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Ruthenium mediated hydroamination of ethylene

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Abstract

We investigated the potential of ruthenium complexes to mediate the hydroamination reaction, using piperidine and ethylene as model substrates. Our main approach was to activate the olefin towards nucleophilic attack by the amine. This might be achieved by co-ordination to a metal centre. We succeeded in identifying ruthenium complexes that mediate this reaction stoichiometrically. We showed that amine co-ordination to ruthenium is strong and that the co-ordinated amine does not take part in the desired reaction. Thus, we tentatively conclude that catalytic results were not achieved due to amine blockage of the essential metal sites. Reaction of higher olefins did not result in any aminated products at all. Dehydroalkylation of piperidine to 2-ethyl-1,2-dehydropiperidine **17** was observed as a side reaction with selected ruthenium compounds. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Hydroamination; Ethylene; Amine; Ruthenium; Homogeneous catalysis

1. Introduction

Amines are of significant industrial importance [1]. Synthetic routes are manifold and diverse. However, the atom efficient amine synthesis via addition of amines to olefins remains one of the challenges in catalysis. Early investigations on this reaction go back to the 1960s and 1970s, when stoichiometric hydroamination reactions were reported [2,3]. The first homogeneously catalysed hydroamination of ethylene with secondary amines was achieved by Coulson with rhodium- and iridium-salts [4]. Rhodium has been of great interest ever since and extensive investigations on rhodium catalysed addition of amines to olefins have been carried out by Taube [5,6] and by Beller [7,8]. Iron and ruthenium compounds were mentioned for the hydroamination reaction in the patent literature [9]. Marks reported the successful intramolecular hydroamination catalysed by lanthanoid metallocenes [10]. These and many more interesting works in this field are summarised in recent reviews covering many approaches in this field of catalysis [11–13].

In summary, there have been extensive investigations, but in general, catalytic hydroamination of non-functionalised olefins has not been satisfactorily realised so far. There is still much potential for finding convincing routes to bring this demanding reaction towards industrial application.

2. Results and discussion

We investigated the potential of ruthenium complexes to mediate the hydroamination reaction, the addition of amines to olefins. The desired reaction of

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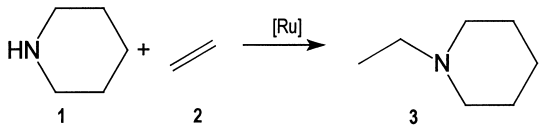


Scheme 1. Hydroamination model reaction.

our model substrates piperidine **1** and ethylene **2** to *N*-ethyl piperidine **3** is shown in Scheme 1.

Ruthenium compounds were chosen according to postulated reaction pathways and their requirements (see Scheme 2). Our main approaches are presented here.

2.1. Reaction mechanism 1 — nucleophilic attack of the amine to the olefin

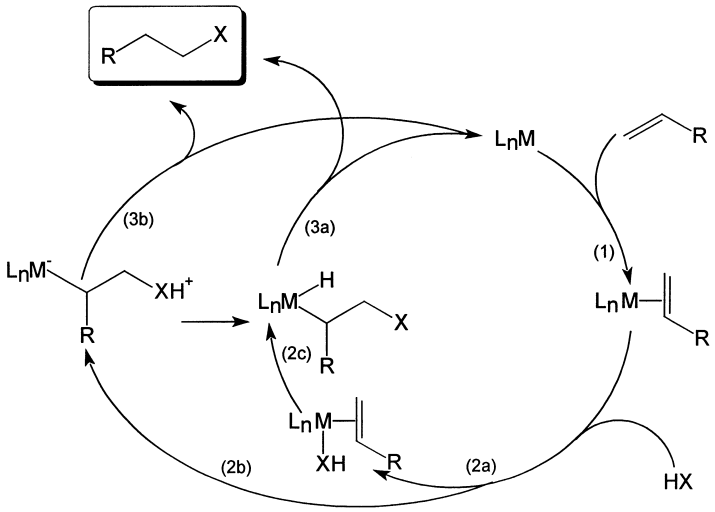
Amine addition to activated olefins is well known. Acrylonitrile, e.g. is even aminated on a technical scale [14,15]. It is the electron withdrawing nitrile group that activates the double bond to undergo nucleophilic attack. An analogous activation of an olefinic bond might be achieved by olefin co-ordination to a metal centre, metal–olefin complexes which exert this behaviour are known from literature. The Wacker–Hoechst process is an industrial example of the required Umpolung of an olefin followed by nucleophilic attack [16]. Umpolung was also described by Bäckvall [17]. Scheme 2 shows the postulated pathways for the hydroamination. Both intramolecular (path a) and intermolecular attack (path b) of the amine are conceivable.

