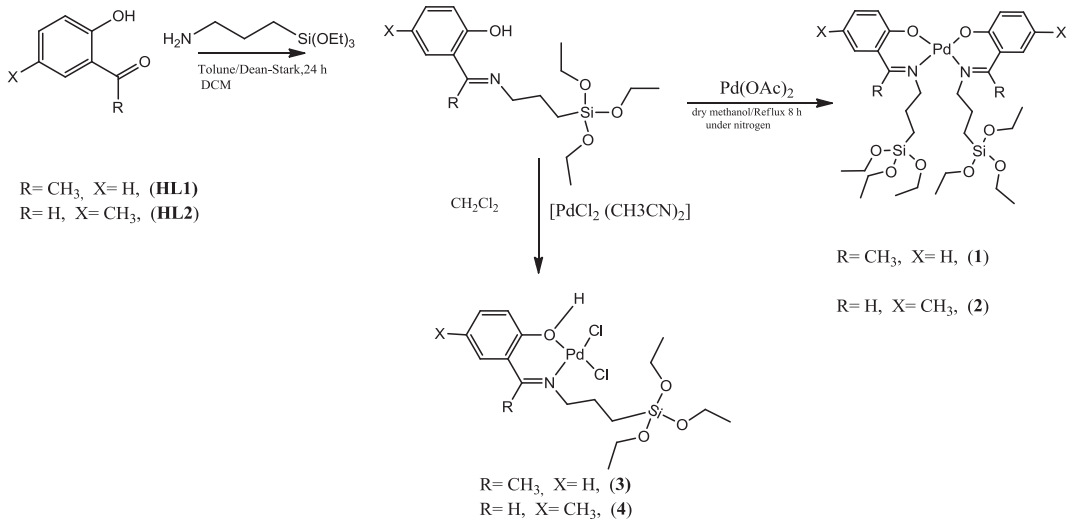
HR-MS spectra of ligands **HL1** and **HL2** were in good agreement with their molecular formulae (Figs. S17 and S18). Similarly, ES-MS data for complexes **1–4** contained m/z signals corresponding to either their molecular ions or fragments of the parent compounds (Table S2, and Figs. S19-S22). As an illustration, ESI mass spectrum of complex **1** exhibited a molecular ion peak at m/z = 805.27 amu, attributed to the [M + Na]$^+$ fragment (Mw = 782.26). Elemental data of complexes **1–4** were consistent with proposed structures in Scheme 1 and also circumstantiated the purity of the bulk materials.

3.2. Catalytic methoxycarbonylation of olefins using complexes 1–4

3.2.1. Determination of the role of complex/ligand structure in the methoxycarbonylation of 1-hexene

Preliminary catalytic studies of complexes **1–4** in the methoxycarbonylation of 1-hexene were carried out at CO pressure of 60 bar, temperature of 90 °C and [1–hexene]:[HCl]:[PPh_3]:[Pd] molar ratio 200:10:2:1, translating to 0.5 mol% of the palladium complex with respect to 1-hexene substrate (Table 1). Under these conditions, percentage conversions between 64% and 85% were realized for complexes **1–4** (Table 1, entries 1–4). The major products formed as identified by GC and GC–MS were methyl 2-methylhexanoate (branched product **A)** and methyl heptanoate (linear product **B**), Scheme 2. Typical GC chromatogram and GC–MS spectra are given in supplementary Fig. S23. To assess the role of the palladium complex, PPh_3 additive and HCl acid promoter in the methoxycarbonylation reactions, we carried out control experiments in the absence of each compound as given in Table 1, entries 5–7. In all cases, no catalytic activity was reported, confirming that these three compounds must be present to achieve any catalytic activity, in line with previous reports [34,35].

