

Synthesis of new ruthenium(II) complexes containing isocyanide and labile nitrile ligands

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ABSTRACT

*A new ruthenium(II) complex containing both acetonitrile and propionitrile moieties as coordinating ligands has been prepared. The treatment of the polymer $[\{\text{RuCl}_2(\text{COD})\}_x]$, (COD = cycloocta-1,5-diene) (**1**) with a mixture of acetonitrile and propionitrile under reflux produced a new precursor $[\text{RuCl}_2(\text{COD})(\text{NCCH}_3)(\text{CH}_3\text{CH}_2\text{CN})]$ (**2**). Also the compound $[\text{RuCl}_2\text{L}_4]$ (**3**) (L = 2,6-dimethylphenylisocyanide) was prepared through a ligand exchange of a derivative of **1**, $[\text{RuCl}_2(\text{COD})(\text{NCCH}_3)_2]$ (**4**), with 2,6-dimethylphenylisocyanide. The two compounds were characterized by elemental analyses, IR and NMR (^1H and ^{13}C) measurements. The ruthenium in both compounds has distorted octahedral coordination geometry.*

Key words: Nitrile ligands, ruthenium(II), 2,6-dimethylphenylisocyanide, spectroscopic analysis

INTRODUCTION

There is continued interest in the study of the chemistry of transition metal complexes containing coordinated acetonitriles as ligands. This is due to high lability of the acetonitriles in these compounds and these complexes have therefore been variously applied as convenient precursors to the synthesis of other active transition metal compounds¹. Since these nitrile ligands are weakly bonded to the central metal ions, they are easily dissociated thereby creating vacant coordination sites which allow the metal center to interact with substrates. This is an important and necessary requirement for homogeneous catalysts to function at optimum capacity². A general synthetic strategy to preparing nitrile containing ruthenium complexes based on the readily

available polymeric species $[\{\text{RuCl}_2(\text{COD})\}_x]$ (**1**) has been developed^{1,3}. The η^4 -coordinated COD ligand in the polymer is very labile in solution and therefore undergoes exchange reactions under very mild conditions⁴. The polymer readily dissolves in refluxing acetonitrile to give a yellow solution on filtration, the yellow solution is then kept at 0 °C for 24 hours after which the product $[\text{RuCl}_2(\text{COD})(\text{NCCH}_3)_2]$ (**2**) crystallized out⁵. The ruthenium complex **2** contains labile ligands that can be easily replaced by other ligands, an extensive range of active ruthenium(II) compounds have been reported based on this technique⁶⁻⁹. There is continued research into isocyanides metal complexes mainly due to their rich

coordination chemistry and wide applications in catalysis¹⁰. Several metal complexes containing isocyanides as coordinating ligands have been reported and many of these complexes have been applied as excellent catalysts in some important reactions. Polymerization of ethylene in the presence of methylaluminoxane have been achieved using nickel(II) isocyanide complexes¹¹. Hydrosilylation of alkene and styrene derivatives have also been carried out in the presence of catalyst systems composed of organoiron(0) or (II) with isocyanides as auxiliary ligands¹². Palladium-*tert*-alkyl isocyanide complexes were applied as catalysts in the intramolecular silylation of C-C multiple bonds catalyzed by have been reported¹³.

The catalytic properties of these ligands highly depend on the steric effect and electronic factors of the alkyl groups in the isocyanides, we have therefore chosen 2,6-dimethylphenylisocyanide as a coordinating ligand to the Ru(II) center in the present study. Synthesis of new ruthenium(II) complexes containing labile nitrile ligands and their applications in catalysis have been a subject of on-going research in our laboratory^{14,15}.

Recently, a highly active transfer hydrogenation catalyst based on acetonitrile and dimethylphenylphosphonite was reported by our group¹⁵. We now report the synthesis of a new ruthenium-organonitrile complex and preparation of tetrakis(2,6-dimethylphenyl isocyanide)dichlororuthenium(II) using **3** as precursor.