2.1.1. Choice of ruthenium compounds

We started our investigations with ruthenium complexes for which the olefin interactions are known from other catalytic reactions, i.e. hydrogenation: $RuCl_2(PPh_3)_3$ **4** and $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ **5** were applied to our model reaction. Both complexes mediated the addition of piperidine to ethylene in stoichiometric amounts (Table 1). Piperidine concentration was of minor influence. Increased temperature, pressure or reaction time did not result in higher yields. No reaction was observed below 20 bar ethylene pressure and 80°C nor in acetonitrile as solvent, which is referred to its more strongly co-ordinating properties.

2.1.2. Variation of the ruthenium environment

Stoichiometric yields were obtained with complexes **4** and **5**. A reason for the stoichiometric reaction might be that the olefin–ruthenium bond is too weak, the strength of which is determined by the surrounding ligands. We, thus, aimed at varying the electronic environment of the ruthenium centre, but were caught in a dilemma, on the one hand, we aimed at creating an electron-poor ruthenium centre to achieve the Umpolung at the co-ordinated olefin, on the other



Scheme 2. Reaction pathway via nucleophilic attack of the amine to the olefin via (a) intramolecular attack, (b) intermolecular attack.

Table 1
Results for model reaction using ruthenium complexes[a]

Entry	Complex[b]	*t* (hour)	Yield (%)[c]	Selective (%)[d]
1	**4**	24	40	98
2	**4**	65	100	98
3	**5**	65	100	23[e]
4	**6**	65	–	
5	**7**	65	3	98
6	**8**	65	22	98
7	**9**	63	100	98
8	**10**	63	–	
9	**11**	63	–	
10	**12**	63	10	98
11	**13**	63	70	98
12	**14**	63	10	3[e]

[a] 0.33 mmol Ru, 10 ml THF, 10 mmol piperidine, 40 bar ethylene, 100°C.

[b] **4** $RuCl_2(pph_3)_3$; **5** $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$; **6** $RuCl_2(Pme_3)_4$; **7** $RuCl_2[P(Oph)_3]_3$; **8** $RuCl_2[P(OMe)_3]_4$; **9** $[(\eta^5\text{-}C_5H_5)\ Ru(PPh_3)_2(C_2H_4)]^+[BF_4]^-$; **10** $[(\eta^5\text{-}C_5H_5)\ Ru(Pme_3)(C_2H_4)]^+[BF_4]^-$; **11** $[(\eta^5\text{-}C_5H_5)\ Ru(dppe)(C_2H_4)]^+[BF_4]^-$; **12** $[(\eta^5\text{-}C_5H_5)\ Ru(P(p\text{-}C_6H_4F_3)_2(C_2H_4)]^+[BF_4]^-$; **13** $[(\eta^5\text{-}C_9H_7)\ Ru(PPh_3)_2(C_2H_4)]^+[BF_4]^-$ and **14** $[(\eta^6\text{-}C_6H_6)Ru(C_5H_{11}N)]Cl_2$.

[c] Calculated on Ru.

[d] Based on detected products.

