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Kinetics and DFT Studies of the Hydrogenation Reactions of Alkenes and Alkynes Catalyzed by (Benzoimidazol-2-ylmethyl)amine palladium(II) Complexes

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Abstract

A series of (benzoimidazol-2-ylmethyl)amine palladium(II) complexes have been employed as catalysts in the homogenous hydrogenation of alkenes and alkynes under mild conditions. A correlation between the catalytic activity and the nature of the ligand was established. Kinetic studies of the hydrogenation reactions of styrene established *pseudo*-first-order dependence on styrene substrate. On the other hand, partial orders with respect to H_2 and catalyst concentrations were obtained consistent with the formation of palladium(II) monohydride species as the active species. The nature of the solvent used influenced the hydrogenation reactions, where coordinating solvents resulted in lower catalytic activities. Density functional theory investigations provided valuable insights into the reactivity trends and influence of complex structure on the hydrogenation reactions.

Keywords: palladium; catalysts; hydrogenation; kinetics; DFT

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1. Introduction

Hydrogenation reactions of alkenes and alkynes are currently one of the dominant industrial processes used for the reduction of unsaturated organic compounds to a wide range of relevant products.[1–3] Several metal-based catalysts derived from nickel, palladium, ruthenium, rhodium, iridium and platinum have been employed in the catalytic hydrogenation of alkenes and alkynes under both homogenous[4,5] and heterogeneous[6,7] conditions. Currently, the major focus in transition metal catalyzed homogeneous molecular hydrogenation reactions has been on ligand design; and the insights gained so far show that the ability to control the catalytic behavior of these catalyst lies in the coordination environment around the metal atom.

To date, palladium(II) catalysts are currently receiving much attention in the hydrogenation of alkenes and alkynes due to their superior catalytic activities and selectivity.[8] Numerous reports have appeared on the homogenous hydrogenation of alkenes and alkynes using palladium(II) catalysts supported on phosphine-donor ligands. For example, Bacchi *et al*[9] and Drago *et al*[10] employed hydazonic phosphine palladium(II) and bidentate (2,5-dimethylphospholano) palladium(II) complexes as effective catalysts in the hydrogenation of alkenes. Even though the phosphine-donor palladium catalysts have been successfully used in the homogeneous hydrogenation reactions of alkenes and alkynes, these systems suffer from lack of stability and sensitivity to moisture and air.[11] As a results, nitrogen-donor palladium(II) catalysts are emerging as suitable alternatives due to their better stability and ease of synthesis in comparison to the phosphine-donor palladium(II) complexes. For example, the pyridine-2-carbaldine palladium(0)[12] and bis(arylimino)acenaphthene palladium(0)[13] complexes have been shown to exhibit good selectivity and stability in the homogenous hydrogenation of alkynes.

We recently reported the use of palladium(II) complexes anchored on (benzoimidazol-2-ylmethyl)amine ligands[14] to give active catalysts in the methoxycabonylation of higher olefins. Due to the promising results obtained in the methoxycabonylation reactions by these systems, we chose to explore their propensity to catalyze the molecular hydrogenation of selected alkenes and alkynes. In addition, kinetics and theoretical studies have been performed and are herein discussed.

2. Experimental section

2.1. Materials and methods

All moisture and air sensitive reactions were performed using standard Schlenk line techniques. Methanol (ACS reagent, ≥99.8%), toluene (ACS reagent, ≥99.5%), dichloromethane (ACS reagent, ≥99.8%), absolute ethanol (ACS reagent, ≥98%) and tetrahydrofuran (anhydrous, ≥99.9%) were purchased from Merck. Solvents were dried and distilled under nitrogen in the presence of suitable drying agents: Toluene and acetone were dried over anhydrous calcium chloride, methanol and absolute ethanol over calcium oxide, dichloromethane over phosphorus pentoxide and stored over 4 Å molecular sieves. The ligands *N*-(1H-benzoimidazol-2-ylmethyl-2-methoxy)aniline (**L1**), *N*-(1H-benzoimidazol-2-ylmethyl-2-bromo)aniline (**L2**), *N*-(1H-benzoimidazol-2-ylmethyl)benzenamine (**L3**) and *N*-(1H-benzoimidazol-2-ylmethylamino)benzenethiol (**L4**), were synthesized following the published literature method.[15] The palladium complexes [Pd(**L1**)Cl_2] (**1**), [Pd(**L2**)Cl_2] (**2**) [Pd(**L3**)Cl_2] (**3**), [Pd(**L4**)Cl_2] (**4**), [Pd(**L2**)ClMe] (**5**) and [Pd(**L2**)ClPPh_3]BAr_4 (**6**), were prepared following our recently published procedure.[14]

2.2. Density Functional Theory (DFT) studies

DFT calculations were performed in a gas phase to identify the energy-minimized structures based on B3LYP/LANL2DZ (Los Almos National Laboratory 2 double ζ) level theory.[16] A split bases set, LANL2DZ for palladium and 6-113G for all other atoms was used to optimize the geometries and energies of the complexes. The Gaussian09 suite of programs was used for all the computations.

