

Synthesis and immobilization of *N*-heterocyclic carbene complexes of Ru(II): catalytic activity and recyclability for the furan formation

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Abstract

Synthesis, characterization and immobilization of ruthenium(II) complexes of the type $[\text{RuCl}_2\text{L}(\eta^6\text{-arene})]$ ($\text{L} = \text{CN}(\text{CH}_2\text{Ph})\text{CH}_2\text{CH}_2\text{N}(\text{CH}_2)_3\text{Si}(\text{OEt})_3$, arene = *p*-cymene, **3** and arene = C_6Me_6 , **4**) and $[\text{RuCl}_2\text{L}]$ ($\text{L} = \eta^1\text{-carbene-}\eta^6\text{-arene}$ bidentate ligand, $\text{CN}[(\text{CH}_2)_3\text{Si}(\text{OEt})_3]\text{CH}_2\text{CH}_2\text{NCH}_2\text{C}_6\text{H}_2\text{Me}_3\text{-}\eta^6$, **5**, morphologically different silicas by sol–gel method are described and their reactivity and recyclability in the furan formation were also reported. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: *N*-Heterocyclic carbenes; Ruthenium complexes; Immobilization; Catalysts for furan formation

1. Introduction

Recently, transition metal complexes of *N*-heterocyclic carbenes have been the focus of considerable attention since they can act as catalyst or catalyst precursors to important transformations, such as Pd-catalyzed Heck type or Suzuki coupling [1], CO–C₂H₄ copolymerizations [2], Rh-catalyzed olefin metathesis [3], cyclopropanations [4], furan synthesis [5] and Rh-catalyzed hydrogenation [6], hydroformylation [7] and hydrosilylations [8]. In contrast to the widely used phosphine complexes, they have been shown to be remarkably stable towards heat, oxygen and moisture. The metal–carbon bonds in the carbene complexes are much stronger than the metal–phosphorus bond of typical phosphine complexes.

This property eliminates the problems associated with weak ligand–metal interactions including deposition of free metal under catalytic conditions.

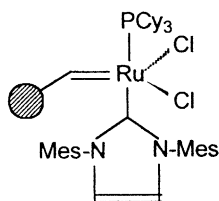
Homogeneous catalysts have been of somewhat limited use, mainly because of the difficulty of separation from the reaction products. A good way of combining the advantages of the homogeneous with those of the heterogeneous catalyst is the attachment of soluble and catalytic active metal complexes on suitable materials [9].

The advantages to be gained in heterogenizing *N*-heterocyclic carbene complexes through polymer attachment have recently been described [10,11]. Recyclable ‘boomerang’ polymer supported catalyst **I** was used for ring closing metathesis reactions [10a]. Palladium(II) complexes of *N*-heterocyclic carbenes, **II**, attached to polystyrene-based Wang resin through ether linkages, exhibit very high efficiency as catalysts for the Heck reaction [11]. However, recovery

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and reuse led to losses in activity after each cycle. Therefore, development of immobilized carbene complexes as active, truly recyclable and reusable catalyst remains a challenging task.



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Furthermore, as far as we are aware, no example of immobilization of such carbene complexes on mineral solids as supports through covalent linkages has been reported. The interest in mineral solids as supports for improvement of catalytic site properties lies in application of solids possessing high surface areas in addition to their insolubility in organic solvents. We report here the preparation of the monosilylated imidazolidinium salts **1** which are converted to the *N*-heterocyclic carbene ligand precursors **2** and then to carbene complexes **3–5**, as well as their immobilization by sol–gel processes and their reactivity and recyclability in the furan from (*Z*)-3-methylpent-2-en-4-yn-1-ol.

