Catalysis Science & Technology

PAPER

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Methylformate as replacement of syngas in one-pot catalytic synthesis of amines from olefins

Cite this: *Catal. Sci. Technol.*, 2014, 4, 540

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Received 30th October 2013,
Accepted 14th November 2013

DOI: 10.1039/c3cy00862b

www.rsc.org/catalysis

A new general approach for the one-pot hydroaminomethylation of olefins using methylformate as formylating agent instead of synthesis gas (syngas) has been proposed. Herein we report that a Ru–Rh catalytic system demonstrates high activity in a tandem conversion of a series of *n*-alkenes into amines using methylformate with yields 58–92% (6 h). The selectivity for the normal amine reached 96% with catalysis by the Ru carbonyl complex $Ru_3(CO)_{12}$, with an overall yield of 55% with respect to amine in this instance. The addition of the Rh complex to Ru catalytic system, sharply increased the hydroaminomethylation rate of both the terminal and internal alkenes and increased the yield of amines to 82–93% (6–12 h).

Introduction

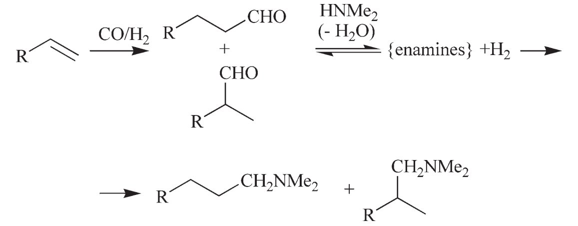
Tandem transformations provide important advantages such as the formation of several bonds and elaboration of the compound structure in a single step. This is an effective pathway for economical synthesis. An important reaction of this type is the hydroaminomethylation of olefins which is a one-pot process that occurs through a sequence of hydroformylation of an unsaturated compound followed by reductive amination of the resulting aldehydes as shown in Scheme 1.

The hydroaminomethylation has continued to draw the attention of researchers since the time of its discovery by Reppe at BASF.[1] This is evident from the large number of publications, both reviews and articles[2–6] dedicated to the syntheses of amines from olefins with terminal and internal double bonds,[7,8] complicated N-containing organic compounds, *e.g.*, heterocycles,[9,10] N-containing macrocycles,[11–13] and dendrimers.[14–16] Reductive aminomethylation of olefins while using Rh complexes with bidentate phosphine ligands that are highly active in hydroformylation have been used for the regioselective preparation of amines.[17–20] The performance of this process in alternative solvents, *i.e.*, ionic liquids[21] and in supercritical ammonia[22] has also been reported. The amination reaction can be applied to the synthesis of various compounds possessing biological activity including a variety of drugs.[23–31] Hydroaminomethylation of higher alkenes for the preparation of "fatty" amines, is an especially valuable application since they are used in the manufacture of surfactants, resins, plastics, crop protectors, *etc.*[32]

Usually, hydroaminomethylation occurs at a high temperature and in presence of a high pressure of syngas enriched in H_2. The use of such a gaseous mixture is unfavorable primarily from the context of ecological and technical safety.

The solution to this problem could be the use of compounds that can act as alternate sources of CO and H_2.[33] Thus, a source of CO for the carbonylation of iodobenzene could be 2-pyridylmethylformate,[34] dimethylformamide (DMF) for the carbonylation of *p*-bromotoluene and iodoaryls,[35,36] various formamides and formates for the carbonylation of norbornene,[37] formic acid and its salts for the hydroxycarbonylation of vinyl, arylhalides and triflates,[38,39] aldehydes in the catalytic Pauson–Khand-type reactions,[40] formaldehyde in the hydroformylation of unsaturated compounds,[41,42] and metal carbonyls, in particular molybdenum carbonyl in the carbonylation of haloaromatic compounds.[43–45]

Methylformate (MF) is promising replacements for syngas in the hydroformylation and hydrocarbonylation reactions. It is a highly reactive compound owing to the presence of both an ester and a labile H atom, and is used as a source of high-purity CO.[46] It was shown that catalytic decomposition of



Scheme 1 General route for the hydroaminomethylation of olefins.