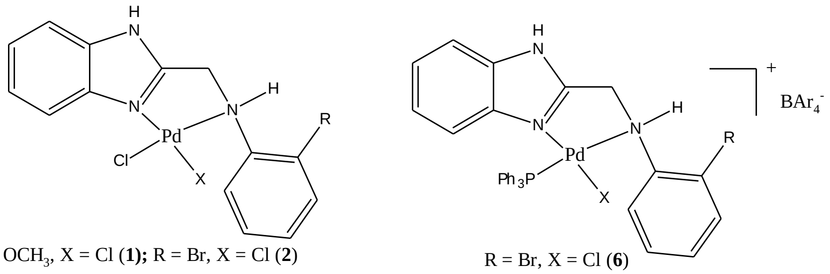
2.3. General procedure for the hydrogenation reactions of alkenes and alkynes

The catalytic hydrogenation reactions were performed in a stainless steel autoclave equipped with temperature control unit and a sample valve. In a typical experiment, styrene (0.5 mL, 4.20 mmol) and complex **2** (3.47 mg, 0.007 mmol, S/C 600) were dissolved in toluene (50 mL). The reactor was evacuated, flushed with nitrogen and the catalytic solution was introduced to the reactor via a cannula. The reactor was purged three times with hydrogen, and then set at the equipped pressure, heated to the desired temperature and the reaction stirred at 500 rpm. At the end of the reaction time, the reactor was cooled, excess hydrogen vented off. Samples for GC analyses were drawn *via* a syringe, filtered using 0.45 µm micro filters and analyzed by Varian CP-3800 GC (ZB-5HT column 30 m × 0.25 mm × 0.10 µm) GC instrument to determine the percentage conversion of styrene to ethylbenzene. Standard ethylbenzene (97%), *trans*-2-hexene (97%), *cis*-2-hexene (98%), *trans*-2-octene (98%) and octane (98%) were purchased from Sigma-Aldrich and used to confirm the presence and composition of hydrogenation products.

3. Results and discussion

3.1. Hydrogenation reactions of alkenes and alkynes using palladium (II) complexes 1-6 as catalysts

Preliminary evaluations of complexes **1-6** (Chat 1) in the hydrogenation of styrene were performed at 5 bar of H_2 pressure, 30 °C and [styrene]:[Cat] = 600:1. Under these conditions, all the complexes showed catalytic activities to afford 100% ethylbenzene with conversions ranging from 54% to 99% within 1.5 h (Fig. S1). In order to fully account for the role of complexes **1-6** in the observed catalytic hydrogenation reactions, control experiments were conducted without the use of the palladium(II) complexes under similar reaction conditions. The low percentage conversions of 4% within 10 h (Table 1, entry 7) confirmed that complexes **1-6** were responsible for the observed higher catalytic activities. We thus further carried out detailed kinetics, selectivity and theoretical studies to establish the structure-activity relationship.



R = OCH_3, X = Cl (**1**); R = Br, X = Cl (**2**)
R = H, X = Cl (**3**); R = SH, X = Cl (**4**)
R = Br, X = Me (**5**)

R = Br, X = Cl (**6**)

Chart 1: Neutral and cationic (benzoimidazol-2-ylmethyl)amine palladium (II) complexes **1-6**[17] used as catalysts in the hydrogenation reactions.

Table 1: Effect of catalyst structure on the hydrogenation of styrene by complexes **1-6**[a]

Entry	Catalyst	Conversion [b](mol%)	k_{obs} (h^{-1})	TOF [c](h^{-1})
1	**1**	74	0.91 (±0.03)	296
2	**2**	92	1.67 (±0.01)	368
3	**3**	78	0.98 (±0.05)	312
4	**4**	86	1.38 (±0.07)	344
5	**5**	54	0.56 (±0.04)	215
6	**6**	99	2.93 (±0.1)	396
7[d]	—	4	—	—

[a]Conditions: styrene, [substrate]/catalyst;600:1; substrate, 4.20 mmol; catalyst; 0.007 mmol; solvent, toluene (50 mL); pressure, 5 bar; temperature, 30 °C; time, 1.5 h. [b]Determined by GC. [c]TOF in $mol_{substrate}mol_{catalyst}^{-1}\ h^{-1}$. [d]Control experiment, no catalyst used, time 10 h.

3.2. Kinetics of styrene hydrogenation reactions

*3.2.1. Effect of complex structure on catalytic hydrogenation of styrene by **1-6***

Kinetics of the hydrogenation reactions of styrene were investigated for complexes **1-6** by monitoring the reactions using a GC chromatography. Table 1 contains the initial rate constants derived from the plots of $\text{In}[\text{Sty}]_0/[\text{Sty}]_t$ *vs* time (Fig. S2). A linear relationship was established consistent with a pseudo-first order kinetics with respect to styrene for all the complexes. The dependence of the rate of the hydrogenation reactions on styrene substrate can therefore be represented as given in equation 1.

