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PAPER

Polyethylene glycol clicked Co(II) Schiff base and its catalytic activity for the oxidative dehydrogenation of secondary amines†

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Copper catalyzed [3+2] cycloaddition "click method" provided an efficient and high yielding immobilization of cobalt(II) Schiff base to the azido-functionalized MeOPEG_{5000}; whereas the direct reaction between MeOPEG_{5000} and Co(II) Schiff base did not produce any immobilization. The prepared catalyst was tested for the oxidative dehydrogenation of various secondary amines using TBHP as oxidant and could be easily recovered by precipitation with diethyl ether at the end of the reaction.

1.0 Introduction

Immobilization of homogeneous metal complexes onto polymeric supports is an area of growing commercial and academic interest as they can combine the advantages of both heterogeneous and homogeneous catalysts. In addition, they are easy to separate from the reaction mixtures, recyclable and are easier to tailor/or fine tune than heterogeneous catalysts.[1] Cobalt(II) Schiff base complexes, due to their high oxidation potential, have gained significant interest in developing highly effective methods in synthetic and industrial chemistry.[2] In recent years, the high costs and tedious synthetic routes has led to an increased interest in immobilizing these catalysts onto a support. These immobilized/supported catalysts can provide the facile recovery and recycling of the catalyst, therefore make the processes cleaner and economically viable. In this regard, a number of solid supports such as organic polymers,[3] silica,[4] clay[5] and mesoporous hybrid materials[6] have been used to immobilize these homogeneous catalysts. Polyethylene glycols,[7] which are well known to be inexpensive and biodegradable, are promising polymeric supports possessing a unique property of being soluble in most organic solvents and being insoluble in some of them, such as in diethyl ether. Thus during the reaction, the PEG-immobilized catalyst behaves like a homogeneous catalyst and at the end of the reaction it can readily be recovered by precipitation with diethyl ether. Despite the potential advantages of PEG, to the best of our knowledge there is no literature report using PEG as a support for the immobilization of cobalt(II) Schiff base complexes.

Oxidative dehydrogenation of secondary amines is an important synthetic transformation[8] and extensively used in the multistep synthesis of bioactive molecules. Stoichiometric reagents such as hypervalent iodine,[9] phenylselecinic anhydride,[10] and *N-tert*-butylphenylsulfinimidoyl chloride[11] are often used, even though they are expensive, generate huge amounts of waste and have lower efficiency, which makes their utility limited from an environmental viewpoint. Thus, catalytic methodologies using transition metal based catalysts with *t*-butyl hydroperoxides are of significant interest, and in this context a variety of metals such as ruthenium,[12] cobalt,[13] rhodium[14] and mixed metal oxides[15] have hitherto been used for this transformation. Maruyama *et al.*[13] have reported the use of a cobalt Schiff base complex for the oxidative dehydrogenation of secondary amines, but the homogeneous nature of the catalyst limited the scope of this method for practical applications. To overcome these limitations we thought it would be worthwhile to develop an efficient yet recyclable heterogenized cobalt(II) Schiff base by using PEG as a promising support. For this purpose, the required cobalt(II) Schiff base **2** was prepared by the reaction of salicylidine-*N*-(methyl 3-(4′-propargyloxy phenyl) propionate and CoCl_2 (Scheme 1) according to the literature procedure.[16] At first we tried to prepare PEG-immobilized Co(II) Schiff base by the direct reaction of MeOPEG_{5000} with Co(II) Schiff base complex **2**. It was surprising to note that no reaction occurred and we could recover MeOPEG_{5000} as such at the end.

Copper catalyzed[17] [3+2] azide-alkyne cycloaddition (CuAAC)[18] is termed a "click reaction" because of its potential advantages such as simplicity, high efficiency, yield and better catalyst loading and has recently been recognized as one of the powerful tools for the ligating molecule fragments in developing immobilized catalysts/reagents.[19,20] Therefore, we thought it would be worthwhile to use the click method for the covalent immobilization of cobalt(II) Schiff to azidofunctionalized MeOPEG_{5000} support **1**, the synthetic strategy for the preparation of PEG-immobilized cobalt(II) Schiff base **4** is shown in Scheme 1.

