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Synthesis and catalytic properties of arene complexes of ruthenium(II) prepared from Si, Zr, Ti and Al alkoxides by the sol–gel process

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Methods of synthesizing materials for catalysis were developed by synthesizing η-arene complexes of ruthenium(II) coordinated to vinylpyridine that was followed by sol–gel polymerization with 3-methacryloxypropyltriethoxysilane. To enforce sufficient catalytic properties, a series of hybrid materials from Si, Zr, Ti and Al alkoxides were prepared by co-condensation. The hydrolysis and polycondensation of materials were performed at different experimental conditions. The monomeric compounds were identified and catalytic activities were tested for cyclization of (*Z*)-3-methylpent-2-en-4-yn-1-ol to 2,3-dimethylfuran.

Introduction

Polymer supported transition metal complexes in catalysis have attracted much attention due to their matrix effect which may enhance the performance of the catalyst.[1] The influence of the polymer structure on the catalytic properties of immobilized metal complex catalysts has been investigated, and a model of the activity of the heterogenized catalytic system has been reported.[2–4]

Recently, preparative and catalytic studies on cyclic diaminocarbene and N-3 bound 2-imidazoline complexes containing an η-arene moiety have been carried out because of their catalytic potential.[5] These complexes are effective catalysis for the intramolecular cyclization of (*Z*)-3-methylpent-2-en-4-yn-1-ol into 2,3-dimethylfuran.[6,7] Tris(2,2′-diimine)ruthenium(II) complexes as water-insoluble free-standing films of partially quaternized poly(1-vinylimidazole)ruthenium(II) complexes were applied to photoinduced hydrogen generation in aqueous solution.[8] The synthesis and characterization of a series of metallopolymers of poly(4-vinylpyridine) and poly(*N*-vinylimidazole) containing $(OC)_3RuCl_2$ and $(2,2'\text{-bipyridine})_2Ru$ moieties have recently been described.[9]

In this study, we examined the possibility to synthesize (η-arene)ruthenium(II) complexes containing pyridine ligands with pendant vinyl groups. It was planned to anchor these complexes on a matrix by sol–gel processing *via* hydrolysis of a γ-methacryloxypropyltriethoxysilane and a metallic alkoxide: $Si(OR)_4$, $Ti(OR)_4$, $Zr(OR)_4$ or $Al(OR)_3$. Further goals are catalytic reactions which will be carried out at the transition metal center of the stationary phase.

Experimental

Materials

4-Vinylpyridine (Aldrich) was fractionally distilled before use, (*Z*)-3-methylpent-2-en-4-yn-1-ol (Aldrich), 3-methacryloxypropyltriethoxysilane (Fluka), and the appropriate amounts of the various alkoxides, $Si(OEt)_4$, $Ti(OPr^i)_4$, $Zr(OPr^n)_4$ and $Al(OBu^s)_3$ (Aldrich) were used.

General methods

Analytical gas chromatography (GC) was performed on a gas chromatograph equipped with a thermal conductivity detector using a 6 ft column of 10% OV-101 on Chromosorp W HP, 100–120 mesh.

