

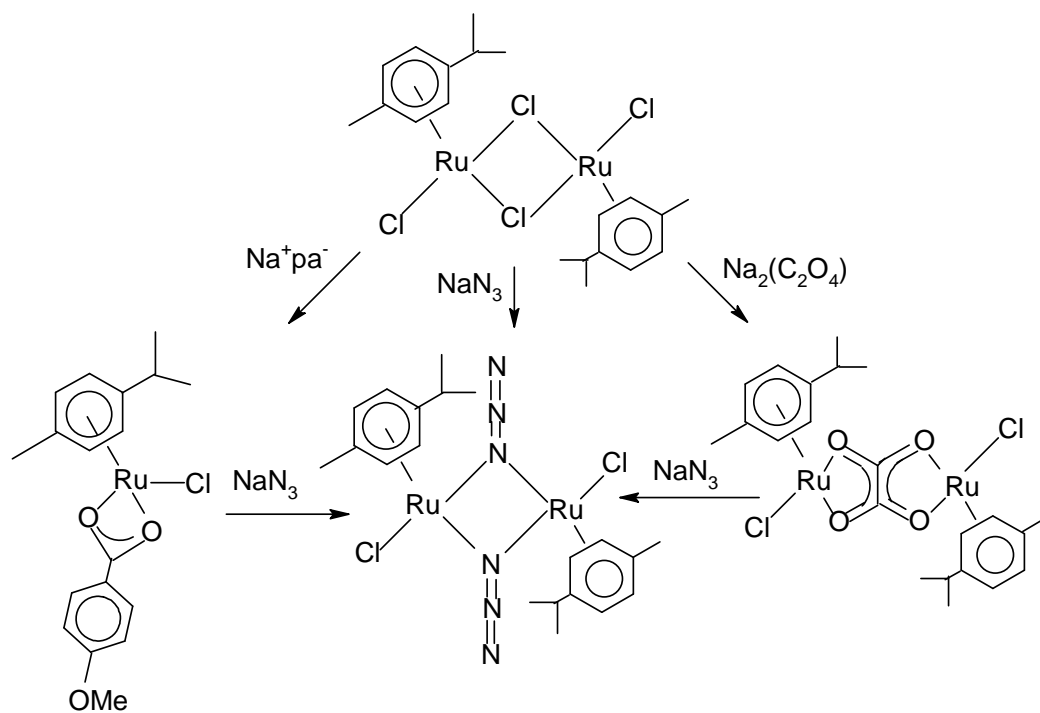
Reactivity studies of η^6 -*p*-cymene ruthenium(II) carboxalato complexes towards azide and some neutral ligands

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A series of η^6 -*p*-cymene ruthenium (II) complexes containing carboxylate ligands have been prepared by the reaction of [$\{\eta^6$ -cymene)RuCl₂]₂ with sodium salt of carboxylic acids. The carboxylate ligands in the complexes [(η^6 -*p*-cymene)Ru(pa)Cl] and [$\{\eta^6$ -cymene)RuCl]₂(μ L)] were readily displaced upon treatment with NaN₃ to give azide bonded complex [$\{\eta^6$ -cymene)Ru(μ N₃)Cl]₂.



Reactivity studies of η^6 -*p*-cymene ruthenium(II) carboxylato complexes
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Abstract

Mono and di-nuclear η^6 -*p*-cymene ruthenium(II) complexes containing carboxylato ligand of formulation $[(\eta^6\text{-}p\text{-cymene})\text{Ru}(\text{pa})\text{Cl}]$ and $[\{(\eta^6\text{-}p\text{-cymene})\text{Ru Cl}\}_2(\mu\text{-LL})]$ [where; pa = O₂CC₆H₄-*p*-OMe (**1**), LL = C₂O₄ (**7**) or C₂CH₂O₄ (**10**)] have been prepared by the reaction of $[(p\text{-cymene})\text{RuCl}_2]_2$ with the corresponding sodium salts of the carboxylic acids. Treatment of $(\eta^6\text{-}p\text{-cymene})$ ruthenium(II) carboxylato complexes with NaN₃ yielded azido complex $[\{(\eta^6\text{-}p\text{-cymene})\text{Ru}(\mu\text{-N}_3)\text{Cl}\}_2]$ whereas halide scavengers such as silver acetate, silvertrifluoroacetate leads to the substitution of chlorine to give neutral complexes of formulation $[\{(\eta^6\text{-}p\text{-cymene})\text{RuY}\}_2(\mu\text{LL})]$ (where, LL = bidentate carboxylate, Y = MeCO₂ or CF₃CO₂). Mono and dicationic complexes were also been prepared by the treatment of complex **1** with the corresponding neutral ligands in the presence of AgBF₄. The complexes were fully characterized on the basis of microanalysis, FT IR and NMR spectroscopic data.

Key words: *p*-cymene, ruthenium, azide, bipyridine, spectroscopy.

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1. Introduction

During the past few decades (η^6 -arene) ruthenium (II) complexes have been subjects of intense research in the field of organometallic chemistry¹. Many of these complexes in particular water soluble complexes are reported to possess anti-tumour² and anticancer activities³ as well as demonstrate catalytic properties towards various reactions⁴. Catalytic activities of these complexes are ranges from hydrogen transfer⁵ to ring closer metathesis⁶. There are several reports, available on the reactivity study of (η^6 -arene) ruthenium (II) dimer with nitrogen base ligands^{7,8}. In contrast, study on (η^6 -arene) ruthenium (II) complexes with oxygen donor ligands is relatively remains unexplored except a few report appeared in recent years⁹⁻¹². In our previous communication, we described the synthesis of a series of (η^6 -arene) ruthenium (II) triazole compounds and azido compounds containing oxygen chelating ligands^{10,11}.

As part of our investigation on (η^6 -arene) ruthenium (II) complexes chelating with oxygen donor ligands, herein, we wish to report the synthesis of mono and di-nuclear arene ruthenium complexes containing carboxylato groups and study their reaction towards azide and some neutral monodentate and bidentate ligands. The complexes were characterized on the basis of microanalysis, IR and NMR spectroscopic data.

