

## Catalytic Carbonylation of Amines using Ruthenium Complexes under Mild Conditions

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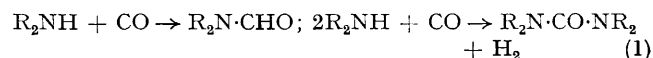
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*Summary* Cyclic secondary amines have been selectively carbonylated to the *N*-formyl derivatives using ruthenium catalysts under homogeneous conditions and a carbon monoxide pressure of 1 atm.

requires severe conditions of temperature and pressure.<sup>1,2</sup>



THE catalytic carbonylation of amines to substituted formamides and ureas [equation (1)] using metal carbonyls

Copper(I) complexes have been used, however, under ambient conditions for the catalytic production of ureas

from amines using carbon monoxide-oxygen mixtures.<sup>3</sup> The mechanisms of these carbonylations are not well understood. We have found that certain ruthenium complexes catalyse the carbonylation of some secondary amines exclusively to the *N*-formyl product under mild conditions (1 atm; 75°) under pure CO, and further, the systems lend themselves to detailed mechanistic studies. Some results are summarized in the Table.

TABLE

Carbonylation of amines at 75°, 1 atm pressure,  $3 \times 10^{-2}$  M ruthenium in 5 ml amine

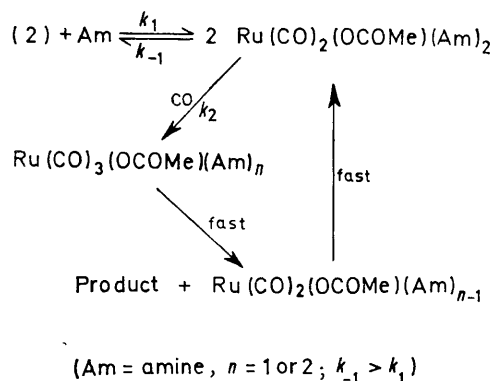
Amine	Catalyst	% Conversion into <i>N</i> -formylamine	Max. rate $\times 10^2$ M h <sup>-1</sup>
Morpholine	(1)	6 (20 h)	1.4
Piperidine	(1) or (2)	15 (30 h); 30 (70 h)	3.6
Pyrrolidine	(1)	35 (35 h)	26.5
Piperidine	Ru <sub>3</sub> (CO) <sub>12</sub>	45 (65 h)	26.0
Piperidine	Ru <sub>2</sub> (OCOMe) <sub>4</sub> <sup>a</sup>	25 (200 h)	2.0

<sup>a</sup> 10% H<sub>2</sub>O added.

The ruthenium(II) bridged acetate dicarbonyl polymer,<sup>4,5</sup> [Ru(CO)<sub>2</sub>(OCOMe)]<sub>n</sub> (1) dissolves in amines such as piperidine and the yellow solutions, *ca.* 10<sup>-2</sup> M in Ru, adsorb CO under mild conditions; the rate curve which is initially autocatalytic reaches a maximum and then slowly decreases after *ca.* 30 h. The sole product, identified by g.l.c., was *N*-formylpiperidine (30% after 70 h); the total gas consumption corresponded to this conversion. The maximum rates (see Table) showed a first-order dependence on CO up to 1 atm total pressure, and a dependence on ruthenium which is first order at concentrations up to *ca.* 0.015M and approaches half order at higher concentrations up to *ca.* 0.06M. Morpholine and pyrrolidine systems behaved similarly but showed lower and higher reactivities, respectively.

The amine solutions of (1) readily yield the complexes [Ru(CO)<sub>2</sub>(OCOMe)(amine)]<sub>2</sub> (2); these compounds give satisfactory analytical data and show three strong ν(CO) i.r. bands in the 1920–2030 cm<sup>-1</sup> region. On comparison with a previously reported pyridine complex<sup>4</sup> they are formulated as dimers. These dimers may be used at the appropriate ruthenium molarities to reproduce exactly the uptake plots observed with the polymeric catalyst. The autocatalytic nature of the reaction indicates that the dimers are precursors to the true catalyst which is probably formed *via* interaction with further carbon monoxide; consistent with this is the finding that amine solutions of the dimers are quite stable at 75° for long periods *in vacuo* and there is no trace of *N*-formylamine. Solution i.r. measurements in regions approaching maximum activity

showed the presence of the amine dimers at the higher catalyst concentrations.



SCHEME

The tentative reaction Scheme shown is consistent with the observations and the kinetics. The autocatalytic region is associated with the build up of a steady state concentration of the active monomer from the dimer (2); this slow equilibrium also accounts for the complex dependence upon ruthenium. Tricarbonyl complexes are known<sup>4,5</sup> to be formed from the dicarbonyl complex (1).

Ru<sub>3</sub>(CO)<sub>12</sub> was more effective than (1) for the carbonylation of piperidine essentially because no induction period was observed; this is again consistent with complexes with more than two carbonyl groups being the active catalyst, although we have not yet been able to characterise the inorganic products formed from reaction of the dodecacarbonyl with amines.

After 70 h, the rate for the piperidine-(1) system for the conditions given in the Table had decreased to 1.7 M h<sup>-1</sup>; at this stage *ca.* 100 mol. of amine had been carbonylated per mol. of ruthenium. The rate decrease is mainly due to accumulation of the formyl product, which poisons the catalyst, and this appears to be due to complexation to the ruthenium, presumably *via* the carbonyl grouping as commonly found for formamide ligands.<sup>6</sup> Decrease in amine concentration also contributes to the fall in rate.

Ruthenium(II) acetate,<sup>5,7</sup> Ru<sub>2</sub>(OCOMe)<sub>4</sub>,<sup>†</sup> can be used as the starting carbonylation complex, but small amounts of water are necessary for solubility, and longer reaction times are required for reasonable conversions (Table).

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<sup>†</sup> A personal communication from Professor G. Wilkinson has informed us that this compound is incorrectly formulated and is probably Ru<sub>2</sub>O(OCOMe)<sub>4</sub> [OCOMe].

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