Comparison of the catalytic activities of complexes **1–4** in these reactions allowed us to deduce the role of complex/ligand structure in regulating catalyst performance. From Table 1, it is clear that the role of ligand was not profound as witnessed in comparable percentage conversions of 84% and 85% for complexes **1** and **2,** containing **HL1** and **HL2** ligands respectively. On the same vein, complexes **3** and **4**, bearing ligands **HL1** and **HL2** gave comparable conversions of 61% and 65%. However, the bis(chelated) complexes **1** (84%) and **2** (85%) were more active than the corresponding mono(chelated) complexes **3** (61%) and **4** (65%). Thus the coordination environment around the palladium(II) atom appeared to be the main contributing factor in regulating catalytic activity. Two reasons can be implicated in this trend. The first is the relative stability of the complexes, where complexes **1** and **2** are expected to be more stable due to the double chelation, thus limit catalyst decomposition [36]. As indicated in the proposed mechanism (Scheme 3), the generation of the active species from the bis(chelated) complexes **1** and **2** may be preceded by dissociation of one ligand unit, resulting in improved stability, in comparison to the mono(chelated) analogues **3** and **4**. The second plausible reason could be the electrophilicity of the metal atoms. This due to the assertion that complexes

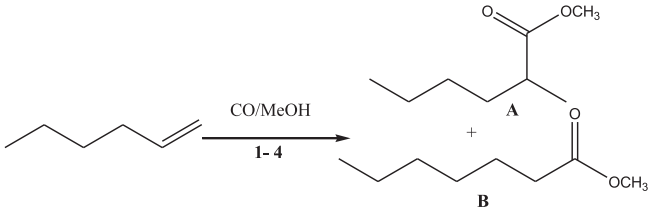


Scheme 1. Synthesis of (phenoxy)imine ligands and their palladium(II) complexes **1–4.**

Table 1
The effect of catalyst structure in the methoxycarbonylation of 1-hexene using **1-4**.[a]

Entry	Catalyst	Conv (%)[b]	TOF (h^{-1})	l/b (%)[c]
1	**1**	84	7.0	58/42
2	**2**	85	7.1	61/39
3	**3**	61	5.0	65/35
4	**4**	65	5.4	60/40
5[d]	–	0	–	–
6[e]	**1**	0	–	–
7[f]	**1**	0	–	–
8	$Pd(OAc)_2/PPh_3$	25		65/37
9	$Pd(OAc)_2$/**HL2**/ PPh_3	8	0.5	100/0
10	$Pd(OAc)_2$/**HL2**	trace	–	–
11[g]	2	76	6.3	60/40

Reaction conditions: [1-hexene]:[HCl]:[PPh_3]:[Pd] = 200:10:2:1; Pd (0.08 mmol), HCl (0.025 mL), 1–1-hexene (2 mL, 16.00 mmol) and PPh_3 (0.04 g, 0.16 mmol); P_{CO}, 60 bar; Temp: 90 °C, Time: 24 h; Solvent: methanol 50 mL and toluene 50 mL; [b]% of 1-hexene converted to esters determined from GC assuming 100% mass balance; [c] Molar ratio between branched and linear ester determined from GC. [d]no Pd complex added; [e]reaction without acid promoter; [f]reaction without PPh_3. [g]Mercury poisoning test.



Scheme 2. Methoxycarbonylation of 1-hexene using complexes **1–4** as catalysts to give branched (**A**) and linear (**B**) esters.

