



A heterogeneous cobalt(II) Salen complex as an efficient and reusable catalyst for acetylation of alcohols and phenols

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ARTICLE INFO

Article history:

Received 3 August 2008

Revised 27 October 2008

Accepted 7 November 2008

Available online 12 November 2008

ABSTRACT

Acetylation of various alcohols and phenols was performed successfully using an immobilized cobalt(II) catalyst in high yield. The catalyst shows high thermal stability and was also recovered and reused at least 10 times without any considerable loss of activity.

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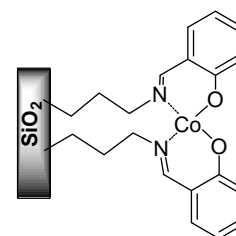
Acylation of alcohols and phenols is a frequently utilized transformation in synthetic chemistry.^{1,2} The acetylation of alcohols and phenols is typically performed using acetic anhydride in the presence of either base^{3–6} or acid catalysts.^{7–25} Although various acetylation methods are available, most have one or more drawbacks including long reaction times, harsh conditions, harmful organic solvents, and tedious work-up procedures. One of the most promising solutions to these problems seems to be immobilization of catalysts or using eco-friendly solvent-free conditions. When an immobilized catalyst is used, the insoluble catalyst can be separated easily by filtration and the catalyst can be recovered and recycled. Furthermore, the reported examples have demonstrated that heterogeneous catalysts give generally higher selectivity and typically require easier work-up procedures. Also, solvent-free synthetic methods are valuable for environmental and economical reasons.^{26–28}

In recent years, various supported catalysts have been reported for operational simplicity as well as environmental compatibility.^{29–42}

However, some require high reaction temperatures, are poorly recyclable, and require toxic organic solvents as reaction media. Therefore, the development of heterogeneous catalysts to overcome such drawbacks which can be used under solvent-free conditions is gaining prominence.

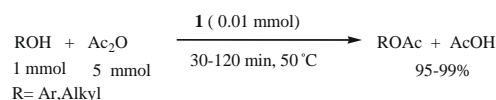
In continuation of our interest in heterogeneous catalysts as well as solvent-free organic reactions,^{43–46} a simple, new, and efficient protocol for the acetylation of alcohols and phenols using a catalytic amount of recyclable cobalt(II) catalyst **1** (Fig. 1) and acetic anhydride under solvent-free conditions is described (Scheme 1).

Initially, the reaction of benzyl alcohol, immobilized cobalt(II) catalyst **1**, and acetic anhydride was chosen as a model, and several sets of reaction conditions were examined (Table 1). The optimized conditions are benzyl alcohol (1 mmol), heterogeneous cobalt(II) catalyst **1** (0.01 mmol), and acetic anhydride (5 mmol). In the



Catalyst **1**

Figure 1.



Scheme 1.

absence of the catalyst **1** using the same reaction conditions, benzyl acetate was obtained in low yield (30%) even after a prolonged reaction time of 5 h.

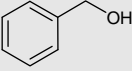
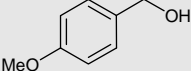
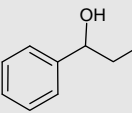
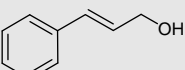
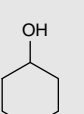
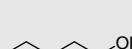
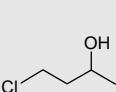
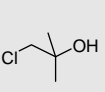
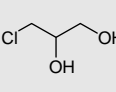
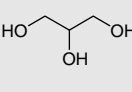
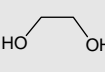

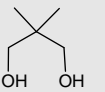
To test the catalytic activity of the supported cobalt(II) catalyst **1**, the reaction was conducted with benzyl alcohol in the presence of catalyst **1** for 20 min which gave a conversion of 65%. The solid was then hot-filtered off. The catalyst-free solution was then left for 10 h, but no further reaction took place. Moreover, analysis of the solution by atomic absorption indicated that no cobalt species had leached into the reaction.

