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Oxidative alkoxycarbonylation of aniline using homogeneous catalysts*

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The oxidative carbonylation of amines has attracted considerable interest due to its importance in the synthesis of carbamates. Based on this non-phosgene route, a new process for the manufacture of methylene diphenyl diisocyanate (MDI) has been developed [1]. Fukuoka *et al.* reported oxidative carbonylation of amines to carbamates using supported Pd and Rh catalysts [2]. Recently, a detailed investigation on effect of reaction conditions on the activity and selectivity of diphenyl urea using a Pd/C–NaI catalyst system has been reported [3]. Oxidative carbonylation of alkyl amines is also known to give corresponding diallyl urea and allyl carbamates as products [4]. In most of the earlier reports, supported Pd catalysts have been used and there are only a few reports on homogeneously catalysed carbonylation of amines, *e.g.* Giannoccaro *et al.*, Alper and Hartstock have reported oxidative carbonylation of aniline to *N,N*-diphenyl urea using Pd complex catalysts [4–6].

In this communication, preliminary data on the homogeneously catalysed oxidative alkoxycarbonylation of aniline to *N,N*-diphenyl urea (I) and *N*-phenyl carbamate (II) has been reported. The reaction is described as:

$$2\mathrm{ArNH_2} + \mathrm{CO} + \tfrac{1}{2}\mathrm{O_2} \xrightarrow{\text{catalyst}} \underset{\text{(I)}}{\mathrm{ArNHCONHAr}} + \mathrm{H_2O} \qquad (1)$$

$$\text{(I)} + \mathrm{CH_3OH} \longrightarrow \underset{\text{(II)}}{\mathrm{ArNHCOOCH_3}} + \mathrm{ArNH_2} \qquad (2)$$

The aim of this work was to evaluate performance of a variety of Pd, Ru and Rh complex catalysts for the above reaction.

Experimental

The transition metal salts such as $PdCl_2$, $RhCl_3 \cdot 3H_2O$ and $RuCl_3 \cdot 3H_2O$ were procured from Arora–Matthey Ltd. and were used as such. Aniline A.R.

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grade was freshly distilled before use. Methanol was dried and doubly distilled before use. Carbon monoxide gas was used from cylinders, the purity of which was found to be greater than 99.5% by GC analysis. Infrared spectra were recorded on a Perkin Elmer 283 B spectrophotometer.

Preparations

$Rh(CO)_2acac$ was prepared according to the procedure described earlier [7]. Ru complexes were prepared by methods described in the literature [8, 9]. $Pd(aniline)_2X_2$ complexes were prepared by refluxing 1.0 g of PdX_2 salts in 90 cm^3 benzene containing 10 cm^3 of aniline for 2 h. The yellow coloured complex was filtered and washed with n-hexane; yield 60–80%.

Catalytic reactions

In a typical procedure, a mixture of aniline (108 mmol), $Pd(aniline)_2I_2$ (0.2 mmol) and solvent methanol (90 cm^3) were charged into a 300 cm^3 capacity Hastelloy C autoclave. The autoclave was pressurized with carbon monoxide and oxygen up to a total pressure of 41 atm ($CO:O_2 = 13:1$). The reaction was carried out at 170 °C for 2 h under stirring. During the course of the reaction the autoclave pressure was maintained at 41 atm by feeding $CO:O_2$ mixture in a 2:1 ratio from the reservior. After cooling the contents, a portion of the wine-red-coloured solution obtained was analyzed on GLC and HPLC for aniline, carbamate and urea. The analysis of the sample showed 65% conversion of aniline, with 100% yield of *N*-phenyl methyl carbamate.

Results and discussion

It has been shown in this study that oxidative alkoxycarbonylation of aniline catalysed by homogeneous transition metal complexes gives carbamate and urea as the main products. Table 1 shows the activity of several transition metal complexes employed in this work, along with the selectivity obtained for carbamate and urea. Comparison of results in this table indicate that for Pd, Rh and Ru complexes, the activity and selectivity of the catalyst varies with the ligand environment around the central metal atom. For example, for $Pd(aniline)_2X_2$, (where $X = Cl$, Br or I) the activity of the catalyst and its selectivity for carbamate increased from Cl to I. The conversion and selectivity for carbamate also increase with increasing catalyst concentration (runs 9, 11 and 14). In absence of alcohol only urea is formed in high yields (runs 17 and 18).

