

The azamacrocyclic derivatives of $H_4Ru_4(CO)_{12}$ and their reactivity with CO and catalytic activity in the methanol carbonylation and in the water–gas shift reaction

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Abstract

The reactions of $H_4Ru_4(CO)_{12}$ with cyclic triazaligands result in the formation of $[LH]^+[H_3Ru_4(CO)_{12}]^-$ salts, (L = 1,4,7-triazacyclononane (1), 1,4,7-trimethyl-1,4,7-triaza-cyclononane (2), 1,5,9-triazacyclododecane (3) and 1,5,9-trimethyl-1,5,9-triazacyclododecane (4)). The compounds were synthesized by refluxing $H_4Ru_4(CO)_{12}$ in hexane followed by precipitation with the corresponding ligand. This is a convenient direct single-step synthetic route to produce $[H_3Ru_4(CO)_{12}]^-$ ion with a high yield. The compounds have been characterized by elemental analysis and spectroscopic measurements. In the 1H NMR spectra they showed a fluxional behavior. Reactivity towards CO at elevated temperature, and the catalytic activity of the new compounds in the water–gas shift reaction (WGS) and in the carbonylation of methanol, have been discussed. © 1997 Elsevier Science S.A.

Keywords: Cluster; Triaza ligand; Synthesis; Reactivity; Homogeneous catalysis; Azamacrocycle

1. Introduction

The chemistry of azamacrocycles has been quite widely researched during the last few decades [1]. Cyclic triamines have been found to form many stable complexes with transition metals, for example with groups 4A, 5A, 6A, 7A, 8, 1B and 3B metals [1]. Most of these complexes are monomeric, but several dinuclear metal complexes are also known, for example with molybdenum, tungsten, iron, ruthenium, cobalt, rhodium and copper. For cyclic diamines, there is one example with 1,2-diazine and metal cluster compound. The crystal structure of a derivative of $Ru_3(CO)_{12}$, in which two *cis* axial CO ligands are replaced by the bidentate ligand 1,2-diazine (pyridazine) has been determined [2].

However, there are very few studies with cyclic triamines and metal carbonyl complexes. Metal carbonyl complexes with macrocyclic azaligands have been prepared at least for molybdenum, chromium and tungsten, which form monomeric complexes with 1,4,7-triazacyclononane, 1,4,7-trimethyl-1,4,7-triazacyc-

lononane and 1,5,9-triazacyclododecane [3–7]. No studies of cyclic triamines with metal carbonyl clusters have been published yet.

We have studied reactions of four cyclic triamines 1,4,7-triazacyclononane, 1,4,7-trimethyl-1,4,7-triazacyclononane, 1,5,9-triazacyclododecane and 1,5,9-trimethyl-1,5,9-triazacyclododecane (Fig. 1) with $H_4Ru_4(CO)_{12}$ cluster, and found that all azaligands form an anionic complex with $H_4Ru_4(CO)_{12}$ cluster producing salts: $H_3Ru_4(CO)_{12}$ (1,4,7-triazacyclononane) (1), $H_3Ru_4(CO)_{12}$ (1,4,7-trimethyl-1,4,7-triazacyclononane) (2), $H_3Ru_4(CO)_{12}$ (1,5,9-triazacyclododecane) (3) and $H_3Ru_4(CO)_{12}$ (1,5,9-trimethyl-1,5,9-triazacyclododecane) (4), which all have been characterized by elemental and spectroscopic analysis.

We have also studied these anionic compounds in catalytic reactions examining first the reactivity towards CO, then the catalytic activity of the new precursors in the carbonylation of the methanol and in the water–gas shift reaction (WGS). Also, the possible active species of the catalyst precursors during the catalytic reactions have been discussed.

Methyl formate is a useful compound in synthetic chemistry [8,9]. It can be used as a starting material for

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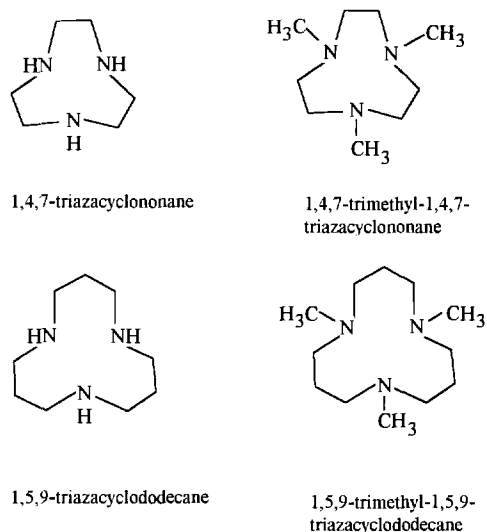
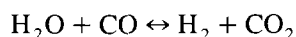


Fig. 1. Schematic structures of the four triazaligands.

the production of formic acid and its derivatives. It can be prepared in large volume from syngas or other C_1 molecules with different catalytic processes. The most common industrial technology to produce methyl formate is the carbonylation of methanol, which is usually catalyzed by alkali methoxide catalysts. They are very efficient but sensitive to even a trace amount of water or carbon dioxide. Transition metal catalysts could prevent the effect of impurities; Choi et al. [10] have shown that the $Ru_3(CO)_{12}/NEt_4Cl/NMP$ catalyst system is much more resistant to poisoning by H_2O and CO_2 compared to alkali methoxide catalysts.