To evaluate the effect of the catalyst concentration, acetylation of benzyl alcohol with acetic anhydride in a ratio of 1:5 was carried out in the presence of different amounts of catalyst **1** (0.5, 1,

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Table 1
Acetylation of alcohols using supported catalyst **1**

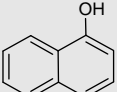
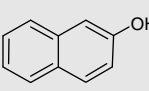
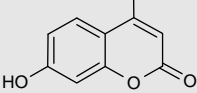
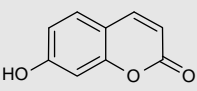
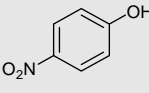
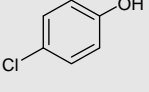
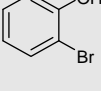
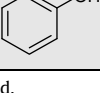
Entry	Substrate	Time (min)	Yield ^a (%)
1		45	99
2		50	99
3		45	99
		45	99
4		45	99
5		50	99
6		55	98
7		60	98
8		60	95 ^b
9		55	99 ^b
10		50	99 ^b
11		50	99 ^b
12		45	99 ^b
13	HC≡CCH ₂ OH	45	99

^a Isolated yield.^b Ratio of Ac₂O/substrate is 10:1.

2 mol %) at 50 °C for 1 h under solvent-free conditions, and the isolated yields of the products were found to be 65%, 99%, and 99%, respectively. Thus, 1 mol % of the supported cobalt(II) catalyst was the optimum amount of catalyst for this reaction. Use of a higher amount of the catalyst (2 mol %) neither improved the yield nor reaction time further.

To investigate the effect of reaction temperature, the acetylation of benzyl alcohol with acetic anhydride was carried out in the presence of 1 mol % of **1** at different temperatures. The reaction rate was found to be very slow at low temperature but increased at higher temperature. At 50 °C, the reaction rate was found to be

Table 2
Acetylation of phenols using supported catalyst **1**

Entry	Substrate	Time (min)	Yield ^a (%)
1		45	99
2		50	99
3		45	99
4		45	99
5		45	99
6		50	99
7		55	98
8		60	98

^a Isolated yield.

maximum and further increase in the temperature did not result in any yield enhancement.

To show the generality and scope of this procedure, the reaction was examined with various alcohols such as primary, secondary, and tertiary alcohols, an allyl alcohol, and diols and triols. The results are summarized in Table 1.

Primary and secondary alcohols were acetylated easily with acetic anhydride in the presence of the supported cobalt(II) catalyst **1** at 50 °C, whereas tertiary alcohols required longer reaction times for completion of the reaction (Table 1, entry 7). Diols and triols were converted to bis- and tris-acetylated products, respectively (Table 1, entries 8–12). Moreover, the efficiency of catalyst **1** was investigated on electron-rich and electron-deficient phenols, all the phenols afforded excellent yields of the corresponding acetates in 45–60 min (Table 2).

Next, the reusability of the catalyst **1** was investigated. After the first use of catalyst **1** in the acetylation of benzyl alcohol (Table 1, entry 1), the recovered catalyst was successfully used in 10 subsequent runs without any significant loss in catalytic activity under similar experimental conditions (Table 3). No pretreatment step was used, although the recovered catalyst was washed with ca. 5 ml of Ac₂O to remove traces of the previous reaction mixture and dried before the next cycle.

In conclusion, an efficient acetylating method for alcohols as well as phenols has been developed using a recyclable supported cobalt(II) catalyst under solvent-free conditions. The simplicity of the procedure and easy work-up are advantages of the present protocol.

Table 3
Reusability of catalyst **1** in the acetylation of benzyl alcohol with Ac₂O

Run no.	1	2	3	4	5	6	7	8	9	10
Yield (%)	99	99	99	99	98	98	95	95	90	86
Time (min)	45	45	45	45	60	60	60	60	90	120