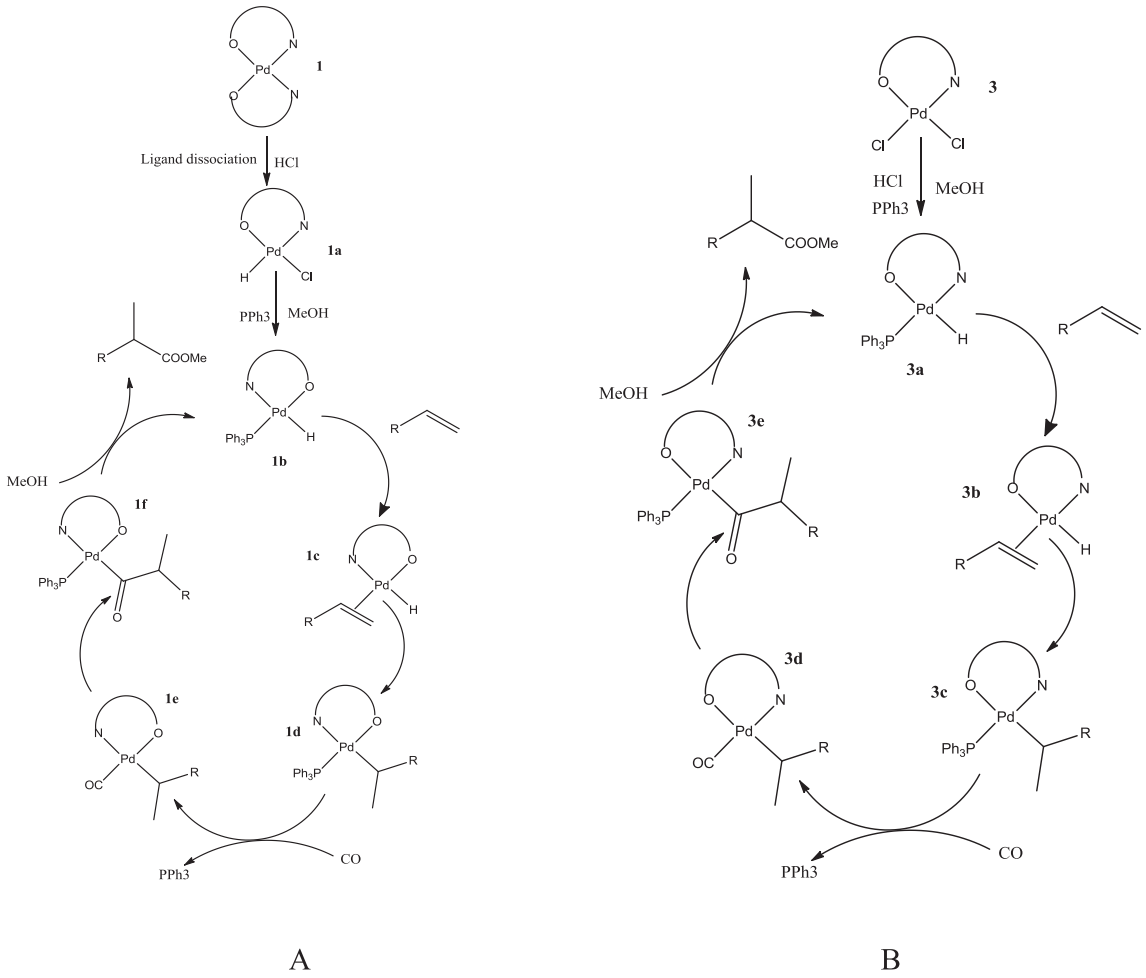
1 and **2**, containing the anionic ligands, are likely to be more electron deficient. In general, the catalyst/ligand structure showed no direct influence on the regioselectivity of the ester products since in all cases, 58%-65% of linear products were realized. This could be attributed to similar active species (palladium hydride,) in line with the mechanistic pathway proposed in Scheme 3 [34].

To further probe the influence and role of the ligand motif in generation of the active species for the methoxycarbonylation reactions, we performed another set of control experiments (Table 1, entries, 8–10) under similar reactions conditions, using HCl as the acid promoter. First, we used the $Pd(OAc)_2/PPh_3$ system and observed significantly lower percentage conversions of 25% in comparison to conversions of 85% reported for complex **2**/PPh_3 system. Additionally, the use of Pd $(OAc)_2$/**HL2**/PPh_3 and $Pd(OAc)_2$/**HL2** systems only gave trace amounts of the products (Table 1, entries 9–10). These findings therefore confirm the significant role of the palladium complexes **1–4** in generating the active species for the methoxycarbonylation reactions. While the catalytic activities of complexes **1–4** are lower in comparison to some of the most active systems reported in literature [23,37], they display comparable catalytic activities to other homogeneous systems reported [13,22]. For instance, the palladium systems bearing naphthyl(diphenyl)phosphines, benzimidazolylemethyl)amine palladium complexes and mixed NˆNˆX (X = O and S) tridentate ligands afford comparable TOF of 11 h^{-1} , 7.1 h^{-1} and 15 h^{-1} respectively [13,20,22] to the TOF values of 5.0–7.1 h^{-1} reported for complexes **1–4**. On the other hand, the palladium catalysts bearing 2-(diphenylphosphinoamino) pyridine display greater TOF values of 28 h^{-1} in the methoxycarbonylation of 1-hexene [23].

