Applied Catalysis A: General 419–420 (2012) 185–193

Contents lists available at SciVerse ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata

Regioselective hydroformylation of vinyl acetate catalyzed by rhodium complex of naphthyl-based monodentate bulky phosphine and phosphite ligands

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ARTICLE INFO

Article history:
Received 1 June 2011
Received in revised form 19 January 2012
Accepted 21 January 2012
Available online 30 January 2012

Keywords:
Hydroformylation
Vinyl acetate
Monodentate bulky phosphite
High rate
Regioselective

ABSTRACT

The hydroformylation of vinyl acetate was carried out using rhodium complex of naphthyl-based monodentate bulky phosphine and phosphite ligands. All the naphthyl-based ligands favored the formation of desire branched aldehyde. High turnover frequency with excellent regioselectivity to branched aldehyde and high selectivity to aldehyde were observed with bulky phosphite ligands. The effect of partial pressure of CO and H_2, concentration of vinyl acetate, stirring rate and solvents on the hydroformylation of vinyl acetate catalyzed by Rh/bulky phosphite were examined precisely in order to improve the catalytic activity and selectivity. In contrast to conventional organic solvents, the significant influence on the activity and selectivity was observed in organic carbonates ('green' solvent) particularly in propylene carbonate (PC). The PC/catalyst system could be recycled without significant loss of activity and selectivity.

1. Introduction

Catalytic hydroformylation is an elegant method to prepare wide range of aldehydes in a single step by the reaction of olefins, CO and H_2 with high selectivity [1,2]. It is mainly used for the preparation of bulk and specialties chemicals. The application of this process has also been extensively explored in pharmaceutical and fine chemical synthesis [1–6]. This powerful atom efficient process is very attractive however; simultaneous control of activity and selectivity (chemo- as well as regioselectivity) is one of the important issue and concern of hydroformylation. Rhodium complexes of modified phosphorous containing ligands display high activity and selectivity for the hydroformylation of olefins under mild reaction conditions. The steric and electronic properties of ligands play an imperative role in concern to activity and selectivity of hydroformylation catalysts. As a result, varieties of modified monodentate and bidentate phosphine/phosphite ligands have been synthesized by fine tuning their electronic and steric properties to address the issues of activity and selectivity [7–11].

Hydroformylation reaction has been mainly studied for terminal and internal olefins. The selective preparation of the linear aldehyde, the starting material for a variety of polymers, detergents, cosmetics and other widespread products by hydroformylation of terminal and internal alkenes have been reported [12–14]. Recently, regioselective hydroformylation of functionalized alkenes such as alkyl acrylate, allyl cyanide, allyl alcohol, enamide and vinyl acetate [19] have also received attention. Hydroformylation of such substrates offers products having two functional groups widely used in organic syntheses [15–19]. Particularly, the hydroformylation of vinyl acetate provides gate way to valuable building blocks for the preparation of bifunctional intermediate which can be further converted into synthetically useful compounds such as 1,2- and 1,3-propanediol, lactic acid and ethyl lactate (Scheme 1).

Indeed, vinyl acetate, less reactive to syngas in comparison to terminal alkenes requires high pressure to achieve high turnover frequency [20], also suffers from a low selectivity and formation of by-products [21]. However, there are few reports wherein hydroformylation of vinyl acetate is carried out under mild conditions with good regioselectivity [22–24]. The hydroformylation reaction proceeds even at 2 atm pressure and 80 °C in the presence of diphosphines in the rhodium complex with large excess of triphenyl phosphine (PPh_3) and resulted in the vinyl acetate conversion from 38 to 60% with branched aldehyde regioselectivity from 53 to 82% [22]. Abatjoglou et al. reported vinyl acetate hydroformylation at low pressure and temperature (8.4 atm, 60 °C) with branched aldehyde regioselectivity from 77 to 86% depending on the phosphine and solvent used [23]. Trzeciak and Ziółkowski also demonstrated vinyl acetate hydroformylation at 1 atm and 40 °C by rhodium/triphenyl phosphite catalyst system [24]. In above cases, the regioselectivity was achieved but at the expense of the reaction rate. In consequent, over past decades, a great deal of efforts

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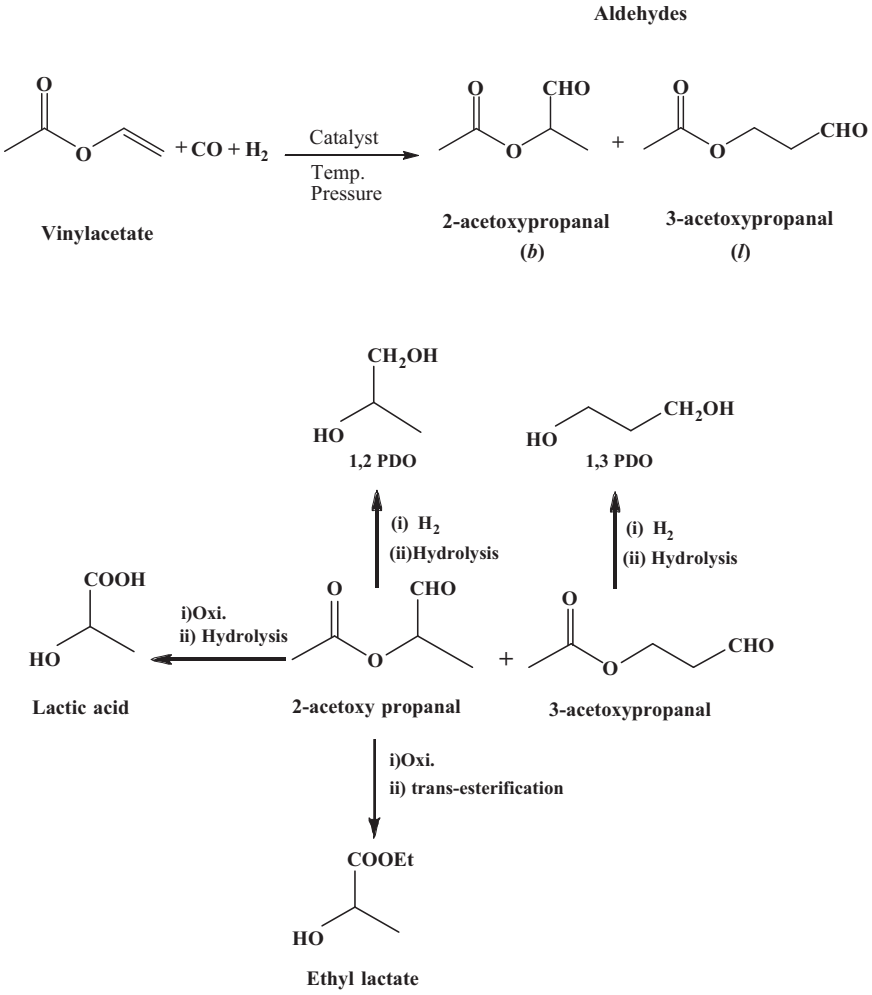
doi:10.1016/j.apcata.2012.01.027