WGSR is a widely examined reaction nowadays [11–19]. In the WGSR the key reaction is:



This is an important route for the production of hydrogen gas from water and the route to increase the hydrogen content of synthetic gas. Soluble group 6 and group 8 metal complexes are attractive, homogeneous alternatives as WGSR catalysts since they are potentially resistant to poisoning by sulfur, and are also active at low temperatures, where very little of CO is present in equilibrium [20]. The most detailed studies to catalyze WGSR by metal carbonyls have been reported for ruthenium carbonyls [21]. Ruthenium carbonyls react in these conditions to form anionic complexes, such as $[HRu_3(CO)_{11}]^-$ and $[H_3Ru_4(CO)_{12}]^-$, which are quite active in catalytic reactions.

2. Experimental

2.1. General comments

$H_4Ru_4(CO)_{12}$ was made by a literature procedure [22]. Ligands: 1,4,7-triazacyclononane, 1,4,7-trimethyl-

1,4,7-triazacyclononane, 1,5,9-triazacyclododecane and 1,5,9-trimethyl-1,5,9-triazacyclododecane were from commercial sources (Aldrich) and the latter three of them were used as methanol solutions because these ligands are quite viscous liquids. All manipulations were carried out under nitrogen, and liquids were bubbled with nitrogen for about 15 min before use. All liquids were p.a. solvent grade and they were stored over molecular sieves. IR-spectra were recorded with Nicolet 750 FT-IR spectrometer and 1H and ^{13}C NMR spectra on Bruker AMX-400 or Bruker AM-250 spectrometer at ambient or at $-60-0^\circ C$ with TMS as reference.

2.2. Preparation of complexes

2.2.1. $[H_3Ru_4(CO)_{12}][H(CH_2)_6(NH)_3]$ (1)

$H_4Ru_4(CO)_{12}$ (100 mg, 0.134 mmol) was dissolved in 25 ml of hexane and heated at $70^\circ C$. When hexane solution was refluxing the 1,4,7-triazacyclononane, $[(CH_2)_6(NH)_3]$, (23 mg, 0.178 mmol dissolved in a small amount of hexane) was added. The mixture was stirred at $70^\circ C$ for 2 h under nitrogen, then cooled down to ambient temperature. Hexane solution was filtered off using the Schlenk technique and the residue was extracted several times with a small amount of hexane, and the yellow-orange residue was dried in vacuum to give $[H_3Ru_4(CO)_{12}][H(CH_2)_6(NH)_3]$, **1**, 116 mg (99.1%); anal/calc: C% 25.49/24.75; H% 2.40/2.19; N% 5.41/4.81; IR (tetrahydrofuran (THF), $\nu(CO)$, cm^{-1}): 2070.6w, 2036.6vs, 2030.0s sh, 2016.8vs, 1999.1s, 1976.4s, 1942.9m sh, 1930.3m; 1H NMR (acetone- d_6 , $20^\circ C$, ppm): -17.07 (s, 3H, RuHRu); ($-60^\circ C$): -16.03 (s, 2H, C_{2v} or C_2 isomer, RuHRu), -17.50 (s, 3H, C_{3v} isomer, RuHRu), -19.07 (s, 1H, C_{2v} or C_2 , RuHRu).

2.2.2. $[H_3Ru_4(CO)_{12}][H(CH_2)_6(NCH_3)_3]$ (2)

$H_4Ru_4(CO)_{12}$ (100 mg, 0.134 mmol) was dissolved in 25 ml of hexane and heated to $70^\circ C$ until refluxing. Then the 1,4,7-trimethyl-1,4,7-triazacyclononane, $[(CH_2)_6(NCH_3)_3]$, (140 μl of 0.973 M methanol solution; methanol was evaporated in vacuum before dissolving in a small amount of hexane) was added. The reaction mixture was stirred at $70^\circ C$ for 2 h, then cooled to room temperature. Hexane solution was filtered off using Schlenk technique and the residue was extracted several times with a small amount of hexane, and the yellow-orange residue was dried in vacuum to give $[H_3Ru_4(CO)_{12}][H(CH_2)_6(NCH_3)_3]$, **2**, 80 mg (65.2%); anal/calc: C% 27.60/27.54; H% 2.75/2.75; N% 4.47/4.59; IR (THF, $\nu(CO)$, cm^{-1}): 2066.4w, 2036.7s, 2029.7s sh, 2016.8vs, 1999.2s, 1975.2m, 1948.0w; 1H NMR (acetone- d_6 , ppm, $20^\circ C$): -17.1 (s, 3H, RuHRu); ($-60^\circ C$): -16.02 (s br, 2H, C_{2v} or C_2 isomer, RuHRu), -17.50 (s, 3H, C_{3v} isomer, RuHRu), -19.05 (s br, 1H, C_{2v} or C_2 isomer, RuHRu).

2.2.3. $[H_3Ru_4(CO)_{12}][H(CH_2)_9(NH)_3]$ (**3**)

Complex **3** was prepared as **2** using $H_4Ru_4(CO)_{12}$ (100 mg, 0.134 mmol) and 1,5,9-triazacyclododecane, $[(CH_2)_9(NH)_3]$, (140 μ l, 0.973 M methanol solution; methanol was evaporated in vacuum before dissolving in a small amount of hexane) to give yellow-orange $[H_3Ru_4(CO)_{12}][H(CH_2)_9(NH)_3]$, **3**, 96.3 mg (78.5%); anal/calc: C% 28.98/27.54, H% 3.13/2.75, N% 5.13/4.59; IR (THF, $\nu(CO)$, cm^{-1}): 2069.2w, 2036.6s, 2031.1s sh, 2016.8vs, 1998.8vs, 1976.4s 1948.7m, 1929.8w; 1H NMR (acetone- d_6 , ppm, 20°C): -17.05 (s, 3H, RuHRu); ($-60^\circ C$): -15.96 (s br, 2H, C_{2v} or C_2 isomer, RuHRu), -17.41 (s, 3H, C_{3v} isomer, RuHRu), -18.94 (s br, 1H, C_{2v} or C_2 isomer, RuHRu).