$$\text{Rate} = k[\text{styrene}]^1 \qquad (1)$$

From the rate constants observed, the cationic complex **6** was the most active compared (Table 1, entries 2 and 6). This higher catalytic activity could be attributed to the improved solubility of complex **6** (due to the bulky Ar groups) compared to complexes **1-5**.[11] Another plausible explanation could be a higher positive charge on the palladium(II) metal atom in the cationic complex **6** relative to the neutral analogues, thus better substrate coordination.[8] A similar trend in the hydrogenation of 1-hexene was reported where higher catalytic activity (TOF = 4000 h^{-1}) for the cationic complex ($[Rh(PPh_3)_2COD]^+$) compared to TOF = 700 h^{-1} for the neutral complex $[Rh(PPh_3)_3Cl]$ was observed.[18,19] We also observed that the ligand motif had an influence on the catalytic activity. For instance, complex **2**, bearing electron withdrawing Br group on the phenyl ring showed higher catalytic activity, (k_{obs} of 1.67 h^{-1}) than the analogues complex **1** (k_{obs} of 0.91 h^{-1}), containing the electron donating OCH_3 substituent (Table 1, entries and 2). This can also be rationalized from electrophilic metal[8] center in **2** compared to **1**, consistent with the argument fronted for the cationic complex **6**. Another factor that appeared to control the catalytic activity was the Pd-Cl/Me bonds on the complex structure. For example, rate constants of 1.67 h^{-1} and 0.56 h^{-1} were observed for complexes **2** and **5** bearing Pd-Cl and Pd-Me groups respectively (Table 1, entries 2 and 5). This can be assigned to the ease of formation of a Pd-H species, usually presumed to be the active species, from the Pd-Cl system compared to the Pd-Me analogues.[20]

3.2.2. *Effect of catalyst concentration and hydrogen pressure on the kinetics of hydrogenation reactions of styrene*

Kinetic experiments were further conducted to establish the effects of catalysts concentrations on the hydrogenation reactions of styrene using complex **2**. This was done by varying [styrene]/[**2**] from 200 to 1000 at constant initial concentration of styrene (Table 2, entries 1-5). A plot of $In[styrene]_0/[styrene]_t$ *vs* time (Fig. S3) gave a linear relationship from which the observed rate constants (k_{obs}) were derived (Table 2). It was observed that an increase in catalyst concentration resulted in an increase in catalytic activity. For instance k_{obs} of 2.66 h^{-1} and 0.91 h^{-1}

were obtained at [styrene]/[**2**] ratios of 600 and 1000 respectively. However, a closer examination of the TOF values at different catalyst loadings paint a different picture. For example, increased [styrene]/[**2**] ratio (decrease in catalyst concentration) from 600 to 1000 was marked by an increase in TOF from 368 h^{-1} and 466 h^{-1} respectively. It is therefore evident that increasing catalyst concentration did not increase the catalytic activity by a similar magnitude and thus higher [substrate]/[catalyst] ratios (lower catalyst loadings) is not only recommended but would also be industrially beneficial with these systems.

The order of reaction with respect to catalyst **2** was extracted from the plot of –In(k_{obs}) *vs* –In[**2**] (Figure 1) and obtained as 0.8 ± 0.08. From our previous work, we reported fractional orders on catalyst concentration in hydrogenation reactions of styrene catalyzed by palladium(II) complexes.[21,22] This fractional order has been associated with possible catalyst aggregation during hydrogenation reactions and/or formation of palladium(0) nanoparticles as the active species.[23,24] To shed some light on this, mercury poisoning test was conducted by adding few drops of mercury to the reaction solution.[23] Appreciable drop in catalytic activity from 92% to 67% was observed (Table 2, entries 3 and 9), consistent with the generation of active palladium(0) nanoparticles in the catalytic mixture.[22] However, from the absence of induction periods (Figs. S1-S6) point to a largely homogeneous catalyst system.

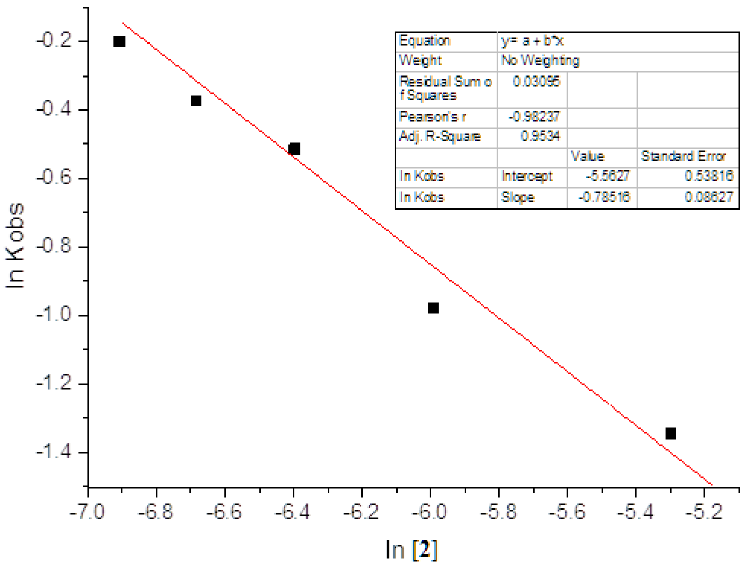


Figure 1: Plot of In(k_{obs}) *vs* In[**2**] for the determination of the order of reaction wit respect to catalyst **2.**