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methylformate in the presence of water (the variation of the water gas shift reaction) leads to the formation of a mixture of gases, the principal components of which are CO and H_2.[46–50] Methylformate was used as carbonylating agent for the catalytic conversion of phenol to methyl phenyl carbonate,[51] in the hydroesterification of alkenes catalysed by Ru complexes[52–59] and hydroformylation of various linear and cyclic (C_5–C_8) alkenes[60,61] using Ru and bimetallic catalytic systems. It should be emphasized that in all these cases indicated the yields of final products (alcohols) rarely exceeded 50% because of the formation of alkane, especially for higher olefins. Thus the yield of octane was 76% in the hydroformylation of 1-octene.[61]

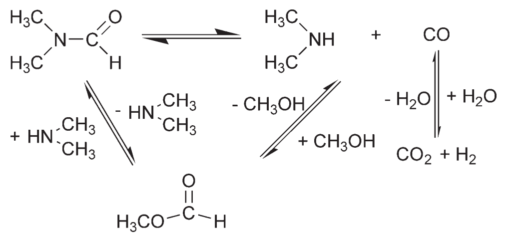
Herein for the first time we report results of the effective use of methylformate as green reagent in the hydroaminomethylation reaction of olefins C_5–C_{16} catalyzed by Ru and Ru–Rh systems with excellent yields of amines with the formation of alkane not exceeding 5%.

Results and discussion

The substitution of methylformate for syngas requires the use of catalytic system which provides the realization of the four processes simultaneously. The system should be active both in the reaction of aqueous methylformate decomposition to form a mixture of CO and H_2 *via* the gas-shift reaction and in the hydroformylation of alkene to form aldehydes which are the first intermediates in the hydroaminomethylation. The metal complex should also participate effectively in the hydrogenation of the second intermediate, which is an enamine formed *via* the reaction of dimethylamine and the aldehyde, in order to produce the final product (amine). The metal centre should also be capable of carrying out these steps with a high rate and specificity. Moreover, the side reaction of DMF formation can run due to dimethylamine (DMA) carbonylation and its interaction with MF. DMF is acting as amine source instead of DMA when syngas used. While using DMF as only formylating agent hydroaminomethylation does not take place.[62]

The equilibrium reactions in the presence of the three components are proposed to be as shown in Scheme 2.

Therefore similarly to the use of syngas the most promising aminating agent is a solution of dimethylamine in dimethylformamide.[61] The use of DMF as the solvent avoids the non-productive consumption of DMA and MF (Scheme 2).



Scheme 2 Equilibrium between the components of the hydroaminomethylation.

This in turn substantially increases the effectiveness of the process.

All the processes indicated can run on the Ru and Rh complexes. We studied the hydroaminomethylation of 1-nonene in MF using a monometallic catalyst system where carbonyl complexes of Ru and Rh acted as catalyst precursors (Table 1). It should be emphasized that the Ru complexes are more active than those of Rh in the hydroformylation of alkenes with methylformate.[48,52,55,60,61,63,64]

Carbonyl complexes such as $Ru_3(CO)_{10}$ and $Rh(acac)(CO)_2$ in combination with PPh_3 were used as the catalysts in most of the experiments. The reaction conditions and catalytic systems were selected based on the decomposition data for MF.[48,61] The Rh and Ru catalysts actively catalyze this process and formed a $CO/H_2 = 1/3$ gas mixture at a MF/H_2O ratio of 3 that was optimal for performing the hydroaminomethylation. We used the excess of PPh_3 because it increases both the linear products yield in the hydroformylation and hydroaminomethylation[64–68] with syngas and the conversion of methylformate during its decomposition.[47,64]

In the course of the reaction with MF in the absence of syngas, the principal linear and branched *N*,*N*-dimethyldecylamines in addition to intermediates such as aldehydes and enamines of the normal and isomerized structures and products originated from the hydrogenation and isomerization of the double bond were identified as shown in Scheme 3. Alcohols and products from the aldol condensation of aldehydes and other side products were not observed.