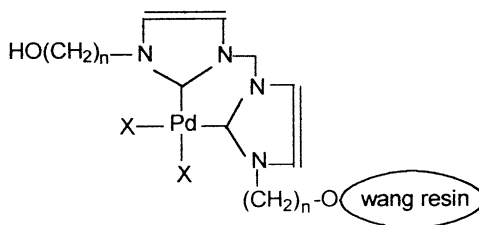
2. Experimental

All synthesis of the 1,3-dialkylimidazolidinium salts (**1**), alkenes (**2**) and the ruthenium complexes (**3–5**) were performed under a nitrogen atmosphere with the use of standard Schlenk techniques. 1-(3-Triethoxysilylpropyl)-2-imidazoline (imeo) was obtained from Fluka. Tetrahydrofuran (THF), diethyl ether and toluene were distilled under nitrogen from sodium benzophenone ketyl just before use. Amorphous mesoporous silicate (AMS) was prepared as reported earlier [12,13].

Solution NMR spectra were recorded on a Bruker 400 MHz. Solid state ^{13}C NMR were measured using a Bruker Avance 300 FT-NMR spectrometer equipped with a cross-polarization (CP)/magic angle spinning (MAS) accessory. FT-IR spectra were recorded on a Mattson 1000 FT-IR spectrometer. Thermal analysis

was performed on Shimadzu DTA System 50 at a heating rate of $10^\circ\text{C}/\text{min}$ in air.

The effect of carbene–Ru(II) concentration on grafting efficiency onto AMS particles was calculated



II

from the thermal gravimetric analysis (TGA), and a thermal behavior was carried out on a Shimadzu System 50 DTA and TGA in air with a heating rate of $10^\circ\text{C}/\text{min}$. Specific surface areas were measured under static process by means of a Micromeritics ASAP 2010 instrument. The specific surface area was calculated by BET method and average pore size was calculated by Barrett, Joyner and Helenda (the BJH method). UV irradiation was performed at 20 Hz, pulse width of 300 ps and 250 kW peak power.

2.1. 1-(3-Triethoxysilylpropyl)-3-benzylimidazolidinium chloride, **1a**

To a DMF solution (5 ml) of imeo (3.99 g, 14.78 mmol) was added 1.87 g, 14.79 mmol of benzyl chloride at 25°C and the resulting mixture was stirred at RT for 24 h. Diethyl ether (20 ml) was added to obtain a crystalline solid which was washed with Et_2O (2×15 ml) and dried in vacuum, 5.09 g, 87%. ^1H NMR (CDCl_3): δ 0.59 (m, 2H, SiCH_2), 1.20 (t, 9H, OCH_2CH_3 , $J = 7.0$ Hz), 1.74 (m, 2H, $\text{SiCH}_2\text{CH}_2\text{CH}_2$), 3.80 (q, 6H, OCH_2CH_3 , $J = 7.0$ Hz), 3.81–4.00 (m, 2H, $\text{NCH}_2\text{CH}_2\text{N}$), 4.90 (s, 2H, CH_2Ph), 7.30–7.42 (m, 5H, C_6H_5), 10.25 ppm (s, 1H, NCHN). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 7.51 (SiCH_2), 18.63 (OCH_2CH_3), 21.50 ($\text{SiCH}_2\text{CH}_2\text{CH}_2\text{N}$), 47.97, 48.43 ($\text{NCH}_2\text{CH}_2\text{N}$), 50.84 (CH_2Ph), 52.27 ($\text{SiCH}_2\text{CH}_2\text{CH}_2\text{N}$), 58.88 (OCH_2CH_3), 129.26, 129.51, 133.14 (C_6H_5), 159.05 ppm (NCHN). Analytically calculated for $\text{C}_{19}\text{H}_{33}\text{N}_2\text{O}_3\text{ClSi}$: C, 56.90; H, 8.24; N, 6.99. Found: C, 56.20; H, 8.40; N, 7.10.