2. Results and discussion

The reaction of [$\{(\eta^6$ -*p*-cymene)RuCl₂]₂] with sodium salts of the ligand, *p*-Anisic acid (pa) in methanol yield an orange yellow mononuclear complex of formulation [$\{(\eta^6$ -*p*-cymene)RuCl(pa)₂] (1) in good yield (Scheme 1). The complex 1 was readily obtained by stirring complex [$\{(\eta^6$ -*p*-cymene)RuCl₂]₂] and sodium salt of ligand (pa) at room temperature for 1 to 2 hrs. The complexes were isolated as air stable orange yellow solid, soluble in most of the chlorinated solvents and isolated in 87% yield. The proton NMR spectrum of 1 is in well agreement with its composition (figure 1).

A closely related compound [$(\eta^6$ -arene)RuCl(O₂R)] (where; R = Me) have been reported by heating η^6 -arene dichloro organoruthenium (II) dimmer with a mixture of carboxylic acid and acid anhydride for 5 hr to 5 days which gave 50-80% yield¹³. Our method for the preparation of *p*-cymene ruthenium(II) carboxylate complexes by using sodium salts of the carboxylic acid is found to be more convenient and yield are comparatively high. Treatment of complex 1 with neutral mono-dentate ligand yielded new cationic complexes of formulation [$\{(p$ -cymene)Ru(pa)(L₁)₂]⁺ (scheme 1) (where L = PyCN, 2; DAMP, 3) while bidentate ligands such as 4,4'-bipy, pyrazine and DCB in the presence of AgBF₄ afforded a dinuclear complexes of formulation [$\{(p$ -cymene)Ru(pa)₂(L₂)₂]⁺² (L₂= 4,4'-bipy, 4; py, 5; DCB, 6) (Scheme 1). The complexes were isolated as their tetrafluoroborate salts in 50-

90% yield. IR spectrum of complex **2** shows absorption band at 2235 cm^{-1} due to $-\text{CN}$ stretching frequency (ν_{CN}). The spectroscopic data are well in agreement with the formulation of these complexes (see experimental section). The mononuclear complexes **2** and **3** were isolated as a dark brown solid soluble in most of the chlorinated solvent. ^1H NMR spectrum of complex **3** exhibited the resonance for methyl protons of isopropyl group as two doublets at around 1.09 and 1.17 ppm, respectively, and more than two sets of doublets for *p*-cymene ring protons was observed at around 6 ppm which could be due to loss of planarity of the cymene ring because of steric hindrance of ligand. The spectrum also displayed a singlet at δ 3.03 assignable to methyl protons of NMe_2 . The spectrum shows four distinct signals in the aromatic region assignable to the ring proton of PyCN. The *p*-cymene ring proton is observed more than two sets of doublets as observed in the complex **3**.

