

## REDUCTIVE CARBONYLATION OF NITROBENZENE TO PHENYLURETHANE CATALYZED BY Ru(III)-SCHIFF BASE COMPLEXES

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(Received December 1, 1988; accepted April 21, 1989)

### Summary

Ruthenium complexes containing Schiff bases with  $N_2O_2$ ,  $N_4$  and  $N_5$  donor groups with the general formula  $[Ru^{III}(X)Cl_{1 \text{ or } 2}]$ , where X = Schiff base such as bis(salicylaldehyde)-*o*-phenylenediimine (saloph), bis(salicylaldehyde)ethylenediimine (salen), bis(picolaldehyde)ethylenediimine (pic-en), bis(picolaldehyde)-*o*-phenylenediimine (pic-opd), bis(picolaldehyde)-diethylenetriimine (pic-dien), were tested for their catalytic activity towards the reductive carbonylation of nitrobenzene in ethanol to give phenylurethane. The five Ru(III) complexes tested towards reductive carbonylation showed different catalytic activities in the range 160 - 200 °C and CO partial pressure of 15 atm.

Among the complexes tested,  $[Ru(\text{saloph})Cl_2]$  showed the highest catalytic activity with a turnover rate greater than 80 mol product per mol catalyst per hour at 160 °C and 15 atm CO.  $[Ru(\text{pic-en})Cl_2]Cl$  and  $[Ru(\text{pic-opd})Cl_2]Cl$  complexes with  $N_4$  donor systems were found to be less active towards carbonylation of nitrobenzene, as indicated by their turnover rates of 20 and 15 mol product per mol catalyst per hour, respectively, at 200 °C and 15 atm CO. The complex  $[Ru(\text{pic-dien})Cl]Cl_2N_5$  donor system was completely inactive even at 200 °C and 15 atm CO, and no conversion of nitrobenzene was seen even after 12 h contact time.

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### Introduction

The chemistry of aromatic isocyanates has gained considerable attention in the last two decades because of the increase in demand for isocyanate raw materials used in making polyurethane foams, fibers and pesticides [1].

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Most commercial production of isocyanates is carried out by phosgenation of the corresponding amines, which are in turn obtained by the catalytic hydrogenation of nitro compounds [2, 3]. This phosgenation route involves serious corrosion problems due to the byproduct hydrochloric acid. To work out an alternative, phosgene-free route, which will eliminate corrosion problems, investigations were made using transition metal complexes as catalysts in the carbonylation of nitro compounds to their corresponding urethanes. Isocyanates can be obtained by the thermal decomposition of the resulting urethanes [4 - 10]. This route has the advantages of giving higher yields than those obtained by direct carbonylation of nitro compounds to isocyanates [11 - 15] and also being free from corrosion problems. Previous studies using Pd(II) complexes [8, 14, 15] have provided poor turnover rates for isocyanates. From the successful utilization of Ru(III) complexes in our laboratory for carbonylation and hydroformylation reactions [16, 17], we tried Ru(III) catalysts for the first time in the reductive carbonylation of nitrobenzene.

In the present study, we report the catalytic activity of [Ru(saloph)Cl<sub>2</sub>] 1, [Ru(salen)Cl<sub>2</sub>] 2, [Ru(pic-en)Cl<sub>2</sub>]Cl 3, [Ru(pic-opd)Cl<sub>2</sub>]Cl 4 and [Ru(pic-dien)Cl]Cl<sub>2</sub> 5 (where saloph = bis(salicylaldehyde)-*o*-phenylenediimine, salen = bis(salicylaldehyde)ethylenediimine, pic-en = bis(picolaldehyde)ethylenediimine, pic-opd = bis(picolaldehyde)-*o*-phenylenediimine and pic-dien = bis(picolaldehyde)diethylenetriimine) in the reductive carbonylation of nitrobenzene at 160 - 200 °C and 15 atm CO in ethanol.

The Schiff bases in the equatorial positions of complexes 1 and 2 contain N<sub>2</sub>O<sub>2</sub>, complexes 2 and 3 contain N<sub>4</sub> donors and complex 5 is a chelated N<sub>5</sub> system. At 15 atm CO and in the temperature range 160 - 200 °C, the reductive carbonylation of nitrobenzene gives exclusively phenylurethane, with turnover rates varying from 15 - 82 mol product per mol catalyst per hour. The catalytic activity of the Ru(III)-Schiff base complexes for reductive carbonylation of nitrobenzene decrease in the order [Ru(saloph)Cl<sub>2</sub>] ≫ [Ru(salen)Cl<sub>2</sub>] > [Ru(pic-en)Cl<sub>2</sub>]Cl > [Ru(pic-opd)Cl<sub>2</sub>]Cl. Complex 5 was completely inactive in the reductive carbonylation of nitrobenzene at 200 °C and 15 atm CO even after 12 h contact time.