2.2.4. $[H_3Ru_4(CO)_{12}][H(CH_2)_9(NCH_3)_3]$ (**4**)

Complex **4** was prepared as **2** using $H_4Ru_4(CO)_{12}$ (100 mg, 0.134 mmol) and 1,5,9-trimethyl-1,5,9-triazacyclododecane, $[H(CH_2)_9(NCH_3)_3]$ (860 μ l 0.156 M methanol solution; methanol was evaporated in vacuum before dissolving in a small amount of hexane) to give yellow-orange $[H_3Ru_4(CO)_{12}][H(CH_2)_9(NCH_3)_3]$, **4**, 120 mg (93.5%); anal/calc: C% 30.39/30.10, H% 3.26/3.26, N% 4.38/4.39; IR (THF, $\nu(CO)$, cm^{-1}): 2071.0w, 2037.7s, 2030.3s sh, 2017.9vs, 1999.0vs, 1977.1m, 1947.7w, 1929.6w; 1H NMR (acetone- d_6 , ppm, 20°C): -17.06 (s, 3H, RuHRu); ($-60^\circ C$): -16.02 (s br, 2H, C_{2v} or C_2 isomer, RuHRu), -17.49 (s br, 3H, C_{3v} isomer, RuHRu), -19.10 (s br, 1H, C_{2v} or C_2 isomer, RuHRu).

2.3. Reactivity towards CO

Reactivity was tested in a 100-ml glass reaction vessel. About 50 mg of the complex to be tested (**1**, **2**, **3** or **4**) was weighed and dissolved in a used solvent, THF or CH_2Cl_2 . The solution was bubbled with carbon monoxide for several hours. If no reaction took place on the basis of the colour or IR, the mixture was heated to the reflux temperature of solvent (40°C for CH_2Cl_2 and 67°C for THF) and carbon monoxide was bubbled for several hours. The reactions were followed with FT-IR.

2.4. The carbonylation of methanol to methylformate catalyzed with **1**, **2**, **3**, **4** and $H_4Ru_4(CO)_{12}$

Methanol 3 ml (0.0741 mol), NEt_3Cl , 20 mg, THF 4 ml or NMP (*N*-methyl-2-pyrrolidinone) 5 ml, and about 10 mg (0.0114, 0.0109, 0.0109 and 0.0104 mmol) of catalyst precursor (**1**, **2**, **3**, **4**, respectively) was weighed and added into the autoclave (100 ml Berghof, containing a Berghof Bar 845 temperature-control and stirring unit) in glovebox under an atmosphere of dry nitrogen. Then the autoclave was charged with carbon monoxide (40 bar, purity $\geq 99.0\%$, impurities $Ar + N_2 \leq 0.2\%$ and $H_2O \leq 10$ ppm) and heated for 2 or 4 (6) h after the

temperature had risen to the set value (200°C) (the temperature rise takes usually about half an hour). After the reaction, the autoclave was cooled with liquid nitrogen, the pressure was released, and the reaction mixture was removed and analyzed. The quantities of methyl formate and unreacted methanol were analyzed with gas chromatograph (Hewlett-Packard Series II 5890 using Chrompack OV 1-column: 50 m, $\phi = 0.53$ mm, phase thickness = 5 μ m). Gas chromatograph was calibrated before sample analysis with known amounts of methanol and methyl formate. The IR spectra of the solution after the reaction were recorded with Nicolet 750 FT-IR spectrometer.

2.5. WGS catalyzed with **1**, **2**, **3** and **4**

The reactions were made in the 100-ml round-bottomed all-glass rotaflo reaction vessel. The catalyst was weighed (5–10 mg, 0.004–0.016 mmol) and packed into the reaction vessel in the N_2 -filled glovebox. Nitrogen atmosphere was replaced with carbon monoxide (purity $\geq 99.0\%$, impurities $Ar + N_2 \leq 0.2\%$ and $H_2O \leq 10$ ppm) and 0.1–0.3 ml H_2O (0.006–0.017 mol) was added with a syringe. Then the reaction vessel was cooled with liquid nitrogen and evacuated in vacuum and charged with carbon monoxide. This cycle was repeated two or three times to verify that the reaction vessel contains only carbon monoxide. The flask was charged to the final reaction pressure of 298–447 mm Hg (0.4–0.6 atm) at room temperature. The Rotaflo reaction vessel was closed tightly and placed to the oil bath so that the whole reaction volume was under the oil. The bottle was heated at the reaction temperature (100–180°C) overnight (17 h). After the reaction, the bottle was cooled to room temperature. Gaseous products, H_2 and CO_2 , and remaining CO, were analysed with a gas chromatograph (Carlo Erba fractovap series 4200 dual columns modular with HWD control Mod. 230, columns: Molecule sieve 5A and Chromosorb 102) using the two-column technique to separate them. The carrier gas in H_2 analysis was argon, and in CO_2 and CO analysis, helium. Gas chromatograph was calibrated with known amounts of H_2 , CO_2 and CO. After the gas analysis, H_2O in the reaction solution was removed in a N_2 flow and the residue was dissolved to THF and analyzed with IR-(Nicolet 750 FT-IR spectrometer) and NMR-(Bruker AM-250, using d_6 -acetone as a solvent and reference) spectrometers.

