Journal of Organometallic Chemistry 772-773 (2014) 152-160

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

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

Polystyrene anchored ruthenium(II) complex catalyzed carbonylation of nitrobenzene and amines for the synthesis of disubstituted ureas



Sk Manirul Islam ^{a, *}, Kajari Ghosh ^a, Anupam Singha Roy ^a, Rostam Ali Molla ^a, Noor Salam ^a, Tanmay Chatterjee ^b, Md. Asif Iqubal ^c

^a Department of Chemistry, University of Kalyani, Kalyani, Nadia 741235, West Bengal, India

^b Department of Organic Chemistry, Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700032, India

activity.

^c Department of Chemistry, IIT Roorkee, Roorkee 247667, Uttarakhand, India

ARTICLE INFO

Article history: Received 3 June 2014 Received in revised form 15 August 2014 Accepted 19 August 2014 Available online 16 September 2014

Keywords: Carbonylation reaction Polymer anchored Ruthenium(II) complex High CO pressure Disubstituted ureas

Introduction

Among the different catalytic processes, carbonylation reactions which make use of carbon monoxide are of great interest as it represents industrial core technologies for converting various bulk chemicals into a diverse set of useful products of our daily life [1–3]. Carbonylation of alkenes to aldehydes [4] and carboxylic acids [5], carbonylation of aryl halides to aryl carboxylic acids [6], aldehydes [7], or amides [8] and the carbonylation of methanol to acetic acid [9] are well known industrial processes with major commercial significance. Although the use of CO as a reductant had been in the past confined to few reactions, its use in organic synthesis, especially in the reductive carbonylation of nitro aromatics and the oxidative carbonylation of aromatic amines, has increased dramatically [10].

Phenyl ureas are a known class of commercially available herbicides. Since phosgene is toxic and expensive, hence there is always a search for comparatively mild non-phosgenation processes [11,12]. These are based on the reductive carbonylation of nitrobenzene to form N,N-diphenylurea (DPU). The conventional N,N- disubstituted urea is an important intermediate for the production of carbamates, which are the raw materials for agrochemicals [13]. Unsymmetrical *N*,*N* -diaryl ureas are found in a variety of biologically active molecules, and their efficient synthesis is of great importance, especially to medicinal chemists [14].

© 2014 Elsevier B.V. All rights reserved.

The catalytically active complex $[Ru(PS-imd)(CO)_2Cl_2]$ (PS-imd = polystyrene anchored imidazole) was

synthesized and characterized using various spectroscopic techniques. The complex is well characterized

and highly stable. The catalytic activity of the resulting species was investigated towards the synthesis of

diphenyl urea and other disubstituted ureas. The experiments were carried out under high CO pressure,

high temperature condition in mild coordinating media. The catalyst was found to produce excellent

yields with high product selectivity. Variable yields are obtained depending on the substituent on nitrobenzene and aniline. The effects of co-solvent and co-catalyst were also studied. The catalyst was

very stable and could be reused for more than five times without any noticeable loss of its catalytic

The conventional method for preparing ureas is the reaction of amines with carbon monoxide in the presence of non-metal catalysts such as *tert*-amine [15]. The yield of urea is increased only if excess sulfur is used for the reaction with amine. The use of sulfur produces hydrogen sulfide as an undesired by-product, which raises the cost of the process because of its toxicity and its special disposal requirements. The other method utilizes selenium, which is a well-known toxic catalyst and which has to be precipitated by a continuous flow of oxygen [16]. Therefore industry has always been on the lookout for new catalyst systems to make symmetric ureas and the more challenging unsymmetric ureas [10]. Among the metal complex catalysts used for this purpose, the complexes of palladium(II), rhodium(I) and ruthenium(II) show very good catalytic activity for the preparation of ureas [17–19]. In homogeneous reactions catalyzed by organometallic compounds, the catalyst gets intimately involved with the reactants to form various intermediates during the course of the reaction [20]. The polymer anchored metal complex catalysts which may be separated easily from the product mixture and reused are expected to have higher

ABSTRACT



^{*} Corresponding author. Tel.: + 91 33 2582 8750; fax: +91 33 2582 8282. *E-mail address:* manir65@rediffmail.com (S.M. Islam).



Scheme 1. Synthesis of polymer anchored Ru(II) complex.

chemical and thermal stabilities. These advantages make the polymer anchored catalysts more attractive than their homogeneous counterpart [21].