Scheme 1. Hydroformylation of vinyl acetate with its application.

has been put to increase the regioselectivity as well as reaction rate; and to decrease the undesired side products [25–27]. Thus far, there are a few examples of successful catalytic system which exhibited high regioselectivity together with rate enhancement. High reaction rate were obtained when the hydroformylation was carried out with bidentate ligands or with electron-deficient ligands such as bulky phosphite ligand [26,27].

We have recently reported the synthesis and use of the monodentate bulky phosphite ligand, tri-1-naphthylphosphite, $P(ONp)_3$ [28]. Rhodium complex of $P(ONp)_3$ showed high activity with high selectivity to aldehyde for the hydroformylation of vinyl acetate [29]. In the present paper, we have synthesized a series of naphthyl-based monodentate bulky phosphine and phosphite ligands and discussed the steric and electronic effect of ligands on the reaction rates and selectivity during hydroformylation reaction. In order to improve activity and selectivity, the effect of partial pressure of CO and H_2, concentration of vinyl acetate, stirring rate and solvents on the hydroformylation of vinyl acetate were examined in detail. Moreover, the hydroformylation of vinyl acetate using Rh/bulky phosphite system was also carried out in the organic carbonates 'green solvent'. The significant advantages of organic carbonate are emphasized compared to the conventional organic solvents along with recycling of the catalyst.

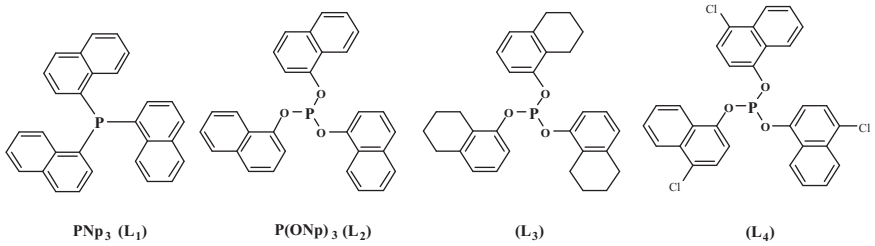
2. Experimental

2.1. Materials

The ligand synthesis was performed using standard Schlenk technique under nitrogen atmosphere. Tetrahydofuran (THF) was distilled from sodium/benzophenone prior to use. Toluene, dichloromethane, and cyclohexane were purchased from Sigma–Aldrich as anhydrous grade material and used as received. Et_3N was distilled from sodium and stored under N_2. PCl_3 and 1-bromo naphthalene were obtained from s. d. fine chemicals, India, and used as received. $Rh(acac)(CO)_2$, PPh_3, $P(OPh)_3$, tricyclohexylphosphine PCy_3, $(p\text{-}CF_3\text{-}C_6H_4)_3P$, 1-naphthol, 5,6,7,8-tetrahydro-1-naphthol, *p*-chloro-1-naphthol, *n*-BuLi (1.6 M solution in hexane), vinyl acetate, PC and dimethyl carbonate (DMC) were purchased from M/s Sigma–Aldrich Chemicals, USA and used as received. The syngas (99.9%) used was from Hydro Gas India Pvt Ltd., India.

2.2. Instrumentation

All the hydroformylation reactions were performed in 100 mL stainless steel autoclave reactor (Autoclave Engineers, EZE–Seal



Scheme 2. The naphthyl-based monodentate bulky phosphine and phosphite ligands.

Reactor, USA). ^{31}P NMR spectra of ligand and complex were measured in $CDCl_3$ solvent and 85% H_3PO_4 as an internal reference, on Bruker Avance 500 MHz FT-NMR. IR spectra were recorded using nujol mull and KBr pellet on Perkin-Elmer spectrum GX FT-IR system in the range 400–4000 cm^{-1} with a resolution of 4 cm^{-1}. CHN analysis has been done on Perkin-Elmer, 2400 C, H, N, S/O analyzer. Products were analyzed with Shimadzu GC-17A gas chromatograph (GC) using flame ionization detector (FID) having 5% diphenyl- and 95% dimethyl siloxane capillary column (60 m length, 0.25 mm diameter). Column temperature was initially kept at 50 °C for 5 min and then raised to 200 °C at 10 °C/min. Nitrogen was used as a carrier gas (1.2 mL/min). n-decane was used as internal standard and the GC was also calibrated using known amount of corresponding aldehydes.

2.3. Synthesis of ligands and characterization

The bulky phosphine, tri-1-naphthylphosphine PNp_3 (L_1) has been synthesized from 1-bromonaphthalene according to reported procedure [30,31]. In typical synthesis of PNp_3, a dried Schlenk flask was charged with 7.09 g (34.25 mmol) of 1-bromonaphthalene in THF (30 mL) under inert atmosphere. A solution of *n*-BuLi (22.5 mL of a 1.6 M solution in hexane, 35.97 mmol) was added drop wise under stirring at −78 °C. The reaction mixture was stirred for 1 h, during this period the temperature of the reaction mixture increased from −78 °C to 0 °C; and the color of the reaction mixture changed to orange. To this the solution of PCl_3 (1 mL, 11.42 mmol) in 10 mL of THF was added slowly at 0 °C over 10 min and stirred additionally for 5 h at 0 °C. After 5 h, the mixture was allowed to warm to room temperature; precipitated out inorganic salt was filtered off and washed with dry THF (2 × 10 mL). The combine filtrates were evaporated in vacuo yielding crude ligand as yellow solid and purified by recrystallization (from ethanol/hexane). Yield: 1.5 g, 32%. ^{31}P NMR ($CDCl_3$): δ – 31.2 ppm, ^{1}H NMR ($CDCl_3$): δ 7.0–8.2 ppm (m, 7H, aromatic).