[e] See Section 2.3.

hand, π-back donation is known to play a major role in ruthenium–olefin bonds, which is why one might consider electron-rich ruthenium centres for strong olefin co-ordination. We tested the more electron-rich ruthenium complex, $RuCl_2(PMe_3)_4$ **6** and the more electron-poor complexes $RuCl_2(P(OPh)_3)_3$ **7** and $RuCl_2[P(OMe)_3]_4$ **8**. All three complexes gave lower yields. In fact, PPh_3 dissociation was observed from complex $RuCl_2(PPh_3)_3$ **4**, whereas no ligand dissociation was observed from complexes **6**–**8**. This extra free co-ordination site at the ruthenium might be essential for the reaction. After the reaction, co-ordinated amine was observed at complex **4**. Applying the cationic ruthenium centres $[RuCl(PPh_3)_3]^+$ and possibly $[Ru(PPh_3)_3]^{2+}$ to the reaction after Cl-abstraction from **4** with $AgBF_4$ did not result in higher yields.

2.1.3. Investigation of cationic ruthenium–olefin complexes

In a parallel approach, we examined preformed cationic ruthenium–olefin complexes such as $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2(C_2H_4)]^+[BF_4]^-$**9**, for which an external nucleophilic amine attack can be postulated according to Scheme 2, path b.

Stoichiometric amounts of *N*-ethylpiperidine **3** were also obtained from the model reaction (Table 1). More severe reaction conditions did not result in higher yields.

On reaction using complex **9**, a ruthenium–amine bond was again detected. PPh_3 dissociated during reaction. On the other hand, no or hardly any product **3** was obtained when using complexes $[(\eta^5\text{-}C_5H_5)\text{-}Ru(PMe_3)_2(C_2H_4)]^+[BF_4]^-$**10**, $[(\eta^5\text{-}C_5H_5)Ru(dppe)\text{-}(C_2H_4)]^+[BF_4]^-$**11** and $[(\eta^5\text{-}C_5H_5)Ru(P(p\text{-}C_6H_4F)_3)_2(C_2H_4)]^+[BF_4]^-$ **12**, no ligand dissociation was observed either. Once more appearances are that an extra co-ordination site is required for the reaction.

To create this free co-ordination site, the cyclopentadienyl ligand $(\eta^5\text{-}C_5H_5)^-$ was replaced by the indenyl ligand $(\eta^5\text{-}C_9H_7)^-$, for which ring slippage from η^5- to η^3-co-ordination is known in catalytic reaction [18]. In the model reaction, complex $[(\eta^5\text{-}C_9H_7)\text{-}Ru(PPh_3)_2(C_2H_4)]^+[BF_4]^-$ **13** gave 70% yield of **3**. No improvements were achieved.

2.1.4. The role of co-ordinated amine

Regularly, co-ordinated amine was detected after the reaction. Therefore, we investigated the influence of amine co-ordinated to the ruthenium centre. Complex $[(\eta^6\text{-}C_6H_6)Ru(C_5H_{11}N)]Cl_2$ **14**, derived from complex **5**, was examined, since complex **5** mediated the reaction. 1 mmol of the piperidine complex **14** was dissolved in 5 ml THF and heated with no further piperidine addition. Neither this complex nor the Cl-abstracted species, which should also allow ethylene co-ordination, led to detection of the desired product **3**. Even acidic work-up did not release any product. No piperidine **1** had been eliminated either. This is a remarkable result, showing how strongly piperidine is bound to the ruthenium centre. With extra piperidine, yields of **3** using complex **14** were under 10%. A cross experiment with complex **14** and 10 mmol morpholine showed traces of *N*-ethyl morpholine, no *N*-ethyl piperidine **3** was detected at all.

These results show that once formed, the Ru–N co-ordination seems too strong for further catalytic reaction in the hydroamination. Of course, these results cannot prove in situ behaviour, however, we have to conclude that no reaction product nor piperi-

dine could be detected from ruthenium–piperidine complexes.

2.1.5. Substrate variation

No products were observed in any reaction using propene or pentene-1. A cross experiment of the ethylene complex **9** with propene showed traces of *N*-ethyl piperidine **3**. The amines tested were piperidine, morpholine, 2,6-dimethyl piperidine, pyrrolidine, dimethyl amine, ethyl amine, cyclohexyl amine and aniline. Diethyl amine was not examined due to disproportionation to ethyl amine and triethyl amine catalysed by many ruthenium complexes. Generally, morpholine gave 50% lower yields compared to piperidine. Methyl propyl amine was obtained in low yields from dimethyl amine and ethylene. All other amines did not react. This shows that any prediction of amine reactivities in this reaction remains difficult.

