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Arene ruthenium (II) azido complexes incorporating N[⊖]O chelate ligands: Synthesis, spectral studies and 1,3-dipolar-cycloaddition to a coordinated azide in ruthenium (II) compounds

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Abstract: Arene ruthenium (II) azido compounds [$\{(p\text{-cymene})\text{Ru}(\text{N}^{\ominus}\text{O})\text{N}_3\}$] have been prepared by the reaction of [$\{(p\text{-cymene})\text{Ru}(\mu\text{N}_3)\text{Cl}\}_2$] with the corresponding ligands. The ruthenium azido compounds [$\{(p\text{-cymene})\text{Ru}(\text{N}^{\ominus}\text{O})\text{N}_3\}$] undergo 1,3-dipolar additions with substituted alkynes at room temperature to give ($\eta^6\text{-arene}$) ruthenium triazolato compounds [$\{(p\text{-cymene})\text{Ru}(\text{N}^{\ominus}\text{O})\{\text{N}_3\text{C}_2(\text{CO}_2\text{R})_2\}$]. The compounds were characterized on the basis of FTIR, NMR (^1H and ^{13}C) and the molecular structure of a representative compound has been established with the help of single crystal X-ray diffraction.

Keywords: Arene, Azide, Quinaldic acid, Glycine, Alkynes, Dipolar cycloaddition.

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1. Introduction

Synthesis of (η^6 -arene) ruthenium (II) complexes has attracted considerable attention owing to their anti-cancer [1-3], antiviral [4] and catalytic properties [5-7]. The catalytic activities of these complexes range from hydrogen transfer to ring closing metathesis via, a variety of C-C bond formation reactions [8, 9]. Water soluble (η^6 -arene) ruthenium compounds bearing carboxylate or pyronate groups show promising catalytic performance in water [10, 11]. Notably, water soluble (η^6 -arene) ruthenium compounds have been prepared by functionalization of the (η^6 -arene) moiety with ethoxyhydroxyl [12] or coordination of a water soluble ligands such as PTA or kojic acid (PTA = 1,3,5-Triazo-7-phosphaadamantane) to the ruthenium centre [6, 13].

Triazole and its derivatives have shown wide application in medicinal chemistry [14]. The most efficient route for synthesizing 1,2,3-triazole compounds is the cycloaddition reactions of an alkyl or aryl azide with alkynes [15,16]. Although such reactions are studied extensively for synthesizing heterocycles [15-18], the dipolar cycloaddition reactions of azide coordinated metal complexes are relatively unexplored. Dori, Ziolo and Fruhauf have reported pioneering work on 1,3-dipolar cycloaddition of coordinated azide and alkynes [19,20]. Later, several other groups have studied cycloaddition reaction of alkynes or nitriles with various azide coordinated metal complexes [21-25].

Previously, we have described the synthesis of various half sandwich ruthenium (II) triazolato complexes bearing (η^6 -arene) [26, 27], (η^5 -indenyl) and (η^5 -C₅Me₅) moieties [28, 29] by cycloaddition reactions of alkynes or nitriles with the corresponding metal azido complexes. In our previous work, we have studied cycloaddition reactions using ruthenium (II) azido complexes bearing either oxygen or phosphine chelate ligands [26-29]. However, insofar as our knowledge goes, these reactions have not been explored with (η^6 -arene) ruthenium (II) azido complexes bearing N[∩]O chelate ligands. In a continuation of our study, herein, we report the synthesis of a series of (η^6 -arene) ruthenium azido complexes bearing N₂O-chelate ligands and the cycloaddition reaction of a coordinated azide with alkynes. The complexes were characterized with the help of IR and NMR spectroscopic data and a representative molecular structure was established by single X-ray diffraction.

2. Experimental:

2.1 *General Remarks:* Solvents were dried according to the standard procedures. RuCl₃.3H₂O (Arrora Matthey), L-proline, glycine, dimethylacetylene dicarboxylate (DMD), diethylacetylene

dicarboxylate (DED) and sodium azide (Sigma Aldrich), were used as received. NMR spectra were recorded on a Bruker Avance 300 MHz spectrometer at 300.13 (^1H), 75.47 MHz (^{13}C) with SiMe_4 as internal reference and coupling constants are given in Hertz. Infra red spectra were recorded in a diffused reflection spectroscopy (DRS) assembly on a Shimadzu-8201PC spectrometer with sample prepared in KBr. The precursor complexes [$\{(\eta^6\text{-}p\text{-cymene})\text{RuCl}_2\}_2$] [30, 31] and [$\{(\eta^6\text{-}p\text{-cymene})\text{Ru}(\mu\text{N}_3)\text{Cl}\}_2$] [32, 33], [$\{(\eta^6\text{-}p\text{-cymene})\text{Ru}(\text{quinto})\text{Cl}\}$] [34] were prepared according to literature procedures.