The bulky phosphite ligand, $P(ONp)_3$ (L_2) was synthesized as per reported procedure [28]. The other bulky phosphites, tris (5,6,7,8-tetrahydro-1-naphthyl) phosphite (L_3) and tris (*p*-chloro-1-naphthyl) phosphite (L_4) (Scheme 2) were synthesized following the similar procedure as for $P(ONp)_3$ using 5,6,7,8-tetrahydro-1-naphthol and *p*-chloro-1-naphthol. For L_3, ^{31}P NMR ($CDCl_3$): δ 130.96 ppm, ^{1}H NMR ($CDCl_3$): δ 6.5–6.9 ppm (m, 3H), 2.78 (dt, 4H), 1.69 (m, 4H) and for L_4, ^{31}P NMR ($CDCl_3$): δ 129.28 ppm, ^{1}H NMR ($CDCl_3$): δ 6.8–8.4 ppm (m, 6H, aromatic).

2.4. Synthesis of Rh–P(ONp)$_3$ complexes

Rhodium complexes of type Rh(acac)(CO)L and $Rh(acac)L_2$ were obtained according to literature procedure [10]. The rhodium complexes of $P(ONp)_3$ were synthesized from $Rh(acac)(CO)_2$ by varying ligand to Rh mmol ratio. For the synthesis of rhodium complex of type Rh(acac)(CO)L, an equimolar amounts of $P(ONp)_3$ (0.019 mmol) was added to the solution of $Rh(acac)(CO)_2$ (0.019 mmol) in toluene (prepared under inert atmosphere). Evolution of CO was observed immediately and the mixture stirred for 5 min afforded rhodium complex Rh(acac)(CO)L. While addition of (0.042 mmol) of $P(ONp)_3$ yielded rhodium complex, $Rh(acac)L_2$. The in situ prepared rhodium complexes using different concentration of $P(ONp)_3$ were characterized by FT-IR and ^{31}P NMR without isolation. Spectroscopic characterizations of the rhodium complexes are summarized in Table 1.

2.5. Catalytic reaction

In a typical hydroformylation experiment, required amount of catalyst, ligand, substrate, solvent were charged into 100 mL autoclave. The reactor was flushed with nitrogen three times followed by flushing syngas twice at room temperature after which reactor was brought to reaction temperature and pressurized with syngas at desired pressure. The reaction was initiated by stirring; reaction started immediately as evidenced by a pressure drop and accompanied increase of the temperature. After desired reaction time, the stirring was stopped, reactor was cooled down to room temperature, depressurized, flushed with N_2 and opened to collect final sample for GC analysis.

The initial turnover frequency (TOF_i) was calculated within 30–40% conversion of vinyl acetate, to avoid inference from the products. The TOF is defined as:

$$\text{TOF} = \frac{\text{number of moles of product form}}{\text{number of moles of rhodium} \times \text{h}}$$

Table 1
Spectroscopic data for rhodium complexes at different $P(ONp)_3$ molar ratios.

Entry	L:Rh	Rh-complex	$^{31}P\{^1H\}$ NMR		FT-IR ν_{CO} (cm^{-1})
			δ (ppm)	$J_{P\text{-}Rh}$ (Hz)	
1	Free ligand	–	130.8	–	–
2	(1:1)	Rh(acac)(CO)L	120.86	291	2009
3	(2.2:1)	$Rh(acac)L_2$	124.37	301	–
4	(3:1)	$Rh(acac)L_2$	124.69	301	–

L: $P(ONp)_3$.

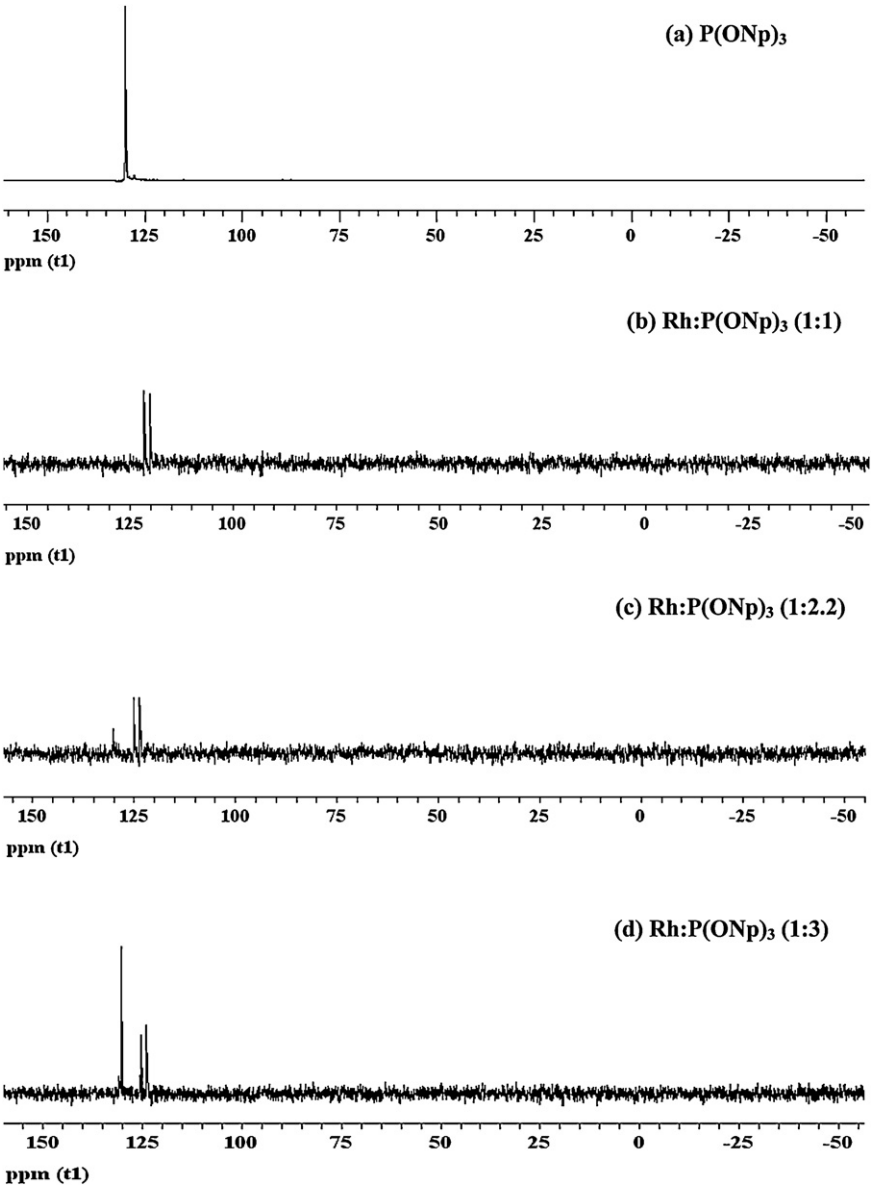
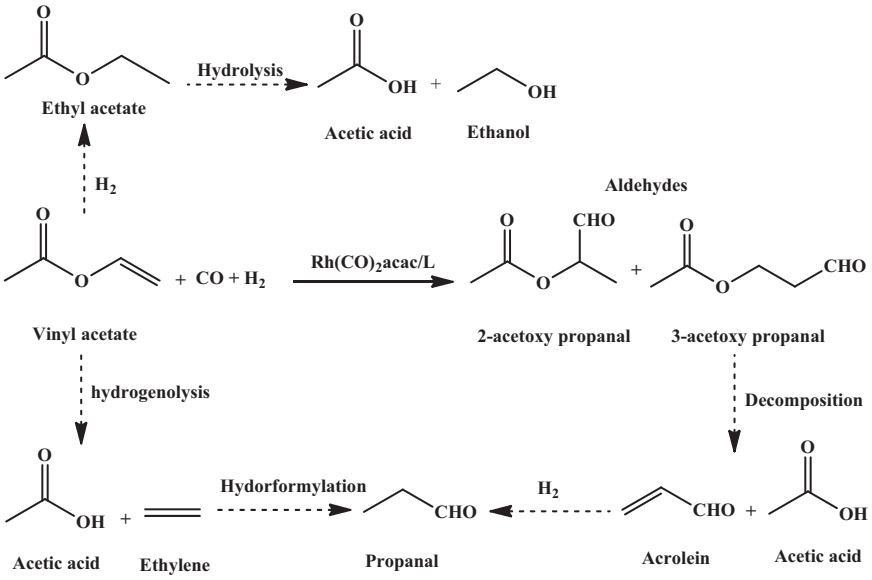