3. Results and discussion

3.1. Synthesis and characterization of complexes **1**, **2**, **3** and **4**

We have studied the reactions of $H_4Ru_4(CO)_{12}$ with different azamacrocyclic ligands: 1,4,7-triazacyc-

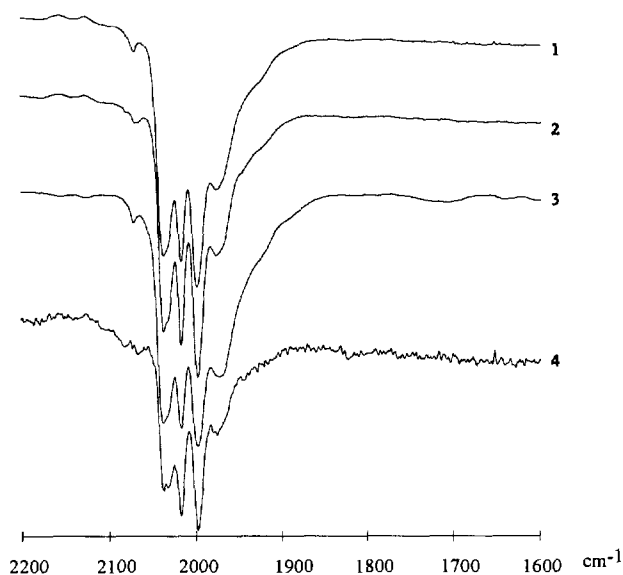


Fig. 2. IR spectra of **1**, **2**, **3** and **4** in THF.

lononane, 1,4,7-trimethyl-1,4,7-triazacyclononane, 1,5,9-triazacyclododecane and 1,5,9-trimethyl-1,5,9-triazacyclododecane and found that $H_4Ru_4(CO)_{12}$ forms with all four ligands an anionic complex $[LH]^+[H_3Ru_4(CO)_{12}]^-$ (L = azamacrocyclic ligand) in a good yield. We have synthesized these complexes with an one-step direct reaction of $H_4Ru_4(CO)_{12}$ with used ligands in refluxing hexane solution. Previously,

this type of complexes were prepared by making first the $[H_3Ru_4(CO)_{12}]^-$ anion in ethanolic KOH-solution and then precipitating the products with an appropriate ligand [23–27]. The anion $[H_3Ru_4(CO)_{12}]^-$ has been claimed to be an important species, for example in hydroformylation and WGSR [16].

Complexes **1**, **2**, **3** and **4** were characterized with elemental analysis, IR and NMR spectroscopies. Chemical analysis results for the complexes **1–4** showed a rather good agreement between found and theoretical values. The IR spectra of clusters **1–4** are, Fig. 2, in the carbonyl stretching region quite similar in the same solvent (THF) indicating that compounds **1–4** have a similar $[H_3Ru_4(CO)_{12}]^-$ cluster framework. The IR spectra of **1**, **2**, **3** and **4** resemble especially well that of $[(Ph_3P)_2N][H_3Ru_4(CO)_{12}]$ [27]. The similarity in the counter ion composition (all have nitrogen) is the obvious reason to this similarity. All four clusters **1**, **2**, **3** and **4** possess a fluxional behaviour in 1H NMR. At ambient temperature in d_6 -acetone 1H NMR consists of one sharp singlet at -17.07 , -17.10 , -17.05 and -17.06 ppm for **1**, **2**, **3** and **4**, respectively. At $-60^\circ C$ 1H NMR spectra consists of a broad signal at -16.03 , -16.02 , -15.96 and -16.02 ppm; a singlet at -17.50 , -17.50 , -17.41 and -17.49 ppm and a broad signal at -19.07 , -19.05 , -18.94 and -19.10 ppm for **1**, **2**, **3** and **4**, respectively. The 1H NMR spectra of the complex **1** is presented at various temperatures in Fig. 3 (the spectra of **2**, **3** and **4** behave in the same way). These spectra

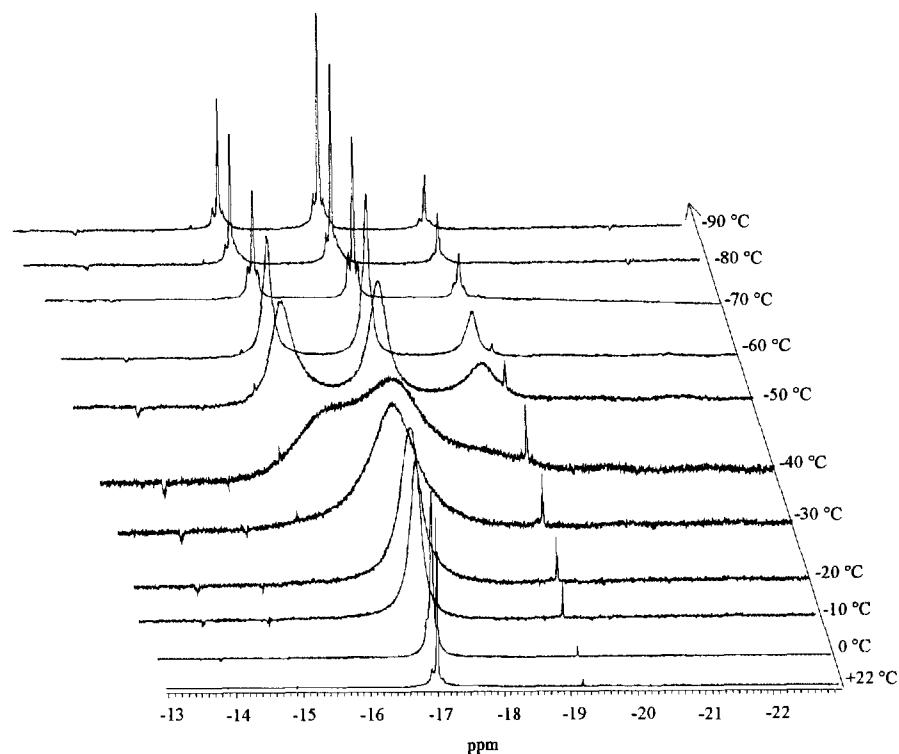


Fig. 3. Variable temperature 1H NMR spectra of **1** in the metal hydride region in acetone- d_6 .