2.2. 1-(Triethoxysilylpropyl)-3-(2,4,6-trimethylbenzyl)imidazolidinium chloride, **1b**

Using a similar procedure, imeo (3.59 g, 13.29 mmol) and 2,4,6-trimethylbenzyl chloride (2.22 g, 13.57 mmol) afforded colorless crystalline solid, 4.64 g, 81%. ^1H NMR (CDCl_3): δ 0.53 (m, 2H, SiCH_2), 1.13 (t, 9H, OCH_2CH_3 , $J = 7.0$ Hz), 1.67 (m, 2H, $\text{SiCH}_2\text{CH}_2\text{CH}_2$), 2.19 (s, 3H, $p\text{-CH}_3\text{C}_6\text{H}_2$), 2.28 (s, 6H, $o\text{-CH}_3\text{C}_6\text{H}_2$), 3.55–3.58, 3.60–3.70 (m, 4H, $\text{NCH}_2\text{CH}_2\text{N}$), 3.72 (q, 6H, OCH_2CH_3 , $J = 7.1$ Hz), 3.86–3.95 (m, 2H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{Si}$), 4.85 (s, $\text{CH}_2\text{C}_6\text{H}_2\text{Me}_3$), 6.81 ppm (s, $\text{CH}_2\text{C}_6\text{H}_2\text{Me}_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 7.43 (SiCH_2), 18.62, 18.69 ($o\text{-CH}_3\text{C}_6\text{H}_2$), 20.47 (OCH_2CH_3), 21.29 ($p\text{-CH}_3\text{C}_6\text{H}_2$), 21.47 ($\text{SiCH}_2\text{CH}_2\text{CH}_2\text{N}$), 46.56 ($\text{CH}_2\text{C}_6\text{H}_2$), 48.02, 48.36 ($\text{NCH}_2\text{CH}_2\text{N}$), 50.72 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{Si}$), 58.86 (OCH_2CH_3), 125.82, 130.14, 130.22, 138.22, 139.38 ($\text{CH}_2\text{C}_6\text{H}_2\text{Me}_3$), 158.77, 158.84 ppm (NCHN). Analytically calculated for $\text{C}_{22}\text{H}_{39}\text{N}_2\text{O}_3\text{ClSi}$: C, 59.63; H, 8.86; N, 6.33. Found: C, 59.50; H, 9.02, N, 6.40.

2.3. Preparation of tetraaminoalkenes, **2**: general procedure

A suspension of the salt **1** (10.0 mmol) and sodium hydride 0.36 g (15 mmol) in THF (20 ml) was heated under reflux for 4 h. The mixture was cooled to 25 °C, volatiles were removed. Toluene (20 ml) was added and filtered. The filtrate was evaporated to dryness. The residue was dissolved in warm hexane (15 ml). Upon cooling cream solid was obtained **2a** (70%) and **2b** (85%). The alkenes were not characterized due to their sensitivity towards oxygen and moisture.

2.4. Preparation of the complexes, **3–5**: general procedure

A solution of the alkene (0.60 mmol), and the corresponding ruthenium dimer (0.60 mmol) in toluene (10 ml) was heated under reflux for 2 h, then cooled to 50 °C and hexane (10 ml) was added. The precipitate formed was filtered off, washed with hexane (2 × 10 ml). The red product was recrystallized from $\text{CH}_2\text{Cl}_2\text{:Et}_2\text{O}$ (5:10 ml).

3, 63%. ^1H NMR (CDCl_3): δ 0.45–0.53, 0.70–0.85 (m, 2H, SiCH_2), 1.23 (t, 9H, OCH_2CH_3 , $J = 7.1$ Hz),