Fig. 1. ^{31}P NMR of $P(ONp)_3$ ligand (a) and Rh–$P(ONp)_3$ complexes at different concentration of $P(ONp)_3$; (b) Rh:$P(ONp)_3$ (1:1); (c) Rh:$P(ONp)_3$ (1:2.2) and (d) Rh:$P(ONp)_3$ (1:3).

3. Results and discussion

3.1. Characterizations

Invariably the active rhodium catalyst for hydroformylation reaction is generated in situ using $Rh(acac)(CO)_2$ as rhodium source. In present study, the rhodium catalysts used for hydroformylation of vinyl acetate were also generated in situ from $Rh(acac)(CO)_2$ and ligands. However, to confirm the coordination of $P(ONp)_3$ to rhodium and to understand the ligand exchange process, the $P(ONp)_3$ was added to a solution of $Rh(acac)(CO)_2$ with different ligand to rhodium molar ratio and the formation of rhodium complexes with $P(ONp)_3$ were probed by FT-IR and ^{31}P NMR (Table 1). The ^{31}P NMR of free $P(ONp)_3$ gave signal at δ 130.8 ppm while infrared spectra of $Rh(acac)(CO)_2$ displayed two band in carbonyl region, one at 2007 cm^{-1} and another at 2089 cm^{-1}. The addition of equimolar amounts of $P(ONp)_3$ to $Rh(acac)(CO)_2$, the substitution of the CO occurred immediately. The infrared spectra of resulting solution displayed only one vibration band in carbonyl region at 2009 cm^{-1} whereas a doublet appeared at δ 120.86 ppm in ^{31}P NMR while signal at δ 130.8 ppm due to free ligand disappear (Fig. 1). These spectroscopic data corroborate the coordination of $P(ONp)_3$ to rhodium; and the formation of Rh(acac)(CO)L complex (L = $P(ONp)_3$). The reaction of $Rh(acac)(CO)_2$ with different phosphorous containing ligands has been studied well as rhodium complex of type Rh(acac)(CO)P plays an important role to understand the σ-donor and π-acceptor behavior of P ligands [10]. The observed CO stretching frequency at high wave number (ν_{CO}, 2009 cm^{-1}) in the case of $Rh(acac)(CO)(P(ONp)_3)$ compare to the $Rh(acac)(CO)PPh_3$ (ν_{CO}, 1975 cm^{-1}) indicates weak σ- and strong π-acceptor behavior of $P(ONp)_3$. With higher excess of $P(ONp)_3$ (ligand/Rh > 2), the further CO substitution occurred and the resulting reaction solution gave no band in CO region and signal at δ 120.86 ppm was shifted to δ 124.37 ppm in ^{31}P NMR (Fig. 1) confirming the formation of complex of type Rh(acac)$(CO)L_2$.



Scheme 3. Decomposition pathway of vinyl acetate hydroformylation.

3.2. Influence of steric and electronic nature of ligands on hydroformylation of vinyl acetate

The selection of an appropriate ligand is one of the critical issues in the transition metal catalyzed hydroformylation reactions as ligands play significant role in the activity and selectivity. Earlier we screened variety of P ligands for rhodium catalyzed hydroformylation of vinyl acetate [29]. It was found that at optimum conditions (temperature 90 °C, syngas pressure 4.0 MPa), the steric and electronic nature of ligands remarkably influences the regioselectivity to branched aldehyde and catalytic activity. Rhodium complex modified with $P(ONp)_3$ ligand having high steric nature and strong π-acceptor ability effectively catalyzed hydroformylation of vinyl acetate with high regioselectivity (99%) to the preferred branched aldehyde with notable high turnover frequency [29]. Thus, to study the influence of naphthyl-based P ligands on the hydroformylation of vinyl acetate, the various naphthyl-based monodentate bulky phosphine and phosphite ligands were synthesized (Scheme 2). The rhodium catalyst was prepared in situ by mixing the appropriate amounts of ligand with $Rh(acac)(CO)_2$. The hydroformylation was carried out with ligand/Rh ratio of 6 using 0.23 mmol/L $Rh(acac)(CO)_2$. The reaction products were 2-acetoxypropanal and 3-acetoxypropanal along with acetic acid and ethyl acetate as side products (Scheme 3).