3.2.2. The effects of acid promoters and phosphine additives on the methoxycarbonylation of 1-hexene

Acid promoters play a crucial role in regulating the catalytic performance of palladium complexes in methoxycarbonylation of olefins. We therefore scrutinized the influence of the acid promoters; *para*-tolyl sulfonic acid (PTSA), HCl, ethyl aluminium dichloride, $EtAlCl_2$ (EADC), trimethyl aluminium, $AlMe_3$ (TMA) and methyl sulfonic acid (MSA) on the catalytic performance of complex **2** (Table 2, entries 1–5). From the results obtained, HCl gave the most active catalyst system (85%), while TMA, only gave conversions of 9%. The reactivity order of TMA < EADC < MSA < PTSA < HCl (Fig. 1) was thus established in line with the strengths and coordinating abilities of the respective acid promoters [14,15]. This contrasts the findings of Tang *et al* in the methoxycarbonylation of acetylene, where PTSA was more active than HCl [38]. In comparison to our previous reports [20,21] where the use of PTSA or MSA did not give any active catalysts, the current systems are thus more industrially relevant (Table 2, entries 2 & 5). In general, all the acid promoters displayed preference to the linear products (> 60%), with exception of TMA, which produced more branched products of 77% (Fig. 1). The reasons for this observation is not clear to us at this stage, since TMA is not the least sterically demanding (HCl is probably the smallest) in the series [39]. It is possible that other than steric hindrance, electronic parameters may also be involved in regulating product composition [40,41].

Due to the corrosive nature of acid promoters especially HCl, we found it prudent to investigate the integrity of the complex **2** under the



Scheme 3. Proposed hydride mechanism for methoxycarbonylation of olefins catalysed by bis(chelated) (A) and the mono(chelated) (B) palladium complexes.

Table 2
The effect of acid promoters and phosphines in the methoxycarbonylation of 1-hexene using complex **1-4**.[a]

Entry	Catalyst	Acid	PR_3	Pd:PR_3	Conv (%)[b]	l/b (%)[c]	TOF
1	**2**	HCl	PPh_3	1:2	85	61/39	7.1
2	**2**	MSA	PPh_3	1:2	75	68/32	6.2
3	**2**	TMA	PPh_3	1:2	9	23/77	0.8
4	**2**	EADC	PPh_3	1:2	63	60/40	5.3
5	**2**	PTSA	PPh_3	1:2	80	67/33	6.7
6	**1**	PTSA	PPh_3	1:2	78	65/35	6.5
7	**3**	PTSA	PPh_3	1:2	60	64/36	4.5
8	**4**	PTSA	PPh_3	1:2	62	62/38	5.2
9	**2**	HCl	$P(Cy)_3$	1:2	61	49/51	5.1
10	**2**	HCl	Dppe	1:2	trace	–	–

Reaction conditions: Pressure: 60 bar, temp: 90 °C, Solvent: methanol 50 mL and toluene 50 mL; [Pd]:[acid]:[hexene] ratio; 1:10:200; time, 24 h; [b]% of hexene converted to esters; [c] Molar ratio between branched and linear ester; TOF (mol. sub/mol. Pd. h^{-1}).

reaction conditions in the presence of HCl using ^{1}H NMR spectroscopy. This was to ascertain if the active species contains a ligand-bound palladium complex or ligand-free palladium nanoparticles. Figures S24 and S25 show ^{1}H NMR spectra acquired at different time intervals for 24 h at room temperature and 80 °C respectively. From both spectra, it was clear that the signature peaks of complex **2** remained unchanged, indicating that the active species is stable under the reaction conditions and contains a ligand bound palladium complex. To further corroborate the true identity of the active species, a mercury poisoning test was performed to establish either the homogeneity or heterogeneity of the active intermediates [42]. Upon addition of a few drops of mercury, we noted a slight drop of conversion from 85% to 76% (Table 1, entries 2 vs 11). The marginal decline in catalytic activity of complex **2** upon addition of mercury is indicative of a largely homogeneous active species in good agreement with NMR experiments.