In order to perform a new contribution to the field of carbonylation reaction, we report here carbonylation reaction for the synthesis of disubstituted ureas using polymer anchored ruthenium(II) catalyst. The effect of various reaction parameters such as mole ratio of reactants, catalyst amount, and temperature was studied to optimize the conditions for maximum conversion. Also the catalyst was regenerated and reused up to five cycles.

Experimental

Materials

Analytical grade reagents and freshly distilled solvents were used throughout. All reagents and substrates were purchased from Merck. Liquid substrates were predistilled and dried by molecular sieve and solid substrates were recrystallized before use. Distillation and purification of the solvents and substrate were done by standard procedures [22]. 5.5% crosslinked chloromethylated polystyrene and ruthenium chloride was purchased from Aldrich Chemical Company, U.S.A. and used without further purification. Carbon monoxide (99.9%) was purchased from IOL Bombay, India.

Physical measurements

The FT-IR spectra of the samples were recorded from 400 to 4000 cm⁻¹ on a Perkin Elmer FT-IR 783 spectrophotometer using KBr pellets. UV–Vis spectra were taken using a Shimadzu UV-2401PC doubled beam spectrophotometer having an integrating sphere attachment for solid samples. Thermogravimetric analysis (TGA) was carried out using a Mettler Toledo TGA/DTA 851e. Surface morphology of the samples was measured using a scanning electron microscope (SEM) (ZEISS EVO40, England) equipped with EDX facility. Ruthenium content in the catalyst was determined using a Varian AA240 atomic absorption spectrophotometer (AAS).

Preparation of the polymer-anchored imidazole ligand (PS-imd)

An outline of the preparation of polymer-anchored Ru(II) complex catalyst is given in Scheme 1. Chloromethylated polystyrene

T-	ы	0	1
Id	v	C	

Chemical composition of polymer anchored ligand and polymer supported catalyst.

Compound	Color	C%	H%	Cl%	N%	Metal%
PS-imd Ru(PS-imd)(CO) ₂ Cl ₂	White Marsh green	76.32 (78.82) 68.62 (69.26)	6.36 (6.57) 5.61 (5.76)	2.15 4.60	9.39 (14.62) 14.71 (14.94)	 5.30

(3 g) was stirred with a 1:1 mixture of acetonitrile and toluene for 30 min. Then imidazole (1.2 g) was added to the above mixture of the polymer, and it was heated for 24 h at 80 °C. The white polymeranchored ligand was filtered out, washed thoroughly with methanol and dried under vacuum (Yield = 60%).

Preparation polymer supported ruthenium(II) catalyst, [Ru(PSimd)(CO)₂Cl₂]

The polymer anchored imidazole ligand (2.0 g) was added to a DMF solution (20 mL) of RuCl₃.3H₂O (1.9 mmol) and the mixture was refluxed for 6 h. Carbon monoxide was bubbled through it under reflux condition when pale green catalyst was formed. It was filtered, washed with ethanol and then dried under high vacuum (Yield = 20%).

Process for the synthesis of ureas

All carbonylation reactions were conducted in a 100 mL glass lined stainless steel autoclave equipped with magnetic stirring. In each reaction, 1.0×10^{-2} mmol of catalyst, 10 mmol of nitrobenzene, 20 mmol of amines and carbon monoxide at 60 atm were charged successively. The reaction proceeded at 120 °C for 5 h, and after the reaction 20 mL of methanol were added to the resulting mixture which was qualitatively analyzed with Varian 3400 gas chromatograph equipped with a 30 m CP-SIL8CB capillary column and a Flame Ionization Detector by the external standard method. All reaction products were identified by using Trace DSQ II GC-MS.

Results and discussion

Catalyst characterization

The polymer supported imidazole ligand was well characterized and established earlier [23]. Due to the insolubilities of the polymer supported metal complex in all common organic solvents, its structural investigation was limited to their physicochemical properties, chemical analysis, SEM, TGA, FT-IR, EPR and UV–Vis spectral data. Table 1 provides the data of elemental analysis of polymer supported ligand and the polymer supported ruthenium catalyst. The metal content of the polymer supported catalyst was estimated by atomic absorption spectrometry.