2.0 Results and discussion

2.1 Synthesis of catalyst

The required azido functionalized $\mathrm{MeO\text{-}PEG}_{5000}\text{-}\mathrm{N}_3$ **1** was prepared by the reaction of MeOPEG_{5000} with sodium azide in

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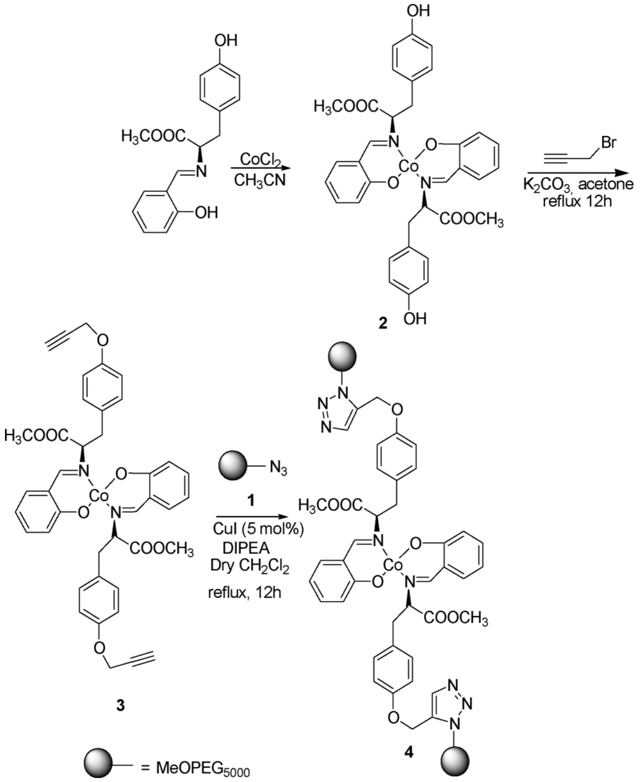
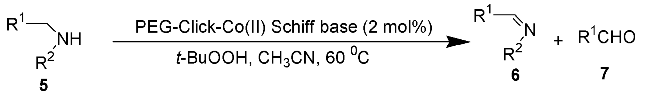


Scheme 1 Synthetic pathway for the PEG-immobilized catalyst **4**.

ethanol under reflux for 12 h. Cobalt(II) Schiff base **2** was treated with propargyl bromide to give propargylated Co(II) Schiff base complex **3**, which on subsequent reaction with **1** in the presence of a catalytic amount of CuI (5 mol%) resulted in the formation of PEG-immobilized Co(II) Schiff base **4**. The $MeOPEG_{5000}$ immobilized complex **4** was separated from the reaction mixture by precipitation with diethyl ether, washed with 2-propanol, diethyl ether and dried under vacuum to give dark brown colored solid in virtually quantitative yield (94%). To confirm the removal of all copper contents from the prepared PEGylated Co(II) Schiff base, we analyzed the catalyst by ICP-AES analysis. We did not find any copper content in this analysis, confirming the absence of copper in the prepared material. The covalent attachment of the complex **3** to the PEG support was confirmed by the disappearance of the typical $-N_3$ band of azido-functionalized $MeOPEG_{5000}$ and appearance of the new bands at υ 1720 and 1605 cm^{-1} corresponding to the C=O of the ester and C=N of the Schiff base respectively. Furthermore, the value of nitrogen content as determined by elemental analysis (0.8%) revealed the loading of the Schiff base to the support to be 0.07 mmol g^{-1}, which is equivalent to 5.6% coverage of the PEG support. The cobalt content per gram of the support was determined by the complexometric titration with EDTA, which was found to be 0.06 mmol g^{-1}.

2.1 Catalytic activity

The catalytic activity of the prepared Co(II) Schiff bases **4** and its comparison with the corresponding homogeneous Schiff base **2** was carried out for the oxidation of secondary amines using *tert*-butylhydroperoxide (TBHP) as oxidant (Scheme 2).



Scheme 2 Oxidative dehydrogenation of secondary amines.