2.2 Preparation of ($\eta^6\text{-arene}$) ruthenium azido complexes:

2.2.1 Preparation of [$\{(p\text{-cymene})\text{Ru}(\text{quinto})\text{N}_3\}$](**1**):

Two routes were used to prepare this complex

Route (a): A mixture of quinaldic acid (0.042 g, 0.24 mmol) and NaOMe (0.013g, 0.24 mmol) in dry MeOH (40 ml) was stirred for 5 minutes. After which the complex [$(p\text{-cymene})\text{Ru}(\mu\text{N}_3)\text{Cl}\}_2$ (0.07g, 0.11 mmol) was added to the mixture and stirring continued for additional 5 h. Solution was rotary evaporated to dryness and the residue was taken in dichloromethane to precipitate out NaCl. The solution was filtered and concentrated to *ca.* 3 ml then excess hexane was added which induces precipitation of a yellow solid. The yellow solid was collected and washed with hexane (2 x 10 ml) and dried under vacuum.

Yield: 0.072g (72 %).

Route (b): A mixture of [$\{(p\text{-cymene})\text{Ru}(\text{quinto})\text{Cl}\}$] (0.07g, 0.168 mmol) and NaN_3 (0.01g, 0.168 mmol) in methanol (20 ml) was stirred for 4 h at room temperature. After which the solution was rotary evaporated then the residue was dissolved in dichloromethane. To this filtrate, an excess hexane was added and kept for 3h. The yellow precipitate was filtered and dried under vacuum.

Yield: 0.045g (63 %).

FTIR (KBr, cm^{-1}): 2030, 1651, 1330.

^1H NMR (CDCl_3 , δ): 8.59 (d, 1H, $J = 8.7$), 8.43 (d, 1H, $J = 8.4$), 8.22 (d, 1H, $J = 8.4$), 7.99 (q, 2H, $J = 8.1$), 7.80 (t, 1H, $J = 7.8$), 5.73 (d, 1H, $J = 6.3$), 5.54 (t, 2H, $J = 4.8$), 5.41 (d, 1H, $J = 5.7$), 2.63-2.61 (sept., 1H, $J = 6.6$), 2.27 (s, 3H), 1.11 (d, 3H, $J = 6.9$), 1.00 (d, 3H, $J = 6.9$).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , δ): 171.35, 152.63, 147.31, 140.18, 131.93, 130.62, 129.18, 128.33, 122.69, 103.51, 100.82, 85.63, 81.62, 80.28, 79.95, 30.93, 22.68, 22.05, 18.08.

2.2.2. Preparation of $[(p\text{-cymene})\text{Ru}(\text{thiq})\text{N}_3](\mathbf{2})$:

This complex was prepared following a similar method as described for **1** (route *a*) using $[(p\text{-cymene})\text{Ru}(\mu\text{N}_3)\text{Cl}]_2$ (0.1g, 0.159 mmol) ligand (0.06g, 0.34 mmol), NaOMe (0.18g, 0.34 mmol) and MeOH (40 ml).

Yield: 0.077g (44 %).

FTIR (KBr, cm^{-1}): 2037, 1631, 1629.

^1H NMR (CDCl_3 , δ): 6.93-6.66 (m, 4H), 5.73 (d, 1H, $J = 5.4$), 5.61 (m, 2H), 5.54 (d, 1H, $J = 5.4$), 4.17 (d, 1H, $J = 15$), 3.90 (t, 1H, $J = 11$), 2.91 (m, 1H), 2.57 (m, 1H), 2.28 (m, 1H), 2.24 (s, 3H), 2.03 (m, 1H), 1.36 (s, 6H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , δ): 180.61, 133.63, 133.37, 129.07, 126.41, 125.80, 125.64, 101.90, 93.95, 83.19, 81.74, 80.99, 79.20, 58.18, 54.39, 30.80, 22.78, 22.26, 17.67.