The attachment of metal onto the support was confirmed by comparing the FT-IR spectra (Fig. 1) of the polymer before and after loading with metal. The IR spectrum of pure chloromethylated polystyrene has an absorption band at 1261 cm⁻¹ due to the C–CI group, which was weak in the ligand and in the catalyst. IR spectra show a stretching vibration for $-CH_2$ at 2918 cm⁻¹ for the polymer bound ligand and its complex. The stretching vibration of C—N bond appeared at 1613 cm⁻¹ for the polymer anchored imidazole ligand which is shifted to 1618 cm⁻¹ in the metal complex, indicating the coordination of azomethine nitrogen to the metal [24,25]. Another band at 1319 cm⁻¹ (in ligand) for C–N stretching is shifted to lower region in the metal complex [26]. A new intense peak at around 1984-2080 cm⁻¹ due to the CO is observed in the



Fig. 1. FT-IR spectra of polymer anchored ligand (a) and polymer anchored ruthenium(II) catalyst (b).



Fig. 2. DRS-UV-visible absorption spectra of polymer anchored Ru(II) complex.

metal complex confirming the metal carbonyl coordination [27]. In the far-IR data, the bands are due to the Ru–N stretching vibrations around at 470 cm⁻¹, which established the formation of the metal complex through Ru–N bonding [28].

The electronic spectrum (Fig. 2) of the polymer anchored metal complex was recorded in diffuse reflectance spectrum mode as MgCO₃/BaSO₄ disks. The polymer anchored ruthenium (II) complex is in the +2 oxidation state. The electronic spectra of the ruthenium complex showed four bands in the region 680–230 nm. The bands around 680–600 nm range have been assigned to the spin allowed d–d transition. The other high intensity bands around 309–492 nm have been assigned to charge transfer transitions (LMCT) arising from the excitation of electrons from the metal t_{2g} level to the unfilled molecular orbitals derived from the π^* level of the ligands. The bands below 300 nm were characterized by intra-ligand charge transfer [29].

Field emission-scanning electron micrographs of polymer anchored ligand (PS-imd) and its complex $[Ru(PS-imd)(CO)_2Cl_2]$ were recorded and it was observed that the morphological changes occurred on the polystyrene beads at various stages of the



Fig. 3. SEM images of polymer anchored ligand (A) and the immobilized ruthenium(II) complex (B).

synthesis. The SEM images of polymer anchored ligand (A) and the immobilized ruthenium(II) complex (B) on functionalized polymer are shown in Fig. 3. The pure chloromethylated polystyrene bead has a smooth surface (not shown) while polymer anchored ligand and complex show roughening of the top layer of polymer beads. This roughening is relatively more in complex. Also the presence of ruthenium metal can be further proved by energy dispersive spectroscopy analysis of X-rays (EDAX) (Fig. 4) which suggests the formation of metal complex with the polymer anchored ligand.

Thermal stability of complex was investigated using TGA-DTA at a heating rate of 10 °C/min in air over a temperature range of 30–600 °C. TGA curve of polymer anchored Ru(II) complex is shown in Fig. 5. Polymer anchored ruthenium(II) complex decomposed at 360–400 °C. So from the thermal stability, it concludes that polymer anchored metal complex degraded at considerably higher temperature.

The X-band EPR (Electron Paramagnetic Resonance) spectra of the Ru-complex in the fresh and used catalyst were recorded in the solid state at room temperature (Fig. 6). The EPR spectra of both the fresh and used catalyst are quite similar and also matches with the EPR spectra of the previously reported Ru(II) complexes [30,31]. Hence, we can predict that the Ru remains in the +2 oxidation state before and after the reaction.

Catalytic activity of [Ru(PS-imd)(CO)₂Cl₂] for carbonylation reaction

In an autoclave, nitrobenzene, aniline, and the catalyst were mixed with solvent. Then co-catalyst was added to it and the autoclave was flushed with CO gas at 120 °C. After 5 h, the formation of diphenyl urea was analyzed by gas chromatograph. The catalyst was found to be highly effective for carbonylation of nitrobenzene and aniline to give *N*,*N*'-diphenyl urea (DPU) as the major product. The above reaction was taken as model and the effects of nitrobenzene and aniline molar ratio, carbon monoxide pressure, temperature, reaction time, solvent, co-solvent, the amount of catalyst and co-catalyst were investigated (Scheme 2).



Fig. 4. EDX images of polymer anchored ligand (A) and its Ru(II) complex (B).