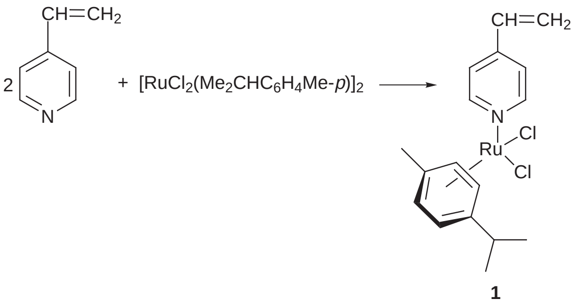
Preparation of catalyst precursors

A solution of 4-vinylpyridine (0.7 g, 4.75 mmol) in toluene (40 ml) and $[RuCl_2(p\text{-}Me_2CHC_6H_4Me)]_2$ (1.40 g, 2.28 mmol) were heated for 3 h under reflux. The product **1** was filtered off, washed with *n*-hexane (2 × 20 ml) and dried in vacuum (yield 88%; mp 144–146 °C). Anal. Calc. for $C_{17}H_{21}N_1RuCl_2$: C: 49.6; H: 5.2; N: 3.4. Found: C: 49.8; H: 5.2; N: 3.4%. ^1H NMR (200.13 MHz, $CDCl_3$, 297 K, δ): 8.86 (d, 2H, $NC_5H_4C_2H_3$; $^3J_{HAHB} = 6.8$ Hz), 7.20 (d, 2H, $NC_5H_4C_2H_3$; $^3J_{HAHB} = 6.8$ Hz), 6.59 (q, H_c, $J_{ac} = 17.6$ Hz, $J_{bc} = 10.8$ Hz), 5.96 (d, H_a, $J_{ab} = 10.8$ Hz), 5.51 (d, H_b, $J_{bc} = 10.8$ Hz), 5.38 and 5.17 (4H, MeC_6H_4, $^3J_{HH} = 6.1$ Hz), 2.91 (sept., 1H, $CHMe_2$, $^2J_{HH} = 6.9$ Hz), 2.03 (s, 3H, $C_6H_4CH_3$), 1.24 [d, 6H, $(CH_3)_2CHC_6H_4$, $^2J = 7.0$ Hz]. $^{13}C\{^1H\}$ NMR (50.32 MHz, $CDCl_3$, 297 K, δ): 156.0, 147.6 and 122.6 (s, C_5H_4N), 134.6 and 122.7 (s, $CH{=}CH_2$), 104.6, 98.5, 84.2 and 83.4 (s, MeC_6H_4), 31.9 (s, $C_6H_4CHMe_2$), 23.6 (s, $C_6H_4CH_3$), 19.5 [s, $CH(CH_3)_2$].

Catalyst preparation

3-Methacryloxypropyltrimethoxysilane (MEMO; 97%, $d = 1.05$ g ml^{-1}, bp 98 °C/5 mmHg, Aldrich) was used as received. The typical procedure for making up the sol solution was as follows. To a stirred solution of MEMO (2.48 g, 10 mmol) isopropanol (26.4 g, 440 mmol) was added. After being stirred for 2 h, the mixture was hydrolyzed with the required amount of water in isopropanol in the presence of an acid catalyst (0.15 M) solution to maintain the pH at 4. The required amount of water, determined with a Karl Fisher Coulometric Titrator, was found to be 1.35 mol per mol of silane. The mixture was stirred in ambient atmosphere at room temperature until a clear sol solution was obtained. Solvent was removed *via* vacuum distillation and an oily residue was collected.

The development of a metal alkoxide, MEMO-1, sol–gel material was carried out as a two step process. First, hydrolyzed MEMO in tetrahydrofuran (15 ml) and distilled water (5 ml) was mixed with the metal alkoxide in 1 : 1 ratio and **1** in 10 ml dichloromethane in a closed vessel and stirred overnight at room temperature. The pH of the solution adjusted at 5.5 by bubbling CO_2 through it. Then free radical polymerization was carried out in toluene at 80 °C with AIBN (recrystallized from methanol) for 8 h to yield the sol–gel materials. The obtained solid products were ground and subjected to further hydrolysis with water in the presence of NaF, followed by co-condensation at 80 °C in the presence of acetic acid (25% solution). Samples were then washed several times with



Scheme 1

dichloromethane in a Soxhlet apparatus to remove impurities, followed by drying in a vacuum oven at 75 °C for 12 h, then at 100 °C for 24 h, until the sample weight became essentially constant.

Catalytic reactions

All the reactions were carried out under nitrogen using freshly distilled dry solvents and reagents. To a known amount of sol–gel matrix (0.1 g) **1–4** in a Schlenk was added a known amount of (*Z*)-3-methylpent-2-en-4-yn-1-ol (100 mg). The mixture was stirred in an oil bath at 80 °C. The progress of the reaction was monitored by GC. The product characterized after purification was determined to be 2,3-dimethylfuran as evidenced by ^{1}H and ^{13}C NMR spectroscopy. For all sol–gel supported catalysts, the Ru content was fixed at 0.1 mM g^{-1}. In the recycling tests, when reaction was complete, the catalyst was removed by filtration from the reaction mixture, washed with 3 × 10 ml toluene, dried in a vacuum oven and used for the next reaction.