2.2.3. Preparation of $[(p\text{-cymene})\text{Ru}(\text{pico})\text{N}_3](\mathbf{3})$:

This complex was prepared following a similar method as described for **1** (route *a*) using $[(p\text{-cymene})\text{Ru}(\mu\text{N}_3)\text{Cl}]_2$ (0.09g, 0.143 mmol) ligand (0.041g, 0.31 mmol), NaOMe (0.017g, 0.31 mmol) and MeOH (40 ml).

Yield: 0.07g (61 %).

FTIR (cm^{-1}): 2029, 1660, 1324.

^1H NMR (CDCl_3 , δ): 8.97 (s, 1H), 8.06 (d, 1H, $J = 7.2$), 7.98 (d, 1H, $J = 6.9$), 7.61 (s, 1H), 5.59 (s, 2H), 5.43 (d, 2H, $J = 12.3$), 2.80 (m, 1H), 2.25 (s, 3H), 1.21 (d, 6H, $J = 6.3$).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , δ): 171.16, 152.13, 150.95, 139.51, 128.14, 127.05, 102.53, 99.20, 83.31, 83.09, 81.09, 80.28, 30.94, 22.61, 22.30, 18.11.

IR (KBr, cm^{-1}): 2036, 1629.

2.2.4. Preparation of $[(p\text{-cymene})\text{Ru}(\text{hquinto})\text{N}_3](\mathbf{4})$: This complex was prepared following a similar procedure as described for **1** (route *a*) using $[(p\text{-cymene})\text{Ru}(\mu\text{N}_3)\text{Cl}]_2$ (0.1g, 0.159 mmol) 8-hydroxyquinoline (0.048g, 0.335mmol), NaOMe (0.018g, 0.335 mmol) and MeOH (40 ml).

Yield: 0.069g (51 %).

FTIR (cm^{-1}): 2036, 1573.

^1H NMR (CDCl_3 , δ): 8.88 (d, 1H, $J = 4.8$), 8.11 (t, 1H, $J = 5.4$), 7.39-7.34 (m, 2H), 6.87 (d, 1H, $J = 11$), 6.86 (t, 1H, $J = 7.8$), 5.59 (d, 1H, $J = 5.4$), 5.50 (d, 1H, $J = 5.7$), 5.39 (d, 1H, $J = 5.7$), 5.28 (d, 1H, $J = 5.7$), 2.75 (m, 1H), 2.30 (s, 3H), 1.16 (d, 6H, $J = 6.6$).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , δ): 168.26, 147.86, 144.19, 137.84, 130.38, 121.83, 115.03, 110.75, 101.29, 99.22, 83.06, 82.06, 80.60, 80.09, 30.93, 30.26, 22.57, 22.41, 18.07.

2.2.5. Preparation of $[\{(p\text{-cymene})\text{Ru}(\text{pyrole-2-carboxylate})\text{N}_3\}](\mathbf{5})$:

This complex was prepared following a similar method as described for **1** (route *a*) using $[(p\text{-cymene})\text{Ru}(\mu\text{N}_3)\text{Cl}]_2$ (0.05g, 0.0799 mmol), pyrole-2-carboxylic acid (0.018g, 0.167 mmol), NaOMe (0.009g, 0.167 mmol) and MeOH (40 ml).

Yield: 0.042 g (68 %).

IR (KBr, cm^{-1}): 2032, 1631.

$^1\text{HNMR}$ (CDCl_3 , δ): 6.98 (s, 1H), 6.25 (s, 1H), 5.48-5.20 (m, 4H), 3.40 (br, 1H), 2.88 (m, 1H), 2.27 (s, 3H), 1.26 (m, 6H).

2.2.6. Preparation of $[\{(p\text{-cymene})\text{Ru}(\text{L-Pro})\text{N}_3\}](\mathbf{6})$:

This complex was prepared following a procedure described for **1** (route *a*) using $[(p\text{-cymene})\text{Ru}(\mu\text{N}_3)\text{Cl}]_2$ (0.05g, 0.079 mmol) L-proline (0.019g, 0.165 mmol), NaOMe (0.01g, 0.18 mmol) and MeOH (40 ml).

Yield: 0.035g (57 %).