Fig. 5. TGA plot for [Ru(p-imd)(CO)₂Cl₂] complex.

To find the effect of amount of nitrobenzene and aniline on the carbonylation reaction, their molar ratio was varied. The results are summarized in Table 2. The yield of DPU was highest (92%) when the ratio was 1:2. Very low DPU yield was observed when no aniline



Fig. 6. The X-band EPR spectra of Ru (II) for (a) fresh catalyst and (b) used catalyst.



Scheme 2. Carbonylation of nitrobenzenes and anilines.

Table 2

Influence of PhNO₂: PhNH₂ molar ratio on the carbonylation reaction.^a

Run	Molar ratio PhNO ₂ : PhNH ₂	Conversion (%)	Yield (%)		
			DPU	PhNH ₂	MPC ^b
1	1:0	100	10	8	82
2	0.5:1	46	15	7	78
3	1:0.5	100	84	6	10
4	1:1	100	88	7	5
5	1:2	100	92	7	1
6	1:4	100	84	9	7

^a Conditions: PhNO₂ + PhNH₂ = 30 mmol, CH₃OH = 60 mmol, FeCl₃ (20 mmol), Catalyst = 1.0×10^{-2} mmol, medium = DMF, T = 120 °C, t = 5 h, $P_{CO} = 60$ atm. Product identified by GC.

^b Methyl-*N*-phenyl carbamate.

Table 3

Effect of solvent on the carbonylation reaction in presence of methanol.^a

Entry	Solvent	Conversion (%)	Yield of DPU (%)
1	DMF	100	92
2	DMSO	98	88
3	CH ₃ CN	84	74
4	C ₆ H ₆	56	35
5	C ₆ H ₅ CH ₃	54	34
6	Hexane	53	34

^a conditions: [nitrobenzene] = 10 mmol, [aniline] = 20 mmol, CH₃OH (60 mmol), FeCl₃ (20 mmol), catalyst amount = 1.0×10^{-2} mmol, T = 120 °C, time (5 h), $P_{\rm CO} = 60$ atm.

was added to the reaction mixture *i.e* when nitrobenzene: aniline molar ratio was 1:0.

The carbonylation reaction using the present catalyst was effective in mild coordinating solvents and in presence of methanol



Fig. 7. Effect of temperature on the production of diphenyl urea catalyzed by polymer anchored ruthenium complex. Reaction condition: [nitrobenzene] = 10 mmol, [aniline] = 20 mmol, CH₃OH (60 mmol), FeCl₃ (20 mmol), DMF (10 mL), catalyst amount = 1.0×10^{-2} mmol, time (5 h), $P_{CO} = 60$ atm.



Fig. 8. Effect of P_{CO} on the production of diphenyl urea catalyzed by polymer anchored ruthenium complex. Reaction condition: [nitrobenzene] = 10 mmol, [aniline] = 20 mmol, CH₃OH (60 mmol), FeCl₃ (20 mmol), DMF (10 mL), catalyst amount = 1.0×10^{-2} mmol, time (5 h).

as co-solvent. Weakly coordinating solvents were found to be more efficient and most of the catalytic runs were taken in DMF and DMSO. Very sluggish reaction occurs in strong coordinating solvents like CH₃CN or in non-polar solvents like C₆H₆, C₆H₅CH₃, and hexane (Table 3). The highest conversion (100%) with DPU selectivity of 92% observed in DMF medium.

Table 4

Effect of co-catalyst and co-solvent on the carbonylation reaction.^a

Run	Co-catalyst	Co-solvent	Conversion (%)	Yield of DPU (%)
1	FeCl ₃	_	94	8
		MeOH	100	92
		EtOH	100	88
2	SnCl ₄	_	92	5
		MeOH	98	90
		EtOH	97	87
3	PTS	-	98	6
		MeOH	99	90
		EtOH	97	88
4	Ру	-	67	1
		MeOH	70	24
		EtOH	65	22
5	Et ₃ N	-	66	3
		MeOH	68	23
		EtOH	67	21
6	KOH	_	67	2
		MeOH	72	27
		EtOH	70	25
7	CH ₃ CONa	-	70	4
		MeOH	76	30
		EtOH	72	27
8	C ₂ H ₅ CONa	_	72	5
		MeOH	78	32
		EtOH	78	29

^a Conditions: PhNO₂ + PhNH₂ = 30 mmol, co-solvent = 60 mmol, co-catalyst (20 mmol), Cat = 1.0×10^{-2} mmol, medium = DMF, T = 120 °C, t = 5 h, $P_{CO} = 60$ atm.