1.20, 1.26 (d, d, 6H, $\text{CH}(\text{CH}_3)_2$, $J = 6.1, 5.5$ Hz), 1.60–1.80, 1.90–2.10 (m, 2H, $\text{SiCH}_2\text{CH}_2\text{CH}_2\text{N}$), 2.84 (s, 1H, $\text{CH}(\text{CH}_3)_2$, $J = 6.9$ Hz), 3.20–3.30 (m, 1H, $\text{SiCH}_2\text{CH}_2\text{CH}_2\text{N}$), 3.30–3.70 (m, 4H, $\text{NCH}_2\text{CH}_2\text{N}$), 3.84 (q, 6H, OCH_2CH_3 , $J = 7.0$ Hz), 4.20–4.30 (m, 1H, $\text{SiCH}_2\text{CH}_2\text{CH}_2\text{N}$), 4.86 (d, 1H, CH_2Ph , $J = 15.2$ Hz), 5.13 (d, 1H, CH_2Ph , $J = 15.0$ Hz), 5.00, 5.31 (d, d, $\text{MeC}_6\text{H}_4\text{Pr}^i$), 7.28–7.39 ppm (m, 5H, C_6H_5). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 7.78 (SiCH_2), 18.76 (OCH_2CH_3), 19.16 ($\text{CH}(\text{CH}_3)_2$), 22.89 (SiCH_2CH_2), 23.65 (CHMe_2), 30.07 ($\text{CH}_3\text{C}_6\text{H}_4\text{Pr}^i$), 49.03, 49.27 ($\text{NCH}_2\text{CH}_2\text{N}$), 55.26 (CH_2Ph), 56.12 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{Si}$), 58.85 (OCH_2CH_3), 83.86, 84.10, 86.79, 87.15, 99.21, 108.79 ($\text{MeC}_6\text{H}_4\text{Pr}^i$), 127.90, 128.02, 129.5, 139.07 (C_6H_5), 207.68 ppm (NCN). Analytically calculated for $\text{C}_{29}\text{H}_{46}\text{N}_2\text{O}_3\text{Cl}_2\text{SiRu}$: C, 51.94; H, 6.86; N, 4.18. Found: C, 52.05; H, 6.91; N, 4.30.

4, 69%. ^1H NMR (CDCl_3): δ 0.45–0.55, 0.70–0.85 (m, 2H, SiCH_2CH_2), 1.20 (t, 9H, OCH_2CH_3 , $J = 7.0$ Hz), 1.60–1.65, 1.80–1.87 (m, 2H, $\text{SiCH}_2\text{CH}_2\text{CH}_2$), 2.03 (s, 18H, $\text{C}_6(\text{CH}_3)_6$), 3.08 (dt, 1H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{Si}$), 3.28–3.69 (m, 4H, $\text{NCH}_2\text{CH}_2\text{N}$), 3.82 (q, 6H, OCH_2CH_3 , $J = 7.0$ Hz), 4.07–4.13 (dt, 1H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{Si}$), 4.08 (d, 1H, CH_2Ph , $J = 14.0$ Hz), 5.75 ppm (d, 1H, CH_2Ph , $J = 13.8$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 7.71 (SiCH_2CH_2), 16.70 ($\text{C}_6(\text{CH}_3)_6$), 18.75 (OCH_2CH_3), 22.64 ($\text{SiCH}_2\text{CH}_2\text{CH}_2$), 48.92, 49.23 ($\text{NCH}_2\text{CH}_2\text{N}$), 54.80 (CH_2Ph), 55.59 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{Si}$), 58.82 (OCH_2CH_3), 94.43 ($\text{C}_6(\text{CH}_3)_6$), 127.82, 128.59, 137.36 (C_6H_5), 210.18 ppm (NCN). Analytically calculated for $\text{C}_{31}\text{H}_{50}\text{N}_2\text{O}_3\text{Cl}_2\text{SiRu}$: C, 53.28; H, 7.16; N, 4.01. Found: C, 53.03; H, 7.69; N, 4.07.