EXPERIMENTAL

Materials and methods

The ruthenium trichloride hydrate was a commercial product from Acros Organics. All other reagents were of analytical grade, commercially sourced from Sigma-Aldrich and were used as received. The methanol and ethanol used in the synthesis of the ruthenium complexes were freshly dried over 3 Å molecular sieves overnight followed by distillation under nitrogen. The other solvents were passed over a column of activated alumina just before use. The known compounds **1** and **4** were prepared using literature procedures^{3,5}. All the reactions were performed in air. Melting points were obtained on a Kofler microhotstage apparatus and were uncorrected. Infrared spectra were recorded on a Bruker Tensor 27 FTIR spectrophotometer at Molecular Sciences Institute, School of Chemistry, University of the Witwatersrand, South Africa. The NMR spectra were recorded on a Bruker Avance 400 MHz instrument at the Department of Chemistry, University of Connecticut, USA. NMR spectra were referenced internally to residual solvent resonances (¹H). Elemental analyses were determined at the Institute of Material Science, University of Connecticut, USA.

Preparation of the ruthenium(II) complexes

Synthesis of dichloro(acetonitrile) (propionitrile) (η^4 -1,5-cyclooctadiene)ruthenium(II)(2)

A suspension of [$\{\text{RuCl}_2(\text{COD})\}_x$] (0.40 g, 1.43 mmol) in a mixture of acetonitrile (5 mL) and propionitrile (5 mL) was heated under reflux overnight. The resulting orange solution was filtered hot to remove the unreacted materials. The volume of the solution was then reduced to 20 mL under a reduced pressure and stored at -5 °C for several hours. A crop of

orange crystals was obtained after 24 hours, and was collected through filtration and washed with diethylether (2×5 mL). Orange crystals; Yield 0.0447 g, 8.2%; m.p. ($^{\circ}\text{C}$): 175–178; IR: 2943 (m); 2913 (m); 2270 (m); 2011 (w); 1452 (m); 1422 (m); 1377 (m); 1315 (w); 1251 (w); 1070 (w); 944 (m); 849 (m); 787 (m); 364 (s); 270 (s). ^1H NMR (CDCl_3) δ (ppm): 1.34 (t, CH_3); 1.61 (s, CH_3); 2.14 (s, CH_2); 2.49 (s, CH_2); 2.81 (q, CH_3); 4.25 (s, CH). ^{13}C NMR (CDCl_3) δ (ppm): 5.09 (s, CH_3); 10.65 (s, CH_3); 13.58 (s, CH_2); 122.15 (s, CH); 126.06 (s, CH). Elemental analysis for $\text{C}_{13}\text{H}_{20}\text{Cl}_2\text{N}_2\text{Ru}$, Calcd. (Found): C, 41.49 (41.58); H, 5.32 (5.71); N, 7.45 (7.48).

Synthesis of tetrakis(2,6-dimethylphenyl isocyanide)dichlororuthenium(II) (3)

A 100 mL Erlenmeyer flask containing a magnetic stirring bar and fitted with a reflux condenser was charged with $[\text{RuCl}_2(\text{NCCH}_3)_2(\text{COD})]$ (0.2 g, 0.5 mmol) and 2,6-dimethyl isocyanide (0.524 g, 4 mmol). Ethanol (20 mL) was added and the resulting solution was heated under reflux for 45 minutes and filtered; a bright yellow solution was obtained. The yellow solution was concentrated under reduced pressure to a volume of 5 mL followed by cooling to -5°C for several hours to give a yellow precipitate. The precipitate was dried under vacuum to obtain the product as a yellow powder. Yellow powder; Yield: 0.25 g, 71%; mp 163–165 $^{\circ}\text{C}$; ^1H NMR (CDCl_3) δ (ppm) 1.67 (6H, s, CH_3); 7.24 (8H, m, C_6H_4), 7.96 (8H, m, C_6H_4), IR $\nu(\text{CN})$ 1589, 829 cm^{-1} . Elemental analysis for $\text{C}_{36}\text{H}_{36}\text{Cl}_2\text{N}_4\text{Ru}$, Calcd. (Found): C, 62.07 (62.19); H, 5.17 (5.26); N, 8.05 (8.41).