The effect of H_2 concentration on the kinetics of styrene hydrogenation reactions was also investigated at different H_2 pressures of 5 bar to 12.5 bar (Table 2, entries 3, 6-8). From the data obtained, it was evident that an increase in H_2 pressure resulted in an increase in the observed rate constants (k_{obs}). For example, k_{obs} of 1.67 h^{-1} and 2.02 h^{-1} were recorded at H_2 pressures of 5 and 10 bar (Table 2, entries 3 and 6). Linear relationships were observed from the plot of In$[Sty]_0/[Sty]_t$ *vs* time at different H_2 pressures (Fig S4) to generate a rate order of 0.7 ± 0.1 with respect to H_2 concentration (Figure 2). This fractional and lower order indicates a complex reaction mechanism with respect to $[H_2]$ and possibly the formation of a Pd-monohydride species as the active species,[25] and possible catalyst aggregation *vide supra*. The rate law for the hydrogenation reactions of styrene using catalyst **2** can therefore be expressed as given in equation 2.

$$\text{Rate} = k[\text{styrene}]^{1}\,[\mathbf{2}]^{0.8}\,[P_{H2}]^{0.7} \qquad (2)$$

Table 2: Effect of catalyst concentration and pressure on the hydrogenation of styrene using catalyst **2**[a]

Entry	**Sub/Cat**	**P_{H2} (bar)**	**T (°C)**	**Conv (%)**[b]	**k_{obs} (h^{-1})**	**TOF[c] (h^{-1})**
1[d]	200	5	30	99	3.84 (±0.02)	158
2	400	5	30	>99	2.66 (±0.02)	267
3	600	5	30	92	1.67 (±0.01)	368
4	800	5	30	84	1.45 (±0.03)	448
5	1000	5	30	70	0.91 (±0.05)	466
6	600	7.5	30	98	2.02 (±0.02)	392
7[d]	600	10	30	99	5.45 (±0.13)	475
8[e]	600	12.5	30	99	6.84 (±0.06)	594
9[f]	600	5	30	67	__	268

[a]Conditions: styrene, 4.36 mmol; solvent; toluene (50mL); time, 1.5 h. [b]Determined by GC. [c]TOF in $mol_{substrate}mol_{catalyst}^{-1}$ h^{-1}.[d]Time, 1.25 h, [e]Time, 1.0 h. [f] Mercury drop test (5 drops of mercury were added to the reaction mixture).

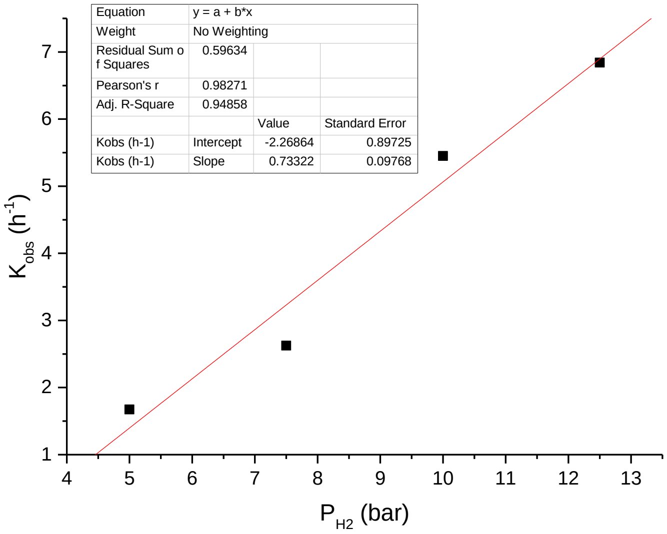
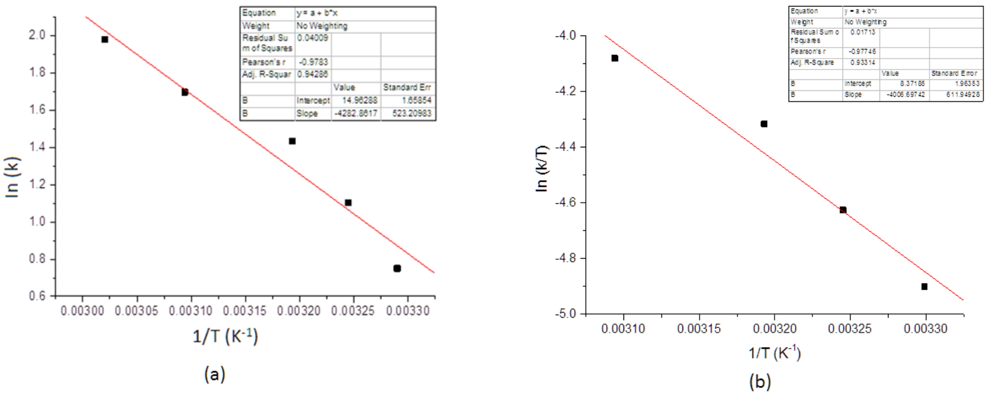


Figure 2: Plot of k_{obs} *vs* P_{H2} (bar) for the determination of the order of reaction with respect to H_2 pressure.