To establish the effect of the nature of phosphine groups on the catalytic performance of complex **2** in the methoxycarbonylation of 1-hexene, we used both monodentate and chelating phosphines such as PPh_3, $P(Cy)_3$ and 1,2- bis(diphenylphosphino) ethane (dppe) (Table 2, entries 9 & 10). The catalytic activities obtained could be connected to the steric property, coordination abilities and basicity of the phosphines. For example, the more basic and bulkier PCy_3 gave lower percentage conversions (61%) than the analogues PPh_3 (85%), while the chelating dppe recorded no catalytic activity. The lower catalytic activity reported for PCy_3 may be a consequence of reduced electrophilicity of the palladium atom. Similarly, for the chelating dppe group, lack of dissociation of the dppe ligand from the palladium coordination sphere may hinder substrate coordination [43]. The nature of the phosphine groups also affected the regioselectivity of the ester products. For instance, PPh_3 and $P(Cy)_3$ groups afforded 39% and 51% of the branched esters respectively (Table 2, entries 1 & 9). Since PCy_3 is relatively bulkier than PPh_3, this observation cannot be explained by steric factors, but rather a stereo-selective phenomenon [40,41].

3.2.3. Investigation of the role of solvent system in methoxycarbonylation of 1-hexene

The role of the solvent system, both in terms of identity and ratios was probed by varying the toluene/methanol ratios in addition to other

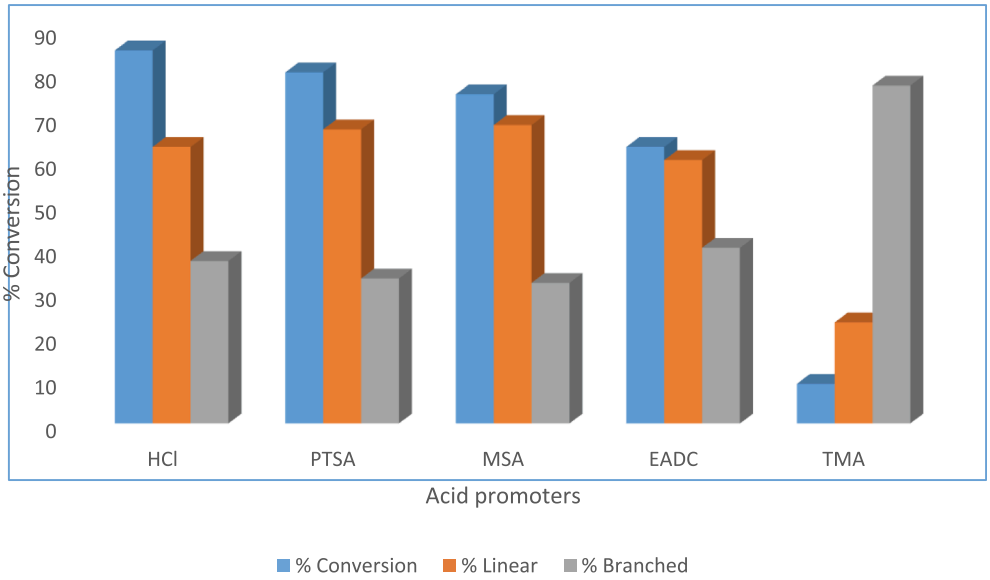


Fig. 1. Effect of acid promoters in the methoxycarbonylation of 1- hexene using complex **2** at [1-hexene]:[HA]:[PPh_3]:[Pd] ratio of 200:10:2:1; [Pd] (0.08 mmol), 1-hexene (2 mL, 16.00 mmol), P_{CO}, 60 bar; temp: 90 °C; time: 24 h; solvent, methanol/toluene (100 mL).