agree well with the spectra of metal hydride region reported and discussed before for $[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$ clusters [23–27]. The ^1H NMR spectra at -60°C contain signals of both isomers (C_2 and C_{3v}). Signals at -17.5 ppm belong to isomer C_{3v} and signals at -16 and -19 ppm belong to C_2 isomer. At ambient temperature, these signals coalesced to one sharp singlet at -17.05 to -17.10 ppm due to the rapid proton change in the NMR scale.

The cluster framework of complexes **1–4** are proposed to be the same as reported earlier [23–25] for the $[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$ anion, the structure of which have been characterized by X-ray crystallographic determination. Two distinct structural isomers have been found with μ_2 -hydrogen ruthenium arrangements in the $[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$ ion approximating C_2 and C_{3v} symmetry. X-ray analysis has been carried out for $(\text{Ph}_3\text{P})_2\text{N}[\text{H}_3\text{Ru}_4(\text{CO})_{12}]$ complex [23–25]. The two other known complexes, $[(\text{C}_6\text{H}_4)_4\text{As}][\text{H}_3\text{Ru}_4(\text{CO})_{12}]$ and $\text{K}[\text{H}_3\text{Ru}_4(\text{CO})_{12}]$, have been characterized by spectroscopic measurements [26,27]. With these evidence it is obvious that all four complexes **1**, **2**, **3** and **4** have the same structure for the metal hydride and carbonyl core as reported earlier.

The formation of $[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$ anion from $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ in an one-step direct reaction of $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ with triaza ligands in refluxing hexane occurs with a deprotonation of $\text{H}_4\text{Ru}_4(\text{CO})_{12}$. One of the hydride ligands in $\text{H}_4\text{Ru}_4(\text{CO})_{12}$ can be easily removed with a moderately basic reagent [28]. Therefore, it is not surprising that an azamacrocyclic affects this reaction, but with triaza ligands, $[\text{H}_3\text{Ru}_4(\text{CO})_{12}]^-$ anion could be easily prepared in a good yield without any intermediates.

The crystallization of suitable crystals for X-ray examinations has not been successful. This is may be due to the low stability of these complexes in air and at ambient temperature in solution. They are quite stable in the solid state when stored under nitrogen or carbon monoxide atmosphere in the freezer (-20°C). At ambient temperature, the decomposition occurs in solution in a few days. At lower temperatures (in a refrigerator) decomposition occurs more slowly (in a few weeks). On evaporation, slowly through the septum instead of crystallization, the decomposition of the complexes occurs both at ambient or lower temperatures. Also, the purification of these complexes is quite difficult, because the separation of products from starting materials could have not been done with chromatographic separation (neither column nor plates), because azaligands bind quite strongly to silica or alumina, causing the decomposition of the complexes.

3.2. Reactivity towards carbon monoxide

Reactivity of **1**, **2**, **3** and **4** towards carbon monoxide has been studied in dichloromethane and THF solution

at ambient and elevated temperature (40 and 70°C) for 3 and 4 h, respectively. The colour of the reaction mixture and the IR spectra measured after the reaction stayed unchanged showing the stability of the tested complexes under these reaction conditions. Therefore, all four complexes proved to be stable under carbon monoxide atmosphere in tested reaction conditions, but all four complexes showed activity in methanol carbonylation and WGSR in much more rigorous conditions.

3.3. The carbonylation of methanol to methylformate catalyzed with **1**, **2**, **3**, **4** and $\text{H}_4\text{Ru}_4(\text{CO})_{12}$

The carbonylation of methanol catalyzed by ruthenium complexes can selectively produce methylformate as a sole liquid product [10,29,30]. All other products were gaseous, mainly CO_2 and CH_4 . The aim of our work was to examine the effect of catalyst precursors to methanol carbonylation when the promoting ligands, cyclic aza ligands, were complexed with ruthenium carbonyl cluster, and compare these results with those measured for pure $\text{Ru}_3(\text{CO})_{12}$ under the same conditions. We used similar reaction conditions as Choi et al. [10] have used, and they have found that NEt_3Cl is very efficient promoter in this reaction. Carbonylation reactions have been done in two different solutions: THF, for best dissolving effect, and NMP for promoting the effect found earlier [10].

In the methanol carbonylation reaction catalyzed with complexes **1–4** in THF solution, methylformate was nearly the sole liquid product, while gaseous products were formed only in small amounts. In NMP, the biggest difference when compared to the reaction carried out in THF solution was the amount of the gaseous products, which was higher for NMP. The explanation for this is not clear, because the gas analysis from reaction mixture did not show the presence of methane, which is one of the decomposing product of methylformate at studied temperatures. Only carbon dioxide and hydrogen was detected. These gaseous products are probably formed in a WGSR, a side reaction taking place due to the presence of water as an impurity in NMP.