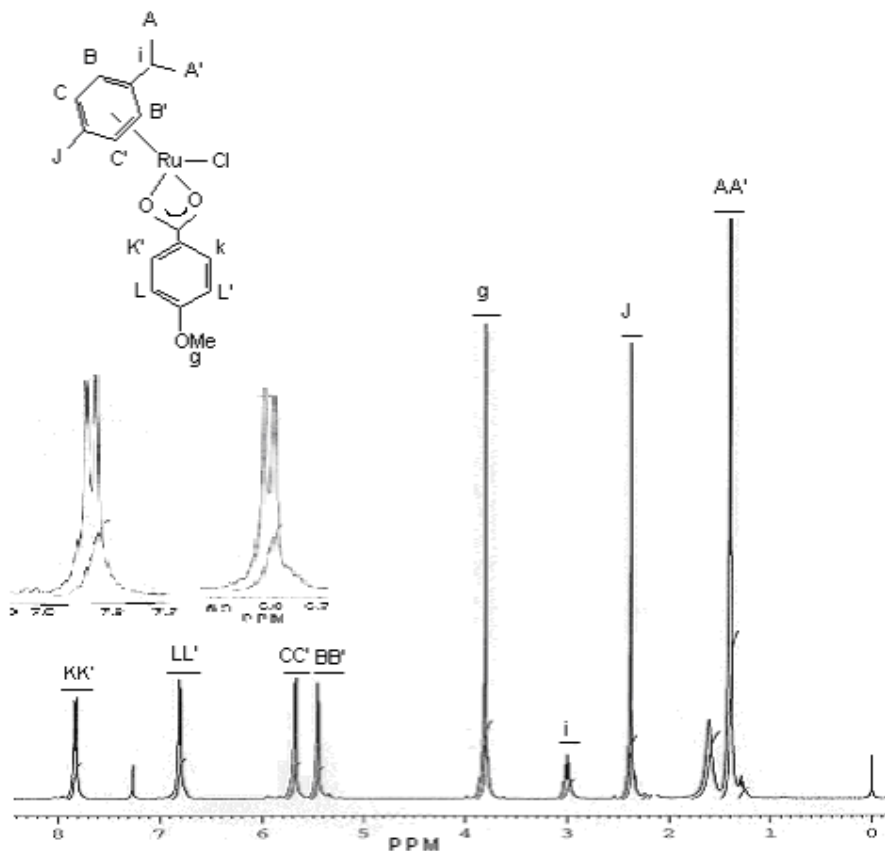
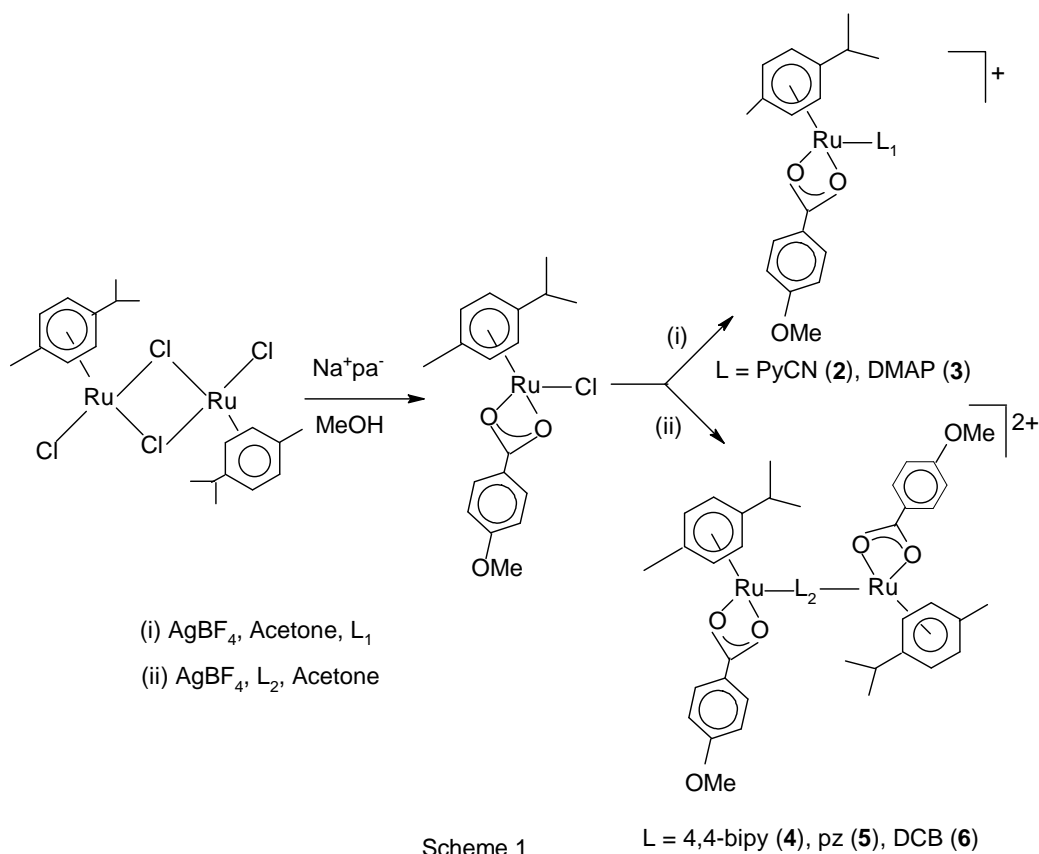
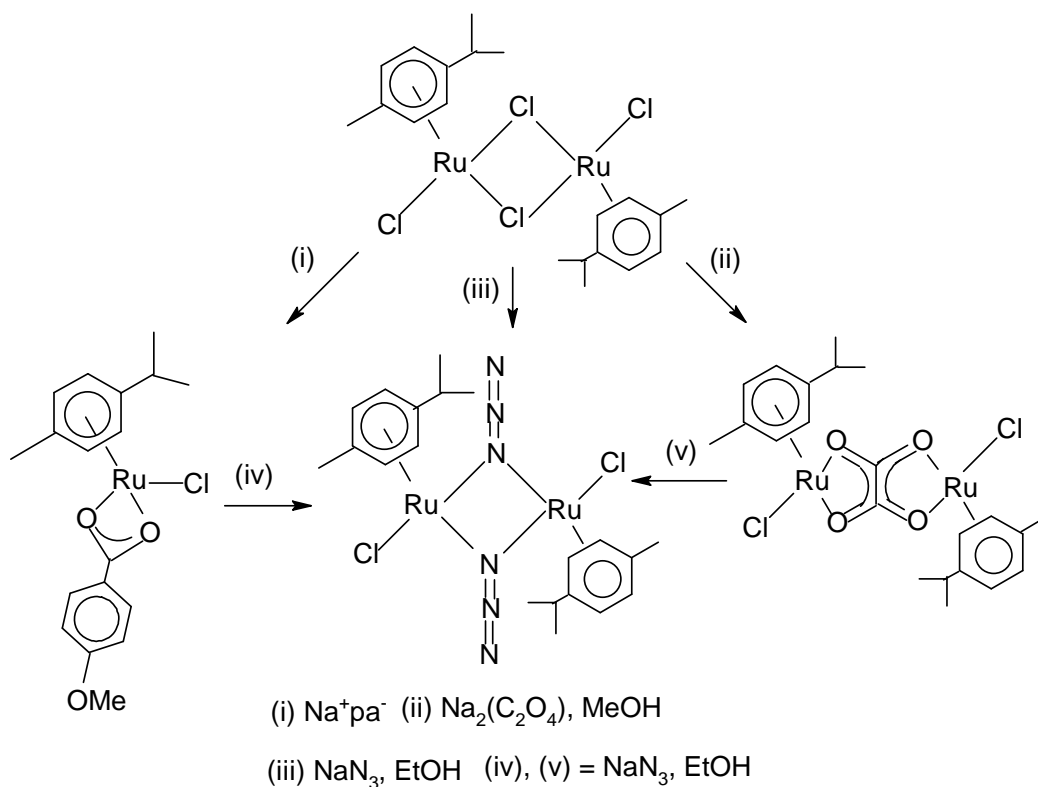


Fig 1: ^1H NMR spectrum of complex **1**



Di-nuclear complexes containing carboxylato group of the type $[\{(\eta^6\text{-p-cymene})\text{Ru}\}_2(\mu\text{LL})]$ ($\text{LL} = \text{C}_2\text{O}_4$, **7**; $\text{C}_2\text{O}_4\text{CH}_2$, **10**) were prepared by treating $[\{(\eta^6\text{-p-cymene})\text{RuCl}\}_2]$ with sodium salts of corresponding carboxylic acids viz *Oxalic acid* or *Malonic acid*. Notably, Süß Fink and coworkers reported the preparation of dinuclear complex **7** by refluxing $[\{(\eta^6\text{-p-cymene})\text{RuCl}\}_2]$ with ammonium oxalate in $\text{CHCl}_3/\text{MeOH}$ for 6hrs¹⁴. We reinvestigated the preparation of this complex and reported here an improved method using sodium salt of the acid instead of ammonium salt. Treatment of equimolar quantity of sodium salt of oxalic acid with $[\{(\eta^6\text{-cymene})\text{RuCl}\}_2]$ afforded a yellow solid of the complex $[\{(\eta^6\text{-cymene})\text{RuCl}\}_2(\eta^4\text{-C}_2\text{O}_4)]$ (**7**) in good yield (93%). The advantage of our method is that complex was precipitated out readily within 1 hour by stirring at room temperature and yield was comparatively high. The IR spectrum of complex **7** showed a sharp single peak at 1619 cm^{-1} characteristic of $\nu(\text{C}=\text{O})$ which is slightly lower than the reported in copper oxalato system¹⁵. The single absorption peak indicates the delocalization of electron in oxalato group. The $^{13}\text{C}\{^1\text{H}\}$ NMR data of complex **7** exhibits a singlet at 171 ppm assignable to the carbon of CO_2 group. The complex **7** has been fully characterized by analytical and spectroscopic data (^1H , $^{13}\text{C}\{^1\text{H}\}$ NMR data, detail are given in experimental section) and confirmed by X-ray crystallography. Since the single crystal data well matched o the one reported by earlier workers¹⁴,