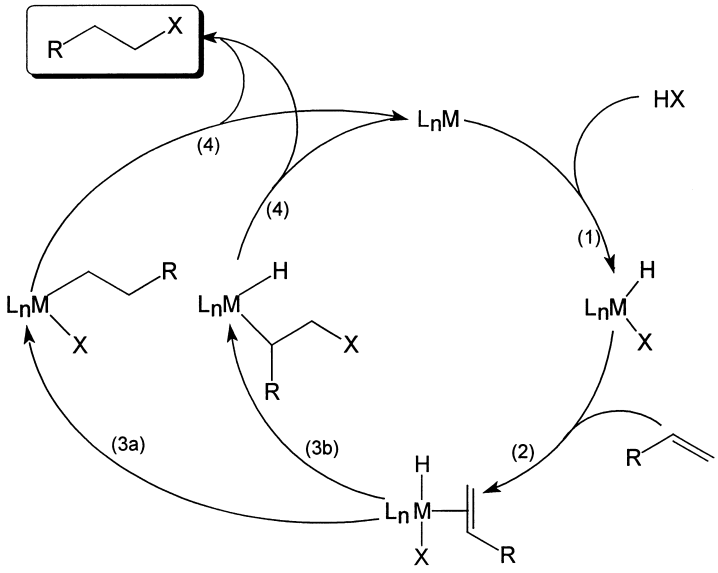
2.2. Reaction mechanism 2 — the hydrocyanation mechanism

The hydrocyanation reaction follows the oxidative addition pathway of HX (HX = HCN) (Scheme 3, path a). The interesting question was whether or not HX could be HNR_2. Consecutive insertion of the olefin into the M–N bond can also taken into consideration and is shown in path b.

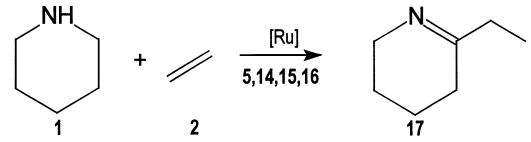
The addition of aniline to norbornene via the oxidative addition of aniline to iridium reported by Casalnuovo, Calabrese and Milstein [19] shows that this mechanism is conceivable. On the other hand, only few oxidative additions of amines to late transition metal centres are known. Overall, it proved difficult to preform amide- or even hydride–amide-complexes due to the general low stability of amide-complexes. All our preliminary experiments showed no hydroamination activity.

2.3. Dehydroalkylation

An interesting side reaction observed when applying complexes $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ **5**, $[(\eta^6\text{-}C_6H_6)Ru(C_5H_{11}N)]Cl_2$ **14**, $[Ru(COD)Cl_2]_2$ **15** or $RuCl_3{\cdot}3H_2O$ **16** was the dehydroalkylation of piperidine **1** to 2-ethyl-1,2-dehydropiperidine **17** (Scheme 4). At present, turn over numbers are low, but on optimisation, this could become a very interesting reaction since cyclic 2-alkylimines such as **17** are very useful synthons for alkaloids [20,21].



Scheme 3. Reaction pathway via oxidative addition of the amine (HX) and (a) olefin insertion into the M–H bond, (b) olefin insertion into the M–X bond.



Scheme 4. Dehydroalkylation.

3. Experimental

3.1. General methods

All solvents were distilled prior to use under an argon atmosphere according to common procedures. Piperidine, morpholine, 2,6-dimethylpiperidine, pyrrolidine, dimetylamine, ethylamine, cyclohexylamine and aniline were purchased from Aldrich and used as-received after degassing. Ruthenium compounds were prepared from $RuCl_3 \cdot 3H_2O$ according to literature methods.

3.2. Analytical methods

GC-analysis was done on Siemens-Sichromat apparatus using a 50 m Pona HP-FS. NMR-data were measured on a Bruker DPX 300: ^{1}H (300 MHz) and ^{13}C (75 MHz) with chemical shifts relative to the solvents used. Elemental analysis was done on a CHN-analyser 1106 from Carlo Erba. IR spectra were taken on a Nicolet P510-spectrometer.