5, 72%. ^1H NMR (CDCl_3): δ 0.50 (m, 2H, SiCH_2), 1.12 (t, 9H, OCH_2CH_3 , $J = 7.0$ Hz), 1.48–1.55 (m, 2H, $\text{SiCH}_2\text{CH}_2\text{CH}_2\text{N}$), 2.07 (s, 6H, $o\text{-CH}_3\text{C}_6\text{H}_2$), 2.22 (s, 3H, $p\text{-CH}_3\text{-C}_6\text{H}_2$), 3.51 (t, 2H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{Si}$, $J = 7.95$ Hz), 3.72 (q, 6H, OCH_2CH_3 , $J = 7.0$ Hz), 3.74 (s, 4H, $\text{NCH}_2\text{CH}_2\text{N}$), 4.06 (s, 2H, CH_2Mes), 5.38 ppm (s, 2H, $\text{C}_6\text{H}_2\text{Me}_3\text{-2,4,6}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 6.87 (SiCH_2), 17.10 ($o\text{-CH}_3\text{C}_6\text{H}_2$), 17.69 ($p\text{-CH}_3\text{C}_6\text{H}_2$), 18.69 (OCH_2CH_3), 22.38 ($\text{SiCH}_2\text{CH}_2\text{CH}_2\text{N}$), 47.35, 48.26 ($\text{NCH}_2\text{CH}_2\text{N}$), 49.93 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{Si}$), 51.87 (CH_2Mes), 58.68 (OCH_2CH_3), 88.49 ($o\text{-C}_6\text{H}_2\text{Me}_3$), 94.44 (*ipso* C), 99.62 ($3,5\text{-C}_6\text{H}_2\text{Me}_3$), 100.25 ($4\text{-C}_6\text{H}_2\text{Me}_3$), 200.17 ppm (NCN). Analytically calculated for $\text{C}_{22}\text{H}_{38}\text{N}_2\text{O}_3\text{Cl}_2\text{SiRu}$: C,

45.67; H, 6.57; N, 4.84. Found: C, 45.41; H, 7.12; N, 4.80.

2.5. Preparation of the P1–P3: general procedure

In a typical synthesis, at first solution was prepared by mixing tetraethylorthosilicate 13.86 g tetraethoxysilane (TEOS) was dissolved in 8 g of ethanol and 8.26 g of ethylene glycol with stirring at 80 °C in an oil bath. After 1 h of stirring, a mixture of 24 g of ethanol, 6 g of water and a catalytic amount of acetic acid was added to the system. After 3 h of reaction under the same conditions, clear, transparent gel was obtained. At the same time, a second solution was obtained by mixing **3–5** (0.1 mmol) in ethanol (10 ml) in the presence of acetic acid catalyst (0.1 ml). The two solutions were then mixed under stirring, and stirring was continued at room temperature for about 3 days. Then stirring was stopped. The resulting gel was recovered, washed with dichloromethane and filtered. Finally, samples were air-dried at room temperature for 24 h. The resulting gel was aged at ambient conditions for 2 days and dried in vacuum oven at 110 °C in a flow of O₂: 305 ± 5 m²/g BET surface area; 25 ± 12 Å pore diameter; 0.56 ± 01 ml/g pore volume.

2.6. Catalytic studies

The ruthenium complexes (0.1 mmol) was added to 10 mmol of neat (*Z*)-3-methylpent-2-en-4-yn-1-ol. The mixture was stirred at 25 or 80 °C for 1–16 h. The product was determined by GC. The immobilized complexes were washed with Et₂O, dried and reused.

3. Results and discussion

The carbene complexes **3–5** were synthesized according to the steps illustrated in Scheme 1. The preparation of the new salts **1** were readily accomplished by quarternization of 1-(3-triethoxysilylpropyl)-2-imidazoline (imeo) with the appropriate benzyl chloride. We chose imeo as starting material for two reasons: (i) it is commercially available and (ii) it has a ‘sticky end’, –Si(OEt)₃, which can be linked to the surface of the inorganic matrix. The salts **1** are colorless, hygroscopic and freely soluble in CHCl₃, but insoluble in hexane or diethyl ether. Their NMR spectra are in agreement with the assigned structures (Table 1). The proton attached to C-2 was observed as a singlet at ca. 10 ppm. This indicates that the proton is very acidic.

Reduction of the salts by sodium hydride gave the corresponding tetraaminoalkenes **2a** and **2b** in high yield. The alkenes were not characterized because of their extreme sensitivity towards oxygen and moisture. They were used directly for complexation reactions.