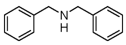
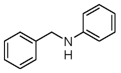
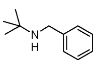
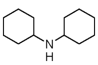
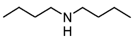
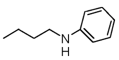
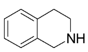
At first, the oxidation of dibenzylamine was studied in various solvents such as methanol, ethanol, acetonitrile and dichloroethane at 60 °C using TBHP as oxidant and PEG-immobilized cobalt Schiff base **4** as catalyst (2 mol%). Interestingly, selective formation of benzaldehyde was obtained in ethanol and methanol; whereas, in acetonitrile *N*-benzylidinebenzylamine was obtained as a major product, these results are presented in Table 1. The reaction was found to be very slow in dichloroethane and gave poor yield of *N*-benzylidinebenzylamine along with trace amounts of benzaldehyde. Next, the reaction was generalized for a variety of secondary amines and the results of these experiments are summarized in Table 1. Although all the substrates (except entries 4 and 7) could be converted completely and afforded corresponding imines **6** along with its hydrolysis product **7** as shown in Scheme 2. The conversion of the substrates and the selectivity (ratio) of the products was determined by GCMS. We also compared the catalytic efficiency of the heterogeneous catalyst **4** with its analogous homogeneous catalyst **2** under identical conditions. These results are presented in Table 1. The catalytic efficiency of both the catalysts was found to be comparable, establishing the advantages of the PEG-immobilized catalysts, as they provide similar catalytic reactivity to the homogeneous ones, with the added benefits of facile recovery and recycling of the catalyst.

Next, to check the recycling and reusability of the catalyst, the recovery of MeOPEG-bound catalyst **4** from the reaction mixture was achieved by precipitation with diethyl ether. The recovered catalyst was reused for 5 runs, and only a very slight decrease in activity of the catalyst was observed in terms of conversion, selectivity and reaction time after each recycling and reuse. The results of these recycling experiments are presented in Table 2. Furthermore, no leaching of the metal/ligand could be observed during the reaction as the metal content (analyzed by ICP-AES) of the recovered catalyst was found to be similar as to the fresh catalyst **4**.

3.0 Conclusion

In summary, we have demonstrated the first successful synthesis of PEG-immobilized Co(II) Schiff base by using click reaction as a simple, efficient and high yielding approach under mild reaction conditions. Interestingly, no immobilization could occur by the direct reaction between $MEOPEG_{5000}$ and Co(II) Schiff base, establishing the superiority of the click method in developing the immobilized catalysts/reagents. The prepared catalyst was tested for the oxidative dehydrogenation of secondary amines with TBHP and could be easily recovered by precipitation with diethyl ether at the end of the reaction. Furthermore, the high product yields, facile recovery/recycling of the catalyst, high catalytic efficiency make the developed methodology superior than existing ones.

Table 1 Oxidation of secondary amines[a]

Entry	Amine **5**	Solvent	Cat. (2 mol%)	Time (h)	Conv. (%)[b]	6 : 7 (%)[b]
1		EtOH	**4**	12.0	100	0 : 100/97[c]
		MeOH	**4**	12.0	100	4 : 96/92[c]
		CH_3CN	**4**	3.0	96	75 : 25
		$ClCH_2CH_2Cl$	**4**	12	30	10 : 2
		CH_3CN	**2**	3.0	98	73 : 27
		CH_3CN	—	12	—	—
2		CH_3CN	**4**	1.5	100	94 : 6/92[c]
			2	1.0	100	96 : 4/93[c]
3		CH_3CN	**4**	1.0	100	65 : 35
			2	1.0	100	82 : 18
4		CH_3CN	**4**	2.5	80	6 : 94
			2	2.5	87	10 : 90
5		MeOH	**4**	2.75	100	0 : 100/96[c]
			2	2.5	100	1 : 98
6		CH_3CN	**4**	3.0	100	92 : 8
			2	2.5	100	95 : 5
7		CH_3CN	**4**	4.5	90	92[c]:0
			2	4.5	94	98 : 2

[a] Reaction conditions: amine (1 mmol), TBHP (6.5 M in decane, 2.5 mmol), catalyst (2 mol %), acetonitrile (2 mL) at 60 °C. [b] Conversion and selectivity determined by GCMS. [c] Isolated yields.