details structural data are not being reported here. In similar manner a closely related dinuclear complex of formulation $[\{(\eta^6\text{-}p\text{-cymene})\text{RuCl}\}_2(\mu\text{-C}_2\text{O}_4\text{CH}_2)]$ (**10**) can be prepared by treatment of complex $[\{(\eta^6\text{-}p\text{-cymene})\text{RuCl}_2\}_2]$ with sodium malonate in methanol at room temperature. In an attempt to synthesis $[\{(\eta^6\text{-}p\text{-cymene})\text{RuN}_3\}_2(\mu\text{-C}_2\text{O}_4)]$ by treating the complex $[\{(\eta^6\text{-}p\text{-cymene})\text{RuCl}\}_2(\mu\text{-C}_2\text{O}_4)]$ (**7**) with sodium azide in ethanol afforded a a dimeric compound $[\{(p\text{-cymene})\text{Ru}(\text{N}_3)\text{Cl}\}_2]$ analogous to the complex obtained by the reaction of $[\{(\eta^6\text{-}p\text{-cymene})\text{RuCl}\}_2]$ with trimethylsilyl azide by Bates *et al.*¹⁶ (Scheme 2). The formation of this complex follows from the complete disappearance of CO stretching frequency at 1619 cm^{-1} and appearance of strong absorption band at 2057 cm^{-1} characteristic band for bridging azide ligands.¹⁶ We believe that the complex was resulted by the displacement of *oxalato* group with azido group yielding a well known azide dimer $[\{(\eta^6\text{-}p\text{-cym})\text{Ru}(\mu\text{N}_3)\text{Cl}\}_2]$ which had already been synthesized and structurally characterized by previous workers¹⁷. A similar observation was found upon treatment of complex **1** and complex **10** with NaN_3 . This leads to our conclusion that $(\eta^6\text{-cymene})$ ruthenium carboxylato complexes gave azide dimer $[(\eta^6\text{-}p\text{-cym})\text{Ru}(\mu\text{N}_3)\text{Cl}]_2$ upon treatment with sodium azide irrespective of the coordinated carboxylate ligands. Substitution of chlorine in the complexes **7** and **10** by other anions was achieved by treatment of the complexes with silver salts. Thus, reaction of complex **7** with silver acetate or trifluoro-silver acetate in ethanol leads to the displacement of chlorine with acetate anion to gave complexes of general formula $[\{(\eta^6\text{-}p\text{-cymene})\text{Ru}(\text{OCOR})_2(\mu\text{-C}_2\text{O}_4)]$ (R = $-\text{CH}_3$ (**8**) $-\text{CF}_3$ (**9**)).



Scheme 2

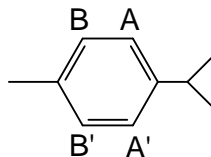
The IR spectrum of the complexes showed absorption peaks for $\nu(\text{C}=\text{O})$ of acetate and *oxalato* group. Similarly, reaction of complex $[\{(\eta^6\text{-}p\text{-cymene})\text{RuCl}_2(\mu\text{-C}_2\text{O}_4\text{CH}_2)\}]$ with silver acetate or silver trifluoro-acetate in ethanol gave a yellow compound of formulation $[\{(\eta^6\text{-}p\text{-cymene})\text{Ru}(\text{OCOR})_2(\mu\text{-C}_2\text{O}_4\text{CH}_2)\}]$ ($\text{R} = \text{CH}_3$, **11** CF_3 , **12**). The complexes are stable in air and soluble in most of the chlorinated solvents.

Experimental

3.1 Materials and methods

All solvents were dried in appropriate drying agents and distilled prior to use. $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ (Arora Matthey Limited) Oxalic acid (SD fine), and *p*-anisic acid (SRL), 4,4'-bipy, pyrazine (Merk), 1,4-dicyanobenzene (Aldrich) were used as received. IR spectra were obtained on a Perkin- Elmer-model 983 Spectrometer or Shimadzu 8201PC with sample prepared in KBr. NMR spectra were recorded in CDCl_3 on a Bruker AMX-400 or Bruker Avance 300 MHz spectrometer with SiMe_4 as internal references and coupling constants are given in hertz. Microanalyses were carried out at the SAIF (NEHU), Shillong, using a perkin-Elmer 2400 CHN/S analyzer. The precursor complex $[\{(\eta^6\text{-}$

$p\text{-Pr}^i\text{C}_6\text{H}_4\text{Me})\text{RuCl}_2\}_2]$ was prepared according to literature method¹⁸. The following atom labelling scheme is used for the ^1H and ^{13}C $\{^1\text{H}\}$ NMR spectroscopic data of p -cymene complexes.



3.2 Preparation of sodium salts of carboxylic acids

Sodium salts of carboxylic acids were prepared by reacting corresponding carboxylic acids with 2 equiv. of NaOH in ethanol as delineated here. Two equiv. of NaOH in 100ml of ethanol were stirred until NaOH is completely dissolved. To this stirring solution 1 equiv. of the corresponding carboxylic acid was added and the resulting mixture was stirred for 24 hr. The white precipitate was filtered and washed with cold ethanol and dried.

3.3. Preparation of compounds

3.3.1. Preparation of $[(\eta^6\text{-}p\text{-cymene})\text{Ru}(\text{pa})\text{Cl}](\mathbf{1})$

The complex $[\{(\eta^6\text{-}p\text{-cymene})\text{RuCl}_2\}_2]$ (150 mg, 0.244 mmol) and the ligand *pa* (86 mg, 0.488 mmol) were stirred in 40 ml of methanol for 3hr. The red solution changed to orange yellow color as the reaction proceeded. The solvent was evaporated in vacuum and the residue was dissolved in dichloromethane. The solution was concentrated to *ca* 5 ml followed by excess of hexane was added whereby compound precipitated out as orange solid. The yellow orange solid was collected and washed with 2x20 ml hexane and dried under vacuum.

Yield: 68 % (140 mg, 0.314 mmol).