3.2.3. Effect of temperature and solvents on styrene hydrogenation kinetics

The effect of temperature on the kinetics of hydrogenation of styrene using catalyst **2** was investigated by comparing the catalytic activities of **2** from 30 °C to 60 °C (Table 3, entries 1-4). The observed rate constants at different temperatures in Table 3 were extracted from the plot of In[styrene]$_0$/[styrene]$_t$ *vs* time (Fig. S5). Expectedly, a significant increase in the rate constant from 1.67 h^{-1} to 6.30 h^{-1} was recorded with an increase in reaction temperature from 30 °C to 60 °C. The overall activation energy (*Ea*) of the hydrogenation of styrene using **2** was calculated from the Arrhenius plot of Ink_{obs} *vs* 1/T (Figure 3a) as 35.61 ± 1.6 kJ mol^{-1}. This value is comparable to the value of 42.05 ± 0.01 kJ mol^{-1} (10.05 ± 0.01 kcal.mol^{-1}) reported by Pelagatti *et. al.*[26] in the hydrogenation reaction of alkenes at 40 ºC. These results in good agreement with the similar TOFs of 600 h^{-1} and 580 h^{-1} obtained for **2** the Pelagatti catalysts respectively. The Eyring plot in Figure 3b was used to obtain the enthalpy of activation ($\Delta H^{\neq}$ = 32.98 ± 1.9 kJ mol^{-1}) and entropy of activation ($\Delta S^{\neq}$ =-1112.74 ± 1.9 J mol^{-1} K^{-1}). The significance of these thermodynamic parameters is that they support homogeneous nature of catalyst as has been previously reported by others.[26,27] Typical heterogeneous catalysts in which the hydrogenation reactions are diffusion controlled display lower E_a between 8 kJ mol^{-1} to 17 kJ mol^{-1} well below the values for E_a and $\Delta H^{\neq}$ of 35.61 ± 1.6 kJ mol^{-1} and 32.98 ± 1.9 kJ mol^{-1} obtained for catalyst **2** respectively.[26]



Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	0.04009		
Pearson's r	-0.9783		
Adj. R-Squar	0.94286		
		Value	Standard Err
B	Intercept	14.96288	1.65854
B	Slope	-4282.8617	523.20983

(a)

Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Squares	0.01713		
Pearson's r	-0.97746		
Adj. R-Square	0.93314		
		Value	Standard Error
B	Intercept	8.37185	1.96353
B	Slope	-4006.69742	611.94928

(b)

Figure 3: Arrhenius plot (a) and Eyring plot (b) for the determination of the E_a= 35.61 ± 1.6 kJ mol^{-1} $\Delta H^{\neq}$ = 32.98 ± 1.9 kJ mol^{-1}, and $\Delta S^{\neq}$ = -1112.74 ± 1.9 J mol^{-1} K^{-1}

We also studied the effects of solvents using toluene, THF, dichloromethane, methanol and DMSO in the hydrogenation reactions of styrene using complex **2** (Table 3, entries 1, 5 - 7). The order of reactivity was established as follows: DMSO < methanol< THF < toluene. For example, higher catalytic activities were obtained in toluene (k_{obs} of 1.67 h^{-1}, TOF = 368 h^{-1}) than methanol (k_{obs} of 0.52 h^{-1}, TOF = 183 h^{-1}). This trend is in line with different coordinating abilities of the solvents; where strongly coordination solvents are known to compete with the alkene substrate, for the active site resulting in diminished activities.[28,29] Consistent with our observations, Unver and Yilmaz recently reported 27% and 63% conversions in DMSO and toluene solvents respectively in the hydrogenation of 1-octene catalyzed by ruthenium complexes.[30]

Table 3: Effect of temperature and solvent the hydrogenation of styrene using catalyst **2**$^{\mathbf{a}}$

Entry	Solvent	T (^{0}C)	Conv (%)^b	k_{obs} (h^{-1})	TOF (h^{-1})^c
1	Toluene	30	92	1.67 (±0.01)	368
2^d	Toluene	40	99	4.19 (±0.03)	475
3^d	Toluene	50	>99	5.46 (±0.1)	480
4^e	Toluene	60	>99	6.30 (±0.07)	600
5	Methanol	30	49	0.61 (±0.08)	196
6	DCM	30	68	0.90 (±0.04)	272
7	THF	30	86	1.40 (±0.03)	343
8	DMSO	30	35	0.52 (±0.06)	183

$^{\mathbf{a}}$Conditions: styrene, 4.36 mmol; solvent; toluene (50mL); [styrene]/[**2**] = 600; time, 1.5 h, pressure, 5 bar. $^{\mathbf{b}}$Determined by GC. $^{\mathbf{c}}$TOF in $mol_{substrate}mol_{catalyst}^{-1}$ h^{-1}.$^{\mathbf{d}}$Time, 1.25 h, $^{\mathbf{e}}$Time, 1.0 h.