Comparison of the activity of metal iodide catalysts shows that the Pd is the most active and selective catalyst for carbamate synthesis, followed by Rh and Ru respectively (runs 1, 8 and 10). It can be seen from this table that iodine-containing complexes show markedly higher activity and selectivity for carbamate than other complexes. It is interesting to note that most of the active catalysts contain halide as a ligand, however the catalyst $Rh(CO)_2$-acac shows activity for oxidative alkoxycarbonylation reaction even in the absence of any halide-containing ligand.

The activity of the catalyst containing Cl ligands increases remarkably when iodine-containing promoters such as NaI are added to the system. The

TABLE 1

Activity and selectivity of transition metal-catalysed oxidative carbonylation of aniline[a]

Run no.	Catalyst	Promoter	Aniline conversion (%)	Selectivity (%)[b]	
				Carbamate	Urea
1	PdI_2	–	63.8	97.6	1.3
2	$Pd(C_6H_7N)_2I_2$	–	65.0	100.0	nil
3	$Pd(C_6H_7N)_2Br_2$	–	54.3	46.9	52.5
4	$Pd(C_6H_7N)_2Cl_2$	–	15.0	36.9	61.8
5	$Pd(C_6H_7N)_2Cl_2$	NaI	59.0	76.1	23.2
6	$Rh(CO)_2acac$	–	10.4	24.5	74.0
7	$Rh(CO)_2acac$	NaI	48.4	74.5	24.3
8	$RhI_3 \cdot 3H_2O$	–	44.6	89.2	09.4
9[c]	$RhI_3 \cdot 3H_2O$	–	62.9	100.0	nil
10	$RuI_3 \cdot 3H_2O$	–	16.1	07.1	91.3
11[c]	$RuI_3 \cdot 3H_2O$	–	37.6	65.4	33.7
12	$Ru(CO)_3I_3$ 18 crown 6 ether	–	38.6	81.1	17.3
13	$Bu_4N[Ru(CO)_3I_3]$	–	30.6	44.0	54.3
14[c]	$Bu_4N[Ru(CO)_3I_3]$	–	44.4	72.7	13.5
15	$Ru(CO)_2(Py)_2Cl_2$	–	16.8	02.4	97.2
16	$Ru(CO)_2(Py)_2Cl_2$	NaI	38.8	62.4	35.1
17[d]	$Bu_4N[Ru(CO)_3I_3]$	–	67.1	nil	100.0
18[d]	$Ru(CO)_3I_3$ 18 crown 6 ether	–	51.7	nil	100.0

[a] Aniline (108 mmol), catalyst precursor (0.2 mmol), NaI (0.6 mmol), initial P_{CO} (38 atm), P_{O_2} (3 atm), methanol (90 cm^3), temperature (170 °C), contact time (2 h).
[b] Selectivity of carbamate and urea calculated based on aniline reacted.
[c] Catalyst precursor (0.4 mmol).
[d] Dimethylformamide (90 cm^3).

results indicate that the activity and selectivity of Pd, Rh and Ru complex catalysts vary depending upon the type of catalyst precursor used. It is known that Rh and Ru precursors employed in this work form anionic species of the type $[Rh(CO)_2I_2]^-$ and $[Ru(CO)_3I_3]^-$ in the presence of CO and NaI [8]. Examination of IR spectra of reaction solutions (runs 12 to 13) clearly indicated two carbonyl frequencies in the ν(CO) range of 2010(sh), 1985(s) cm^{-1} and 1955(sh), 1930(s) cm^{-1}. It is indicated from runs 12–13 that if iodide is present in the catalyst precursor, the active catalytic intermediate is formed even in the absence of a promoter such as NaI. The higher activity observed in runs 12 and 13, wherein $[Ru(CO)_3I_3]^-$ is used as a catalyst precursor, indicates that anionic intermediates are the most likely reactive species. The IR spectrum of reaction solution containing the catalytic intermediate of Pd complexes did not show any carbonyl frequency, as Pd carbonyl complexes are highly unstable and were found to decompose to metallic Pd during recording of the spectrum.

Conclusion

In conclusion, these results indicate that metal carbonyl complexes of the type $[M(CO)_m X_m]^-$ (where X = halogen and $m = 2$ or 3) are the key catalytic intermediates in the homogeneously catalysed oxidative carbonylation of amines. The activity and selectivity of the catalyst are highest with iodine-containing ligands and depend on the ease with which the catalyst precusor can be converted into active catalytic intermediate, *viz.* $M(CO)_m I_m$ (see runs 5, 7 and 16).

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