The carbene complexes were prepared by bridge splitting reaction of the dimers [RuCl₂(η⁶-arene)]₂ with the alkenes in toluene at 110 °C. It is worth noting that the alkene (**2b**), bearing bulky mesityl benzyl group on the N atom, simultaneously displaces the arene (*p*-cymene) attached to the Ru(II), resulting in a chelated carbene complex **5**. Previously we have reported thermally stable novel ruthenium complexes possessing carbene-η⁶-arene bidentate ligands [14].

The new complexes **3–5** were characterized by NMR spectroscopy and elemental analysis. Diagnostic ¹³C{¹H} and ¹H NMR data for the carbene complexes

Table 1
Selected IR, ¹³C{¹H} and ¹H NMR spectral data for the new compounds^a

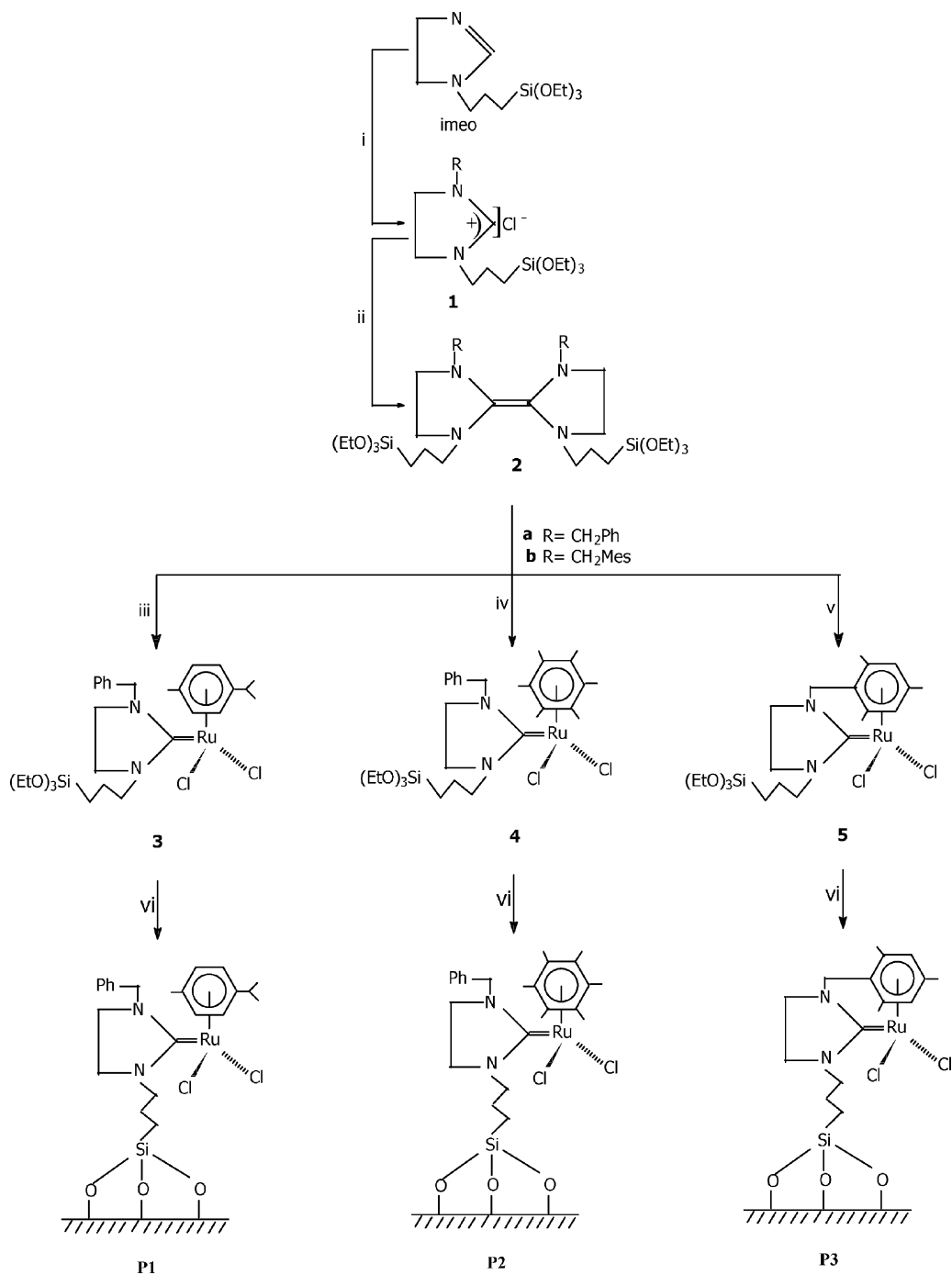
Compound number	ν(CN)	δ (¹³ C)			δ (¹ H) ^b		
		Ru = C	² C	² C–H	CH ₂ Ar	OCH ₂ CH ₃	OCH ₂ CH ₃
1a	c		159.05	10.25	4.90	3.80 (7.0)	1.20 (7.0)
1b	c		158.77	9.79	4.85	3.72 (7.0)	1.13 (7.0)
3	1497	207.68			4.86 ^d , 5.13	3.84 (7.0)	1.23 (7.1)
4	1489	210.18			4.08, 5.75	3.82 (7.0)	1.20 (6.95)
5	1520	200.17			4.06	3.72 (7.0)	1.12 (7.0)

