Selective Ruthenium Carbonyl Catalysed Reductive Carbonylation of Aromatic Nitro Compounds to Carbamates

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$Ru_3(CO)_{12}$ and $Ru(CO)_3(PPh_3)_2$ catalyse the reductive carbonylation of aromatic nitro compounds to the corresponding carbamates with high selectivity in the presence of $NEt_4^+Cl^-$ as co-catalyst.

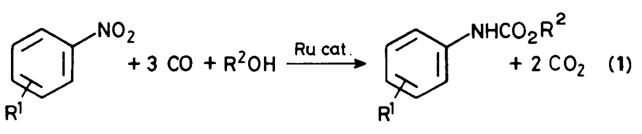
Isocyanates are usually prepared by the reaction of phosgene with amines and they are transformed into carbamates by their reaction with alcohols.[1] On the other hand carbamates, which are important pesticides, can be transformed into isocyanates by thermal cracking. Thus an alternative synthesis of carbamates would also give a phosgene-free route to isocyanates, which are of practical interest in the manufacture of polyurethanes. In the patent literature there are reports on the synthesis of carbamates by reductive carbonylation of aromatic nitro compounds in the presence of alcohols catalysed by heterogeneous, usually complex, catalytic systems.[2]

A novel catalytic synthesis of carbamates by oxidative alkoxycarbonylation of amines in the presence of palladium and iodide has recently been reported.[3] As a continuation of our studies on the reactivity of nitroso[4] and nitro[5] compounds which are bound to a transition metal centre, we report here that ruthenium carbonyl complexes such as $Ru_3(CO)_{12}$ (**1**) and $Ru(CO)_3(PPh_3)_2$ (**2**) are very efficient homogeneous catalysts

$Ru_3(CO)_{12}$ $Ru(CO)_3(PPh_3)_2$
(**1**) (**2**)

in the reductive carbonylation of aromatic nitro compounds to carbamates, when tetraethylammonium chloride is used as a co-catalyst. The reaction is also very selective in the formation of the carbamates [equation (1)]. Thus when nitrobenzene (15.5 mmol) in toluene (23 ml) was allowed to react with CO (82 atm.) and methanol (2 ml) at 160—170 °C for 5 h in a 200 ml autoclave,† in the presence of (**1**) (0.156 mmol) and $NEt_4^+Cl^-$ (1.09 mmol), methyl *N*-phenylcarbamate (R^1 = H, R^2 = Me) (14.4 mmol) and aniline (1.00 mmol) were obtained (g.l.c. analysis).[6] The conversion of nitrobenzene was 100% and the selectivity in the formation of the carbamate 92.7%. Similar results were obtained using (**2**) as the catalyst (Table 1), while $Fe_3(CO)_{12}$ and $Fe(CO)_3(PPh_3)_2$ were inactive under the reaction conditions used. At the end of the reaction, catalyst (**1**) was recovered unchanged while catalyst (**2**) had been transformed into a new carbonyl complex (i.r. evidence), which was probably the true catalyst (or catalyst precursor) for this reaction, since it maintained the catalytic activity observed for $Ru(CO)_3(PPh_3)_2$.

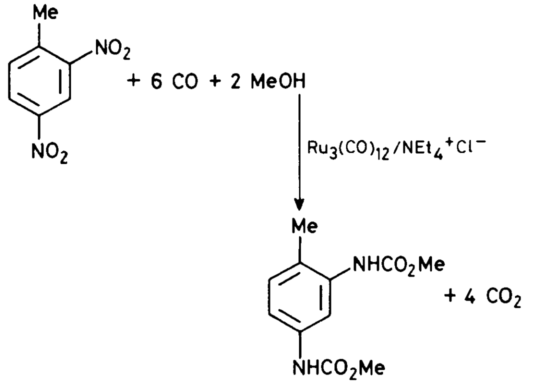
In the absence of the alkylammonium salt, aniline was the main product of the catalytic reactions (Table 1, entries 1 and 2). The experimental conditions used were optimal (CO pressure, reaction temperature, the amount and nature of the added alcohol, and the catalyst/co-catalyst ratio).