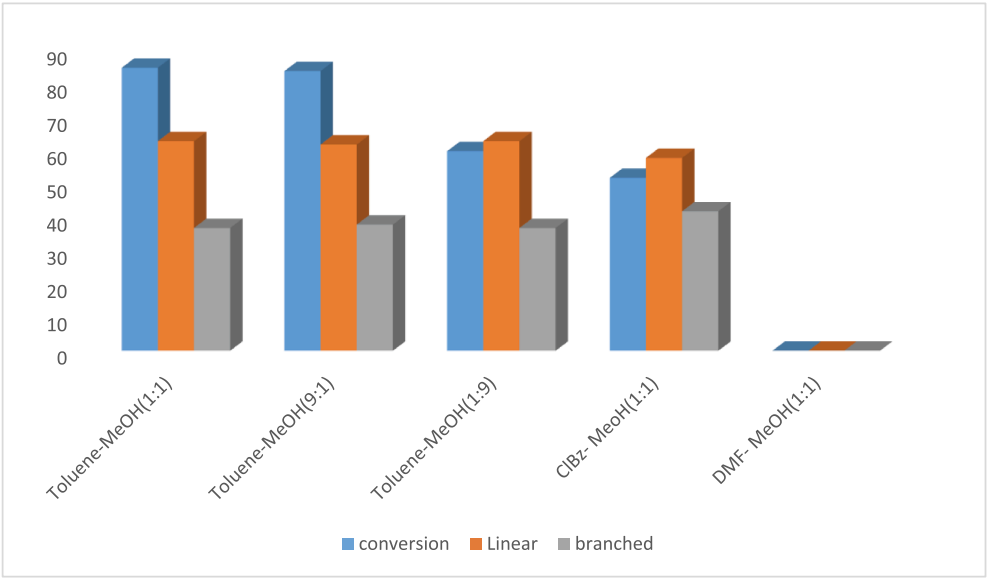


Fig. 2. Effect of solvent mixtures in the methoxycarbonylation of 1- hexene. Reaction conditions: complex **2** (0.08 mmol); [Pd]:[HCl]:[hexene] ratio, 1:10:200; time, 24 h; P_{CO}: 60 bar; temp, 90 °C; solvent, methanol/toluene (100 mL).

solvents such as chlorobenzene and DMF using complex **2** (Fig. 2). It has been reported that the role of solvent in promoting methoxycarbonylation is largely dependent on solvent polarity and coordination ability [38,44]. The results obtained in this study showed that toluene/methanol was the best system (85%), while DMF/methanol was found to give inactive catalyst system. The data thus agrees with reduced catalytic activity with increased polarity and coordinating ability of the solvents. The lower percentage conversions of 60% observed for toluene/methanol ratios of 1/9 (greater volume of methanol) may also be assigned to a hindered substrate coordination. Recently, Unver *et al.* reported percentage conversions of > 99% and 23% in toluene and DMSO solvents respectively [45]. With respect to product distribution, there was no significant effect of the solvent system employed, as comparable compositions of the branched esters (37%-42%) were realized.

3.2.4. The impact of reaction conditions in methoxycarbonylation of 1-hexene

In order to optimize the reaction conditions, we varied the reaction time, temperature, CO pressure and catalyst concentration using complex **2** and 1-hexene substrate (Table 3). We observed that decreasing the temperature from 90 °C to 60 °C was accompanied with a decline in conversions from 85% to 51% (Table 3, entries 1 and 2). This is expected [46] and also points to thermal stability of catalyst **2**, as there was no decomposition even at higher temperatures of 90 °C. Similarly, percentage conversions of 60% and 85% were reported at CO pressures of 40 and 60 bar respectively (Table 3, entries 1 and 3) and can be associated with rapid CO insertion at elevated pressure [47]. We also studied the effect of catalyst loading by varying the [1–hexene]/[2] ratios from 100 (1 mol%) to 400 (0.25 mol%) as given in Table 3, entries 1, 6–7. From the results, an optimum catalyst loading of 0.5 mol% was established, giving percentage conversion of 85% and TOF of