^a The salts were included for comparison.

^b Coupling constants in parenthesis.

^c Not recorded due to hygroscopic property.

^d Not well resolved.



Scheme 1. Pathways to the synthesis of imidazolidinium salts **1**, tetraaminoalkenes **2**, carbene complexes **3–5** and their immobilization. Reagents and conditions: (i) PhCH₂Cl (or MesCH₂Cl), DMF, 25 °C; (ii) NaH, THF, 25 °C then 4 h, 65 °C; (iii) [RuCl₂(*p*-cymene)]₂, PhMe, 110 °C; (iv) [RuCl₂(η⁶-C₆Me₆)]₂, PhMe, 110 °C; (v) [RuCl₂(*p*-cymene)]₂, PhMe, 110 °C; (vi) TEOS (1:1 ratio), HCl, methanol.

are compared in Table 1. The carbene carbon chemical shifts all occur between 200 and 210 ppm. In the ^1H NMR spectrum of **3** the methylenes are well separated AB doublets. Furthermore, all methylene protons on the imidazolidine backbone and the spacer $-(\text{CH}_2)_3\text{Si}(\text{OEt})_3$ were observed as separated two multiplets.

Recently, the sol–gel process has been used to prepare hybrid organic–inorganic materials by hydrolysis and polycondensation of organometallic molecules substituted by more than one hydrolyzable $\text{Si}(\text{OR})_3$ groups with TEOS [15]. Co-condensation of **3**, **4** and **5** with TEOS in the presence of aqueous HCl results in the formation of powdery or granular water insoluble solids (Scheme 1).

All the evidences from FT-IR, TGA, DTA and elemental analysis supported the successful grafting of carbene–Ru(II) on the surface of silica. The grafting efficiency of carbene–Ru(II) (P1–P3) on silica was studied as a function of reaction temperature, which was changed from room temperature to the boiling point of the solvent. The results showed that the grafting efficiency was improved by raising the temperature. The grafting efficiency of P1 as a function of reaction time was also studied from 4 to 24 h. It was found that the reaction time between 18 and 24 h was necessary for optimal grafting. The effect of carbene–Ru(II) concentration on grafting efficiency was revealed that depending upon the amount of silanol (SiOH) groups present on the silica surface that is less than 0.034 mol/g, the theoretical amount of carbene–Ru(II) for 1 g of silica is $0.034/3 = 0.011$ mol. This evidence was supported by TGA analysis, from 0.01 to 1 mol ratio the grafting efficiency was increased to 9.2 to 12.7% , and then remains constant with further increase in carbene–Ru(II) concentration so the optimum carbene–Ru(II) concentration was found to be 0.025 mol/g silane.

