MCM-Silylamine Pd(II)Complex: A Heterogeneous Catalyst for Selective Azide Reductions

M. Lakshmi Kantam,* N. Sreenivasa Chowdari, Ateeq Rahman, B.M. Choudary

Indian Institute of Chemical Technology, Hyderabad 500 007, India Fax: +91 40 7173378; E-mail: mlakshmi@iict.ap.nic.in *Received 8 July 1999*

Abstract: Palladium complex immobilized on MCM-41 catalyses the reduction of alkyl, aryl and arylsulfonyl azides to the corresponding amines in excellent yields under mild conditions.

Keywords: reduction, MCM-41, palladium complex, azides, amines

Azides are generally prepared with good regio-, stereoand enantio control and subsequent reduction permits a controlled introduction of amino function.¹ The reduction of azides to amines is an important protocol in organic synthesis of intermediates applicable in fine chemical industry. A wide variety of reagents, lithium aluminum hydride,² sodium borohydride,³ borohydride,⁴ zinc borohydride exchange regin (BER),⁵ lithium amino borohidrides,⁶ sodium borohydride/copper(II) sulfate,⁷ benzyl triethyl ammonium tetrathio molybdate,8 SmI2.9 SnCl2.10 triphenylphosphine,¹¹ iodotrimethylsilane¹² etc. have been reported for reduction of azides. These methods generate an enormous amount of effluents and suffer with tedious workup procedures. Stringent environmental laws and cutting edge competition in fine chemical industry prompted to opt highly desirable selective ecofriendly catalytic hydrogenation of azides to amines in the presence of variety functional groups. A catalytic method for azide reductions using inexpensive and non-polluting reagents is therefore highly desirable particularly if it can be reused.

The recently discovered family of mesoporous materials MCM possesses compatible tunable larger pores to large molecules will find conceivable application in fine chemical industry. Accordingly we designed anchored catalysts using MCM-41 as a support for nitrogroup reduction and hydrodehalogenation reactions.¹³ We report in this letter selective azide reductions by a heterogeneous MCM-sil-ylamine Pd(II) complex for the first time affording excellent yields.

The MCM-silylamine Pd(II) complex was prepared¹³ as described below: The mesoporous material MCM-41 (pure silica) was synthesized ¹⁴ by stirring a solution of tetraethyl ortho silicate (1 mol), ethanol (6 mol), isopropanol (1 mol) with hexadecylamine (0.3 mol) in water (36 ml) at room temperature for 1h. The resultant mixture was aged for 12 h and the solid was filtered, washed with excess of distilled water, dried for 24 h at room temperature. 1g of MCM-41 was calcined at 550 °C overnight and refluxed with 0.686 mmol of 3-aminopropyltriethoxysilane

in dry toluene under inert atmosphere for 48h. MCM-silylpropyl amine (1g) was complexed with Bis(benzylcyanide)palladium(II) chloride (2 mmol) in dry benzene under stirring at room temperature. The bright yellow coloured complex thus obtained was filtered, Soxhlet extracted with benzene for 8 h and dried under vacuum. Pd content of the catalyst was determined by plasma analysis (1.99% Pd). The IR spectra of the ligand and the complex showed the silylpropylamine bands. The complex showed an additional band at 356 cm⁻¹ indicating the presence of terminal Pd-Cl.¹⁵

 $R-N_3 \xrightarrow{MCM-Pd}_{MeOH, r.t.} R-NH_2$

R= aryl, alkyl, arylsulfonyl **Scheme**

As shown in Table 1. a number of aryl, alkyl and arylsulfonyl azides have been reduced to the corresponding amines in excellent yields at room temperature indicating a broader scope of application of our catalytic system unlike other reagents. The rate of hydrogenation of the azides is very faster and impressive even at room temperature when compared with NaBH₄ and heterogenised borohydride exchange resin, which requires reflux conditions, stoichiometric quantity of reagent, longer reaction times (3-18h) and whose application is confined to the reduction of aromatic azides.^{5,16} The secondary alkyl azides are also reduced to the corresponding amines in good yields (entry10&13). A selective azido reduction in presence of other functional groups such as carbonyl, sulfonyl, nitro and benzyl under the conditions employed is a significant achievement. However in case of cinnamyl azide both olefin and azido groups are reduced simultaneously without any preference. Further, as part of the ongoing asymmetric catalysis programme this selective reduction has also been applied for the reduction of 3.4-diazido-1benzylpyrrolidine to the corresponding diamine without debenzylation and racemization. The catalyst is reused for five cycles with consistent activity, for example 3,4,5- trimethoxy phenyl azide (entry 1).