## Experimental

### Materials

Ruthenium chloride trihydrate was obtained from M/s. Arora Mathey Ltd. (Calcutta). The various ligands used in the preparation of Ru(III) complexes, such as salicylaldehyde, picolaldehyde, ethylenediamine, *o*-phenylenediamine and diethylenetriamine were obtained from Aldrich Chemicals Co., U.S.A. The ethanol and nitrobenzene (AR grade) were distilled and dried (moisture-free) by passing through a column containing activated molecular sieves just before use. Carbon monoxide gas was obtained from B.O.C., U.K. and had a purity of ~99.9%.

### Preparation of complexes

Complexes having the general formula  $K[Ru(X)Cl_{1-2}]$  (where X = Schiff base ligand) were prepared using  $K_2RuCl_5$  as a starting material [18]. In a general procedure, stoichiometric amounts of the Schiff base ligand were dissolved in hot ethanol to which  $K_2RuCl_5$  was added in an appropriate mole ratio and the resulting mixture refluxed up to 15 h. After the completion of the reaction, verified by TLC, the reaction mixture was filtered on a sintered glass crucible and the filtrate concentrated to a small volume by heating on a water bath. To this solution, ether was added to precipitate the complexes. All the complexes were purified and dried under vacuum. Their compositions were established by C, H and N analysis and other physico-chemical methods. The structure of complexes used in the carbonylation experiments are given in Fig. 1.

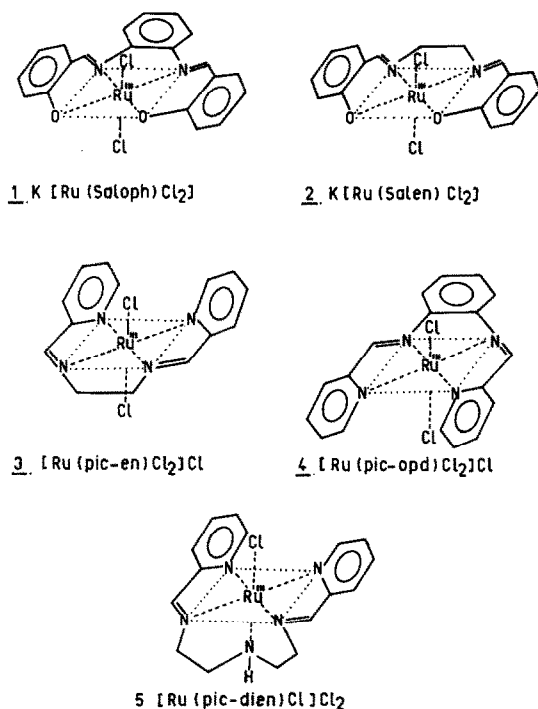


Fig. 1. Schiff base complexes of ruthenium.

### Reductive carbonylation of nitrobenzene

The reductive carbonylation of nitrobenzene was conducted in a 300 ml stainless steel pressure reactor (Parr Instrument Co., U.S.A.) as described in an earlier publication [17]. In a typical experiment, the carbonylation run was carried out by charging known amounts of nitrobenzene, carbon monoxide,

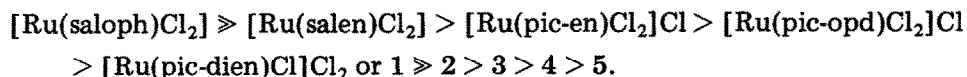
CO to the desired value when the required temperature was attained. The reaction was initiated by starting the agitation of the cell mixture. Liquid samples were withdrawn at different time intervals and were analyzed for nitrobenzene and phenylurethane using GLC (Shimadzu, GC-9A) to monitor the progress of reaction. A stainless steel column having 5% SE-30 support on Carbowax 80/100 mesh (2.5 m in length) was used in the GLC with FID detector. Other conditions of GLC analysis were column temperature programmed in the range 120 - 250 °C, injector temperature 275 °C and N<sub>2</sub> carrier gas (30 ml min<sup>-1</sup>).

## Results and discussion

The Ru(III) complexes tested for their catalytic activity towards reductive carbonylation of nitrobenzene to phenylurethane in ethanol solvent (Fig. 1) are classified as:

(a) those containing Schiff bases with two nitrogen and two oxygen atoms (N<sub>2</sub>O<sub>2</sub> system), which include [Ru(saloph)Cl<sub>2</sub>] 1 and [Ru(salen)Cl<sub>2</sub>] 2; (b) those containing four nitrogen donor atoms (N<sub>4</sub> system) which include [Ru(pic-en)Cl<sub>2</sub>]Cl 3 and [Ru(pic-opd)Cl<sub>2</sub>]Cl 4; (c) complex containing five nitrogen donor atoms (N<sub>5</sub> system) [Ru(pic-dien)Cl]Cl<sub>2</sub> 5.