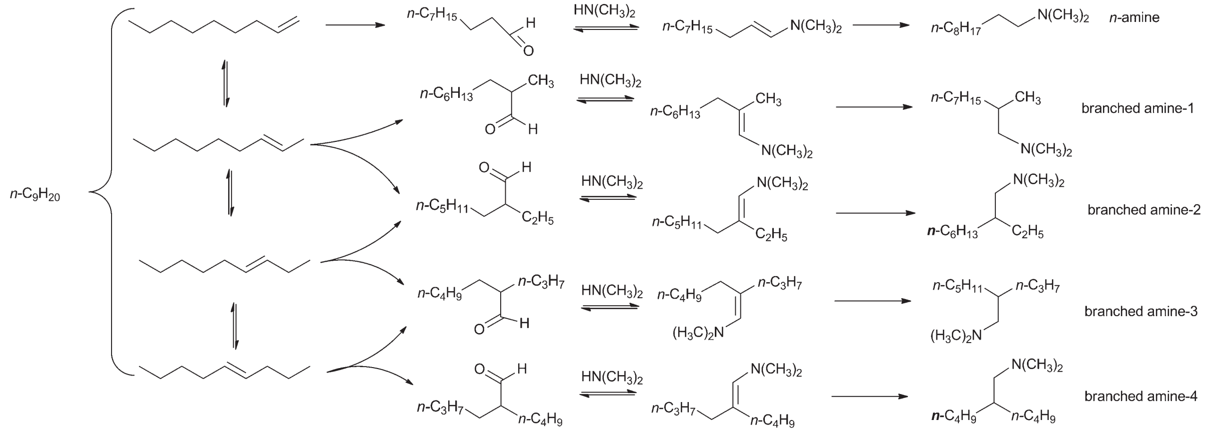
The use of the Ru catalyst was attractive as it leads to high selectivity for the normal product only in conversion and reaches as much as 60%. The best result was 55% total yield of the amines with 96% selectivity and was achieved at a Ru concentration of 2.52 mol% (Table 1, entry 4) due to the essential difference in the rates of hydroformylation in internal and terminal double bonds. Thus the increase of the reaction time from 12 to 36 h led to the increase of conversion by 11% at the decrease of selectivity by 3% (Table 1, entry 2 and 3). At high temperature the selectivity decreases due to the partial involvement of isomeric alkenes in the reaction. Neither aldehyde nor enamine was observed in the final products while using $Ru_3(CO)_{12}$. The reaction occurred much more slowly than that with rhodium because of the lower activity of ruthenium phosphine complexes in hydroformylation.[69] The results are in good agreement with literature data. The Ru systems are considerably more active for the hydrogenation and much less active for the hydroformylation reaction, especially of internal double bonds.[70–75] In addition the Ru-catalyst is much more effective in syngas formation from MF. Its activity is twice as much in the presence of the amines.[76–78]

The Rh system was more active. The use of the Rh complex resulted in high yields of the amines, the fraction of *N*,*N*-dimethyldecylamine was less than 30% at 130 °C and only 15% at 170 °C (Table 1; entries 8, 9). A significant amount of aldehydes (with an isomerized skeleton) and a small amount of enamines remained after 12 h at 130 °C.

Table 1 Hydroaminomethylation of 1-nonene using monometallic catalytic systems[a]

Entry	Mol%	Temperature [°C]	Time, h	Reaction mixture composition[b] [%]						% *n*-amine[c]
				1-Nonene	Isononenes	Nonane	Aldehydes	Enamines	Amines	
$Ru_3(CO)_{12}$										
1	0.63	130	12	4	52	5	0	0	39	92
2	1.26	130	12	3	44	6	0	0	47	91
3	1.26	130	36	4	25	13	0	0	58	88
4	2.52	130	12	2	32	7	0	3	55	96
5	0.63	170	12	4	26	7	1	1	61	66
6	1.26	170	12	3	31	15	0	0	51	82
$Rh(acac)(CO)_2$										
7	0.63	130	12	0	5	13	22	8	52	50
8	0.63	130	36	0	0	14	0	0	86	30
9	0.63	170	6	0	0	6	0	2	92	15

[a] *Reaction conditions*: PPh_3 (8.3×10^{-4} mol), 1-nonene (6.2×10^{-4} mol), DMA (5.6×10^{-3} mol), DMF (1 mL), methylformate (2 mL), H_2O (0.2 mL), 12 h. [b] The yield of amines was determined using GC with *n*-decane as internal standard. [c] % *n*-amine = [(yield of *n*-amine)/(yield of amines)] × 100%.



Scheme 3 Products observed during the hydroaminomethylation using methylformate.

After 36 h the reaction went to completion and only amines (total yield: 86%, Table 1, entry 8) were observed in the products. The fraction of *n*-amine was 30%. The complexes of rhodium and PPh_3 in the hydroformylation with syngas are very active both in the terminal and internal olefins.[65]

Due to the isomerisation of alkenes high amounts of iso-amines are formed. In addition the Rh catalyst was most active in the hydroformylation and far less active in the hydrogenation of enamines.[69]