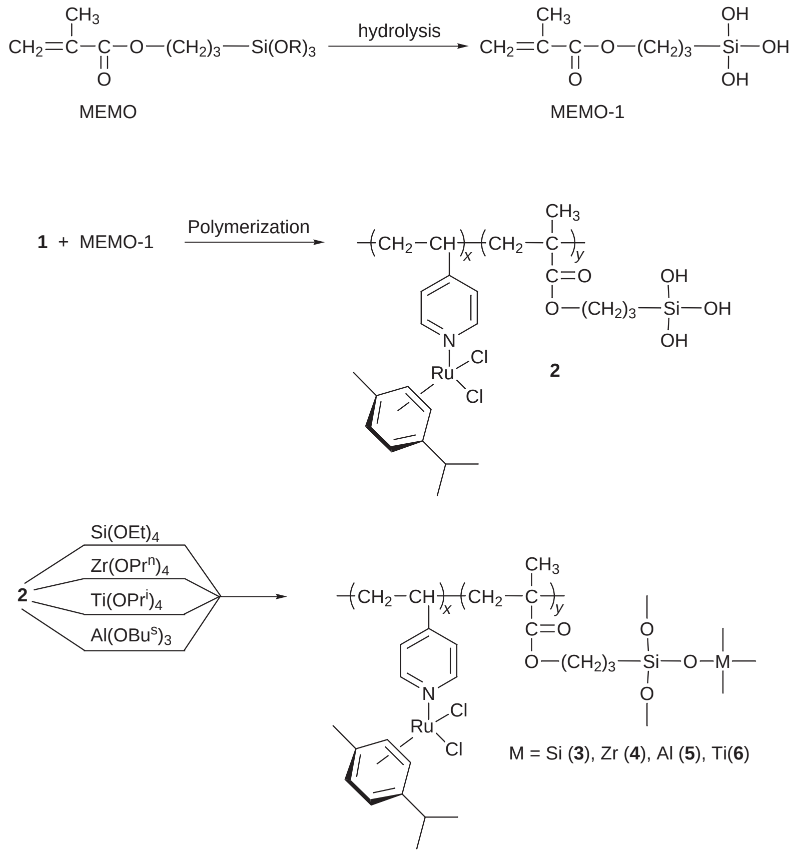
Results and Discussion

The ability of ruthenium dimers, [(η-arene)RuCl$_2$]$_2$, to react with heteroatomic nucleophiles allowed the convenient synthesis of monomer **1** as shown in Scheme 1. The divalent ruthenium cation is classified as a borderline acid; it shows affinity for borderline bases such as pyridine. The monomer was identified on the basis of elemental analysis and spectroscopic measurements.

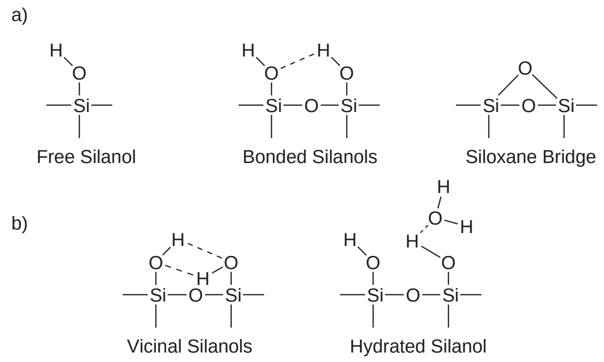
The methacrylate substituted alkoxysilane (MEMO), in which a reactive double bond is present, is very interesting for the synthesis of inorganic–organic polymers by polymerization of the organic groups (Scheme 2). In this approach, an organic network is formed in the matrix of the initially formed inorganic network. The use of metal complexes in sol–gel chemistry to prepare catalysts has been investigated.[10–15] The chemistry of such complexes was mainly developed with regard to the heterogenization of catalytically active metal complexes by anchoring them on an inorganic matrix.

Structural analysis of the expected product from the prehydrolysis of MEMO-1 gives a mixture of oligomers: polysiloxanes, silanols and ethoxysilanes, as shown in Scheme 3. The identification of Si(OH)$_3$ was made using a multichannel Raman spectrometer (DILOR xy) equipped with a CCD detector. The band positions were accurate to ±1 cm^{-1}. All spectra were taken at 20–40 mW on the sample. Tentative assignment of bands found in the laser Raman spectrum was as follows. The band at 430–440 cm^{-1} (s) is the Si—O—Si in-plane vibration.[16] The band at 490–500 cm^{-1} was attributed to the structures sketched in Scheme 3. Si—O—Si symmetric stretching and Si—O—Si asymmetric stretching bands appeared at 800 and 1100 cm^{-1} respectively. Internal and surface silanol stretching bands at 910–920 and 970–985 cm^{-1} were also observed (see Fig. 1).[17,18]

The expected product from the prehydrolysis of MEMO-1



Scheme 2



Scheme 3 (a) Silica framework, (b) silanols and siloxane bridges

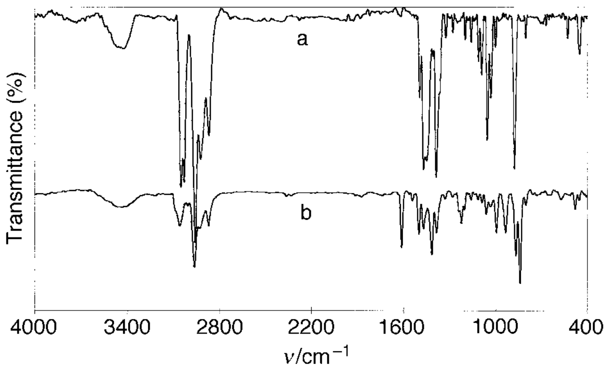


Fig. 1 Comparison of the solid-state FT-IR spectra of (a) $[RuCl_2(Me_2CHC_6H_4Me\text{-}p)]_2$ and (b) compound **1**