In conclusion we have demonstrated a novel inexpensive and eco-friendly method for selective azide reductions by a heterogeneous MCM-silylamine Pd(II) complex for the first time affording excellent yields. The advantages of

 Table 1 Reduction of azides to amines catalyzed by MCM-silylamine Pd (II) complex

Entry	Substrate	Time(h)	product ^a	Yield(%) ^b
1	McO N ₃ McO	1	MeO NH ₂ MeO NH	99(98) ^c
2	MeO N ₃	1	MeO NH2	98
3	MeO N3	1.5	MeO NH ₂	97
4	Me N3	1		94
5	OC N ₃ COOH	3	OT NH ₂ COOH	98
6	O2N ON3	2	O2N NH2	84
7	Me SO ₂ N ₃	2	Me SO ₂ NH ₂	95
8	~~~~N ₃	1.5	~~~~ NH ₂	97
9	~~~N ₃	2	₩ NH ₂	90
10	\bigcirc^{N_3}	2	\bigcirc ^{NH₂}	92
11		0.5		86
12	Ph N ₃	1	Ph NH ₂	95
13	$Ph \sum_{n=1}^{n} N_{n_3}^{n}$ $[\alpha]_{p}-85(c=1, McOH)$	2	$Ph \stackrel{\text{NH}_2}{\longrightarrow} NH_2$ $[\alpha]_D - 14 \text{ (c=1, MeOH)}$	98

^aAll products were characterised by ¹H NMR and IR Spectra. ^bIsolated yield

^cYield for fifth cycle.

our methodology are (1) operational simplicity, (2) environmental acceptability (3) mild reaction conditions, and (4) reusability of the catalyst The present heterogeneous catalytic system may be a potential candidate to practical organic synthesis.

Acknowledgement

The authors are grateful to the Council of Scientific and Industrial Research, India and Commission of the European Communities (Contract No.: CII-CT94-0050 (DG 12 HSMU)) for financial support.

References and Notes

- IICT Communication No.: 4279
- (1) Scriven, E.F.V.; Turnbull, K. Chem. Rev. 1988, 88, 297.
- (2) Bose, A. K.; Kistner, J. F.; Farber, L. J. Org. Chem. 1962, 27, 2925.
- (3) Casini, G.; Goodman, L. J. Am. Chem. Soc. 1964, 86, 1427.
- (4) Ranu, B. C.; Sarkar, A.; Chakraborty, R. J. Org. Chem. 1994, 59, 4114.
- (5) Kabalka, G.W.; Wadgaonkar, P. P.; Chatla, N. Synth. Commun. **1990**, 20, 293. Yoon, N. M.; Choi, J.; Shon, Y. S. Synth. Commun. **1993**, 23, 3047.
- (6) Alvarez, S. G.; Fisher, G. B.; Singaram, B. *Tetrahedron Lett.* 1995, 36, 2567.
- (7) Rao, H. S. P.; Siva, P. Synth. Commun. 1994, 24, 549.
- (8) Ramesha, A. R.; Bhat, S.; Chandrasekaran, S. J. Org. Chem. 1995, 60, 7682.
- (9) Huang, Y.; Zhang, Y.; Wang, Y. Tetrahedron Lett. 1997, 38, 1065.
- (10) Maiti, S. N.; Singh, M. P.; Micetich, R. G. *Tetrahedron Lett.* 1986, 27, 1423.
- (11) Vaultier, M.; Knouzi, N.; Carrie, R. *Tetrahedron Lett.* **1983**, 24, 763.
- (12) Kamal, A.; Rao, N. V.; Laxman, E. *Tetrahedron Lett.* 1997, 38, 6945.
- (13) Kantam, M. L.; Bandyopadhyay, T.; Rahman, A.; Reddy, N. M.; Choudary, B. M. *J. Mol. Catal.* **1998**, 133, 293. Kantam, M. L.; Rahman, A.; Bandyopadhyay, T.; Harita, Y. *Synth. Commun.* **1999**, 29, 691.
- (14) Tuel, A.; Gontier, S. Chem. Mater. 1996, 8, 114; CA: 124, 44015s, 1996.
- (15) Pinnavaia, T. J.; *Science* **1983**, 220, 365. Terasawa, M.; Kaneda, K.; Imanaka, T.; Teranishi, S. *J. Catal.* **1978**, 51, 406.
- (16) Nicello, M.; Mauriello, G.; Scafato, P. J. Org. Chem. **1995**, 60, 2254.
- (17) Typical procedure for azide reductions: The catalyst (25 mg, 0.0046 mmol of Pd) was suspended in dry methanol (2ml) and treated with molecular hydrogen for 20 min and then a solution of 3,4,5- trimethoxy phenyl azide (209 mg, 1 mmol) in methanol (2 mL) was added to it dropwise via syringe. A hydrogen balloon was fitted to the flask and the resultant solution was stirred at room temperature. On completion of the reaction (monitored by TLC), the reaction mixture was filtered (to remove the catalyst), washed with methanol and evaporated under reduced pressure to give trimethoxy aniline as a white solid (181 mg, 99% yield).

Article Identifier: 1437-2096,E;1999,0,09,1413,1414,ftx,en;L07499ST.pdf