Bimetallic catalysts have been used successfully for many catalytic processes, including olefin aminomethylation in the presence of synthesis gas.[79] Earlier we showed[62] that the addition of ruthenium carbonyl to rhodium systems leads to the essential increase of catalytic activity at the retained selectivity of *N*,*N*-dimethyldecylamine up to 74%. The most effective was the system containing 3.9×10^{-6} mol $Rh(acac)(CO)_2$ and between 3.9×10^{-6} mol and 15.6×10^{-6} mol $Ru_3(CO)_{12}$. Therefore we studied the behavior of bimetallic Ru–Rh systems in hydroaminomethylation by methylformate. We studied the influence of the amount of Rh-complex in presence of a fixed amount of Ru carbonyl on the yield and selectivity towards the formation of normal amine (Fig. 1). The reaction with a low Rh content occurred rather slowly but with excellent selectivity (70–95% of normal amine). At a Ru/Rh ratio greater than three (0.45 mol% Rh), the amount of isomerized nonenes decreased sharply and the overall yield of amines reached 80% with the yield of *N*,*N*-dimethyldecylamine remaining at the previous level, *i.e.*, the contribution of the reactions occurring at the internal double bonds increased substantially upon reaching this concentration (Fig. 1).

Thus, the principal product was the branched amine-1 that can be formed from both 1-nonene and 2-nonene (Fig. 2).

Fig. 3 and 4 present the results obtained at 170 °C using Ru/Rh ratios 3 and 12 in the catalytic system. Amines produced almost quantitatively (>90%), the majority of it was formed in the first two hours. The fraction of *n*-decanal in the aldehydes was less than 2–3%. After two hours, the overall yield of amines increased due to the accumulation of branched products that were formed by the hydroformylation of isomeric nonenes containing internal double bonds that reacted more slowly. With this, the selectivity for the *n*-amine did not actually change. The amount of unreacted aldehydes that was converted into the isomeric amines decreased sharply. A comparison for the change of selectivity for the formation of aldehydes in case of the Ru/Rh = 3 and Ru/Rh = 12 catalytic system indicated that increasing the Ru concentration

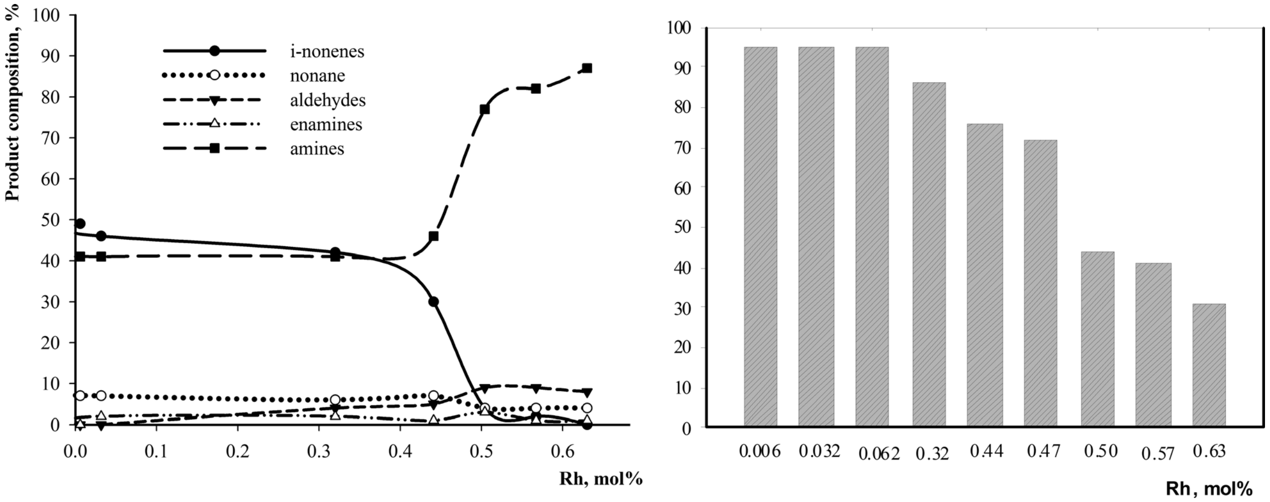


Fig. 1 Hydroaminomethylation of 1-nonene. *Reaction conditions*: $Ru_3(CO)_{12}$ (7.8×10^{-6} mol), PPh_3 (8.3×10^{-4} mol), 1-nonene (6.2×10^{-4} mol), DMA (5.6×10^{-3} mol), DMF (1 mL), methylformate (2 mL), H_2O (0.2 mL), 130 °C, 12 h, conversion of 1-nonene 100%.