Table 3
The effect of reaction conditions in the methoxycarbonylation of 1-hexene using **C2**.[a]

Entry	P_{CO} (bar)	Temp (^{0}C)	Time (h)	[Pd]:[hexene]	Conv (%)[b]	l/b (%)[c]	TOF (h^{-1})
1	60	90	24	1:200	85	61/39	7.1
2	60	90	12	1:200	33	66/34	5.5
3	60	90	36	1:200	89	60/40	4.9
4	40	90	24	1:200	60	64/36	4.5
5	60	60	24	1:200	51	61/39	4.3
6	60	90	24	1:100	86	63/37	3.6
7	60	90	24	1:400	27	68/32	4.5

Reaction conditions: [Pd]: [PPh_3]:[HCl acid]: [1-hexene]; 1:2:10: 200, [b]% of 1-hexene converted to esters; [c] Molar ratio of branched to linear esters; TOF (mol. sub/mol. Pd h^{-1}).

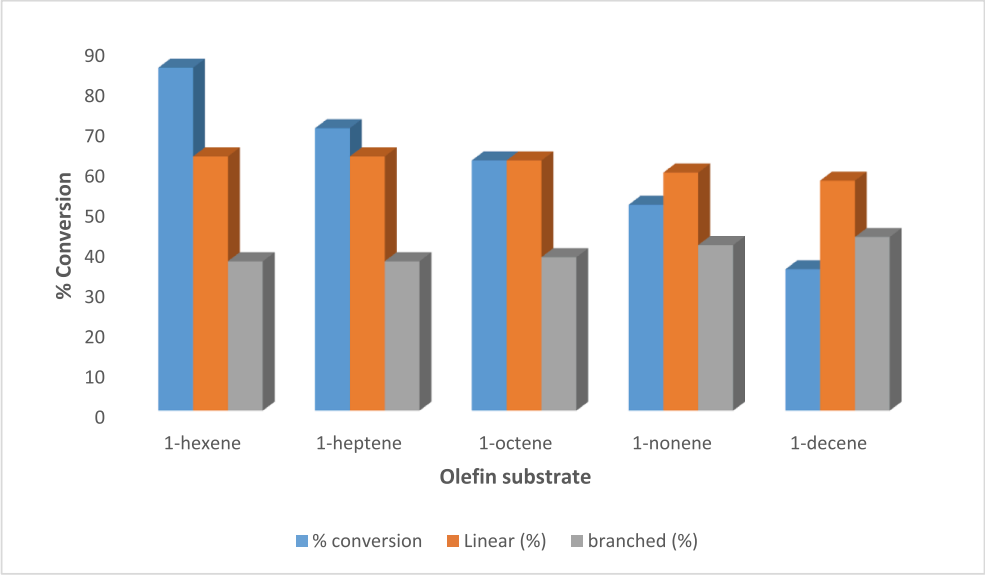


Fig. 3. The effect of olefin substrate in the methoxycarbonylation of 1-hexene using **2** (0.08 mmol) at [Pd]:[PPh_3]:[HCl]:[olefin] ratio of 1:2:10: 200, P_{CO}; 60 bar; temp, 90 °C, solvent, methanol/toluene (100 mL); time, 24 h.

7.1 h^{-1}. It is important to note that, even though lower conversions of 27% was achieved at 0.25 mol% catalyst loading, this corresponds to a higher TOF of 4.5 h^{-1} compared to TOF of 3.6 h^{-1} (86%) recorded at 1 mol%. It is therefore conceivable that higher catalyst loading of 1 mol % is not beneficial, possibly due to enhanced catalyst aggregation [48].