Synthesis of bis(acetonitrile)dichloro(η^4 -1,5-cyclooctadiene)ruthenium(II) acetonitrile monosolvate (4)

This compound was prepared by following a reported procedure⁵. A suspension of the polymer $[\{\text{RuCl}_2(\text{COD})\}_x]$ (0.6 g, 2.14 mmol) in acetonitrile (50 mL) was heated under reflux for 5 hours. Then 1,5-cyclooctadiene (1 mL) was added to the mixture during reflux to suppress the formation of $[\text{RuCl}_2(\text{NCCH}_3)_4]$. The bright orange solution obtained was filtered hot and reduced in volume to 15 mL, it was then cooled to -5°C for several hours. A crop of yellow crystals was obtained after six hours. The yellow crystals were collected through filtration and washed with chilled acetonitrile (2 mL) and diethylether (2×5 mL). The crystals were suitable for X-ray diffraction studies. Yellow crystalline solids; Yield 0.4782 g, 56%; m.p. ($^{\circ}\text{C}$): 173–175; IR: 3480 (m); 2966 (w); 2924 (w); 2858 (w); 2411 (w); 2308 (w); 2151 (w); 1612 (w) 1449 (w); 1421 (m); 1374 (w); 1341 (w); 1308 (w); 1042 (m); 1007 (w); 953 (w); 871 (w); 841 (w); 782 (w); 565 (w); 554 (w); 540 (w); 383 (s). ^1H NMR (CDCl_3) δ (ppm): 4.27 (s, CH , 4H); 2.61 (s, CH_3 , 6H); 2.42 (m, CH_2 , 4H); 2.02 (m, CH_2 , 4H); 1.72 (s, CH_3 , 3H). ^{13}C NMR (CDCl_3) δ (ppm): 4.87 (s, CH_3); 29.45 (s, CH_2); 89.95 (s, CN); 125.76 (s, CH). Elemental analysis for $\text{C}_{14}\text{H}_{21}\text{Cl}_2\text{N}_3\text{Ru}$, Calcd. (Found): C, 41.69 (41.86); H, 5.21 (5.23); N, 10.42 (10.56).

RESULTS AND DISCUSSION

The synthesis and crystal structure of **4** derived from the polymer $[\{\text{RuCl}_2(\text{COD})\}_x]$ has been reported by us previously⁵. The same procedure was adopted in the preparation of **2**

while complex **3** was derived from **4** through ligand exchange of the labile CH_3CN group with 2,6-dimethylphenyl isocyanide. Spectroscopic and X-ray diffraction analyses has provided sufficient evidence for assigning a *trans*-arrangement of the acetonitrile ligands in **4**^{1,5}. It is therefore believed that the nitrile ligands in the new complex **2** are also in *trans*-positions (Fig. 1a). The IR spectral data of **2** contain $\nu(\text{CN})$ bands which are to higher frequency than is observed in the free nitrile in agreement with previous reports^{1,5,16}. This has been attributed to the coordination mode of the nitrile ligands to the ruthenium centre through the nitrogen atom^{1,5}. The protons of the propionitrile ligands in **3** were observed at δ_{H} 1.47 and 2.84 ppm with extra ^1H resonances at δ_{H} 2.59 and 2.48 ppm attributable to the presence of acetonitrile in its structure¹. In the ^{13}C NMR of **2** (Fig. 1b), propionitrile CH_3 was observed at δ_{C} 13.58 ppm while its CH_2 appeared at δ_{C} 10.65 ppm. This spectrum also contains an extra line at δ_{C} 5.09 ppm attributable to the CH_3 of the acetonitrile moiety. It can therefore be concluded that a complex containing both aceto- and propionitrile moieties attached to a ruthenium(II) centre is formed.

