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Selective hydroformylation–acetalization of various olefins using simple and efficient Rh-phosphinite complex catalyst

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ABSTRACT

A simple and efficient Rh-phosphinite complex catalyst was studied for the selective hydroformylation of various olefins. The influence of various reaction parameters including the effect of temperature, pressure, catalyst loading, time, and solvents was studied. The protocol was also applied for the synthesis of various acetals via tandem hydroformylation–acetalization of olefins in alcohols as solvents. High activity and selectivity for acetal formation was achieved in the absence of co-catalysts with admirable substrate to catalyst mole ratio (TON 2500). The developed protocol works for a wide range of olefins to synthesize corresponding aldehydes and acetals under optimized reaction conditions.

Hydroformylation is one of the well studied homogeneously catalyzed reaction and also one of the large scale industrial applications of homogeneous catalysis. The annual production of several million tons of oxo chemicals attests its importance. The catalytic hydroformylation is an elegant, clean, and atom-efficient method to prepare wide range of aldehydes by the reaction of olefins with syngas.[1] In many cases, aldehydes are not the final products and are further converted into alcohols, esters, amines, acetals, and many more.[2] The tandem reaction is always advantageous over multistep synthesis since it minimizes the waste, multiple reaction steps and the number of purification processes which fulfills the criteria of sustainability and green chemistry. Several transition metal-based catalysts involving Rh, Pt, Co, and Ru are used for this reaction. Rhodium complexes of modified phosphorous containing ligand show high activity and selectivity at mild reaction conditions and hence are generally preferred for hydroformylation reactions.[3]

The direct synthesis of acetals from olefins is one of the interesting applications of tandem reaction. Acetal formation under hydroformylation conditions may be needed either to protect the sensitive aldehyde group from side reactions or for synthetic purposes.[4] Considering the importance of acetals as organic solvents, additives for fuel and intermediates in the pharmaceutical, perfumery, and agricultural industries,[5] several methods have been developed for their synthesis. Fernandez and Castillon reported the acetalization of olefins using $[Rh_2(\mu\text{-}OMe)_2\text{-}(cod)_2]$ with pyridinium *p*-toluenesulfonate (PPTS) as co-catalyst.[6] The acetal formation under hydroformylation condition can be increased in the presence of acid catalyst or by acidified resins,[7] and special ligands with rhodium which can provide an acidic pH.[8] Besides this, there are a few reports wherein acetal formation was achieved under acid-free conditions. El Ali et al. reported acid-free acetalization of alkenes using $RhCl_3{\cdot}3H_2O/P(OPh)_3$ as an effective catalytic system for this transformation.[9] Recently, Gusevskaya and co-workers reported the synthesis of fragrance acetals using $Rh/P(O\text{-}o\text{-}tBuPh)_3$ catalytic system in the absence of acid co-catalyst.[10] In spite of their potential utility, most of the reported protocols suffer from one or more drawbacks such as use of acid co-catalysts, harsh reaction conditions, or low substrate to catalyst mole ratio. Literature reports reveal that the hydroformylation as well as hydroformylation–acetalization reactions using rhodium metal with phosphite/phosphinite ligands are more effective than the conventional Rh-triphenyl phosphine based catalysts.[11] Even with high activity, performance, and stability there are very few reports on Rh-phosphite/phosphinite complexes.[12] Some of the best results with these ligands are obtained using the family of calixarenes, which are known as sophisticated molecular cages and claw-like ligands,[13] pyranoside,[14] and furanoside[15] ligands. However, multistep synthetic procedures and high cost of these ligands limit their industrial applications.

Hence, the development of simple and atom efficient catalytic system is always a key issue in the case of hydroformylation and related reactions. In continuation of our interest in the development of homogeneous catalytic system,[16] we herein report a facile

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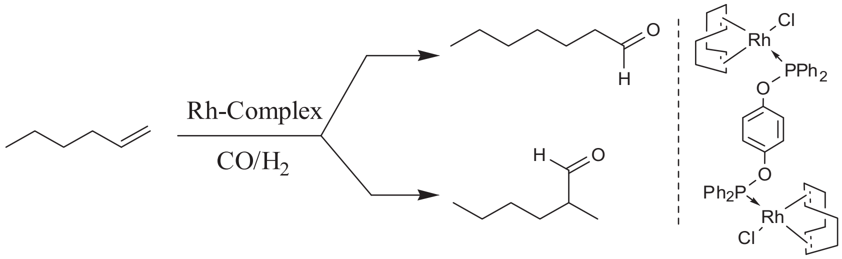
and highly efficient protocol for hydroformylation reaction and for one-pot hydroformylation–acetalization process under acid-free condition using a known Rh-phosphinite complex catalyst.