Fig. 9. Effect of amount of catalyst on the production of diphenyl urea catalyzed by polymer anchored ruthenium complex. Reaction condition: [nitrobenzene] = 10 mmol, [aniline] = 20 mmol, DMF (10 mL), temperature (120 °C), time (5 h), $P_{CO} = 60$ atm.

Effect of carbon monoxide pressure and temperature on the carbonylation of nitrobenzene and aniline was therefore studied to optimize the yield of DPU. Reaction at room temperature and low carbon monoxide pressure (20 atm) even in presence of methanol did not yield any product. Highest conversion (100%) was achieved at 60 atm and 120 °C and at a methanol concentration of 60 mmol. The products were majorly DPU (92%) with a little amount of aniline (6%) and MPC (2%) as the by-product. No product formation occurred at low temperature (less than 35 °C) and at carbon monoxide pressure maintained below 20 atm. The concentration of DPU increased gradually when the temperature was increased from 35 °C to 50 °C and finally to 100 °C. The DPU yield obtained 85% at 100 °C. Finally, the optimized temperature for the carbonylation reaction was 120 °C when the yield of DPU was 92% (Fig. 7).

At a carbon monoxide pressure of 20 atm or below, no carbonylation reaction takes place, as nitrobenzene and aniline concentration remained unchanged and no reaction products were observed even after 16 h of a catalytic run (Fig. 8). As the pressure of carbon monoxide was slowly raised from as low as 20–80 atm, the percentage of diphenylurea increased gradually and reached the optimum value of 92% at $P_{co} = 60$ atm.

Table 5

Synthesis of di-substituted ureas using nitrobenzene and different amines.





Conditions: substrates = 30 mmol, MeOH = 60 mmol, FeCl₃ (20 mmol), Cat = 1.0×10^{-2} mmol, medium = DMF, T = 120 °C, t = 5 h, $P_{CO} = 60$ atm.

In absence of methanol, low DPU yield was recorded even when the carbon monoxide pressure was increased to 80 atm and temperature raised to 100 °C. The presence of a co-solvent such as ROH (R = $-CH_3$, $-C_2H_5$) was therefore necessary for the reaction between PhNO₂, PhNH₂ and CO to proceed under high pressure and high temperature conditions. Presence of moisture in the system greatly hinders the catalytic conversion to DPU and almost 90% aniline was recorded. High aniline formation may also be due to hydrolysis of any DPU formed.

$(PhNHCONHPh) + H_2O \rightarrow 2PhNH_2 + CO_2$

Carbonylation reactions in presence of both co-solvent and cocatalyst were tried out to optimize the yield of DPU (Table 4). Investigations were made with both acidic and basic co-catalysts in the presence of alcohol in the reaction medium. In presence of methanol concentration (60 mmol), addition of acid co-catalysts such as FeCl₃, AlCl₃ and p-toluene sulphonic acid (PTS) increased the yield of DPU. The selectivity of the co-catalysts for the conversion of nitrobenzene and aniline to DPU is comparable, though highest yield of DPU was obtained using FeCl₃. Again, it is seen that the addition of basic co-catalysts like KOH, Et₃N, Pyridine, RONa (R = $-CH_3$, $-C_2H_5$) not only lowers the total conversion, it also reduces the yield of DPU and increases the yield of carbamates.

The effect of amount of catalyst was studied for the carbonylation reaction. It was found that the highest yield of DPU was obtained when 1.0×10^{-2} mmol of the catalyst was taken (Fig. 9).

The successful yield of DPU using the polymer anchored Ru(II) catalyst encouraged us to study the efficiency of the present catalyst to obtain other disubstituted urea from substituted

nitrobenzene and substituted aniline. The substrates and their corresponding products under optimized reaction conditions are given in Tables 5 and 6. Syntheses of ureas were also tested when aniline was replaced with n-butylamine, n-hexylamine and cyclohexylamine (Table 5, entries 2–4). The corresponding ureas were also formed with high conversion and selectivity (94–97%). Finally, several other aromatic amines, *i.e.*, *p*-methylaniline and *p*-methoxyaniline, were subjected to the reaction (Table 5, entries 5 and 6), with sufficient high catalytic performance. No reaction occurred on using *o*-nitroaniline as substrate (Table 5, entry 7), suggesting that the presence of the electron-attracting $-NO_2$ severely weakened the activity of the NH₂.