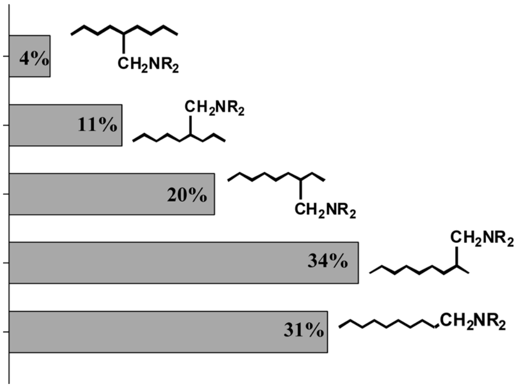


Fig. 2 Isomeric composition of amines after hydroaminomethylation of 1-nonene in MF. *Reaction conditions*: = $Rh(acac)(CO)_2$ (3.9×10^{-6} mol), $Ru_3(CO)_{12}$ (7.8×10^{-6} mol), PPh_3 (8.3×10^{-4} mol), olefin (6.2×10^{-4} mol), DMA (5.6×10^{-3} mol), DMF (1 mL), methylformate (2 mL), H_2O (0.2 mL), 130 °C, 12 h.

enabled the aldehydes to be consumed at much faster rates. Even after conducting the reaction for 5 h the amount of alkenes is 4% and that of aldehydes is 10% for the ratio Ru/Rh = 3. At the ratio Ru/Rh = 12 the alkenes are not observed at all, and the amount of aldehydes does not exceed 2%.

Our experiments on the use of different catalytic precursors showed (Fig. 5) that combinations of other complexes and salts of Rh and Ru could also be used successfully to perform this reaction with high chemoselectivity. However it can be seen that the fraction of *N*,*N*-dimethyl-*n*-decylamine formed decreased if Rh-cyclooctadienyl complexes or trivalent Ru salts were used. This is because the complexes mentioned facilitated isomerization.[80]

The Ru–Rh catalytic system was highly active for the hydroaminomethylation of a number of unsaturated compounds (Table 2). The yields of amines from the linear C_5–C_9 alkenes reached 90% after 6 h. The reaction was slightly

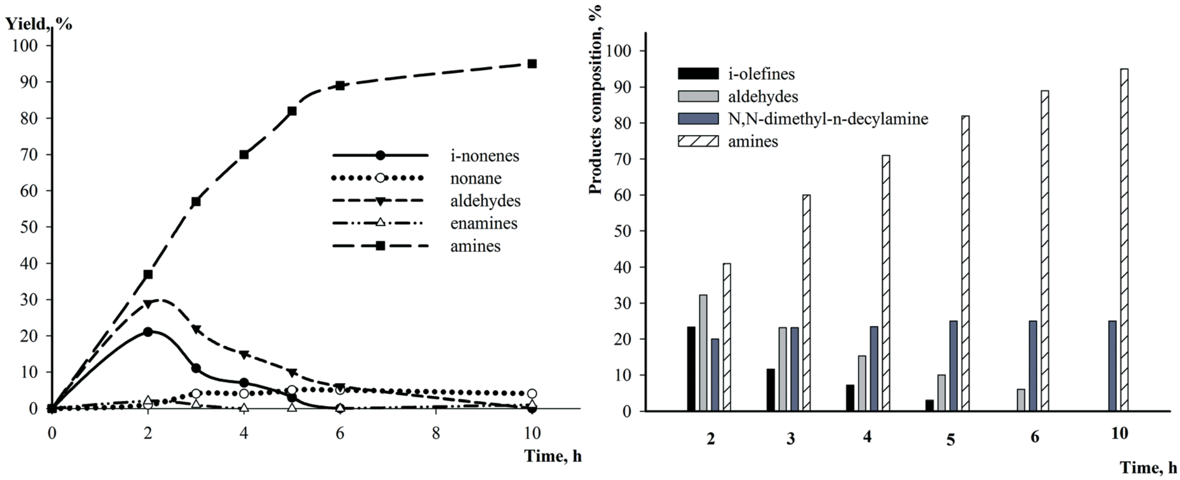


Fig. 3 Hydroaminomethylation of 1-nonene at ratio Ru/Rh = 3. *Reaction conditions*: $Rh(acac)(CO)_2$ (3.9×10^{-6} mol), $Ru_3(CO)_{12}$ (3.9×10^{-6} mol) PPh_3 (8.3×10^{-4} mol), 1-nonene (6.2×10^{-4} mol), DMA (5.6×10^{-3} mol), DMF (1 mL), methylformate (2 mL), H_2O (0.2 mL), 170 °C. Conversion of 1-nonene 100% after 2 h.