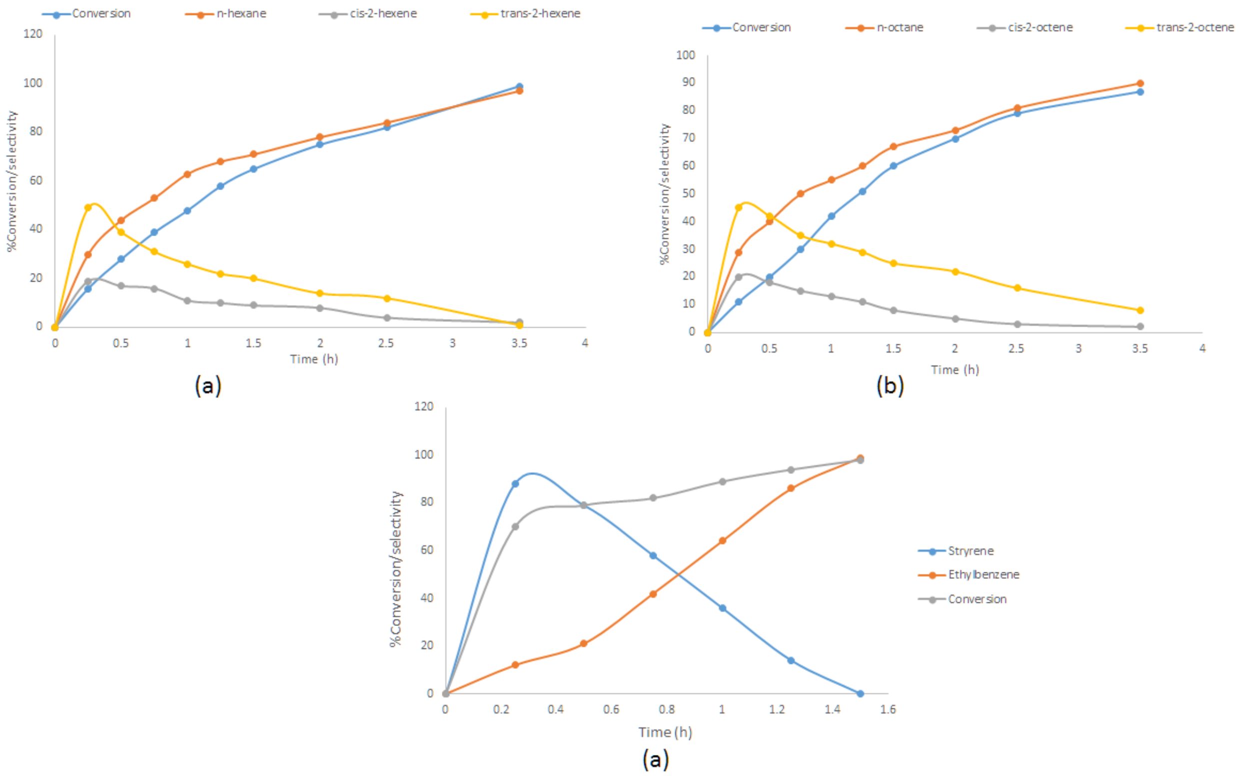
Effect of alkene and alkyne substrates on styrene hydrogenation kinetics and selectivity

Complex **2** was further used to investigate the hydrogenation reactions of a range of alkene and alkyne substrates: 1-hexene, 1-octene, 1-nonene, 1-decene, phenyl-acetylene, 1-hexyne and 1-octyne. The initial rate constants (k_{obs}) of each substrate were determined from the plot of In$[Sty]_0/[Sty]_t$ *vs* time (Fig. S6). The results obtained generally showed that alkynes were more reactive compared to the corresponding alkenes.[31,32] For example, k_{obs} of 0.69 h^{-1} and k_{obs} of 2.92 h^{-1} were obtained for 1-hexene and 1-hexyne (Table 4, entries 2 and 7). The alkyl chain length had a profound effect on the reactivity of the substrates, in which shorter chains were more reactive. For instance, k_{obs} of 0.69 h^{-1} and 0.50 h^{-1} were observed for 1-hexene and 1-decene respectively (Table 3, entries 2 and 5). The decrease in catalytic activity with alkene chain has been attributed to poor coordinating abilities of higher alkenes to the active metal center.[11] With respect to alkenes, the best catalytic activity was obtained using styrene (k_{obs} = 1.67 h^{-1}); a feature that has largely been assumed to arise from the delocalized double bonds in the phenyl ring.[33] The product distribution of terminal alkenes and alkynes was similar to our recent reports;[21,22] hydrogenation reactions of terminal alkenes were followed by isomerization reactions to give the corresponding internal alkenes, while alkyne hydrogenation reactions occurred in two steps to produce the respective alkenes and alkanes (Figure 4).