When comparing the activities of different catalysts **1–4** in methanol carbonylation reactions, we found that the activities were higher in THF than those in NMP. The highest activity was found for **4** in THF, the turnover number being 16.3 mol methylformate/mol Ru-atoms h^{-1} . Other three catalysts **1**, **2** and **3** seemed to be nearly equally good catalysts under these reaction conditions (Table 1). Some reactions in NMP were also done using 4-h reaction time, and these studies showed that the activity was maintained despite the longer reaction time.

When studying the effect of the initial amount of methanol on the catalytic rate, we found that doubling

Table 1
Activity of compounds **1–4** (mol methylformate (mol Ru)⁻¹ h⁻¹) in the methanol carbonylation reaction in THF and NMP solutions

Catalyst	A ^a	B ^a	C ^b	D ^b	E ^b
1	13.2	19.6	11.3	8.14	
2	12.2	19.4	6.94	10.3	
3	13.3	23.3	7.28	6.42	
4	16.3	24.8	11.3	13.2	
H ₄ Ru ₄ (CO) ₁₂	15.0		8.43		
Ru ₃ (CO) ₁₂	14.2	19.7			21.7

^a200°C, 40 bar CO, 10 mg (0.0104–0.0114 mmol) catalyst precursor, 4 ml THF.

^b200°C, 40 bar CO, 10 mg (0.0104–0.0114 mmol) catalyst precursor, 5 ml NMP.

A: reaction time 2 h, 3 ml MeOH; B: reaction time 2 h, 6 ml MeOH; C: reaction time 2 h, 3 ml MeOH; D: reaction time 4 h, 3 ml MeOH; E: reaction time 2 h, 6 ml MeOH.

the methanol amount from 3 ml to 6 ml increases the activity for all four catalysts being the highest for **4** 24.8 mol/mol Ru h⁻¹ (Table 1). When the amount of methanol is higher in the reaction, there is, under the high temperature and pressure reaction conditions, more methanol in liquid phase than in reactions with smaller amounts of methanol. Because the catalytic reaction takes place homogeneously in liquid phase, the bigger amount of methanol in liquid phase increases the rate of carbonylation reaction.

The clusters Ru₃(CO)₁₂ and H₄Ru₄(CO)₁₂ showed also catalytic activity in methanol carbonylation under the present conditions in both solutions (Table 1). Turnover frequencies do not significantly differ from the best values found for azacomplexes.

The reaction mixtures from the methanol carbonylation reactions were studied with IR to characterize the metal species present in the catalyst solutions. Including the signals of **2**, **3** and **4**, the IR spectra of the THF solutions (IR from the catalyst solution of **2**: 2060.0w, 2034.0m, 2014.0s, 2001.7sh, 1978.5vs, 1963.8sh, 1779.3w; IR from the catalyst solution of **3**: 2059.7w, 2013.8vs, 2001.7sh, 1987.7m, 1949.7w, 1779.3w; IR from the catalyst solution of **4**: 2060.7w, 2014.4s, 2000.9sh, 1978.2vs, 1949.7w, 1779.3w) showed the presence of Ru₃(CO)₁₂ and [HRu₃(CO)₁₁]⁻ anion (IR for Ru₃(CO)₁₂ in THF: 2060s, 2030m, 2010sh and IR for [N(PPh₃)₂]⁺[HRu₃(CO)₁₁]⁻ in CH₂Cl₂: 2073vw, 2014vs, 1985s, 1952m, 1698w) [31]. Only the bands of Ru₃(CO)₁₂ were observed in the IR spectrum of the catalyst solution of **1** (IR from the catalyst solution of **1**: 2060.8vs, 2028.8m, 2010sh). In Fig. 4, the IR spectra of the catalyst solution of **3** in THF are shown before and after the reaction. In NMP, the IR spectra of all four catalyst solutions showed the signals due to [HRu₃(CO)₁₁]⁻ anion. In Fig. 5, the IR spectra of the catalyst solution of **3** in NMP before and after the reaction are presented (other compounds **1**, **2** and **4**

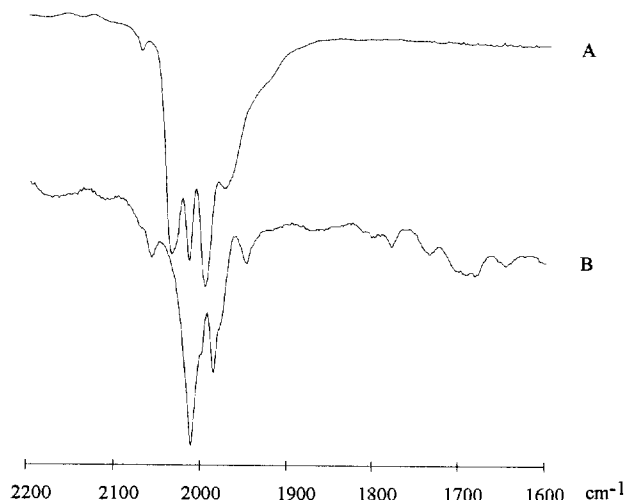
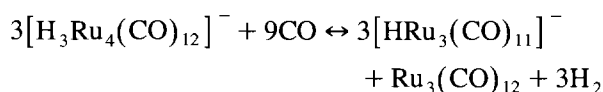


Fig. 4. IR spectra of **3** before (A) and after (B) the methanol carbonylation reaction in THF solution.

have similar spectra). Based on the IR results, the catalytically active species in the carbonylation of methanol with ruthenium catalysts seems to be the [HRu₃(CO)₁₁]⁻ anion which has been formed from catalysts precursors under carbon monoxide atmosphere at the reaction temperature and pressure.