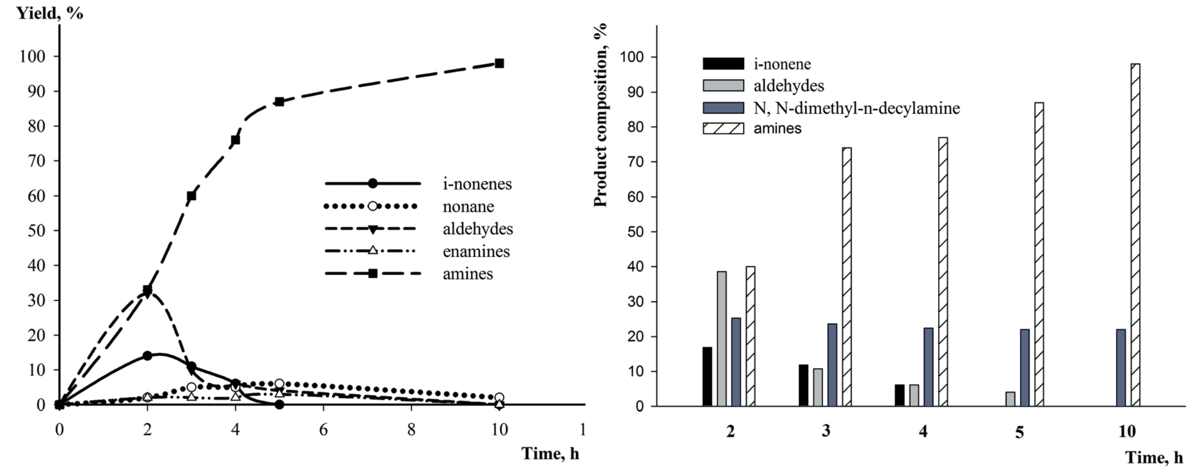


Fig. 4 Hydroaminomethylation of 1-nonene at ratio Ru/Rh = 12. *Reaction conditions*: $Rh(acac)(CO)_2$ (3.9×10^{-6} mol), $Ru_3(CO)_{12}$ (15.6×10^{-6} mol) PPh_3 (8.3×10^{-4} mol), 1-nonene (6.2×10^{-4} mol), DMA (5.6×10^{-3} mol), DMF (1 mL), methylformate (2 mL), H_2O (0.2 mL), 170 °C. Conversion of 1-nonene 100% after 2 h.

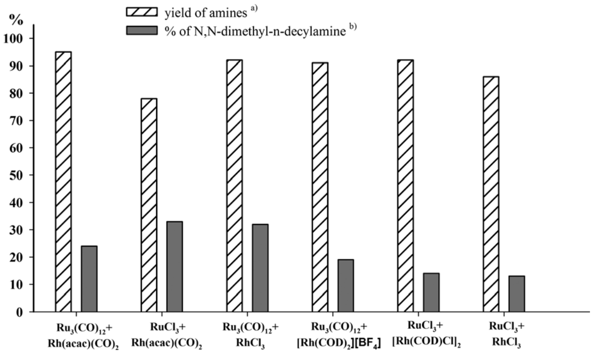


Fig. 5 Hydroaminomethylation of 1-nonene using various catalytic precursors. *Reaction conditions*: PPh_3 (8.3×10^{-4} mol), 1-nonene (6.2×10^{-4} mol), DMA (5.6×10^{-3} mol), DMF (1 mL), methylformate (2 mL), H_2O (0.2 mL), 170 °C, 12 h. Conversion of 1-nonene – 100%. a) Yields of amines were determined using GC with *n*-decane as internal standard. b) % of *N*,*N*-dimethyl-*n*-decylamine = [(yield of % of *N*,*N*-dimethyl-*n*-decylamine)/(yield of amines)] × 100%.

slower for higher *n*-olefins (C_{10}–C_{16} alkenes) and much worse for cyclic ones. It is interesting that an internal alkene such as 3-heptene was just as reactive as terminal 1-heptene. As expected, only the yields of linear *N*,*N*-dimethyloctylamine differed substantially (32 and 7%, respectively). In general, the selectivity towards the formation of linear products decreased with increasing length of the carbon chain from 50% (for 1-pentene) to 20% (for 1-nonene). This resulted from the considerable increase in the number of possible isomeric alkenes with an internal double bond from which amines with only the iso-structure can be formed. Thus, there can be only one such olefin for 1-pentene (*i.e.* 2-pentene); 3 for 1-octene (*i.e.* 2-octene, 3-octene, and 4-octene); 4 for 1-decene (*i.e.* 2-decene, 3-decene, 4-decene, and 5-decene) *etc.*

The corresponding amines were also readily formed if other amine components (Table 3) and MF were used. For these instances, the reaction was carried out in MF/amine/alkene and was accompanied by the formation of the corresponding formamide from the amine and MF.