Analytical and spectroscopic data are as follows:

Analytical Calc. for $\text{C}_{20}\text{H}_{21}\text{O}_3\text{ClRu}$: C, 53.86; H, 4.71%.

Found: C, 53.48; H, 4.52%.

IR (KBr, cm^{-1}): 1605 $\nu(\text{C}=\text{O})$.

^1H NMR (CDCl_3 , δ): 1.39 (d, 6H, $\text{CH}(\text{CH}_3)_2$, $J_{\text{H-H}} = 6.92$ Hz), 2.32 (s, 3H, (CH_3)), 2.98 (m, 1H, $\text{CH}(\text{CH}_3)_2$), 3.80 (s, OMe), 5.44 (d, 2H, $J_{\text{H-H}} = 6.96$ Hz), 5.67 (d, 2H, $J_{\text{H-H}} = 6.0$ Hz), 6.79 (d, 2H, $J_{\text{H-H}} = 8.76$ Hz), 7.81 (d, 2H, $J_{\text{H-H}} = 8.76$ Hz).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , δ): 18.81 (s, CH_3), 22.40 (s, CH_3 , $\text{CH}(\text{CH}_3)_2$), 31.59 (s, CH , $\text{CH}(\text{CH}_3)_2$), 55.35 (s, CH_3 (OCH_3)), 78.56 (s, $\text{C}_{\text{AA}'}$), 79.12 (s, $\text{C}_{\text{BB}'}$), 94.20 (s, CMe), 100.44 (CPr^1), 113.23 (s), 124.16 (s), 130.60 (s), 163.29 (s, $\text{C}(\text{CO}_2)$), 184.38 (s, (CO_2)).

3.3.2. Preparation of $[(\eta^6\text{-}p\text{-cymene})\text{Ru}(\text{pa})(\text{L}_1)]\text{BF}_4$ ($\text{L}_1 = \text{PyCN}$, **2**; DMAP, **3**)

A suspension of the complex $[(\eta^6\text{-}p\text{-cymene})\text{Ru}(\text{pa})\text{Cl}]$ (**1**) (50mg, 0.12 mmol), NaBF_4 (46mg, 0.24 mmol) and ligand (L_1) were stirred in 30 ml of acetone for 3 hrs at room temperature. During the course of reaction, the solution became bright red in colour and white solid precipitated out. The insoluble material was filtered off and solvent was removed under reduce pressure. The solid was dissolved in minimum amount of dichloromethane then filtered. The filtrate on subsequent concentration to *ca* 3 ml followed by addition of hexane afforded a dark red solid. The solid was collected, washed with hexane (2 x10 ml) and dried under vacuum.

Complex 2

Yield: 0.062g (90%); IR (KBr, cm^{-1}): 2235, 1691, 1602, 1558, 1215, 1029.

$^1\text{HNMR}$ (CDCl_3 , δ): 9.30 (d, 1H, $J_{\text{H-H}} = 6.2$), 8.84 (s, 1H), 8.05 (d, 1H, $J_{\text{H-H}} = 7.5$), 7.84 (d, 1H, $J_{\text{H-H}} = 7.5$), 7.56 (d, 2H, $J_{\text{H-H}} = 4.9$), 6.94 (d, 1H, $J_{\text{H-H}} = 7.2$), 6.82 (d, 1H, $J_{\text{H-H}} = 5.6$), 5.69 (d, 1H, $J_{\text{H-H}} = 5.7$), 5.46 (t, 2H, $J_{\text{H-H}} = 6.3$), 5.27 (d, 1H, $J_{\text{H-H}} = 6$), 3.89 (s, 3H), 2.99 (sept, 1H), 2.39 (s, 3H), 1.40 (d, 3H, $J_{\text{H-H}} = 6.9$), 1.28 (t, 3H, $J_{\text{H-H}} = 6.9$).

Complex 3

Yield: 0.056g (80%); IR (KBr, cm^{-1}): 1680, 1601, 1215, 1046.

$^1\text{HNMR}$ (CDCl_3 , δ): $^1\text{HNMR}$ (CDCl_3 , δ): 8.43 (d, 2H, $J_{\text{H-H}} = 6.9$), 8.34 (d, 1H, $J_{\text{H-H}} = 6.9$), 7.91 (d, 1H, $J_{\text{H-H}} = 8.7$), 6.88 (d, 2H, $J_{\text{H-H}} = 8.7$), 6.51 (m, 2H), 6.14 (d, 1H, $J_{\text{H-H}} = 6$), 5.80 (d, 2H, $J_{\text{H-H}} = 4.6$), 5.54 (d, 1H, $J_{\text{H-H}} = 5.7$), 3.81 (s, 3H, OMe), 3.03 (s, 6H, NMe_2), 2.62 (m, 1H, CHMe_2), 1.76 (d, 3H, CMe , $J_{\text{H-H}} = 10.8$), 1.17 (d, 3H, CHMe_2 , $J_{\text{H-H}} = 6.9$), 1.09 (d, 3H, CHMe_2 , $J_{\text{H-H}} = 6.9$).

3.3.3 Preparation of $[\{(\eta^6\text{-}p\text{-cymene})\text{Ru}(\text{pa})\}_2(\mu\text{-}4,4\text{-bipy})](\text{BF}_4)_2$ (**4**)

A suspension of the complex $[(\eta^6\text{-}p\text{-cymene})\text{Ru}(\text{pa})\text{Cl}]$ (**1**) (100mg, 0.23 mmol) and AgBF_4 (89mg, 0.46 mmol) in 30 ml of acetone was stirred for 45 min. The white precipitate of AgCl was filtered off. To this solution 4,4-bipy (18 mg, 0.11 mmol) was added and the resulting mixture was stirred at room temperature for 3 hrs. After which the solution was concentrated to *ca* 5 ml and excess diethyl ether was added which gave a yellow crystalline solid. The solid was collected and dried under vacuum.

Yield: 73 mg (58%).

Analytical Calc. for $C_{46}H_{50}O_6N_2B_2F_8Ru_2$: C, 50.08; H, 4.53; N, 2.54%.

Found: C, 49.23; H, 4.28; N, 2.17%.