Table 1 Catalytic synthesis of 2,3-dimethylfuran at 80 °C by Ru^{II} complexes

catalyst	time/h	yield (%)[a,b]
1	1.5	77
1	6	80
1	14	85 (77)[b]
2	1	3
2	15	17
2	45	56
2	72	60
2	92	87 (78)[b]
3	1	5
3	15	63
3	45	76
3	72	88 (78)[b]
4	1	4
4	15	27
4	45	72
4	72	85 (74)[b]
5	15	20
5	70	65
5	85	87
6	15	66
6	70	80
6	85	89

[a] Yield determined by GC. [b] Isolated yield after distillation.

is a mixture of oligomers as described. Note that the term silanols herein refers to the mixture of products. A mixture of functionalized polymers was prepared from **1** and 3-methacryloxypropyltriethoxysilane in high yields by free radical polymerization using AIBN as initiator in toluene at 80 °C. The polymers were then hydrolyzed and co-condensed with $Si(OEt)_4$, $Ti(OPr^i)_4$, $Zr(OPr^n)_4$ and $Al(OBu^s)_3$ with an acid catalyst. The molar ratios of $Si(OEt)_4$, $Ti(OPr^i)_4$, $Zr(OPr^n)_4$ and $Al(OBu^s)_3$ to MEMO-1 used were in the range of 1 : 1. When the ratio is greater than 1.4 : 1, precipitation took place in all cases. The ratio was optimized as 0.8 : 1 for $Al(OBu^s)_3$, 0.92 : 1 for $Ti(OPr^i)_4$ and 1.1 : 1 for $Zr(OPr^n)_4$, no gelation took place when $Si(OEt)_4$ was used. After the gelation, the gel was dried in a vacuum oven. Further thermal treatments were performed at 60 and 200 °C until the sample weight became essentially constant. The ceramer network was formed after mixing the Ti, Al or Zr sol with MEMO-1. An IR absorption peak at 1055 cm^{-1} was observed as shown in Fig. 2(b); this was attributed to Si—O—Al linkage. For the Ti/MEMO-1 system, a peak at 914 cm^{-1} [Fig. 2(c)] was believed to be due to the Si—O—Ti linkage, an assigment that agrees well with that reported in the literature.[19–22] A band at 1612 cm^{-1} was attributed to C=C bonds. The peaks at 1558 cm^{-1} and 1452 cm^{-1} were assigned to COO asymmetric and symmetric stretching frequencies [Fig. 2(a)] which are believed to result from CO groups bonded to Zr as a bidentate chelating ligand.[23]

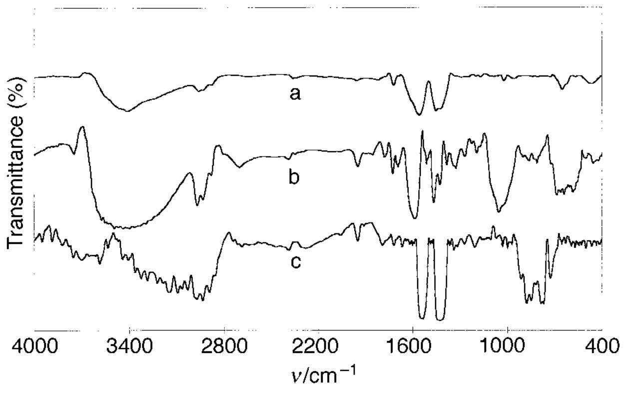


Fig. 2 FT-IR spectra of arene complexes of Ru^{II} prepared from Ti (a), Zr (b) and Al (c) alkoxide by the sol–gel process

The other objective of the present work was a comparison of the catalytic reactivity of a given metal fragment in various environments, with the emphasis on a material obtained by the sol–gel route. We chose **1** as a model compound because it is a highly active homogeneous catalyst in the cyclization of (*Z*)-3-methylpent-2-en-4-yn-1-ol to 2,3-dimethylfuran; results are given in Table 1.

At present, catalysts **3–6** were not optimized; however, like homogeneous catalysts, **3–6** operate under relatively mild conditions but they offer the advantage that they can be applied like a heterogeneous catalyst.

The degree of Ru incorporation in a sol–gel matrix was fixed at 0.1 mM g^{-1}, which is the required amount to maintain maximum conversion. The sol–gel matrix without Ru did not speed up the reaction as much as the matrix containing Ru, as shown by the lower yield in the cyclization of (*Z*)-3-methylpent-2-en-4-yn-1-ol to 2,3-dimethylfuran.

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