When substituted nitro aromatic compounds and aniline were subjected to react in 60 atm pressure of CO at 120 °C in the presence of [Ru(PS-imd)(CO)₂Cl₂] using DMF as solvent, disubstituted ureas were produced in variable yields depending on the substituents (Table 6). For methyl substitution in the *para* position, the yield of disubstituted urea was dramatically decreased to 30% (Table 6, entry 1). The Fluoro, cyano, and methoxycarbonyl groups in the *para* position led to the formation of the corresponding disubstituted ureas in 60%, 88%, and 76% yield, respectively (Table 6, entry 2–4).

Based on earlier reported mechanistic studies of catalytic carbonylations of nitobenzene [20,32], the reaction mechanism of this DPU synthesis is proposed in Scheme 3.

Heterogeneity test

To determine whether the catalyst actually functions in a heterogeneous manner, a test was performed on the

Table 6

Synthesis of di-substituted ureas using substituted nitrobenzene and aniline.



$$X = CH_3$$
, F, CN, COOCH₃



Conditions: substrates = 30 mmol, MeOH = 60 mmol, FeCl₃ (20 mmol), Cat = 1.0×10^{-2} mmol, medium = DMF, T = $120 \degree$ C, t = 5 h, P_{CO} = 60 atm.



Scheme 3. Proposed reaction mechanism of ruthenium catalyzed carbonylation nitrobenzene.

carbonylation of nitrobenzene and aniline. During the catalytic carbonylation of nitrobenzene and aniline, the solid catalyst was separated from the reaction mixture after 3 h. The obtained DPU at this point was 78%. The reaction was carried out for a further 3 h without the catalyst. The gas chromatographic analysis showed no increase in the conversion, whereas there was an increase in conversion in the uninterrupted experiment. AAS analyses of the liquid phase of the reaction mixtures collected by filtration confirmed that Ru is absent in the reaction mixture. These results suggest that the Ru is not being leached out from the catalyst during the carbonylation reaction. Furthermore, when the reaction was carried out in the absence of catalyst (blank reaction), no product was observed. This result suggested the catalytic role is played by the Ru centre in this carbonylation reaction.



Fig. 10. Recycling efficiency for the production of diphenyl urea catalyzed by polymer anchored ruthenium complex.

Recycling of the catalyst

One of the main advantages of a heterogeneous catalyst is to enhance the lifetime of the catalyst. To investigate the reusability of the polymer anchored Ru(II) complex, the catalyst was separated by filtration after the first run, dried under vacuum and then subjected to a second run under the same reaction conditions. Recycling efficiency was tested for the carbonylation of nitrobenzene and aniline with further addition of substrates in the appropriate amount under optimum reaction conditions, and the nature and yield of the final products were found to be comparable to that of the original one. As seen in Fig. 10, the catalyst can be reused up to five times without any appreciable loss of its catalytic activity.

Conclusion

A versatile polymer anchored ruthenium catalyst has been introduced for carbonylation reaction. The reaction conditions and catalyst system employed in the present study were found to be exceptionally efficient in *N*,*N*'–diphenylurea synthesis from aniline, nitrobenzene, and carbon monoxide. The catalyst is also effective for the selective production of other disubstituted ureas. The system allows facile product separation and catalyst recovery. The polystyrene-supported ruthenium complex can be recycled several times without substantial loss of catalytic efficiency.

Acknowledgments

SMI acknowledges the Council of Scientific and Industrial Research (CSIR), 02(0041)/11/EMR-II, dated: 19-12-2011 and Department of Science and Technology (DST), New Delhi, India, SB/S1/PC-107/2012; dated 10.06.2013 for funding. RAM acknowledges UGC, New Delhi, India for his Maulana Azad National Fellowship.

