One-pot Synthesis of Amines by Aminomethylation of Alkenes catalysed by Dinuclear Rhodium Complexes under Mild Conditions

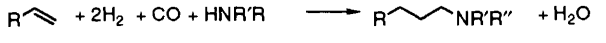
Thierry Baig and Philippe Kalck*

Laboratoire de Chimie des Procédés, Ecole Nationale Supérieure de Chimie, 118, route de Narbonne, 31077 Toulouse Cédex, France

The complex $[Rh_2(\mu\text{-S-Bu}^t)_2(CO)_2(PPh_3)_2]$ with a slight excess of PPh_3 catalyses the aminomethylation reaction of terminal alkenes under low pressures of carbon monoxide and hydrogen.

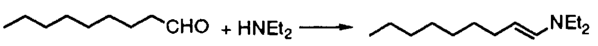
Hydroformylation of alkenes has been extensively studied[1] and in organic chemistry it is well known that condensation of an aldehyde with a primary or a secondary amine affords an imine and an enamine respectively.[2] As early as 1949, Reppe and Kindler[3] showed that it is possible to perform the two previous reactions and to hydrogenate the C=N or C=C bond to obtain in a one-step reaction the secondary or tertiary amine. This so-called aminomethylation reaction can be described by eqn. (1) where only the linear amine has been written. The catalytic conditions were rather harsh (above 150 °C and 15 MPa). Since this period, the academic and patent literature is quite scarce so that, even if, as more recently, rhodium has been used, only a few studies have been concerned with this reaction. Some rhodium precursors have been used such as $HRh(CO)(PPh_3)_3$,[4] $Rh_6(CO)_{16}$ and $Ru_3(CO)_{12}$[5] or even Rh_2O_3 in the presence of $Fe(CO)_5$[6] but the conditions used reached 150 °C and more than 15 MPa. More recently cobalt containing diphosphine complexes[7] were found to afford good yields but under the same conditions.

We have recently recognised the catalytic properties of $[Rh_2(\mu\text{-S-Bu}^t)_2(CO)_2(PPh_3)_2]$, **1**, for the low pressure (<1 MPa) hydroformylation of terminal alkenes provided a slight excess of triphenylphosphine is added.[8] As this catalytic system is not sensitive to the presence of water, it appeared to be a good candidate for the aminomethylation reaction of interest.

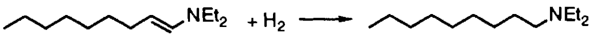


(1)

(2)



(3)



(4)

Complex **1** catalyses the one-pot synthesis of *N*,*N*-diethylnonylamine starting from oct-1-ene and diethylamine provided slightly higher pressures (0.8–1.8 MPa) than those required for the hydroformylation reaction are used. For the three successive reactions, described by eqns. (2)–(4), which occur in this catalysis, Table 1 shows the distribution of the linear and branched amines of interest as well as the intermediate aldehyde and enamine products. The sole by-products detected in our tests for less than 5% were oct-2-ene and small amounts of oligomers of enamines and aldehydes, except in dichloroethane (DCE) were extensive polymerisation was observed. The nature of the solvent plays a dramatic influence on the course of the reaction. In dimethylformamide (DMF), small quantities of amines were detected as well as significant amounts of the linear enamine; however, too many by-products are produced in this reaction. Satisfactory results were obtained in tetrahydrofuran (THF); two pressures were tested. We observed that addition of some ethanol to THF improved the rate of the reaction by 4–5%. The two tests reported in Table 1 were carried out with ethanol for 10% of the total reaction volume. As shown in Table 1, high conversions were reached, particularly at 1.8 MPa, as 97% of products of interest were formed among them 82% of amines. As evidenced by the last row, the linear aldehyde is more easily condensed with $NHEt_2$ and hydrogenated into the linear amine than the branched isomer.

Some other reacting amines have been explored (Table 2). Morpholine reacts more slowly than diethylamine since 20% of the linear enamine is still present. Probably, the hydrogenation step is retarded by morpholine which competes with the enamine for coordination on a rhodium metal centre. The effect of steric hindrance is shown by using diisopropylamine since the reaction mainly gave the two aldehydes, the enamines and expected amines being produced very slowly. Finally, a bulky primary amine, *i.e.* *tert*-butylamine was used

Table 1 Aminomethylation of oct-1-ene by diethylamine catalysed by $[Rh_2(\mu\text{-S-Bu}^t)_2(CO)_2(PPh_3)_2]$ **1**[a,b]

		Aldehydes		Enamines		Amines		
Solvent	Conversion (%)	n (%)	iso (%)	n (%)	iso (%)	n (%)	iso (%)	n/n + iso (%)
DCE	97	Polymerisation and side reactions						—
DMF	98	1.5	14	24	4	2	5	—
THF	98[c]	0.5	17	0.5	3	69	4	94.5
	99[d]	Trace	13	Trace	2	80	2	98

[a] **1** = 0.13 mmol; PPh_3 = 0.82 g; V_{total} = 30 ml; oct-1-ene = 38 mmol; Et_2NH = 58 mmol; P = 0.8 MPa ($CO:H_2$ = 1); T = 80 °C; t = 15 h; [b] All the ratios of products were determined by gas chromatography with anisole as the internal standard (precision better than 5%), the standardization curves being made from the commercial substrates and authentic samples prepared by classical condensation of the aldehydes and amines followed by hydrogenation and purification. [c] P = 0.8 MPa. [d] P = 1.8 MPa.

Table 2 Aminomethylation of oct-1-ene by various amines[a]

		Aldehydes		Enamines		Amines	
Amine	Conversion (%)	n (%)	iso (%)	n (%)	iso (%)	n (%)	iso (%)
Morpholine	99.5	3	6	20	6	42	13
Diisopropylamine	99	61	22	3	0.5	7	1
tert-Butylamine	98.5	1	0.5	71[b]	20[b]	1	2

[a] **1** = 0.13 mmol; PPh_3 = 0.82 g; oct-1-ene = 38 mmol; amine = 58 mmol; V_{total} = 30 ml; T = 80 °C; t = 15 h; P = 0.8 MPa ($CO:H_2$ = 1); solvent = 15 ml THF + 3 ml EtOH. [b] Imines.

(entry 3). Distribution of the products show that hydroformylation and formation of imines took place with significant rates, but these imines are too sterically overcrowded to be hydrogenated since about only 3% of amines were produced.

In conclusion, complex **1** $[Rh_2(\mu\text{-S-Bu}^t)_2(CO)_2(PPh_3)_2]$ appears to be a very useful catalyst for the aminomethylation reaction of non-activated alkenes under mild conditions.

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