Treatment of a mixture of the polymer $[\{\text{RuCl}_2(\text{COD})\}_x]$ and four equivalent of 2,6-dimethylphenyl isocyanide in acetonitrile under reflux for 5 hours yielded a complex $[\text{RuCl}_2\text{L}_4]$ ($\text{L} = 2,6\text{-dimethylphenyl isocyanide}$) (**3**) shown

in Fig. 1b. In the ^1H NMR of this complex, the methyl groups on the ligand are symmetric and therefore were observed as a singlet at δ_{H} 2.55 ppm integrating to 24 protons while the phenyl protons were present between δ_{H} 7.01 – 7.26 ppm¹⁷. The presence of two weak resonances at δ_{H} 2.01 and 5.30 ppm in the ratio of 2:1 integrating to 12 protons suggest that the complex might contain a trace amount of another compound with a coordinated cyclooctadiene. This complex was, however, produced without any trace of impurity by the treatment of ethanolic solution of **4** and 2,6-dimethylphenyl isocyanide in the ratio 1:4 under reflux for 45 minutes. As observed in the NMR of compound **3**, no traces of cyclooctadiene ligand could be observed at the expected regions in the NMR spectrum (Fig. 2). A sharp band at ν 2130 cm^{-1} in the IR spectrum of the complex indicated a weakly bonded Ru-CN which will make the ligand a labile one in this complex. A strong isocyanide peak at ν 2116 cm^{-1} in the IR of compound **3** also indicate a weakly bonded 2,6-dimethylphenyl isocyanide to the ruthenium(II) center⁹. However, we could not prepare compound **3** by direct reaction of the polymer, $[\{\text{RuCl}_2(\text{COD})\}_x]$ and 2,6-dimethylphenylisocyanide as in the case of compound **2**.