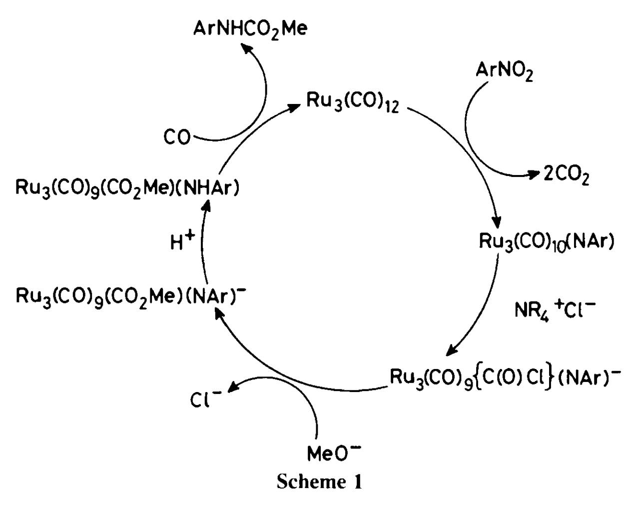
Moisture poisoned the reaction severely, and its presence led mainly to the formation of aniline. Tetraethylammonium chloride was a much more efficient co-catalyst than the corresponding bromide and iodide. It was also more active than other alkylammonium salts such as $NMe_4^+Cl^-$ and $NBu^n{}_4^+Cl^-$, and than tetra-n-butyl phosphonium chloride (Table 1). LiX (X = F, Cl, I) compounds were not selective co-catalysts in this reaction; when they were very active (X = F), the product was mainly aniline. Compound (**1**) also catalysed the conversion of 2,4-dinitrotoluene into the corresponding dicarbamate [equation (2)].

Reaction (2) has not been optimized, and preliminary results showed that the dicarbamate was formed with *ca.* 50% selectivity for a 100% conversion, another product being identified as methyl *N*-(3-nitro-*p*-tolyl)carbamate, while no 2,4-diaminotoluene was formed. It is known that (**1**) reacts with nitrobenzene to give phenylimido (or phenylnitrene) complexes.[7]

Alper has shown that in the presence of sodium methoxide the $M_3(CO)_{12}$ (M = Fe, Ru) complexes catalyse the carbonylation of aromatic nitro compounds to carbamate esters, ureas, formamides, and amines, probably *via* $[M_3(CO)_{11}(CO_2Me)]^-$ species.[8] He has also reported that tetrabutyl-



(**2**)



Scheme 1

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† The reactants were put into a glass liner, constructed to fit the autoclave, and a cap, filled with glass wool which avoids splashing of the solvent was used. Magnetic stirring was applied.

Table 1. Conversion of nitrobenzene into *N*-phenylcarbamates catalysed by $Ru_3(CO)_{12}$ (**1**) and $Ru(CO)_3(PPh_3)_2$ (**2**) and co-catalysts.[a]

Entry	Catalyst	Co-catalyst	Conversion (%)	Aniline (%)[b]	*N*-Phenylcarbamates (%)[b,e]
1	(**1**)	none	36.4	34.1	22.2
2[c]	(**2**)	none	25.5	32.5	19.9
3	(**1**)	$NEt_4^+Cl^-$	100	6.5	92.7
4[c]	(**2**)	$NEt_4^+Cl^-$	100	7.9	86.7
5[d]	(**2**)	$NEt_4^+I^-$	45.5	64.0	27.7
6[d]	(**2**)	$NMe_4^+Cl^-$	93.8	28.5	53
7[d]	(**2**)	$NBu^n{}_4{}^+Cl^-$	86.3	27.6	53.8
8[d]	(**2**)	$PBu^n{}_4{}^+Cl^-$	83.7	33.8	42.8
9[c,d]	(**1**)	LiCl	88.9	49	21.5
10[c,d]	(**2**)	LiCl	44.2	65.4	8
11[c,d]	(**2**)	LiF	100	57.8	5.9

[a] See text for conditions. [b] Calculated as a percentage of the converted nitrobenzene, thus representing selectivity. [c] Reaction time 7 h and then the autoclave was left to cool overnight. [d] In these experiments toluene (20 ml) and ethanol (5 ml) were used, $PhNHCO_2Et$ being obtained. [e] In some experiments, phenylisocyanate was also present in the gas-chromatographic analysis (*ca.* 5%). However it originates from the thermal cracking of carbamate which occurs during the analysis.

ammonium fluoride can catalyse the reduction of nitrobenzenes to anilines by $Fe_3(CO)_{12}$, suggesting the attack of fluoride ion on co-ordinated carbon monoxide.[9] Moreover we have observed that the activity of (**1**) (Table 1, entry 1) is not significantly modified when $NEt_4^+BF_4^-$ is used as the co-catalyst. Thus, it seems reasonable to propose the reaction mechanism shown in Scheme 1 for our catalytic reaction, at least when (**1**) is the catalyst. The methoxycarbonyl group should favour the opening of one Ru–N bond of the triply bridging[7] arylimido ligand, thus allowing the protonation reaction to take place.

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