To optimize the reaction conditions, series of experiments were performed on the hydroformylation of hexene as a model system using Rh-phosphinite complex as a catalyst (Scheme 1). The Rh-phosphinite complex used was synthesized according to the reported procedure in the literature.[18] The influences of various reaction parameters such as effect of temperature, solvent, catalyst loading, syngas pressure, and time were studied and the results obtained are summarized in Table 1.

Initially, the reaction was studied at different temperatures in the range of 50–110 °C (Table 1, entries 1–4). A high temperature significantly promotes the side reaction like hydrogenation with suppression of α-formylation and thus provided higher branched selectivity (Table 1, entry 1).[19] It was found that regioselectivity for linear aldehyde formation increases with a decrease in temperature to 60 °C without affecting the conversion. Further decrease in the reaction temperature to 50 °C led to the poor conversion of hexene. Thus, further studies were carried out at 60 °C, which was found to provide optimum conversion and selectivity toward desired aldehyde (Table 1, entry 3). It was observed that the nature of solvent affects the selectivity of the reaction product. The small amount of substrate isomerization was observed when toluene was used as a reaction solvent provided moderate conversion and poor selectivity for linear aldehyde, whereas low conversion and considerable amount of acetal formation were obtained in methanol (Table 1, entries 5 and 6). It was observed that tetrahydrofuran (THF) provides good yield and selectivity of the desired product and hence was used for further studies (Table 1, entry 3). Next, we studied the substrate to catalyst molar ratio. It was found that increasing the molar ratio from 1000:1 to 2500:1 does not have a significant impact in the conversion and selectivity of the desired aldehyde products (Table 1, entries 7, 3, and 8), whereas, with further increase in the substrate to rhodium mole ratio up to 3333:1, decreases the conversion of hexene (Table 1, entry 9). This decrease in conversion was due to a decrease in the amount of catalyst from 0.04 mol % (Sub/Rh mole ratio 2500:1) to 0.03 mol % (Sub/Rh mole ratio 3333:1). The influence of syngas (CO/H_2) pressure on the hydroformylation reaction was then investigated. It was observed that lowering the syngas pressure from 40 to 30 bar did not have any prominent effect on the reaction outcome, but with further decrease in pressure to 25 bar decreases the conversion of the desired product (Table 1, entry 11). We further studied the effect of reaction time ranging from 8 to 4 h and it was found that within a period of 6 h, reaction provided maximum yield and selectivity for linear aldehyde formation (Table 1, entries 3, 12, and 13). To check the activity and selectivity of the developed Rh-phosphinite complex with a ligand-free system, the reaction of 1-hexene was carried out using $[Rh(cod)Cl]_2$ as a catalyst and was compared. However, low conversion addresses the importance of the ligand in hydroformylation reaction (Table 1, entry 14). Hence, the optimized reaction conditions for the hydroformylation of hexene were; hexene (5 mmol), Rh-phosphinite complex (0.002 mmol), and CO/H_2 (30 bar) at a temperature of 60 °C for 6 h in THF (15 mL) as solvent.

With these optimized reaction conditions, the scope of the developed protocol was extended for the hydroformylation of a variety of aliphatic, aromatic, and cyclic olefins and the results obtained are summarized in Table 2.[20] The model reaction of hexene provided good conversion and selectivity toward linear aldehyde (Table 2, entry 1).



Scheme 1. Hydroformylation of hexene using Rh-phosphinite complex catalyst.

Table 1
Effect of reaction parameters on hydroformylation of hexene[a]

Entry	Temp (°C)	Solvent	Sub/Rh (mole ratio)	CO/H_2 pressure (bar)	Time (h)	Conversion[c] (%)	Aldehyde (%)	Linear:iso[c] (%)	Reduction (%)
1	110	THF	2000	30	8	100	92	43:57	8
2	90	THF	2000	30	8	100	95	49:51	5
3	60	THF	2000	30	8	100	99	71:29	–
4	50	THF	2000	30	8	44	99	69:31	1
5	60	Toluene	2000	30	8	94	97	52:48	3
6	60	MeOH	2000	30	8	68	13:87[d]	67:33	–
7	60	THF	1000	30	8	100	99	71:29	–
8	60	THF	2500	30	8	100	99	72:28	1
9	60	THF	3333	30	8	73	97	69:31	3
10	60	THF	2500	40	8	100	96	65:35	4
11	60	THF	2500	25	8	88	99	70:30	1
12	60	THF	2500	30	6	100	99	72:28	–
13	60	THF	2500	30	4	89	99	73:27	1
14[b]	60	THF	2500	30	6	34	73	67:33	27

[a] Reaction conditions: hexene (5 mmol), Rh-phosphinite complex (as indicated), solvent (15 mL), 600 rpm.
[b] $[Rh(cod)Cl]_2$ used as a catalyst.
[c] Conversion and selectivity (lin/iso) were determined by GC analysis.
[d] Acetal formation.

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