Preparation of cobalt(II) catalyst 1: The preparation of the catalyst is straightforward and is analogous to the procedure described in Ref. 46 with slight modification. Salicylaldehyde (2 mmol, 0.244 g) was added to excess absolute MeOH, to which 3-amino-propyl (trimethoxy)silane (2 mmol, 0.352 g) was then added. The solution instantly became yellow due to imine formation. After 3 h, cobalt(II) acetate, Co(OAc)₂·2H₂O (1 mmol, 0.248 g), was added to the solution, and the mixture was stirred for a further 3 h to allow the new ligands to complex the cobalt and a color change from pink to olive green was observed. Mesoporous silica (average pore diameter 60 Å, 3 g) was activated by refluxing in concentrated hydrochloric acid (6 M) and then washed thoroughly with deionized water and dried before undergoing chemical surface modification. Hydrated mesoporous silica was then added, and the mixture was stirred overnight. The solvent was removed using a rotary evaporator, and the resulting olive green solid dried at 80 °C overnight. The final product was washed with MeOH and water until the washings were colorless. Further drying of the solid product was carried out in an oven at 80 °C for 8 h (Scheme 1). The loading achieved was about 0.3 mmol g⁻¹, as determined from the 11.5% loss in mass between 200 and 600 °C, as well as atomic absorption analysis of the HNO₃-digested material. Surface analysis showed the surface area as 197 m²/g (Kieselgel 60 has a surface area of 458 m²/g) and the catalyst has a single point total pore volume of 0.461 cm³/g, compared to 0.69 cm³/g for the support. This indicates that supporting the complex brings about a substantial reduction in surface area, possibly due to pore blockage from the bulky silane limiting access to some very narrow-entrance pores in the material. The infrared spectrum of the catalyst showed the expected bands, including a distinctive band at 1561 cm⁻¹ due to C=N stretching, which is lowered in frequency on complexation to cobalt(II).

General procedure for the acetylation of alcohols and phenols: To a solution of substrate (1 mmol) and acetic anhydride (5 mmol) was added supported cobalt(II) catalyst **1** (0.01 mmol, 0.33 g) and the mixture was stirred at 50 °C. After completion of the reaction (TLC), the reaction mixture was filtered and the catalyst rinsed with acetic anhydride and dichloromethane and thus recovered. The organic layer was washed with saturated NaHCO₃ and water, and dried over anhydrous Na₂SO₄. Evaporation of the solvent under reduced pressure gave the almost pure acetates.

Acknowledgment

The author thanks the Payame Noor University for partial financial support of this work.

Supplementary data

Supplementary data (copies of thermogravimetric analysis, surface analysis (nitrogen adsorption/desorption experiments), and diffuse reflectance fourier transform infrared spectroscopy of catalyst **1** before and after recovery) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2008.11.024.