Table 2 Results of recycling experiments[a]

Run	1	2	3	4	5
Time (h)	3.0	3.0	3.5	3.5	3.5
Conv.[b]	96	96	94	92	92
6 : **7**[b]	75 : 25	78 : 22	76 : 24	74 : 26	78 : 22

[a] Conditions: dibenzylamine (1 mmol), TBHP (6.5 M in decane, 2.5 mmol), catalyst (0.02 m mol), acetonitrile (2 ml) at 60 °C. [b] Conversion and ratio of 6 : 7 was determined by GCMS.

4.0 Experimental

4.1 Materials

All the substrates were purchased from Aldrich and used as received. L-(−) Tyrosine, salicylaldehyde and propargylated bromide (80 wt% solution in toluene) were commercially available and used as obtained. The Co(II) Schiff base **2** and bispropargylated Co(II) Schiff base **3** were prepared according to the published method.[3c] $CoCl_2$ was heated at 110 °C for 3–4 h under vacuum prior to use.

4.2 Techniques used

The melting points were determined in open capillaries on a Buchi apparatus and are uncorrected. The ^1H NMR spectra were recorded on Bruker 300 MHz spectrometer and the chemical shifts are expressed in δ parts per million relative to tetramethylsilane (TMS) as internal standard. The IR spectra were recorded on a Perkin Elmer FTIR X 1760 instrument. Elemental analysis was done by using ASTM D-3828 (Kjeldhal method). Analysis for metal contents were carried out by using inductively coupled plasma atomic emission spectrometer (ICP-AES, PS-3000UV) by Leeman Labs. GCMS analysis were done on HP 5972 MSD coupled with HP 5890 GC by using CP-Sil 5 column.

4.3 MeOPEG$_{5000}$-Immobilized Co(II) Schiff base 4

A mixture containing azido functionalized MeO-PEG$_{5000}$-N_3 (20 g, 4 mmol), and propargylated Co(II) Schiff base **3** (1.10 g, 2.0 mmol) in dry dichloromethane (30 mL) was added CuI (5 mol%) and DIPEA (10 mmol), the resulting mixture was refluxed for 24 h. After being cooled at room temperature, the polymer was separated from the reaction mixture by precipitation with diethyl ether, washed with 2-propanol, diethyl ether and dried under vacuum to yield dark brown colored PEG-supported catalyst 4 in 94% yield (19.41 g). IR (cm^{-1}): 3260, 2879, 1720, 1605, 1466, 1154. Analytical calc. for nitrogen (found; 0.8%). The loading of the cobalt to the PEG support was determined by the complexometric titration using EDTA. The loading of the cobalt was found to be 0.06 mmol g^{-1}.

4.4 General experimental procedure for oxidative dehydrogenation of secondary amines using TBHP as oxidant

Into a stirred mixture of secondary amine (1 mmol), *t*-BuOOH (6.5 M in decane, 2.5 mmol) in acetonitrile (2 mL) was added polymer bound catalyst (2 mol%). The resulting mixture was heated at 60 °C for the time reported in Table 1. Completion of the reaction was analysed by TLC. After completion of the reaction, the catalyst was recovered from the reaction mixture by precipitation with diethyl ether and reused as such for subsequent experiments. The filtrate so obtained was concentrated under reduced pressure and dissolved in dichloromethane (10 mL). The organic layer was washed with water (2 × 15 mL), dried over anhydrous $MgSO_4$. The solvent was removed under vacuum to give corresponding products. The conversion and selectivities for the formation of imine and its hydrolyzed products were determined by GCMS. The identity of the products was confirmed by comparing their physical and spectral data with those of literature compounds.[21]

4.5 Product charaterization data

N-(Benzylidine)benzylamine (Table 1, entry 1): mp (51–52 °C);[21a] IR (KBr): 3041, 1634, 1610, 1580, 1180, 976 cm^{-1}; ^1H NMR ($CDCl_3$, δ ppm): 8.10 (s, 1H, CH═N), 7.92–7.15 (m, 10 H, ArH), 4.82 (s, 2H).; ^{13}C NMR ($CDCl_3$): $\delta = 165.1$, 156.1, 142.1, 140.0, 57.7, 15.5 ppm.