Complexes 1 to 5 tested for the reductive carbonylation of nitrobenzene to phenylurethane in the temperature range 160 - 200 °C and 15 atm CO showed different catalytic activities. 100% conversion of nitrobenzene is achieved in cases 1 and 2, but for relative comparison only the turnover rates obtained with different complexes at 25% conversion of nitrobenzene are presented in Table 1. It is seen from the results in Table 1 that the highest turnover rate of 82 mol product per mol catalyst per hour was obtained with 1 at 160 °C and 15 atm CO, and the lowest turnover rate of 15 mol product per mol catalyst per hour with 4 at 200 °C and 15 atm CO. But 5 under similar conditions and at 200 °C did not show any activity, even after 12 hours contact time. The activities of five complexes tested for reductive carbonylation of nitrobenzene to give phenylurethane lie in the following order:



The observations made with respect to catalytic activity towards carbonylation of nitrobenzene clearly show that the complexes with (N<sub>2</sub>O<sub>2</sub>) Schiff base systems showed higher catalytic activity, followed by N<sub>4</sub> systems, while the N<sub>5</sub> system is catalytically inactive.

On comparison of the catalytic activity of complexes with 5, it is evident that the presence of labile *trans* chlorides in the coordination sphere of the metal ion is essential for catalytic activity. The blocking of a *trans* position by a chelated nitrogen atom in 5 makes the complex inactive as a

TABLE 1

Catalyst activity towards reductive carbonylation of nitrobenzene to phenylurethane<sup>a</sup>

Sample No.	Catalyst precursor	Temperature (°C)	Turnover rate <sup>b</sup>
1	K[Ru(saloph)Cl <sub>2</sub> ]	160	82
2	K[Ru(salen)Cl <sub>2</sub> ]	160	30
3	[Ru(pic-en)Cl <sub>2</sub> ]Cl	200	20
4	[Ru(pic-opd)Cl <sub>2</sub> ]Cl	200	15
5	[Ru(pic-dien)Cl]Cl <sub>2</sub>	200	—

<sup>a</sup>Reaction conditions: nitrobenzene 0.04 M, ethanol 96.0 ml, catalyst precursor 1 mmol,  $P_{CO}$  15 atm.

<sup>b</sup>Turnover rate = mol product per mol catalyst per hour.

*trans* chlorides thus provides vacant coordination sites for the coordination of CO and C<sub>6</sub>H<sub>5</sub>NO<sub>2</sub> to the metal ion, a requirement essential for catalytic activity. Complexes with N<sub>2</sub>O<sub>2</sub> coordination on the Schiff bases, which form more flexible complexes than a rigid N<sub>4</sub> system, allow rearrangement in the coordination sphere of the metal ion. This explains the higher catalytic activity of the N<sub>2</sub>O<sub>2</sub> Schiff bases over the N<sub>4</sub> systems.

## References

- 1 R. G. Arnold, J. A. Nelson and J. J. Verbanc, *Chem. Rev.*, **57** (1957) 47.
- 2 M. Sittig, in *Amines, Nitriles and Isocyanates Processes and Products*, Noyes Development Corporation, NJ, 1969.
- 3 K. Othmer, in *Encyclopedia of Chemical Technology* Vol. 12, Wiley, New York, 1967, pp. 673 - 702.
- 4 S. Cenini, C. Crotti, M. Pizzotti and F. Porta, *J. Org. Chem.*, **53** (1988) 1243.
- 5 C. Crotti, S. Cenini, B. Rindone, S. Tollari and F. Demartin, *J. Chem. Soc., Chem. Commun.*, (1986) 784.
- 6 Y. Watanabe, Y. Tsuji, R. Takeuchi and N. Suzuki, *Bull. Chem. Soc. Jpn.*, **56** (1983) 3343.
- 7 Y. Watanabe, Y. Tsuji and N. Suzuki, *Chem. Lett.* (1982) 105.
- 8 A. Bontempi, E. Alessio, G. Chanos and G. Mestroni, *J. Mol. Catal.* **42** (1987) 67.
- 9 G. Besenyei, P. Viski, L. I. Simandi and F. Nagy, *Inorg. Chim. Acta*, **90** (1984) 43.
- 10 F. Benedini, M. Nali, B. Rindone, S. Tollari, S. Cenini, L. Monica and G. Porta, *J. Mol. Catal.*, **34** (1986) 155.
- 11 B. K. Nefedov, V. I. Manov-Yuevenskii and S. S. Nowkov, *Dokl. Chem., Eng. Ed.*, **234** (1977) 826.
- 12 *Jap. Kokai* 73 64 048 (1973) to T. K. Yamahara, S. Takamatsu and K. Hirose.
- 13 K. Unverferth, R. Hontsch and K. Schwetlick, *J. Prakt. Chem.*, **321** (1979) 86.
- 14 S. B. Halligudi, R. V. Chaudhari and L. K. Doraiswamy, *Ind. Eng. Chem. Proc. Des. Dev.*, **23** (1984) 793.
- 15 S. P. Gupte and R. V. Chaudhari, *J. Mol. Catal.*, **24** (1984) 197.
- 16 M. M. Taqui Khan, S. B. Halligudi and S. H. R. Abdi, *J. Mol. Catal.*, **44** (1988) 179.
- 17 M. M. Taqui Khan, S. B. Halligudi and S. H. R. Abdi, *J. Mol. Catal.*, **45** (1988) 215.
- 18 M. M. Taqui Khan, A. Kumar and Z. Shirin, *J. Chem. Res.*, **5** (1986) 130.