Table 4: Effect of substrate on the catalytic activity of complex **2**[a]

Entry	Substrate	k_{obs} (h^{-1})	TOF (h^{-1})[b]	%Alkane[c]
1	Styrene	1.67 (±0.01)	368	92
2	1-Hexene	0.69 (±0.06)	284	71
3	1-Octene	0.58 (±0.13)	268	67
4	1-Nonene	0.56 (±0.05)	236	59
5	1-Decene	0.50 (±0.07)	220	55
6	Phenyl-acetylene	2.40 (±0.05)	400	100
7	1-Hexyne	2.92 (±0.04)	260	65
8	1-Octyne	2.29 (±0.02)	208	52

[a]Conditions: substrate, substrate/catalyst = 600; solvent, toluene; pressure, 5 bar; temperature, 30 °C; time, 1.5 h. [b]TOF in $mol_{substrate}mol_{catalyst}^{-1}$ h^{-1}. [c]Selectivity towards alkane hydrogenation products after 1.5 h.



(a)

(b)

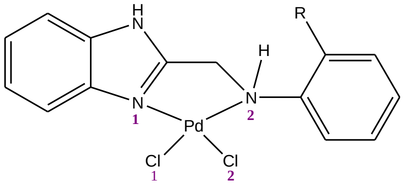
(a)

Figure 4. Product distribution over time in the hydrogenation of (a) 1-hexene, (b) 1-octene and (c) phenyl-acetylene using complex **2** as a catalyst.

3.4. Theoretical insights of the hydrogenation reactions of alkenes

Density Functional Theory (DFT) calculations were conducted in order to have an understanding of the effect of the ligand motif and catalyst structure on the catalytic activities of complexes **1-4**. The geometries-optimized structures and frontier orbital energy (HOMO and LUMO) maps are summarized in Table 4 and Fig. S7, respectively. The relationship between HOMO-LUMO energy gaps and the catalytic activity was established to show a significant correlation. For example, while complex **1** with HOMO-LUMO energy gap of 121.28 kcal mol^{-1} displayed k_{obs} of 0.91 h^{-1}, complex **2**, with HOMO-LUMO energy gap of 104.48 kcal mol^{-1} had k_{obs} of 1.67 h^{-1} (Table 4). HOMO-LUMO energy gaps promote coordination of the substrate to the metal center[34], which is in good agreement with the observed catalytic trends. The charge on the metal ion was also observed to influence the catalytic activities of complexes **1-4** (Fig. S8). For instance, catalyst **2** carrying a positive charge of 0.392 was more active than catalyst **1**, with a charge of 0.326 on the palladium (II) atom. This trend is in agreement with a more facile substrate coordination to an electrophilic palladium atom.[34]

Table 4 DFT calculated data for palladium (II) complexes



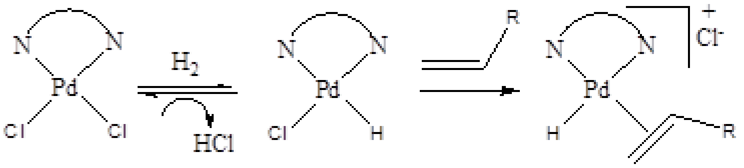
R = OCH_3 (**1**); Br (**2**); H (**3**); SH (**4**)

Parameter	**1**	**2**	**3**	**4**
LUMO (eV)	-1.87	-1.83	-1.77	-1.81
HOMO (eV)	-7.13	-6.38	-6.75	-6.35
$\Delta E_{L\text{-}H}$	5.26	4.55	4.98	4.54
$\Delta\varepsilon$[kcal mol^{-1}]	121.28	104.48	114.92	104.69
NBO charges (Pd)	0.326	0.392	0.354	0.358
TOF (h^{-1}) [a]	296	368	312	344
k_{obs} (h^{-1})	0.91	1.67	0.98	1.38

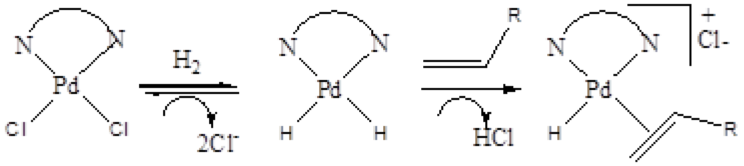
[a] TOF in $mol_{substrate}\ mol_{catalyst}^{-1}\ h^{-1}$

3.5. Proposed mechanism of the hydrogenation of styrene

The dependency of the rate of hydrogenation reactions on styrene, catalyst and hydrogen pressure (eq. 2) is consistent with either of the following equations 3 and 4. The partial and lower order of reaction with respect to [H_2] of 0.7 ± 0.1 support the formation of a monohydride species as the rate determining step. This points to the first mechanism (3) as the most probable pathway.[35]