The naphthyl-based P ligands were then evaluated for the rhodium catalyzed hydroformylation of vinyl acetate (temperature 90 °C, syngas pressure 4.0 MPa). The PPh_3 and $P(OPh)_3$ were taken as reference ligands in this study. The rhodium complex modified with monodentate bulky phosphine ligand PNp_3 (L_1) resulted in the high regioselectivity but low activity as compare to PPh_3 (Table 2, entries 2 and 3). However the initial rate of vinyl acetate hydroformylation was better compared to unmodified $Rh(acac)(CO)_2$ catalyst. This result clearly indicates that the steric nature of ligands remarkably influences the regioselectivity to branched aldehyde. The rhodium complex modified with phosphite ligands displayed high TOF as well as high selectivity. In fact, an excellent regioselectivity (99%) for the preferred branched aldehyde and selectivity to aldehyde (93%) with high TOF were attained with monodentate bulky phosphite ligands (Table 2). The $P(OPh)_3$ gave high TOF than phosphines but lower than bulky phosphites ligands. Among the naphthyl-based bulky phosphite ligands, $P(ONp)_3$ afforded notable catalytic activity (Table 2, entry 5). The observed TOF is ~1.7 times higher compared to the $Rh/P(OPh)_3$ catalytic system. These results clearly demonstrate that the ligands having π-acceptor ability along with high steric nature enhance reaction rate and selectivity considerably.

In order to perceive whether further improvements are possible in activity and selectivity using $Rh/P(ONp)_3$, the effect of partial pressure of CO and H_2, concentration of vinyl acetate, stirring rate and solvents on the hydroformylation of vinyl acetate were examined.

3.3. Effect of partial pressure of pCO and pH_2

It is established that the hydroformylation of vinyl acetate proceeds slowly at low syngas pressure and minimum 4.0 MPa syngas pressure is require to achieve reasonable TOF [29]. As a consequence, the effect of CO partial pressure on the vinyl acetate

Table 2
Influence of various ligands on the hydroformylation of vinyl acetate.[a]

Entry	Ligand	Conv. (%)	Time (min)	TOFi[b] (h^{-1})	$S_{aldehyde}$ (%)	b/l
1	–	12	60	480	89	95/5
2[c]	PPh_3	28	30	2240	92	93/7
3	PNp_3	15	60	600	82	99/1
4[c]	$P(OPh)_3$	30	15	4800	93	92/8
5[c]	$P(ONp)_3$	34.5	10	8280	93	99/1
6	L_3	34	10	8160	94	99/1
7	L_4	32	10	7680	93	99/1

[a] Reaction conditions: Sub/cat., 4000; $[Rh(CO)_2acac]$, 0.23 mmol/L; P/Rh, 6.0; temperature, 90 °C; syngas pressure (1:1), 4.0 MPa; solvent (toluene), 50 mL.
[b] Turnover frequency, determined based on 30–35% GC conversion.
[c] Reported earlier, Ref. [29].

Table 3
Effect of partial pressure of pCO and pH_2 on $Rh/P(ONp)_3$ catalyzed hydroformylation of vinyl acetate.[a]

Entry	*p*CO (bar)	pH_2 (bar)	Conv. (%)	TOF (h^{-1})	$S_{aldehyde}$ (%)	b/l
1	15	15	23.5	5640	92.0	98/2
2	25	15	21.5	5160	93.0	99/1
3	35	15	19.0	4560	92.0	99/1
4	45	15	15.0	3600	93.0	99/1
5	15	25	40.0	9600	93.0	99/1
6	15	35	54.0	12960	93.0	99/1
7	15	45	67.5	16200	92.0	99/1

[a] Reaction conditions: [vinyl acetate], 0.93 mol/L; $[Rh(CO)_2acac]$, 0.23 mmol/L; P/Rh, 6.0; temperature, 90 °C; solvent (toluene), 50 mL; reaction time, 10 min.

hydroformylation was studied at 90 °C and constant H_2 partial pressure (1.5 MPa) by varying the CO partial pressure (2.5–4.5 MPa). The TOF of vinyl acetate hydroformylation decreased with an increase of CO partial pressure (Table 3, entries 2–4) exhibiting an inverse dependency on CO partial pressure. The rate inhibition trend at higher CO partial pressure, common characteristic of hydroformylation catalyzed by rhodium complexes modified with P ligands [32] is mainly due to the formation of inactive acyl species (H) (Fig. 5) at higher CO partial pressure. The species (H) is in equilibrium with the catalytic species (F) and is affected by CO partial pressure. The equilibrium can shift from (F) to (H) significantly at higher CO partial pressure resulted in the lower TOF.

The effect of H_2 partial pressure on the vinyl acetate hydroformylation was studied at 90 °C, at constant CO pressure (1.5 MPa) by varying the H_2 partial pressure (2.5–4.5 MPa). The TOF of vinyl acetate hydroformylation increased linearly on increasing the partial pressure of hydrogen indicating first order dependency on H_2 partial pressure (Table 3). This trend indicates that the oxidative addition of hydrogen to the acylrhodium intermediate (F) would be a rate determining step (Fig. 5). In all conditions, the chemo selectivity to aldehyde and regioselectivity to branch aldehyde (2-acetoxypropanal) were unaffected.