IR (KBr, cm^{-1}): 1606 $\nu(C=O)$, 1083 $\nu(BF_4)$

1H NMR ($CDCl_3$, δ , $SiMe_4$): 1.28 (d, 12H, $J_{H-H} = 6.7$ Hz), 2.21 (s, 6H), 2.87 (sept., 2H), 3.86 (s, 6H, OMe), 5.47 (d, 4H, $J_{H-H} = 6.2$ Hz), 5.78 (d, 4H, $J_{H-H} = 6.4$ Hz), 6.82 (d, 4H, $J_{H-H} = 5.7$ Hz), 7.86 (d, 4H, $J_{H-H} = 6.2$ Hz), 7.83 (d, 4H, $J_{H-H} = 6.4$ Hz), 8.60 (d, 4H, $J_{H-H} = 5.8$ Hz).

3.3.4. Preparation of $[(\eta^6\text{-}p\text{-cymene})Ru(pa)]_2(\mu\text{-pyrazine})(BF_4)_2$ (**5**)

This complex was prepared by following a similar method as described for complex **4** using the ligand, pyrazine instead of 4,4-bipyridine.

Yield: 65 mg (53%).

Analytical Calc. for $C_{40}H_{46}O_6N_2B_2F_8Ru_2$: C, 46.77; H, 4.48; N, 2.72%.

Found: C, 46.28; H, 3.98; N, 2.53%.

IR (KBr, cm^{-1}): 1604 $\nu(C=O)$, 1083 $\nu(BF_4)$

1H NMR ($CDCl_3$, δ , $SiMe_4$): 1.34 (d, 12H, $J_{H-H} = 6.4$), 2.10 (s, 6H), 2.78 (sept., 2H), 3.80 (s, 6H, OMe), 5.26 (d, 4H, $J_{H-H} = 5.9$), 5.48 (d, 4H, $J_{H-H} = 6.2$), 6.78 (d, 4H, $J_{H-H} = 5.7$), 7.72 (d, 2H, $J_{H-H} = 6.8$), 7.88 (d, 4H, $J_{H-H} = 6.0$), 8.69 (d, 2H, $J_{H-H} = 6.7$).

3.3.5. Preparation of $[(\eta^6\text{-}p\text{-cymene})Ru(pa)]_2(\mu\text{-DCB})(BF_4)_2$ (**6**)

The complex was prepared following a similar method as described in the preparation of complex **4** using the ligand DCB instead of 4,4-bipy.

Yield: 64 mg (50%).

Analytical Calc. for $C_{44}H_{46}O_6N_2Ru_2B_2F_8$: C, 49.15; H, 4.28; N, 2.60%.

Found: C, 49.87; H, 4.62; N, 2.86%.

IR (KBr, cm^{-1}): 2228, $\nu(C=N)$, 1604, $\nu(C=O)$, 1083, $\nu(BF_4)$.

1H NMR ($CDCl_3$, δ , $SiMe_4$): 1.38 (d, 12H, $J_{H-H} = 6.2$), 2.16 (s, 6H), 2.81 (sept., 2H), 3.86 (s, 6H, OMe), 5.36 (d, 4H, $J_{H-H} = 5.9$), 5.47 (d, 4H, $J_{H-H} = 6.2$), 6.58 (d, 4H, $J_{H-H} = 4.8$, DCB), 6.78 (d, 4H, $J_{H-H} = 5.8$), 7.26 (d, 2H, $J_{H-H} = 4.8$, DCB), 7.86 (d, 4H, $J_{H-H} = 6.0$).

3.3.6. Preparation of $[\{(\eta^6\text{-}p\text{-cymene})\text{RuCl}_2\}_2(\mu\text{-}\eta^4\text{-C}_2\text{O}_4)]$ (**7**)

To a solution of $[\{(\eta^6\text{-}p\text{-cymene})\text{RuCl}_2\}_2]$ (200 mg, 0.32 mmol) in MeOH (30 ml) was added $\text{Na}_2\text{C}_2\text{O}_4\cdot\text{H}_2\text{O}$ (48 mg, 0.32 mmol). The mixture was stirred for 1 hr at room temperature. During the period the starting materials dissolved completely. As reaction progress a yellow orange solid precipitated out. The solid was collected centrifuged, washed with cold methanol then finally with (2x10 ml) diethyl ether and dried under vacuum. Additional product can be obtained from the liquid by evaporating the liquid to dryness and filtered to remove NaCl and precipitated out the complex with hexane.

Overall yield: 191 mg (93%).

Anal. Calc. for $\text{C}_{22}\text{H}_{28}\text{Cl}_2\text{O}_4\text{Ru}_2$: C, 41.93; H, 4.44%.

Found: C, 41.67; H, 4.26%.

IR (KBr, cm^{-1}): 1619 $\nu(\text{C}=\text{O})$.

^1H NMR (CDCl_3 , δ): 1.30 (d, 6H, $J_{\text{H-H}} = 6.86$), 2.22 (s, 3H), 2.63 (m, 1H), 5.33 (d, 2H, $J_{\text{H-H}} = 6.08$), 5.56 (d, 2H, $J_{\text{H-H}} = 6.02$).

^{13}C $\{^1\text{H}\}$ NMR (CDCl_3 , δ): 18.64 (s, CH_3), 22.55 (s, CH_3 , $\text{CH}(\text{CH}_3)_2$), 31.23 (s, CH , $\text{CH}(\text{CH}_3)_2$), 78.52, 80.53, 95.60, 99.95 (C_6H_4), 171.80 (s, CO).

3.3.7. Preparation of $[\{(\eta^6\text{-}p\text{-cymene})\text{Ru}(\text{OCOCH}_3)\}_2(\mu\text{-}\eta^4\text{-C}_2\text{O}_4)]$ (**8**)

To a round bottom flask charged with complex $[(\eta^6\text{-}p\text{-cymene})\text{Ru}(\mu\text{-}\eta^4\text{-C}_2\text{O}_4)\text{Cl}]_2$ (**7**) (100 mg, 0.158 mmol) and AgCO_2CH_3 (53 mg, 0.317 mmol) and 30 ml of ethanol. After stirring the mixture for 15 hrs at room temperature, the solvent was removed under reduced pressure and the residue was extracted with dichloromethane. The extract was filtered to remove insoluble solid and subsequent concentration to *ca* 5 ml follow by addition of excess hexane afforded a yellow crystalline solid. The solid was collected and washed with hexane then dried under vacuum.