References and notes

- Green, T. W.; Wuts, P. C. M. *Protective Groups in Organic Synthesis*, 3rd ed.; Wiley: New York, 1999.
- Kocienski, P. J. *Protecting Groups*; Thieme: Stuttgart, 1994.
- Steglich, W.; Hofle, G. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 981.
- Vedejs, E.; Diver, T. S. *J. Am. Chem. Soc.* **1993**, *115*, 3358.
- Scriven, E. F. V. *Chem. Soc. Rev.* **1983**, *12*, 129.
- Tomohumi, S.; Kousaburo, O.; Takashi, O. *Synthesis* **1991**, 1141.
- Orita, A.; Tanahashi, C.; Kakuda, A.; Otera, J. *Angew. Chem., Int. Ed.* **2000**, *39*, 2877.
- Alleti, R.; Perambuduru, M.; Samanha, S.; Reddy, V. P. *J. Mol. Catal. A: Chem.* **2005**, *226*, 57.
- Karimi, B.; Maleki, J. *J. Org. Chem.* **2003**, *68*, 4951.
- Ahmed, N.; Van Lier, J. E. *Tetrahedron Lett.* **2006**, *47*, 5345.
- Tale, R. H.; Adude, R. N. *Tetrahedron Lett.* **2006**, *47*, 7263.
- Reddy, T. S.; Narasimulu, M.; Suryakiran, N.; Mahesh, K. C.; Ashalatha, K.; Venkateswarlu, Y. *Tetrahedron Lett.* **2006**, *47*, 6825.
- Phukan, P. *Tetrahedron Lett.* **2004**, *45*, 4785.
- Saravanan, P.; Singh, V. K. *Tetrahedron Lett.* **1999**, *40*, 2611.
- Dalpozzo, R.; De Nino, A.; Maiuolo, L.; Procopio, A.; Nardi, M.; Bartoli, G.; Romeo, R. *Tetrahedron Lett.* **2003**, *44*, 5621.
- Alleti, R.; Perambuduru, S.; Samanha, S.; Reddy, V. P. *J. Mol. Catal. A: Chem.* **2005**, *226*, 57.
- Kamal, A.; Khan, M. N. A.; Reddy, K. S.; Srikanth, Y. V. V.; Krishnaji, T. *Tetrahedron Lett.* **2007**, *48*, 3813.
- Velusamy, S.; Borpuzari, S.; Punniyamurthy, T. *Tetrahedron Lett.* **2005**, *61*, 2011.
- Kanta De, S. *Tetrahedron Lett.* **2004**, *45*, 2919.
- Mukaiyama, T.; Shiina, I.; Miyashita, M. *Chem. Lett.* **1992**, 625.
- Iqbal, J.; Srivastava, R. R. *J. Org. Chem.* **1992**, *57*, 2001.
- Ishihara, K.; Kubota, M.; Kurihara, H.; Yamamoto, H. *J. Org. Chem.* **1996**, *61*, 4560.
- Bartoli, G.; Bosco, M.; Dalpozzo, R.; Marcantoni, E.; Massaccesi, M.; Sambri, L. *Eur. J. Org. Chem.* **2003**, 4611.
- Garsa, G. A.; Singh, R.; Nolan, S. P. *Synthesis* **2004**, 971.
- Izumi, J.; Shiina, I.; Mukaiyama, T. *Chem. Lett.* **1995**, 141.
- Tanaka, K.; Toda, F. *Chem. Rev.* **2000**, *100*, 1025.
- Walsh, P. J.; Li, H.; de Parrodi, C. A. *Chem. Rev.* **2007**, *107*, 2503.
- Garay, A. L.; Pichon, A.; James, S. L. *Chem. Soc. Rev.* **2007**, *6*, 846.
- Zhihong, P.; Akihiro, O.; Delie, A.; Junzo, O. *Tetrahedron Lett.* **2005**, *46*, 3187.
- Baleizao, C.; Gigante, B.; Das, D.; Alvaro, M.; Garcia, H.; Garcia, A. *Chem. Commun.* **2003**, 1860.
- Yin, L. X.; Liebscher, J. *Chem. Rev.* **2007**, *107*, 133.
- Babu, N. S.; Pasha, N.; Rao, K. T. V.; Prasad, P. S. S.; Lingaiah, N. *Tetrahedron Lett.* **2008**, *49*, 2730.
- Jain, S. L.; Prasad, V. V. D. N.; Sain, B. *Catal. Commun.* **2008**, *9*, 499.
- Iranpoor, N.; Firouzabadi, H.; Jamalian, A. *Tetrahedron Lett.* **2005**, *46*, 7963.
- Joseph, J. K.; Jain, S. L.; Sain, B. *J. Mol. Catal. A: Chem.* **2007**, *267*, 108.
- Das, B.; Thirupathi, P. *J. Mol. Catal. A: Chem.* **2007**, *269*, 12.
- Cusati, C.; Djakovitch, L. *Tetrahedron Lett.* **2008**, *49*, 2499.
- Wu, H.; Shen, Y.; Fan, L.; Wan, Y.; Shi, D. *Tetrahedron Lett.* **2006**, *62*, 7995.
- Yoon, H. J.; Lee, S. M.; Kim, J. H.; Cho, H. J.; Choi, J. W.; Lee, S. H.; Lee, Y. S. *Tetrahedron Lett.* **2008**, *49*, 3165.
- Baleizao, C.; Garcia, H. *Chem. Rev.* **2006**, *106*, 3987.
- De Vos, D. E.; Dams, M.; Sels, B. F.; Jacobs, P. A. *Chem. Rev.* **2002**, *102*, 3615.
- Rajabi, F.; Saidi, M. R. *Synth. Commun.* **2004**, *34*, 4179.
- Rajabi, F.; Saidi, M. R. *Synth. Commun.* **2005**, *35*, 483.
- Rajabi, F.; Clark, J. H.; Karimi, B.; Macquarrie, D. *J. Org. Biomol. Chem.* **2005**, *5*, 725.
- Rajabi, F.; Karimi, B. *J. Mol. Catal. A: Chem.* **2005**, *232*, 95.
- Chisem, I. C.; Rafelt, J.; Shieh, M. T.; Chisem, J.; Clark, J. H.; Jachuck, R.; Macquarrie, D. J.; Ramshaw, C.; Scott, K. *Chem. Commun.* **1998**, 1949.