

## Oxidative Carbonylation of Amines Catalysed by Metallomacrocyclic Compounds

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Metallomacrocyclic compounds, such as metalloporphyrins, have been shown to catalyse the oxidative carbonylation of amines to carbamates which are precursors to isocyanates.

Non-phosgene methods for the production of isocyanates have attracted much attention in the past two decades. One of the approaches being advanced is to first synthesize the precursor carbamates *via* oxidative carbonylation of an amine with carbon monoxide and oxygen in the presence of an alcohol, followed by the thermal cracking of the carbamates to form the isocyanates.<sup>1</sup> While it is well known that metalloporphyrins and other metallomacrocyclic compounds can catalyse the oxidation of various organic substrates, little has been reported in the literature on the oxidative carbonylation of amines to carbamates using metallomacrocyclic compounds as catalysts. Recently, a few reports were published describing the use of certain cobalt and ruthenium Schiff base complexes as catalysts for the oxidative carbonylation of amines.<sup>2</sup> We do not know of any reports which describe the use of other metallomacrocyclic compounds, such as metalloporphyrins, as catalyst for this particular reaction. We report our recent findings which show that the oxidative carbonylation of an amine can be catalysed by metallomacrocyclic compounds,

including metalloporphyrins, metal Schiff base complexes and metal phthalocyanines.

When an amine, such as cyclohexylamine, was allowed to react with CO and O<sub>2</sub> (7% O<sub>2</sub>) at 1000 psi (1 psi ≈ 6.9 × 10<sup>5</sup> Pa) in the presence of ethanol using Co(tpp) (tpp = tetraphenylporphyrinato dianion) as the catalyst, *N*-cyclohexyl *O*-ethyl carbamate formed in close to quantitative yield [eqn. (1)]. Iodide was found to be a promoter for the catalyst system, enhancing the rate of the reaction.

Table 1 shows some results on the oxidative carbonylation reactions of various amines using different metallomacrocyclic compounds. Among the metallomacrocyclic compounds that

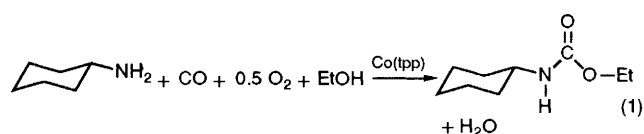


Table 1 Examples of oxidative carbonylation of amines with several catalysts<sup>a</sup>

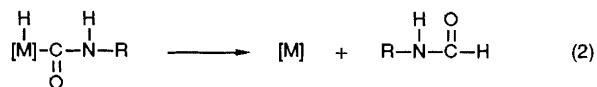
Example	Substrate amine-alcohol	Catalyst	Cocatalyst	Conversion (%)	Selectivity <sup>b</sup> (%)	Turnover frequency <sup>d</sup>
1	Bu <sup>t</sup> NH <sub>2</sub> -EtOH	Co(tpp) <sup>c</sup>	None	30	41	10
2	Bu <sup>t</sup> NH <sub>2</sub> -EtOH	Co(tpp) <sup>c</sup>	NaI	100	96	≥33
3	Bu <sup>t</sup> NH <sub>2</sub> -EtOH	Co(pc) <sup>c</sup>	NaI	100	96	≥33
4	Bu <sup>t</sup> NH <sub>2</sub> -EtOH	Co(salen) <sup>c</sup>	NaI	100	99	≥33
5	Bu <sup>t</sup> NH <sub>2</sub> -EtOH	Cu(pc)	NaI	63	81	21
6	Bu <sup>t</sup> NH <sub>2</sub> -CF <sub>3</sub> CH <sub>2</sub> OH	Co(tpp)	NaI	100	95	≥33
7	CyNH <sub>2</sub> -EtOH	Co(tpp)	NaI	100	98	≥33
8	<i>m</i> -Toluidine-EtOH	Co(tpp)	NaI	86	99	29
9	PhNH <sub>2</sub> -EtOH	Co(tpp)	NaI	80	52	27
10	PhNH <sub>2</sub> -EtOH	Rh(tpp)Cl	NaI	73	77	24
11	PhNH <sub>2</sub> -EtOH	Pd(tpp)	NaI	94	83	31
12	PhNH <sub>2</sub> -EtOH	Co(salen)	NaI	100	99	≥33
13	PhNH <sub>2</sub> -EtOH	Co(pc)	NaI	77	84	26
14	PhNH <sub>2</sub> -EtOH	Cu(pc)	NaI	63	42	21
15	Hexane-1,6-diamine-EtOH	Co(tpp)	NaI	100	95	≥33
16	Isophorone diamine-EtOH	Co(tpp)	NaI	100	70	≥33
17	Isophorone diamine-EtOH	Co(tpp)	KI	100	73	≥33

<sup>a</sup> Typical experimental conditions: 1000 psi CO-O<sub>2</sub>(7% O<sub>2</sub>); 180 °C; reaction time = 3.0 h; 50 mmol of amine; 0.50 mmol of catalyst; 5.0 mmol NaI, 1.0 mol of alcohol. <sup>b</sup> Selectivity to corresponding carbamate or dicarbamate in the case of diamine. The balance of the products is mainly the *N,N'*-disubstituted ureas which are an intermediate in the reactions. <sup>c</sup> Abbreviations used: tpp = tetraphenylporphyrinato dianion; salen = *N,N'*-bis(salicylidene)ethylenediamine dianion; pc = phthalocyanato dianion. <sup>d</sup> Turnover frequency, mol amine converted per mol catalyst per hour.

we have studied, we found that salen and porphyrin complexes are the most active catalysts. Among the metalloporphyrins that we have studied, Co, Rh and Ru porphyrins gave the best results. The role of iodide as a promoter for the catalyst system is not yet clear.

We also carried out experiments using metal carbonyl compounds, such as  $\text{Co}_2(\text{CO})_8$  or  $\text{Ru}_3(\text{CO})_{12}$ , as the catalyst. We found that they are less effective as catalysts compared with the corresponding metallomacrocyclic compounds. We also observed no formation of formamide side products in experiments using metallomacrocycles as the catalyst, while substantial amount of formamides were observed in experiments using metal carbonyls as the catalyst.

We speculate that formamide formation, resulting from carbonylation of the amine, may be due to the reductive elimination of an amido intermediate with a hydride ligand [eqn. (2)].



Since it is unlikely that a square-planar coordination complex, such as  $\text{Co}(\text{tpp})$ , could have a hydride and an amido group *cis* to each other owing to the unavailability of two adjacent coordination sites, the above side reaction to form a formamide can apparently be avoided by using such complexes as catalysts for the oxidative carbonylation of amines. This would help explain the high selectivities for the carbamate formations of the catalytic reactions as shown in Table 1. The detailed reaction mechanism is the subject of our future study.

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## References

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