Benzaldehyde (Table 1, entry 1): IR (KBr) 3086, 2860, 1703, 1697, 1204, 1168 cm^{-1}. ^1H NMR ($CDCl_3$, δ ppm): 10.02 (s, 1H, CH), 7.87 (m, 2H, ArH), 7.64 (m, 2H, ArH), 7.52 (m, 2H, ArH). ^{13}C NMR: ($CDCl_3$): $\delta = 192.8$, 135.2, 134.8, 129.0, 127.7, 47.0 ppm.

N-Phenyl-*N*-(1-phenylmethylidine)amine (Table 1, entry 2): mp (55–56 °C); IR (KBr): 3044, 1629, 1598, 1580, 1180, 970 cm^{-1}; ^1H NMR ($CDCl_3$, δ ppm): 8.42 (s, 1H, CH═N), 7.80 (m, 2H, ArH), 7.49–7.34 (m, 5H, ArH), 7.26–7.19 (m, 3H, ArH).

N-(Benzylidine)-*t*-butylamine (Table 1, entry 3): colorless oil, IR (cm^{-1}): 3028, 2980, 1632, 1618, 1550, 972.; ^1H NMR ($CDCl_3$, δ ppm) 8.19 (s, 1H, CH═N), 7.61 (m, 2H, ArH), 7.15 (m, 2H, ArH), 2.38 (s, 3H, $ArCH_3$), 1.26 (s, 9H, $C(CH_3)_3$). ^{13}C NMR ($CDCl_3$): $\delta = 160.1$, 157.5, 136.1, 62.7, 23.5

Cyclohexanone (Table 1, entry 4): IR (KBr) 2941, 2864, 1717, 1460, 1018 cm^{-1}. ^1H NMR ($CDCl_3$, δ ppm): 2.35 (m, 4H), 1.56–2.06 (m, 6H). ^{13}C NMR ($CDCl_3$): $\delta = 210.6$, 44.03, 27.4, 25.0 ppm.

N-Butylidinebutylamine (Table 1, entry 5): ^1H NMR ($CDCl_3$, δ ppm): colorless oil, IR (cm^{-1}): 2948, 2910, 2875, 1630, 1576, 972 cm^{-1}. ^1H NMR ($CDCl_3$, δ ppm): 7.58 (t, 1H, CH═N), 3.3.2 (t, 2H), 2.18 (m, 2H), 1.53–1.28 (m, 4 H), 0.88 (m, 3H). ^{13}C NMR ($CDCl_3$): $\delta = 164.30$, 62.0, 38.2, 32.7, 22.0, 19.6, 13.6 ppm.

N-Butylidinebenzylamine (Table 1, entry 6): IR (KBr): 3041, 2920, 1662, 1628, 1570, 899 cm^{-1}; ^1H NMR ($CDCl_3$, δ ppm): 7.78 (t, 1H, CH═N), 7.34–7.30 (m, 5H), 4.57 (s, 2H), 2.32 (m, 2H), 1.62 (m, 2H), 0.98 (m, 3H). ^{13}C NMR ($CDCl_3$): $\delta = 166.30$, 128.4, 65.05, 37.9, 19.3, 13.7 ppm.

3,4-Dihydroisoquinoline (Table 1, entry 7): IR (KBr): 3020, 2935, 1627, 1575, 1454, 1210, 1005, 879 cm^{-1}. ^1H NMR ($CDCl_3$, δ ppm): 8.32 (s, 1H), 7.42–7.45 (m, 1H), 7.29–7.22 (m, 2H), 7.15 (d, $J = 7.5$ Hz, 1H), 3.89–3.82 (m, 2H), 2.69 (t. $J = 7.5$ Hz, 2H). ^{13}C NMR ($CDCl_3$): $\delta = 162.4$, 134.2, 130.8, 128.0, 127.8, 47.40, 25.0 ppm.

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