A significant amount of unreacted aldehydes remained in the reaction mixture even after 12 h at 130 °C when morpholine and piperidine were used, in contrast to dimethyl and diethylamines. In analogy with dimethylamine, the structure of the amines formed was determined from the isomerization of the starting olefin. In all the instances, the maximum fraction observed was that of the branched amine-1; followed by the *n*-amine (Fig. 6).

Experimental

All reagents were purchased from either Aldrich Chemicals or Acros Chemicals and were of high purity. Water was distilled twice under a N_2 atmosphere. All liquid reagents and solvents were degassed by bubbling N_2 for 15 min before use or by two freeze–pump–thaw cycles.

$Ru_3(CO)_{12}$,[81] $[Rh(COD)Cl]_2$ and $[Rh(COD)_2]^+BF_4^-$(ref. 82) were prepared according to literature methods. Dimethylamine (DMA) was used as a solution (25%) in DMF that was prepared as follows: a two-necked flask equipped with a dropping funnel and gas outlet tube was charged with base (KOH or NaOH). A saturated solution of dimethylamine hydrochloride in water was added dropwise. The released gaseous DMA was passed into an ice-cooled container containing DMF. The mass fraction of dissolved DMA in the solution was determined from the change in mass of the DMF and was monitored by GC.

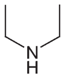
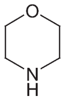
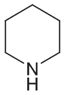
The hydroaminomethylation was carried out in a steel thermostatted custom-made autoclave (7 mL) equipped with a magnetic stirrer. The following general order of operations was carried out during the experiments: catalytic precursor (Rh- and/or Ru in the required amounts), PPh_3 (0.214 g, 0.83 mmol), olefin (0.614 mmol), MF (2 mL), H_2O (0.2 mL), 25% DMA in DMF (1.3 mL) (or 0.056 mmol of a different amine) were placed into the autoclave. Then the reactor was

Table 2 Hydroaminomethylation of various substrates[a]

Olefin	Time [h]	Reaction mixture composition[b] [%] 1-Alkene	Isoalkenes	Alkane	Aldehydes	Enamines	Amines	% *n*-amine[c]
1-Pentene	6	2	0	6	0	0	92	48
1-Hexene	6	0	0	6	1	1	92	36
1-Heptene	6	7	7	2	0	2	82	39
3-Heptene	6	0	4	3	0	0	93	8
1-Octene	6	6	4	2	0	0	88	17
1-Nonene	6	5	6	1	0	1	87	19
1-Decene	6	11	27	2	1	1	58	29
1-Decene	12	0	0	6	0	6	88	23
1-Undecene	12	0	0	6	0	12	82	20
1-Tetradecene	12	0	0	6	7	8	79	20
1-Hexadecene	12	16	11	7	0	7	59	29
Cyclohexene	12	64	—	0	3	9	24	100
Cycloheptene	12	87	—	0	0	4	9	100
Vinylcyclohexane	6	7	15	4	3	4	77	66
Allylbenzene	6	11	25	3	0	1	60	27
Propenylbenzene	6	0	39	5	0	0	56	—

[a] *Reaction conditions*: Rh(acac)(CO)$_2$ (3.9×10^{-7} mol), Ru$_3$(CO)$_{12}$ (3.9×10^{-6} mol), PPh$_3$ (8.3×10^{-4} mol), olefin (6.2×10^{-4} mol), DMA (5.6×10^{-3} mol), DMF (1 ml), methylformate (2 ml), H$_2$O (0.2 ml), 170 °C. [b] The reaction mixture composition was determined using GC with *n*-decane or *n*-octane as internal standard. [c] % *n*-amine = [(yield of *n*-amine)/(yield of amines)] × 100%.