The transformation of [K]⁺[H₃Ru₄(CO)₁₂]⁻ to the triruthenium cluster species has been detected earlier by Bricker et al. [15,16]. Under carbon monoxide atmosphere, [H₃Ru₄(CO)₁₂]⁻ reacts with carbon monoxide with displacement of the hydride ligands with CO:



In this equilibrium reaction, the presence of H₂ favors the formation of [H₃Ru₄(CO)₁₂]⁻ while the presence of CO favors the formation of [HRu₃(CO)₁₁]⁻. In our case, the higher CO partial pressure than that of H₂

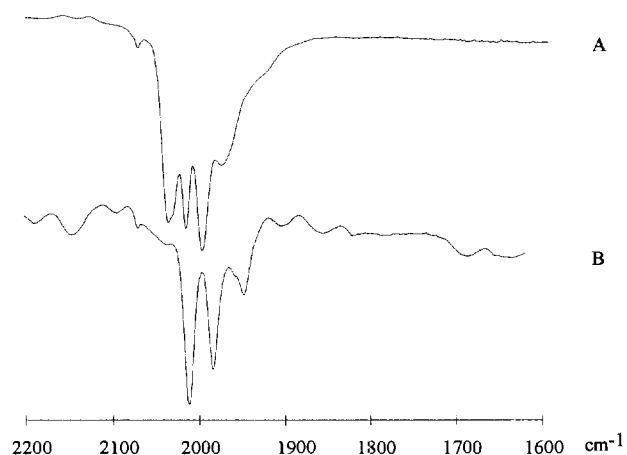


Fig. 5. IR spectra of **3** before (A) and after (B) the methanol carbonylation reaction in NMP solution.

Table 2
Catalytic activity of the ruthenium catalysts in the carbonylation of methanol

Catalyst system	<i>T</i> (°C)	<i>P</i> (bar)	TO	Reference
Ru ₃ (CO) ₁₂ /MeOH	200	450	183 ^a	[28]
[HRu ₃ (CO) ₁₁] ⁻ /PPN/MeOH	125	17	4.4 ^a	[29]
[H ₃ Ru ₄ (CO) ₁₂] ⁻ /PPN/MeOH	125	17	3.7 ^a	[29]
Ru ₃ (CO) ₁₂ /NEt ₄ Cl/NMP	200	300	440 ^a	[10]
[H ₃ Ru ₄ (CO) ₁₂] ⁻ /1,4,7-triazacyclononane/NEt ₄ Cl/NMP	200	40	11.3 ^b	This work
[H ₃ Ru ₄ (CO) ₁₂] ⁻ /1,5,9-trimethyl-1,5,9-triazacyclododecane/NEt ₄ Cl/THF	200	40	16.3 ^b	This work
[H ₃ Ru ₄ (CO) ₁₂] ⁻ /1,5,9-trimethyl-1,5,9-triazacyclododecane/NEt ₄ Cl/THF	200	40	24.8 ^c	This work
Ru ₃ (CO) ₁₂ /THF/NEt ₄ Cl	198	40	14.2 ^b	This work
Ru ₃ (CO) ₁₂ /THF/NEt ₄ Cl	200	40	19.7 ^c	This work
Ru ₃ (CO) ₁₂ /NMP/NEt ₄ Cl	198	40	21.7 ^c	This work
Ru ₃ (CO) ₁₂ /KOMe/MeOH	125	250	80 ^d	[8]

^a mol formate(mol metal catalyst)⁻¹ h⁻¹.

^b mol formate(mol metal atom)⁻¹ h⁻¹, 3 ml MeOH.

^c mol formate(mol metal atom)⁻¹ h⁻¹, 6 ml MeOH.

^d mol formate(mol metal catalyst)⁻¹ day⁻¹.

clearly favors the presence of triruthenium species in solutions.

Complexes 1–4, Ru₃(CO)₁₂ and H₄Ru₄(CO)₁₂ have a moderate activity in the carbonylation of methanol to methylformate. The reactions with H₄Ru₄(CO)₁₂ and Ru₃(CO)₁₂ showed that the azaligands have no significant promoting activity in this reaction, since the activities of H₄Ru₄(CO)₁₂ and Ru₃(CO)₁₂ were similar to those found for Ru azacomplexes (Table 1). These activities are comparable to those found earlier for Ru clusters (Table 2). The differences and lower activities are probably due to the lower carbon monoxide pressure used as the results with Ru₃(CO)₁₂ showed. One of the

best formate yields from methanol has been obtained in the experiments [29] carried out at 500 bar of carbon monoxide. Thus, it seems that the activity is remarkably enhanced when the pressure of the carbon monoxide increases.