Proof for the structures of the complexes P1–P3 was given through the carbene atom resonances (P1 $\delta = 206.32$, P2 $\delta = 205.98$ and P3 $\delta = 197.74$) which are in a typical range of starting monomeric metal carbene complexes (**3–5**). The infrared spectra of the polymeric materials show about the same $\nu(\text{CN})$ bands as starting complexes. This further indicates that the complexes have been successfully anchored to the silica surface. Standard conditions (monomer:TEOS = 1:1) were used for all condensation reactions. The reaction

behavior of the materials were determined by differential thermal analysis at a heating rate of $10^\circ\text{C}/\text{min}$. On heating the sample sharp exotherms appeared at 363, 364 and 394°C for materials P1, P2 and P3, respectively. This indicates thermal stability of the materials are higher than corresponding monomers. The results are in accordance with the proposed structures where P3 possess more rigid structure as outlined. The curing temperature could be chosen as the approximate midpoint between the start of exothermic

Table 2
Catalytic synthesis of 2,3-dimethylfuran

Entry	Catalyst	Temperature ($^\circ\text{C}$)	Time (h)	Yield (%) ^a
1	3	RT	0.5	59
2	3	RT	2.5	61
3	3	RT	16	87
4	4	RT	0.5	13
5	4	RT	16	41
6	5	RT	0.5	61
7	5	RT	2	97
8	3	80	1	95
9	4	80	1	86
10	5	80	1	97
11	P1	RT	1	21
12	P1	RT	6	36
13	P2	RT	1	09
14	P2	RT	8	14
15	P3	RT	1	39 ^b
16	P3	RT	3	43 ^b
17	P3	RT	1	37 ^c
18	P3	RT	4	40 ^c
19	P3	RT	1	36 ^d
20	P3	RT	4	38 ^d
21	P1	80	1	84
22	P1	80	3	90
23	P2	80	1	62
24	P2	80	5	84
25	P3	80	1	93 ^b
26	P3	80	1	82 ^c
27	P3	80	2	91 ^c
28	P3	80	1	81 ^d
29	P3	80	2	90 ^d
30	P3	80	1	79 ^e
31	P3	80	2	92 ^e
32	P3	80	1	81 ^f
33	P3	80	2	92 ^f

^a Determined by GC.

^b First run.

^c Second run.

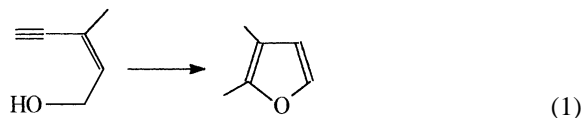
^d Third run.

^e Fourth run.

^f Fifth run.

peak (approximately 350 °C) and the thermal decomposition of materials (approximately 400 °C).

In a preliminary catalytic study, we used (*Z*)-3-methylpent-2-en-4-yn-1-ol to investigate potential of monomeric (**3–5**) and immobilized complexes (P1–P3) for the furan formation. The reaction (Eq. (1)) proceeded smoothly at 25–80 °C.



The reaction rate and yield increases in the series $4 < 3 < 5$. The presence of bulky 2,4,6-trimethylbenzyl as *N*-substituent with the chelated form (**5**) has an extremely positive effect on catalytic activity (Table 2). Although, slower at 25 °C, the polymer P3 was found to be active in this reaction at 80 °C. Moreover, P3 can be recycled up to five times without losing significant activity (Table 2, entries 25–33).

4. Conclusion

We have developed a convenient synthetic route to heterogenize catalytically active *N*-heterocyclic carbene complexes by hydrolyzing and condensation of $-\text{Si}(\text{OEt})_3$ group attached through $-(\text{CH}_2)_3-$ spacer to *N* atom of the carbene ligand. All immobilized complexes display catalytic activity in the furan formation. However, the activity of the mesityl chelated complex (**5**) is comparable to that of most active binuclear Ru(II) complexes. P3 is the most active among the polymers and can be recycled at least five times (Table 2). We are currently investigating scope and application of these complexes as catalysts for various organic reactions. Performing the reaction at elevated temperature (80 °C) increases the yield.

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