Table 3 Hydroaminomethylation of 1-nonene with amines[a]

Amine	Temperature [°C]	Time [h]	Reaction mixture composition[b] [%] Hydrocarbons	Aldehydes	Enamines	Amines	% *n*-amine[c]
	130	6	53	4	4	43	91
		12	25	15	—	60	72
	170	6	14	1	5	80	36
	130	6	35	47	2	15	87
		12	22	48	4	26	85
	170	6	5	7	18	70	31
	130	6	29	22	8	41	68
		12	22	19	7	52	62
	170	6	7	3	11	79	33

[a] *Reaction conditions*: Rh(acac)(CO)$_2$ (3.9×10^{-6} mol), Ru$_3$(CO)$_{12}$ (7.8×10^{-6} mol), PPh$_3$ (8.3×10^{-4} mol), 1-nonene (6.2×10^{-4} mol), amine (5.6×10^{-3} mol), methylformate (2 ml), H$_2$O (0.2 ml), 170 °C, 12 h. [b] Reaction mixture composition was determined using GC with *n*-decane as internal standard. [c] % *n*-amine = [(yield of *n*-amine)/(yield of amines)] × 100%.

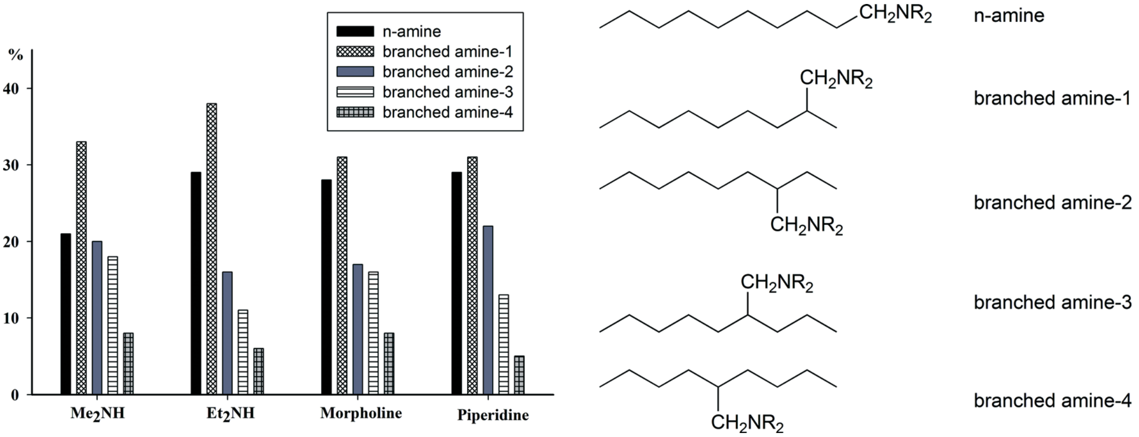


Fig. 6 Isomeric compositions of amines after hydroaminomethylation of 1-nonene in MF using various amines. *Reaction conditions*: Rh(acac)(CO)$_2$ (3.9×10^{-6} mol), Ru$_3$(CO)$_{12}$ (7.8×10^{-6} mol), PPh$_3$ (8.3×10^{-4} mol), 1-nonene (6.2×10^{-4} mol), amine (5.6×10^{-3} mol), methylformate (2 mL), H$_2$O (0.2 mL), 170 °C, 12 h.

heated either to 130, 150, or 170 °C. The reaction time was varied within the range of 2–36 h. After the reaction was complete, the autoclave was cooled to room temperature and the pressure was slowly released before opening it. An internal standard was added before analyzing the products by GC. The analysis was carried out on an HP 6990 chromatograph with a flame-ionization detector, SE-30 column (30 m × 0.25 mm), and temperature programming from 90 to 230 °C. Each experiment was repeated a minimum of two times in order to obtain reliable results.

Conclusions

Ru–Rh catalytic systems were found to be highly active in a tandem one-pot conversion of a series of alkenes into amines using MF as the formylating agent instead of syngas. The yields of the amines were >90%. The selectivity for the formation of the normal amine reached 96% in case of catalysis by the Ru carbonyl complex $Ru_3(CO)_{12}$, the overall yield of amines in this instance was 55%. Adding a Rh complex with a fixed amount of Ru sharply accelerated the hydroaminomethylation of both the terminal and internal olefins.

The results indicate that the use of MF as an alternative source of syngas for the development of new approaches towards the synthesis of higher amines from alkenes is promising.

Acknowledgements

This work was supported financially by the Ministry of the Russian Federation for Education and Science under the auspices of the Federal Targeted Program "Scientific and Scientific-Pedagogical Departments of Innovation Russia" for 2009–2013 (Program Activity 1.2.1, natural sciences; grant no. 8449/2012-1.2.1-12-000-1004-005). We thank Dr. Jeff Scheibel (P&G Chemicals) who provided some technical insights to the research programme.

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