Yield: 76 mg (70%).

Anal. Calc. for $\text{C}_{26}\text{H}_{34}\text{O}_8\text{Ru}_2$: C, 46.14; H, 5.02%. Found: C, 45.92; H, 4.86%.

IR (KBr, cm^{-1}): 1672, 1626 $\nu(\text{C}=\text{O})$.

^1H NMR (CDCl_3 , δ): 1.26 (d, 6H, $J_{\text{H-H}} = 6.90$, $\text{CH}(\text{CH}_3)_2$), 1.92 (s, 3H, CH_3), 2.23 (s, 3H, CH_3), 2.79 (m, 1H, CH , $\text{CH}(\text{CH}_3)_2$), 5.50 (d, 2H, $J_{\text{H-H}} = 5.94$), 5.76 (d, 2H, $J_{\text{H-H}} = 5.93$). ^{13}C $\{^1\text{H}\}$ NMR (CDCl_3 ,

δ): 18.30 (s, CH₃), 22.37 (s, CH₃, CH(CH₃)₂), 24.01 (s, CH₃, CO₂(CH₃)), 31.05 (s, CH, CH(CH₃)₂), 80.09, 80.60, 93.95, 98.23 (C₆H₄), 171.86 (s, (CO₂)), 177.89 (s, (CO₂)).

3.3.8. Preparation of [$\{(\eta^6\text{-}p\text{-cymene})\text{Ru}(\text{OCOCF}_3)_2(\mu\text{-}\eta^4\text{-C}_2\text{O}_4)\}$] (**9**)

This complex was prepared by following a similar method as described in the preparation of complex (**8**) by using AgCO₂CF₃ instead of AgCO₂CH₃.

Yield: 76 mg (61%).

Anal. Calc. for C₂₆H₂₈O₈F₆Ru₂: C, 39.7; H, 3.57. Found: C, 38.52; H, 3.28%.

IR (KBr, cm⁻¹): 1668,ν(C=O); 1626 ν(C=O).

¹H NMR (CDCl₃, δ): δ: 1.29 (d, 6H, J_{H-H} = 6.8, CH(CH₃)₂), 2.20 (s, 3H, CH₃), 2.83 (m, 1H, CH, CH(CH₃)₂), 5.52 (d, 2H, J_{H-H} = 6.0), 5.80 (d, 2H, J_{H-H} = 6.0).

3.3.9. Preparation of [$\{(\eta^6\text{-}p\text{-cymene})\text{Ru}(\text{Cl})_2(\mu\text{-}\eta^4\text{-C}_2\text{CH}_2\text{O}_4)\}$] (**10**)

A round bottom flask was charged with [$\{(\eta^6\text{-}p\text{-cymene})\text{RuCl}_2\}_2$] (120 mg, 0.195 mmol), Na₂CH₂(CO₂)₂ (ma) (32 mg, 0.195 mmol) and methanol (40 ml). The mixture was stirred at room temperature for 6 hrs. The red solution turned into orange yellow solution as the reaction proceeded. The solvent was removed under reduced pressure then the solid residue was extracted with dichloromethane. After which the solution was filtered to remove insoluble materials. The filtrate on subsequent concentration to *ca* 5 ml and addition of excess hexane induced a yellow solid of the complex. The solid was collected and washed with hexane 2x10 ml and dried under vacuum.

Yield: 120 mg (98%).

Anal. Calc. for C₂₃H₃₀Cl₂O₄Ru₂: C, 42.91; H, 4.66%. Found: C, 42.53; H, 4.57%.

IR (KBr, cm⁻¹): 1633.

¹H NMR (CDCl₃, δ): 1.26 (d, 12H, J_{H-H} = 6.9), 2.08 (s, 6H), 2.82 (m, 2H, CH(CH₃)₂), 3.47 (s, 2H, (CH₂)), 5.32 (d, 4H, J_{H-H} = 5.8), 5.46 (d, 4H, J_{H-H} = 5.7).

¹³C {¹H} NMR (CDCl₃, δ): 18.39 (s, Me), 22.07 (s, CH₃, CH(CH₃)₂), 30.76 (s, CH, CH(CH₃)₂), 40.76 (s, -CH₂-), 77.33-101.20 (C₆H₄), 172.43 (s, CO₂).

3.3.10. Preparation of [$\{(\eta^6\text{-}p\text{-cymene})\text{Ru}(\text{OCOCH}_3)_2(\mu\text{-}\eta^4\text{-C}_2\text{CH}_2\text{O}_4)\}$] (**11**)

To a round bottom flask charged with complex [$\{(\eta^6\text{-}p\text{-cymene})\text{RuCl}_2\}_2(\mu\text{-}\eta^4\text{-C}_2\text{CH}_2\text{O}_4)$] (100 mg, 0.155 mmol), silver acetate (51 mg, 0.31 mmol) and ethanol (40 ml). The mixture was stirred at room temperature for 20 hrs. The insoluble materials were filtered off and solvent was

removed by rotary-evaporator. The residue was extracted with dichloromethane followed by addition of excess hexane afforded a yellow solid of the complex.

Yield: 67 mg (63%).

Anal. Calc. for $C_{27}H_{36}O_8Ru_2$: C, 42.96; H, 4.77%.

Found: C, 42.27; H, 4.98%.

IR (KBr, cm^{-1}): 1630, $\nu(C=O)$, $\nu(C=O)$ 1678.

1H NMR ($CDCl_3$, δ): 1.28 (d, 12H, $J_{H-H} = 6.2$), 1.98 (s, 6H), 2.27 (s, 6H), 2.82 (m, 2H), 3.28 (s, 2H), 5.30 (d, 4H, $J_{H-H} = 5.6$), 5.48 (d, 4H, $J_{H-H} = 5.7$).

3.3.11. Preparation of [$\{\eta^6\text{-}p\text{-cymene}\}Ru(OCOFCF_3)_2(\mu\text{-}\eta^4\text{-}C_2CH_2O_4)$] (**12**)

This complex was prepared following a similar procedure as described in the preparation of complex (**11**) using silver trifluoro acetate instead of silver acetate.

Yield: 88 mg (71%).

Anal. Calc. for $C_{27}H_{30}O_8F_6Ru_2$: C, 40.59; H, 3.75%. Found: C, 40.12, H, 3.21%.