References

- [1] A. Brennführer, H. Neumann, M. Beller, Angew. Chem. Int. Ed. 48 (2009) 4114-4133
- [2] M. Seayad, J. Seayad, P.L. Mills, R.V. Chaudhari, Ind. Eng. Chem. Res. 42 (2003) 2496-2506
- [3] S.P. Gupte, V.P. Krishnamurthy, R.V. Chaudhari, Chem. Eng. Sci. 51 (1996) 2069–2078.
- [4] J. Xie, Z.Z. Huang, Chem. Commun. 46 (2010) 1947–1949.
- [5] H. Alper, W. Lee, J. Org. Chem. 60 (1995) 250–252.
- [6] V.P. Boyarskii, T.E. Zhesko, S.A. Lanina, Russ. J. Appl. Chem. 78 (2005) 1844-1848
- [7] T. Ueda, H. Konishi, K. Manabe, Angew. Chem. Int. Ed. 52 (2013) 8611-8615.
- [8] M.V. Khedkar, T. Sasaki, B.M. Bhanage, ACS Catal. 3 (2013) 287–293.
 [9] A. Haynes, Top. Organomet. Chem. 18 (2006) 179–205.
- [10] A.M. Tafesh, J. Weiguny, Chem. Rev. 96 (1996) 2035-2052.
- [11] J. March, Advanced Organic Chemistry, John Wiley & Sons, New York, 1985, p. 370.
- [12] M. Carafa, V. Mele, E. Quaranta, Green. Chem. 14 (2012) 217-225.
- [13] A. Ion, C.V. Doorslaer, V. Parvulescu, P. Jacobsa, D.D. Vos, Green. Chem. 10 (2008) 111-116.
- [14] T.M.E. Dine, S. Chapron, M.-C. Duclos, N. Duguet, F. Popowycz, M. Lemaire, Eur. J. Org. Chem. 24 (2013) 5445–5454.
- [15] R.A. Franz, F. Applegath, F.V. Morriss, F. Baiocchi, J. Org. Chem. 26 (1961) 3309-3312.
- [16] N. Sonoda, T. Yasuhara, K. Kondo, T. Ikeda, J. Am. Chem. Soc. 93 (1971) 6344.

- [17] N. D Ca, P. Bottarelli, A. Dibenedetto, M. Aresta, B. Gabriele, G. Salerno, M. Costa, J. Catal. 282 (2011) 120-127.
- [18] D.K. Mukherjee, C.R. Saha, J. Mol. Catal. A: Chem. 193 (2003) 41-50.
- [19] F. Shi, O. Zhang, Y. Gu, Y. Deng, Adv. Synth. Catal. 347 (2005) 225-230.
- [20] J.H. Kim, D.W. Kim, M. Cheong, H.K. Kim, D.K. Mukherjee, Bull. Korean Chem. Soc. 31 (2010) 1621-1627.
- [21] K.C. Gupta, A.K. Sutar, J. Mol. Catal. A Chem. 280 (2008) 173-185.
- [22] A.I. Vogel, Test Book of Practical Organic Chemistry, fifth ed., Longman, London 1989 [23] M. Islam, S. Mondal, P. Mondal, A.S. Roy, D. Hossain, M. Mobarak, Transit. Met.
- Chem. 36 (2011) 1–11. [24] V.V. Raju, K.P. Balasubramanian, C. Jayabalakrishnan, V. Chinnusamy, Nat. Sci.
- 3 (2011) 542-591.
- [25] B. Prabhakaran, N. Santhi, M. Emayavaramban, Phys. Astronomy 3 (2013) 53-66.
- [26] N. Nakamoto, Infrared Spectra and Raman Spectra of Inorganic and Coordination Compounds, Wiley, New York, 1997. [27] G.N. Krishnamurthy, N.J. Shashikala, Serb. Chem. Soc. 74 (2009) 1085–1096.
- [28] J.R. Dyer. Prentic-Hall, Upper Saddle River, 1978.
- [29] P. Anitha, R. Manikandan, A. Endo, T. Hashimoto, P. Viswanathamurthi, Spectrochim. Acta Part A Mol. Biomol. Spectro. 99 (2012) 174–182.
- [30] A.K. Das, B. Sarkar, C. Duboc, S. Strobel, J. Fiedler, S. Zalis, G.K. Lahiri, W. Kaim, Angew. Chem. Int. Ed. 48 (2009) 4242–4245.
- [31 E. Sondaz, A. Gourdon, J.P. Launay, J. Bonvoisin, Inorg. Chim. Acta 316 (2001) 79-88
- [32] D.K. Mukherjee, C.R. Saha, J. Catal. 210 (2002) 255-262.