The stability of complex **2** was also investigated by monitoring the reaction times from 12 h to 36 h (Table 3, entries, 1–3). From the results, a two stage process could be extracted. First, is the initiation stage, as evident from increased TOFs from 5.5 h^{-1} to 7.1 h^{-1} from 12 h to 24 h respectively. The second phase between 24 h (85%) and 36 h (86%), is typical of catalyst deactivation [49] as seen from a drop in TOF from 7.1 h^{-1} to 4.9 h^{-1} respectively. Another reasonable argument for this trend could be saturation kinetics at higher product compositions [50]. This is strongly supported by near constant conversions of 85% and 86%, which does not reflect catalyst deactivation alone.

Analyses of the product composition showed that changing the reaction temperature and CO pressure did not discernibly shift the regioselectivity, as about 36% − 39% of branched esters were obtained. However, changes in catalyst concentration and time of the reactions did confer some variations in regioselectivity. For example, 32% and 39% of the branched esters were observed at catalyst loadings of 0.25 mol% and 1 mol% respectively. Increased branching with increase in catalyst loading is not well documented, but may be ascribed to enhanced isomerization with increase in catalytic activity [51]. With respect to time of reaction, 34% and 40% of branched esters were reported within 12 h and 36 h respectively, consistent with isomerization reactions over time [52].

3.2.5. Role of olefin chain length in methoxycarbonylation reactions

Next, we focused our attention to the scope of olefin substrates by further studying 1-heptene, 1-octene, and 1-decene substrates using complex **2** (Fig. 3). It was evident that the catalytic activity of complex **2** was greatly altered by the identity of the olefin substrate. For instance, conversions of 85% and 35% were reported for 1-hexene and 1-decene respectively (Fig. 3). The decrease in catalytic activity with increase in olefin chain length could result from increased steric hindrance, in addition to higher electron density; both of which have the overall effect of limiting substrate coordination to the metal center [53]. In terms of product composition, higher olefins produced more branched esters, as exemplified from values of 37% and 43% reported for 1-heptene and 1-decene respectively. This agrees with literature reports and has been associated with higher number of possible isomers with increase in olefin chain length [53,54].

3.2.6. Proposed mechanism for the methoxycarbonylation catalysed by complexes *1–4*

Methoxycarbonylation of olefins catalysed by palladium complexes is known to proceed through either carbomethoxy and hydride pathways [55]. However, most studies have shown that the hydride route is the most common [56–60]. We thus propose a hydride mechanism for complexes **1–4** using (Scheme 3). For the bis(chelated) complexes **1** and **2** (Scheme 3A), we hypothesize that the process starts with the dissociation of one ligand unit to give the palladium hydride complex (**1a**), as the active species. On the other hand, for the mono(chelated) complexes (Scheme 3B), the generation of the hydride complex (**3a**) occurs directly from the pre-catalysts without ligand dissociation. These

variations in the mechanism may account for the relatively higher catalytic activities observed for the bis(chelated) complexes **1** and **2**, in comparison to the mono(chelated) analogues **3** and **4**. The stabilization by the second ligand unit in complexes **1** and **2**, is also expected to confer improved stability of their respective active intermediates. Subsequent coordination of the olefin substrate gives the pi-bonded olefin complexes **1c** and **3b,** followed by hydride migration to afford the palladium alkyl complexes **1d** and **3c**. Coordination of the CO ligand which is then accompanied by migratory insertion forms the acyl complexes **1f** and **3e**. Finally, methanolysis reaction occurs to form the desired ester products and also results in the regeneration of the active species, **1b** and **3a**.

4. Conclusions

In conclusion, four palladium complexes supported on (phenoxy) imine ligands bearing silane alkoxy groups have been synthesized and established to form mono(chelated) and bis(chelated) monometallic complexes depending on the metal precursor. These palladium complexes form active catalysts in the methoxycarbonylation of higher olefins, in which the catalytic activity is largely influenced by the coordination environment around the palladium atom. The ligands display comparable steric encumbrance around the metal atom, producing mainly linear esters. Both the nature of the acid promoter and phosphine additive influenced the catalytic activities of the complexes. In addition, the type of solvent system used, temperature, pressure, catalyst concentration, time of reaction and nature of the olefin substrate influenced the catalytic behaviour of the complexes.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ica.2019.02.025.

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