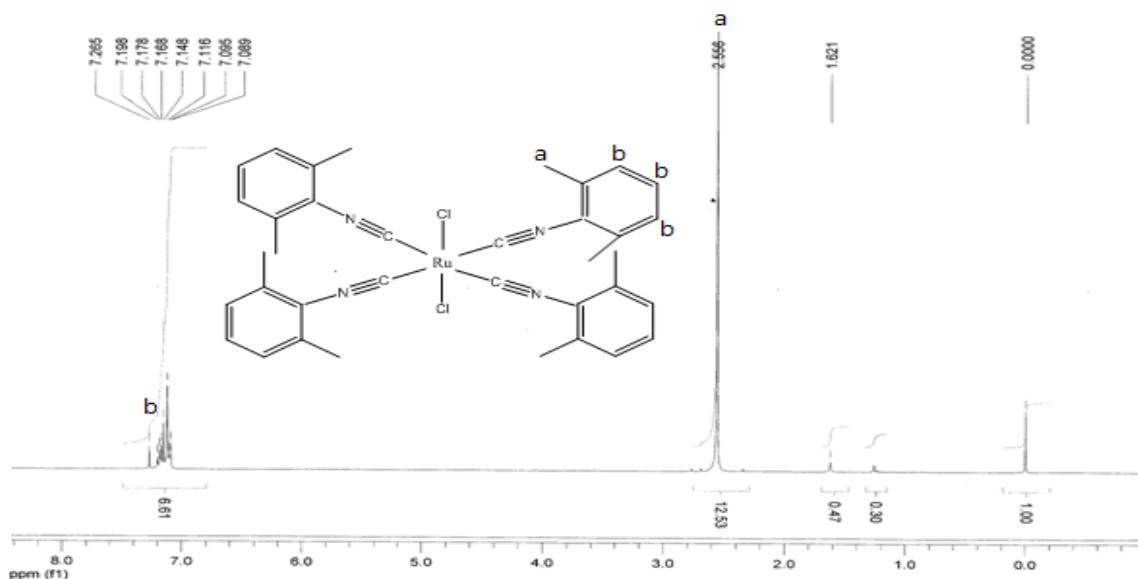
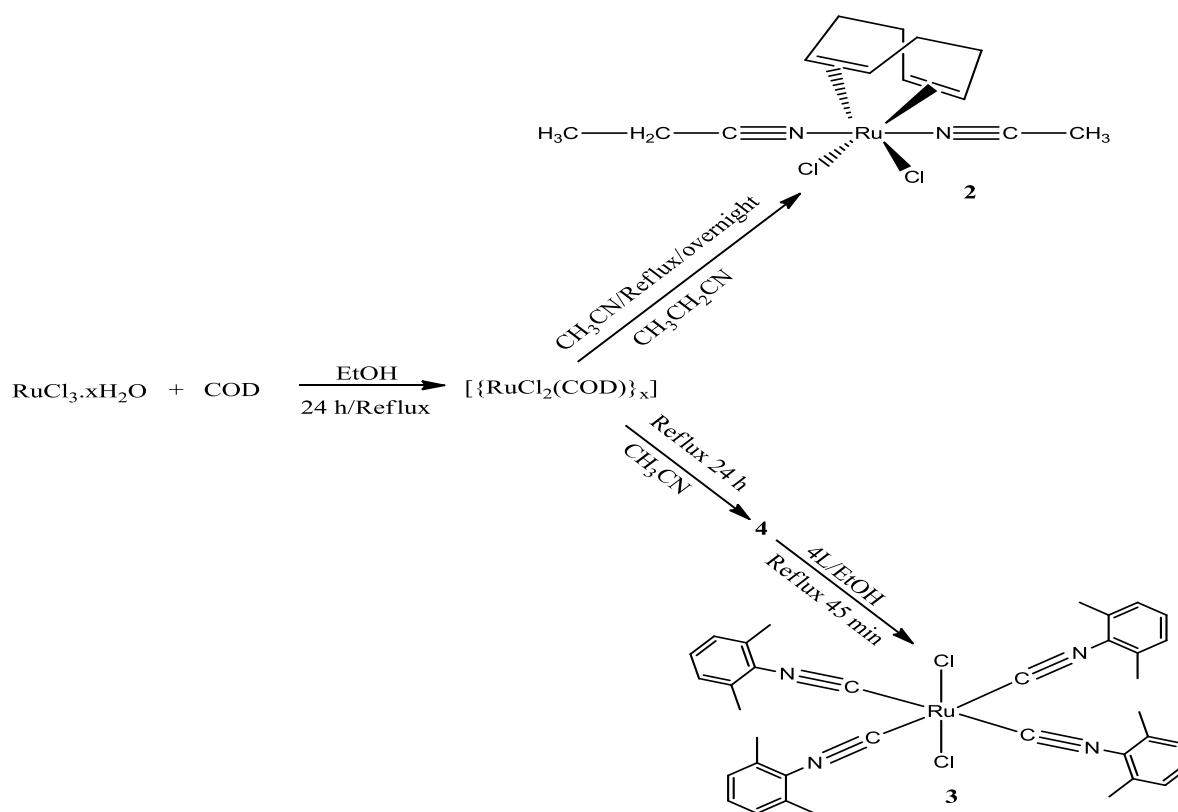


Fig. 2. ^1H NMR spectrum of complex **3**



Scheme 1: The synthetic route to the ruthenium(II) complexes (COD = cycloocta-1,5-diene; L = 2,6-dimethylphenylisocyanide)

CONCLUSIONS

The reaction of the polymer $[\{ \text{RuCl}_2(\text{COD}) \}_x]$ with a mixture of acetonitrile and propionitrile under reflux produced a new ruthenium(II)-organonitrile precursor

$[\text{RuCl}_2(\text{COD})(\text{NCCH}_2\text{CH}_3)(\text{NCCH}_3)]$ while the treatment of $[\text{Ru}(\text{COD})(\text{NCCH}_3)_2]$ with 2,6-dimethylphenylisocyanide in ethanol gave a new compound $[\text{RuCl}_2\text{L}_4]$ ($\text{L} = 2,6$ -dimethylphenylisocyanide). The two complexes were isolated as air and moisture stable solids and were characterized by IR and NMR spectroscopic techniques as well as elemental analysis. Work is in progress on the applications of compound **2** as a precursor to the preparation of catalytically active Ru(II) compounds.

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