3.4. Effect of initial vinyl acetate concentration

The effect of vinyl acetate concentration on the rate of hydroformylation was studied at 90 °C, 4.0 MPa syngas pressure and ligand/Rh of 6.0 by varying the vinyl acetate initial concentration (0.7–1.63 mol/L). The TOF of vinyl acetate hydroformylation increased at lower vinyl acetate concentration, particularly from 0.7 to 0.93 mol/L (Fig. 2) whereas it decreased at higher concentration (from 0.93 to 1.63 mol/L) indicating substrate inhibition trend. The similar substrate inhibition has been reported in the hydroformylation of vinyl acetate using $HRh(CO)(PPh_3)_3$ as catalyst [32]. Generally, a positive order dependency with respect to olefin concentration has been observed up to a critical substrate/catalyst ratio, after that a negative or zero dependence was observed. The similar trend observed in a present system is mainly due to the coordination of the substrate to the rhodium catalyst (Fig. 5, species E and E_2) in which carbonyl group of vinyl acetate coordinates with rhodium to form chelates. At higher vinyl acetate concentration, the rhodium catalyst present in the chelates form which resulted in the decrease in TOF. The variation of the initial vinyl acetate concentration scarcely influenced the selectivity to branched aldehyde and selectivity to aldehyde. Moreover, in order to ascertain that high selectivity is maintained throughout the course of the reaction, the hydroformylation reaction was studied till the complete consumption of vinyl acetate. At regular intervals, the samples were collected and analyzed by GC. The kinetic profile for the $Rh/P(ONp)_3$ catalyzed hydroformylation of vinyl acetate showed the gradually increase of conversion with time (Fig. 3). The complete conversion of vinyl acetate was at 50 min while selectivity (chemo- as well as regio) was high from the beginning and remained almost unaffected throughout the course of the reaction (Fig. 3). Also, the acrolein (form due to the decomposition of 3-acetoxypropanal, Scheme 3) was not detected in GC analysis. This signifies that no decomposition of 3-acetoxypropanal occurred confirming high regioselectivity observed in present study was mainly due to the nature of ligand.

3.5. Effect of stirring rate

In order to see the impact of gas liquid mass transfer resistance, the effect of agitation speed on the TOF and selectivity of

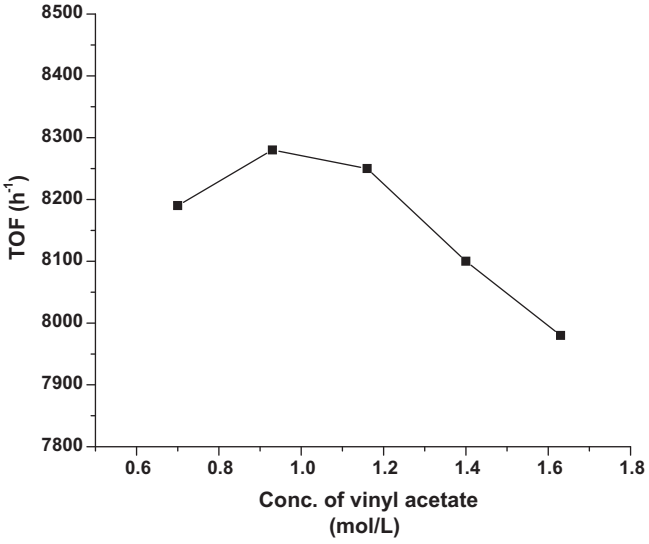


Fig. 2. Effect of initial vinyl acetate concentration on $Rh/P(ONp)_3$ catalyzed hydroformylation of vinyl acetate.

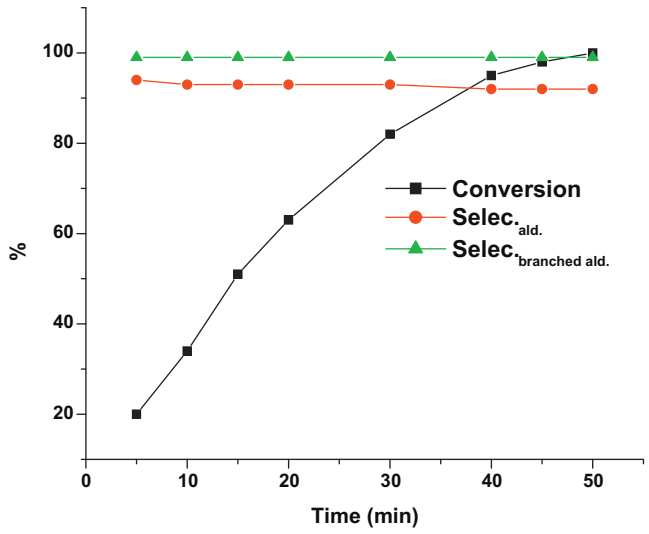


Fig. 3. The kinetic profile of the rhodium catalyzed vinyl acetate hydroformylation using ligand $P(ONp)_3$.

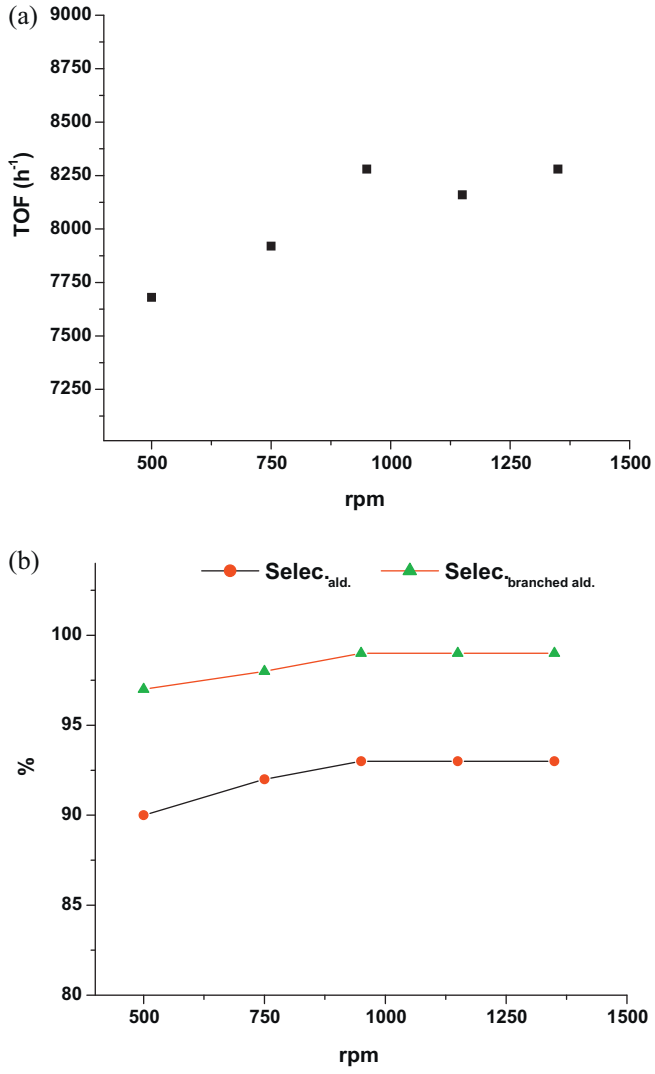


Fig. 4. Effect of stirring rate on TOF (a) and selectivity (b) of vinyl acetate hydroformylation catalyzed by Rh/P(ONp)$_3$.

vinyl acetate hydroformylation was studied by varying the stirring speed (Fig. 4). The other reaction parameters were kept constant. It was observed that at low stirring rate, the reaction proceeded slowly with diffusion limitation. Whilst at higher stirring speed, the CO diffuse rapidly and hence increases the rate of the reaction. For example, the TOF as well as selectivity were low at lower stirring rate (500 rpm). With an increase in stirring rate from 500 to 950 rpm substantially enhanced both TOF and selectivity (Fig. 4). These results clearly indicate that the TOF depend on the stirring rates, particularly when the stirring rate is low. Moreover, at low stirring speed the formation of byproduct is somewhat higher due to the slow diffusion of CO. A further increase in stirring rate from 950 to 1350 rpm, no significant changes in TOF and selectivity were observed. Therefore, in all the experiments the stirring rate was maintained at 950 rpm.