IR (KBr, cm^{-1}): 1630, $\nu(C=O)$, $\nu(C=O)$ 1668

1H NMR ($CDCl_3$, δ): 1H NMR ($CDCl_3$, δ): 1.29 (d, 12H, $J_{H-H} = 6.2$), 1.98 (s, 6H), 2.87 (m, 2H), 3.41 (s, 2H), 5.32 (d, 4H, $J_{H-H} = 5.6$), 5.48 (d, 4H, $J_{H-H} = 5.6$).

4. Conclusion

This paper described an improved method for the synthesis of η^6 -arene ruthenium (II) complexes incorporating carboxylato groups. A series of new mono and dinuclear complexes of arene ruthenium complexes incorporating carboxylate ligands were prepared by treating complex **1** with the corresponding neutral ligands in the presence of $AgBF_4$. The coordinated carboxylato ligands in the complexes **1**, **7** and **10** were readily displaced by azide when treated the complexes with NaN_3 , to give a well known azide complex [$\{\eta^6\text{-}p\text{-cym}\}Ru(\mu\text{-}N_3)Cl_2\}_2$]. However, reaction of these carboxylato complexes (**7&10**) with halide scavenger such as silver acetate leads to the substitution of chlorine from complexes **7** and **10** to give complexes **8** and **9** or **11** and **12**, respectively.

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References

1. H. L. Bozec, D. Touchard, P. H. Dixneuf, *Adv. Organomet. Chem.*, 1989, **29**, 163.
2. (a) C. A. Vock, W. H. Ang, C. Scolaro, A. D. Phillips, L. Lagopoulos, J. L. Jeanneret, G. Sava, R. Scopelliti, P. J. Dyson, *J. Med. Chem.*, 2007, **50**, 2166; (b) F. Wang, H. Chen, J. A. Parkinson, P. S. Murdoch, P. J. Sadler, *J. Med. Chem.*, 2002, **41**, 4509.
3. (a) C. S. Allardyce, P. J. Dyson, D. J. Ellis, S. L. Health, *Chem. Commun.*, 2001, 1396; (b) R. E. Morris, R. E. Aird, P. D. Murdoch, H. M. Chen, J. Cummings, N. D. Huges, S. Parsons, A. Parkin, G. Boyd, D. I. Jodrell, P. J. Sadler, *J. Med. Chem.*, 2001, **44**, 3621; (c) C. Scolaro, A. Bergamo, L. Brescacin, R. Delfino, M. Cocchietto, G. Laurencyzy, T. J. Geldbach, G. Sava, P. J. Dyson, *J. Med. Chem.*, 2005, **48**, 4161.
4. D. L. Davies, J. Fawcett, S. A. Garratt, D. R. Russell, *Chem Commun.*, 1997, 1351.
5. C. S. Hauser, C. Sulugove, K. Mereiter, R. Schmid, K. Kirchner, L. Xiao, W. Weissensteiner, *J. Chem. Soc. Dalton Trans.*, 2001, 2989.
6. (a) A. Fürstner, M. Picquet, C. Bruneau, P. H. Dixneuf, *Chem. Commun.*, 1998, 1315; (b) B. C. G. Soderberg, *Coord. Chem. Rev.*, 2003, **241**, 147.
7. (a) R. Lalrempuia, P. J. Carroll, M. R. Kollipara, *J. Chem. Sci.*, 2004, **116**, 21; (b) R. Lalrempuia, M. R. Kollipara, *Polyhedron*, 2003, **22**, 3155; (c) R. Lalrempuia, M. R. Kollipara, P. J. Carroll, *Polyhedron*, 2003, **22**, 605; (d) S. K. Mandal, A. R. Chakravarty, *Polyhedron*, 1992, **11**, 823.
8. I. Moldes, E. D. Encarnacion, J. Ros, A. Alvarez-Larena, J. F. Piniella, *J. Organomet. Chem.*, 1998, **566**, 165.
9. (a) M. A. Bennett, T. R. B. Mitchell, M. R. Stevens, A. C. Willis, *Can. J. Chem.*, 2001, **79**, 655; (b) D. Carmona, J. Ferrer, L. A. Oro, *J. Chem. Soc. Dalton Trans.*, 1990, 1463.
10. (a) K. S. Singh, K. A. Kreisel, G. P. Yap, M. R. Kollipara, *J. Organomet. Chem.*, 2006, **691**, 3509; (b) K. Pachhunga, B. Therrien, M. R. Kollipara, *Inorg. Chim. Acta*, 2008, **361**, 3294.
11. K. S. Singh, V. Svitlyk, P. Devi, Y. Mozharivskyj, *Inorg. Chim Acta*, 2009, **362**, 5252.
12. (a) N. P. E. Barry, B. Therrien, *Eur. J. Inorg. Chem.*, 2009, 4695; (b) J. Freudenreich, N. P. E. Barry, G. S. Fink, B. Therrien, *Eur. J. Inorg. Chem.*, 2010, 2400.
13. D. A. Tocher, R. O. Gould, T. A. Stephenson, *J. Chem. Soc. Dalton Trans.*, 1983, 1571.
14. H. Yan, G. S. Fink, A. Neels, H. S. Evans, *J. Chem. Soc. Dalton Trans.*, 1997, 4345.
15. K. Köhler, J. E. Meyer, F. D. Vodovic, *Organometallics*, 2003, **22**, 4426.
16. R. S. Bates, M. J. Begley, A. H. Wright, *Polyhedron*, 1990, **9**, 1113.
17. (a) Z. Dori, R. F. Ziolo, *Chem. Rev.*, 1973, **73**, 247; (b) W. Beck, W. P. Fehlhammer, P. Pöllman, E. Schuierer, K. Feldl, *Chem. Ber.*, 1967, **100**, 2325; (c) R. Mason, G. A

Rusholme, H. Engelman, K. Joos, B. Lindenberg, H. S. Smedal, *J. Chem. Soc. Chem. Commun.*, 1971, 496.

18. (a) M. A. Bennett, T. N. Huang, T. W. Matheson, A. K. Smith, *Inorg. Synth.*, 1985, **21**, 75;
(b) M. A. Bennett, T. W. Matheson, G. B. Robertson, A. K. Smith, P. A. Tucker, *Inorg. Chem.*, 1980, **10**, 1014.