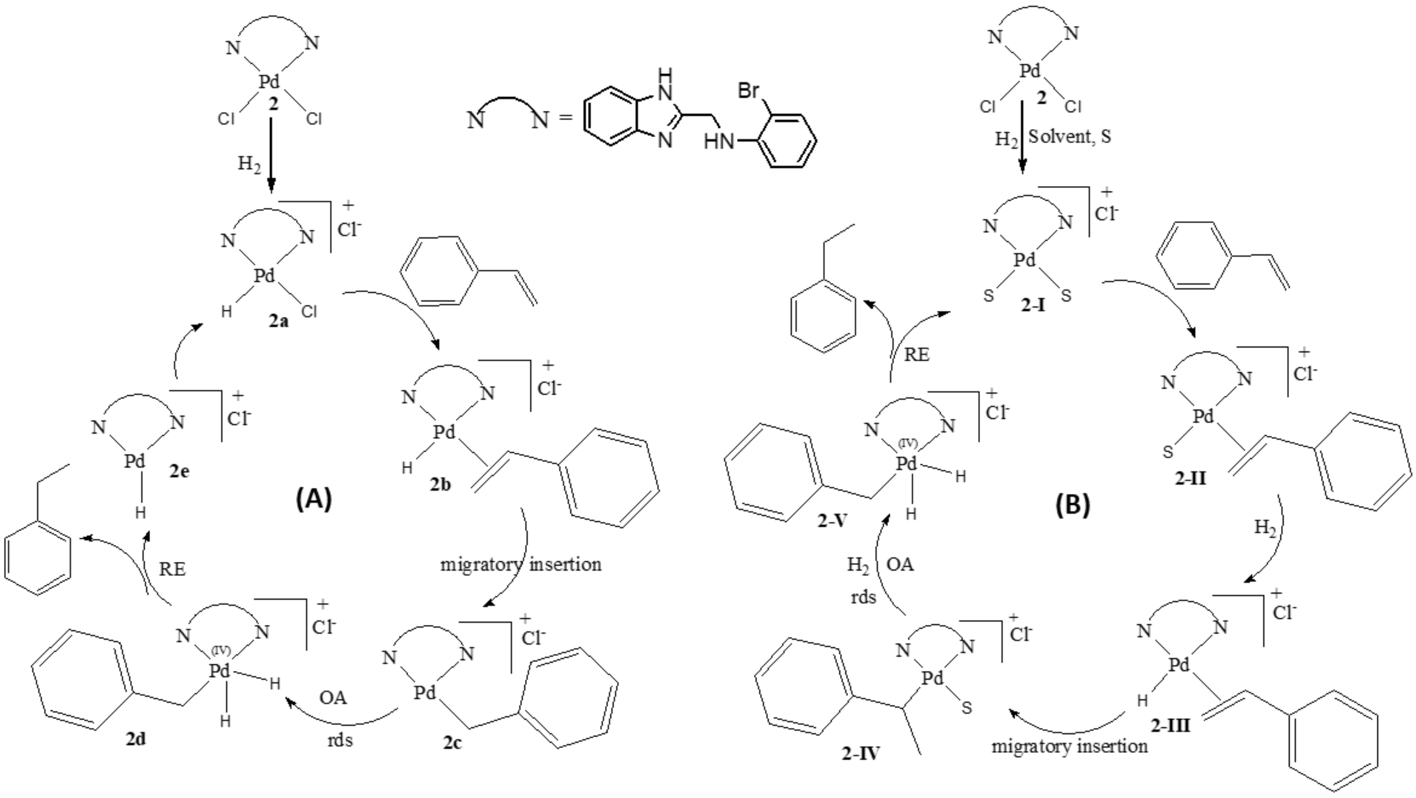


(3)



(4)

Based on the kinetics data and the dependency of the rates of hydrogenation reactions on the coordinating ability of the solvent used, we can now propose two mechanisms as shown in Scheme 1. The first pathways is a classical route usually observed for bidentate systems where dihydride species is not favored, thus formation of the monohydride species **2a**.[36] In the second pathway (B), the presence of a coordinating solvent leads to the formation of the solvated species **2-I**, consistent with the earlier proposals by Halper.[37] Depending on the coordinating ability of the solvent used, substrate addition to give **2b-II** may be hindered leading to lower catalytic activities, consistent with the observed lower activities in methanol in comparison to toluene. In both, routes, the rate-determining step is the oxidative addition of hydrogen to give the $Pd^{(IV)}$ species **2d** and **2-IV**, in line with observed lower partial orders of 0.7 with respect to [H_2].



Scheme 1: Proposed mechanistic pathway for the hydrogenation of styrene catalyzed by complex **2** in the presence of non-coordinating (**A**) and coordinating (**B**) solvents.

4. Conclusions

In summary, we have established that neutral and cationic palladium (II) complexes anchored on (benzoimidazol-2-ylmethyl)amine ligands form active catalysts for the hydrogenation reactions of alkenes and alkynes in which isomerization of terminal alkenes also occur. The electrophilicity of the metal palladium atom of the complexes atom as supported by DFT calculations, enhanced the reactivity of the respective catalysts. Longer chain alkenes showed diminished reactivity while alkynes were generally more reactive compared to the correspond alkenes. Kinetics, thermodynamics and mercury drop experiments point to largely homogeneous systems. A mechanistic pathway in which olefin coordination precedes oxidative hydride addition and stabilization of the active species by a coordinating solvent is proposed.

Conflict of interest statement

The authors declare no conflict of interests in this manuscript with any other third party, individual or organization.

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