3.6. *Effect of various solvents*

The choice of solvent is crucial for a particular reaction to achieve high activity and selectivity besides the choice of the appropriate ligand. The formation of side products are affected by solvent used (Table 4). In the cases of conventional organic solvents such as cyclohexane and toluene, the hydroformylation of vinyl acetate proceeds well with high activity and selectivity (Table 4, entries 1 and 2). While catalytic activity was low in tetrahydrofuran and dichloromethane (DCM) (Table 4, entries 3 and 4) with comparable aldehyde selectivity and regioselectivity. The reaction performed in these commonly used solvents present several drawbacks like toxicity, volatility and high flammability. Subsequently, ionic liquids have been used widely as alternative solvents [33–35]. The recent research focused is on the use of organic carbonates (as green solvent) for catalysis [36–39] particularly cyclic carbonates (propylene carbonate, PC) which display some remarkable properties like high boiling point, odorless, low toxicity, low viscosity, noncorrosive, inflammable and biodegradable [36–39]. The PC has been used as solvent for the asymmetric hydrogenation [36,38], asymmetric allylic alkylation, amination [37], and in sonogashira reaction [40]. Thus, we have investigated the viability and beneficial effect of organic carbonate as solvent in hydroformylation of vinyl acetate catalyzed by Rh/bulky phosphites. The significant influence of organic carbonates as solvent on the catalytic activity and selectivity can be seen by comparing results summarized in Table 4. In particular, the high TOF with high selectivity for aldehyde and comparable regioselectivity to branched aldehyde was achieved when the reactions were performed in PC. The high boiling point (242 °C) is another advantage of solvent PC as product can be separated by vacuum distillation [27,38]. In order to reuse rhodium based catalyst in PC, the hydroformylation experiments with a consecutive run were carried out in PC. The reactions were run until no uptake of syngas was observed to ensure complete conversion of vinyl acetate as reaction slow down after 90% conversion. The product was separated from the catalyst/PC by distillation under reduce pressure and the catalyst/PC was then recycled (Table 5). Consequently, PC/catalyst system was recycled three times without significant loss in activity and selectivity.

4. Mechanism

On the basis of experimental results and reported literature on vinyl acetate hydroformylation, the proposed mechanism for the rhodium catalyzed hydroformylation of vinyl acetate using bulky phosphite, P(ONp)$_3$ as ligand is articulated (Fig. 5). The naphthyl-based monodentate bulky phosphite ligands gave noticeably high activity and selectivity than phosphine ligands. Bulky phosphites are weak σ-donor and strong π-acceptor ligands than phosphine ligands; and are known to enhance the rate of the hydroformylation reaction [41–44]. The high activity in the case of bulky phosphite ligand is ascribed to the stronger π-acceptor characteristic and high steric nature, lead to the formation of monoligated electron deficient rhodium complex, HRh(CO)$_3$L [45]. P(ONp)$_3$, a sterically bulky ligand (cone angle of P(ONp)$_3$ is 166° while for PPh$_3$ is 145°) have high π-acceptor character as compare to PPh$_3$. Under syngas environment reaction solution containing Rh(acac)(CO)$_2$ and L (L = P(ONp)$_3$) generates catalytically active species having one P(ONp)$_3$ coordinated to rhodium, HRh(CO)$_3$L (A) confirmed by in situ IR and NMR [28]. The HRh(CO)$_3$L (A) 18e complex easily dissociate CO to form species (B), facilitates alkene coordination and hence enhance rate of reaction. The formation of 16e species (B) is influence by electron-donating or withdrawing ability of ligands and is in equilibrium with 18e complex (A) (Fig. 5). The ligand with comparative more σ-donor ability increases electron density on rhodium, improves substantial π-back donation to CO, reduce CO dissociation and lead to low rate and selectivity. The bulky phosphine ligand PNp$_3$ even having high steric nature was less effective than bulky phosphite in terms of activity and selectivity. In contrast, ligands with π-acceptor capability compete with CO for the electron back donation. Thus, electron density

Table 4
Effect of various solvents on Rh/bulky phosphites catalyzed hydroformylation of vinyl acetate.[a]

Entry	Ligand	Solvent	TOF (h^{-1})	$S_{aldehyde}$ (%)	b/l
1	$P(ONp)_3$	Toluene	8280	93.0	99/1
2	$P(ONp)_3$	Cyclohexane	8328	93.0	>99/1
3	$P(ONp)_3$	DCM	3040	93.5	>99/1
4	$P(ONp)_3$	THF	3200	90.5	>99/1
5	$P(ONp)_3$	PC	12240	95	95/5
6	L_3	PC	12120	95	95/5
7	L_3	DMC	10320	95	98/2
8	L_4	PC	11760	95	94/6

[a] Reaction conditions: $[Rh(CO)_2acac]$, 0.23 mmol/L; P/Rh, 6.0; [vinyl acetate], 0.93 mol/L; temperature, 90 °C; syngas pressure (1:1), 4.0 MPa; solvent, 50 mL; reaction time, 10 min.

Table 5
Recycling experiments with the catalyst system (PC/Rh-L_3).[a]

Entry	Catalyst	Conv. (%)	Time (min)	$S_{aldehyde}$ (%)	b/l
1	Rh-L_3	100	30	95	95/5
2[b]	Recycled catalyst	100	30	95	95/5
3[b]	Recycled catalyst	100	40	93	95/5
4[b]	Recycled catalyst	100	45	92	93/5

[a] Reaction conditions: $[Rh(CO)_2acac]$, 0.23 mmol/L; P/Rh, 6.0; [vinyl acetate], 0.93 mol/L; temperature, 90 °C; syngas pressure (1:1), 4.0 MPa; solvent (PC), 50 mL.
[b] The catalyst system was reused after separation of product by vacuum distillation.