Obviously, the triaza derivatives of H₄Ru₄(CO)₁₂ are less water-sensitive than alkali methoxide catalysts used commonly in the methyl formate synthesis. Although triaza derivatives of H₄Ru₄(CO)₁₂ are less stable than, for example, the corresponding [PPN]⁺ salt, they are suitable for catalysis use, because of their easy preparation. Moreover, the literature example shows that the activity of the [PPN]⁺ salt is not significantly higher in

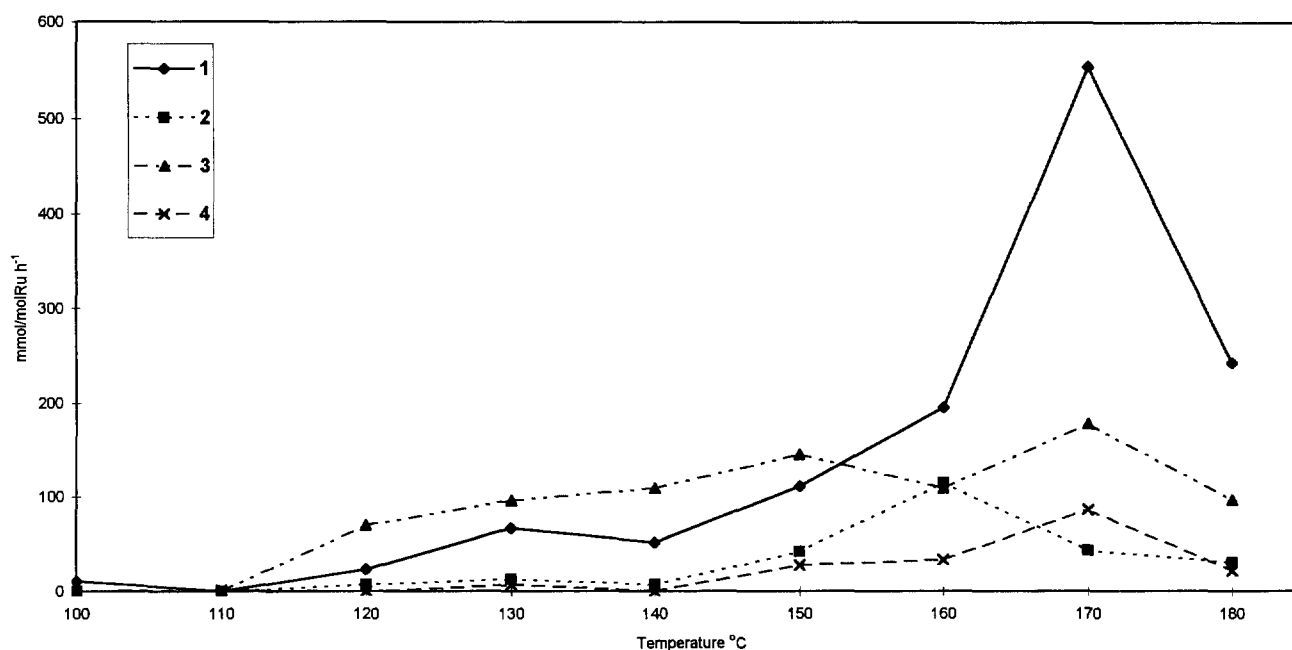


Fig. 6. The activity (mmol H₂/mol Ru h⁻¹) of 1, 2, 3 and 4 in WGSR at different temperature.

Table 3
Conversion of CO, CO₂ and H₂ and activity of the catalysts **1**, **2**, **3** and **4** at 170°C in the WGSR

Catalyst	Conversion of CO (%)	Mol% H ₂	Mol% CO ₂	Activity ^a H ₂	Activity ^a CO ₂
1	8.13	8.13	8.94	13.31	14.63
2	0.60	0.60	1.90	1.05	3.32
3	3.83	3.83	3.23	4.27	3.60
4	1.29	1.29	0.83	2.07	1.33

^a mol CO₂ or H₂ (mol Ru)⁻¹ day⁻¹.

the methanol carbonylation reaction to methyl formate than the activities we have found for triaza derivatives of H₄Ru₄(CO)₁₂ (Table 2).

3.4. WGSR catalyzed with **1**, **2**, **3** and **4**

WGSR catalyzed by complexes **1–4** were carried out in a wide temperature range: 100–180°C for **1**, 110–180°C for **2**, 120–180°C for **3** and 110–180°C for **4**. For all complexes **1–4** we found that at low temperatures, the activity of the catalysts was not very high. But when the temperature goes up, the activity increases (Fig. 6). The best activity for **1** and **4** was achieved at 170°C, for **2** at 160°C and for **3** at 150°C (Table 3). Clearly the most active catalyst was **1** with a turnover number of 12.26 and 12.15 mol (mol Ru atoms)⁻¹ day⁻¹ calculated from formed hydrogen and carbon dioxide, respectively. At temperatures above 170°C, the activity decreases, probably due to the decomposition of the catalysts.

4. Conclusion

The reaction of H₄Ru₄(CO)₁₂ with triazaligands (1,4,7-triazacyclononane, 1,4,7-trimethyl-1,4,7-triazacyclononane, 1,5,9-triazacyclododecane and 1,5,9-trimethyl-1,5,9-triazacyclo-dodecane) produces [LH]⁺[H₃Ru₄(CO)₁₂]⁻-type complexes **1**, **2**, **3** and **4**, respectively, in a high yield. This is a direct synthetic route to [H₃Ru₄(CO)₁₂]⁻ ion which has been earlier prepared by forming first the corresponding anion in ethanolic KOH solution, then precipitating the product with an appropriate ligand. Characteristic for compounds **1–4** is air-sensitivity and low stability in solution at ambient temperature under nitrogen atmosphere. However, reactivity tests at elevated temperatures with CO show that these compounds are stable in CO atmosphere at 67°C in THF solution. The compounds are also stable in solid state when stored under nitrogen or carbon monoxide atmosphere at low temperatures.

The catalytic activity tests in WGSR and the carbonylation of the methanol showed low or moderate activity for compounds **1–4**. These compounds are expected to be suitable catalyst precursors in both reactions because the anionic compounds form easily active

catalysts under these reaction conditions. In the methanol carbonylation, the active catalyst formed is the same as found earlier for Ru-catalyst precursors in the carbonylation reactions under basic conditions.

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