3.3. Preparation of $[(\eta^6\text{-}C_6H_6)Ru(C_5H_{11}N)]Cl_2$ **14**

A slurry of 2 mmol of $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ **5** and 5 mmol piperidine in 5 ml THF was stirred overnight at room temperature. Meanwhile, the colour changed from brown/red to yellow. The solid product was filtered, washed with ethanol and acetone and dried in high vacuum. It was recrystallised from chloroform (yield 85%).

^{1}H-NMR δ ($CDCl_3$) = 1.39–1.60 (m, 6H, C$\underline{H}_2$); 3.02 (m, 2H, NH–C$\underline{H}_{ax}$); 3.82 (m, 2H, NH–C$\underline{H}_{eq}$); 5.55 (s, 6H, Ar–H).

^{13}C-NMR δ ($CDCl_3$) = 24.2 (NH–CH_2–$\underline{C}H_2$–CH_2); 29.2 (NH–CH_2–$\underline{C}H_2$); 56.4 (NH–$\underline{C}H_2$); 83.0 (Ar–$\underline{C}$).

Elemental analysis: C (calc. 31.7%, found 31.9%); H (calc. 3.99%, found 3.97%); N (calc. 3.08%, found 3.06%).

3.4. Hydroamination reactions

A 75 ml stainless steel autoclave was charged with the catalyst mixture, piperidine, pressurised to 40 bar ethylene and stirred for the given times at the given temperatures. After the reaction, the autoclave was cooled to 0°C, vented carefully and the reaction mixture was flashdistilled and analysed by GC. The catalyst residue was analysed by NMR, when appropriate.

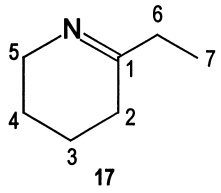
3.5. Experiments with piperidine complex $[(\eta^6\text{-}C_6H_6)Ru(C_5H_{11}N)]Cl_2$ **14**

About 1 mmol of $[(\eta^6\text{-}C_6H_6)Ru(C_5H_{11}N)]Cl_2$ **14** was dissolved in 5 ml THF and heated for 66 h with/without further piperidine addition at 100 and 180°C, respectively. Further work-up followed the described procedure.

3.6. Characterisation and identification of 2-ethyl-1,2-dehydropiperidine **17**

2-Ethyl-1,2-dehydropiperidine **17** was observed as a by-product when using $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$ **5**, $[(\eta^6\text{-}C_6H_6)Ru(C_5H_{11}N)]Cl_2$ **14**, $[Ru(COD)Cl_2]_2$ **15** or $RuCl_3 \cdot 3H_2O$ **16**. It was isolated with preparatory GC.

NMR



17

^{1}H-NMR δ ($CDCl_3$) = 1.066 (t, 3H, H7);1.55 (m, 2H, H4); 1.67 (m, 2H, H3); 2.13 (m, 4H, H2, H6); 3.55 (m, 2H, H5).

^{13}C-NMR δ ($CDCl_3$) = 10.6 (C7); 19.6 (C3); 22.1 (C4); 28.9 (C6); 33.8 (C2); 49.3 (C5); 171.4 (C1).

IR ν (in $CHCl_3$) = 2800 (N–CH_2–), 1680 (C=N).

4. Summary and conclusions

Ruthenium compounds could be identified to mediate the hydroamination reaction of ethylene and

piperidine in stoichiometric amounts. In many cases, amine co-ordination was observed after the reaction. Experiments with preformed ruthenium–amine complexes showed no reaction of the bound amine nor was amine eliminated from the complex.

Thus, none of the two paths shown in Scheme 2 is exactly followed. An extra co-ordination site seems to be necessary. A conclusive answer to the actual pathway cannot be given yet. We tentatively conclude that co-ordination of the amine to the ruthenium centre blocks the olefin co-ordination site essential for the catalytic reaction. This is seen as a potential hindrance for the realisation of catalytic hydroamination with these systems.

Acknowledgements

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