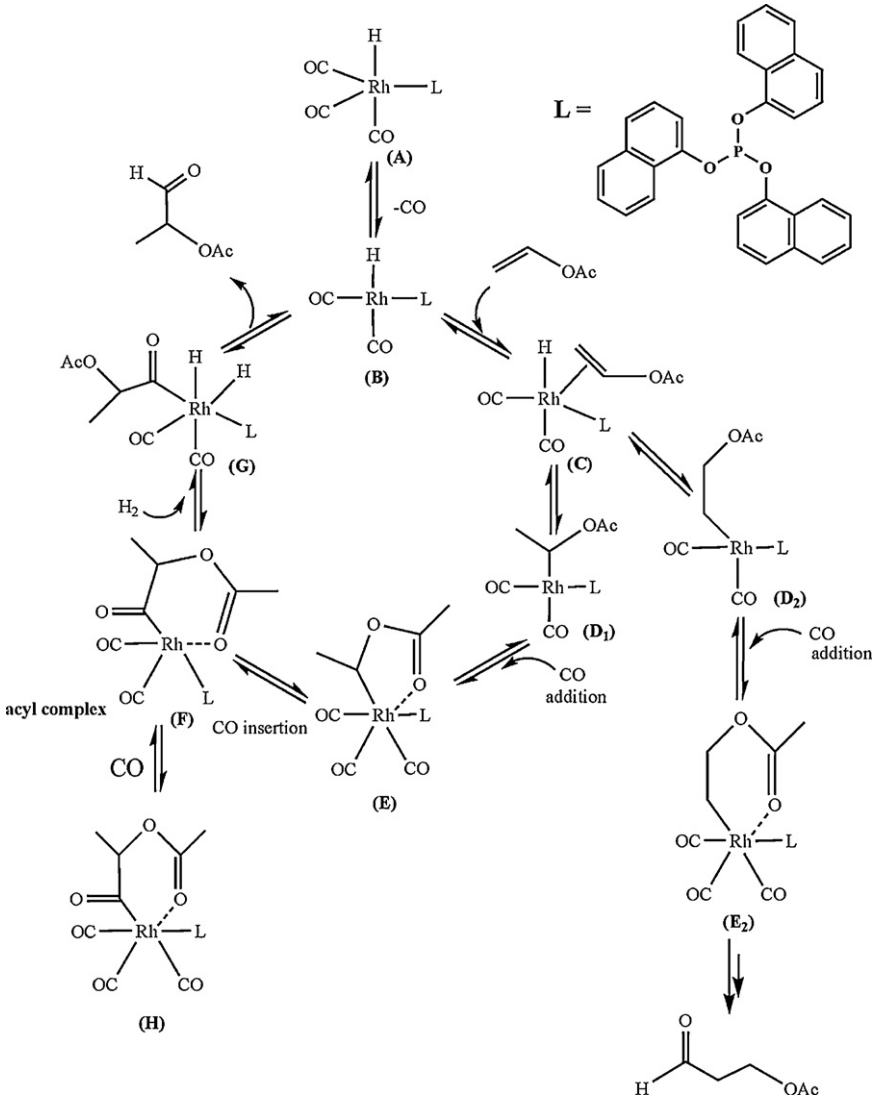


Fig. 5. Proposed mechanism for the rhodium catalyzed hydroformylation of vinyl acetate using $P(ONp)_3$.

around metal center decreases thereby increases the reaction rate due to facile CO dissociation and easily alkene association.

In view of above, the vinyl acetate hydroformylation has some discrete features: (i) vinyl acetate is less reactive to the hydroformylation compared to terminal alkenes, (ii) the regioselectivity of the vinyl acetate hydroformylation is contradictory to that of non-functionalized linear olefins, the branched aldehyde predominates, and (iii) the reaction rate, regioselectivity and formation of side products depend distinctly on steric and electric nature of ligands used. The less reactivity, reversed regioselectivity, and formation of side products were attributed probably to the double bond polarization due to the inductive effect of the ester carbonyl group and chelating effect of the vinyl ester carbonyl group to metal center. The ester carbonyl group influences the intermediates stability during hydroformylation by the formation of thermodynamically stable five and/or six membered rings through coordination to the rhodium (Fig. 5, species E and E_2) and can slow down carbon monoxide insertion and responsible for the less hydroformylation reactivity of vinyl acetate and formation of side products. Consequently, the initial rate of hydroformylation of vinyl acetate using rhodium complex modified by bulky $P(ONp)_3$ ligand (at 80 °C, 3.0 MPa syngas pressure) for vinyl acetate hydroformylation) was ~16 times slower than initial rate of 1-hexene hydroformylation [28].

5. Conclusions

The naphthyl-based monodentate bulky phosphine and phosphite ligands were evaluated in rhodium catalyzed hydroformylation of vinyl acetate. The reaction rate activity and selectivity (chemo- as well as regio-) depend conspicuously on steric and electronic nature of ligands. The ligand PNp_3 having high steric nature than PPh_3 and offered high regioselectivity toward branched aldehyde with low activity and low chemo selectivity toward aldehyde. While an excellent regioselectivity to branched aldehyde and high selectivity to aldehyde with high TOF were realized with monodentate bulky phosphite ligands having π-acceptor ability with comparative more steric nature. Among the naphthyl-based bulky phosphite ligands, $P(ONp)_3$ afforded notable catalytic activity. The observed TOF is 3.6 times higher than those observed for the Rh/PPh_3 catalyst. Moreover, the viability and beneficial effect of organic carbonate as 'green' solvent in hydroformylation of vinyl acetate catalyzed by Rh/bulky phosphites were also investigated. The substantial advantages of organic carbonates were found compared to the conventional organic solvents and also allow the recycling of the catalyst.

Acknowledgments

Authors are thankful to analytical section of the institute for assistance with analyses and CSIR and DST for financial support under CSIR Network Programme NWP 010 and SR/S1/OC-56/2009. AAD thanks CSIR, New Delhi, for the award of Senior Research Fellowship.

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