Alternative method: A mixture of complex $[\{(p\text{-cymene})\text{Ru}(\mu\text{N}_3)\text{Cl}\}_2]$ (0.07g, 0.11 mmol), L-proline (0.026g, 0.23 mmol) and K_2CO_3 (0.034g, 0.25 mmol) were stirred in acetonitrile (30 ml) for 18 h. The reaction mixture was rotary evaporated and the residue was extracted with CH_2Cl_2 . The solution was filtered through celite and washed the cake with several times with CH_2Cl_2 . The filtrate was concentrated to *ca.* 5 ml and excess pentane was added. The solution was kept for 2h at room temperature and the yellow solid formed was collected and dried under vacuum.

Yield: 0.045g (52 %).

IR (KBr, cm^{-1}): 2036, 1651, 1624.

$^1\text{HNMR}$ (CDCl_3 , δ): 5.43 (m, 2H), 5.34 (d, 1H, $J = 5.7$), 5.20 (d, 1H, $J = 6$), 4.09 (bs, NH, 1H), 3.81 (m, 1H), 3.45 (m, 1H), 3.05 (m, 1H), 2.91 (m, 1H, cym), 2.26 (s, 3H), 2.21 (m, 2H), 1.97-1.95 (m, 2H), 1.33 (m, 6H, cym).

2.2.7. Preparation of $[\{(p\text{-cymene})\text{Ru}(\text{Gly})\text{N}_3\}](\mathbf{7})$: This complex was prepared following a similar procedure as described for **1** (route *a*) using $[(p\text{-cymene})\text{Ru}(\mu\text{N}_3)\text{Cl}]_2$ (0.1g, 0.159 mmol) and sodium salt of glycine (0.034 g, 0.351 mmol) in methanol.

Yield: 0.076g (68%).

Alternative method: This complex was prepared using an alternative method as described for complex **6** using $[(p\text{-cymene})\text{Ru}(\mu\text{N}_3)\text{Cl}]_2$ (0.072g, 0.115 mmol), glycine (0.018 g, 0.24 mmol), K_2CO_3 (0.036g, 0.26 mmol) and acetonitrile (30 ml). Yield: 0.035g (44 %).

FTIR (cm⁻¹): 2036, 1620, 1576.

¹H NMR (CDCl₃, δ): 5.62 (d, 1H, *J* = 5.7), 5.56 (d, 1H, *J* = 5.7), 5.39 (dd, 2H, *J* = 9.3, 5.7), 3.18 (d, 1H, *J* = 8.1), 3.05 (d, 1H, *J* = 7.8), 2.86 (sept, 1H, *J* = 6.9), 2.22 (s, 3H), 1.32 (dd, 6H, *J* = 6.6, 3.0).

¹³C {¹H} NMR (CDCl₃, δ): 181.96, 100.36, 96.26, 83.21, 80.78, 80.12, 79.37, 45.29, 30.70, 22.80, 22.52, 17.94.

2.3 Synthesis of (*η*⁶-*p*-cymene) ruthenium (II) triazolato complexes:

2.3.1 Preparation of [(*p*-cymene)Ru(*quinto*){N₃C₂(CO₂Me)₂}] (**8**):

A mixture of complex **1** (0.05g, 0.11 mmol) and five folds excess of dimethylacetylenedicarboxylate in dry dichloromethane (20 ml) was stirred for 16-18 h at room temperature then the solution was reduced to *ca.* 3 ml in a rotary evaporator. To this solution 30 ml of hexane was added and volume of the solution was reduced in a rotary evaporator whereby the compound precipitated out as a yellow solid. The solid was collected and washed with 2x20 ml of hexane and dried under vacuum to afford the complex as yellow solid.

Yield: 0.058 g (88%).

FT (IR, cm⁻¹): 1720, 1662.

¹H NMR (CDCl₃, δ): 8.65 (d, 1H, *J* = 8.7), 8.31 (t, 1H, *J* = 8.1), 8.15 (d, 1H, *J* = 8.4), 7.93 (m, 2H), 7.73 (m, 1H), 5.93 (d, 1H, *J* = 5.1), 5.81 (t, 1H, *J* = 6.3), 5.72 (t, 2H, *J* = 6.3), 3.76 (s, 6H), 2.86 (m, 1H), 1.96 (s, 3H), 1.04 (d, 3H, *J* = 7.2), 0.96 (d, 3H, *J* = 6.9).

¹³C {¹H} NMR (CDCl₃, δ): 171.94, 162.69, 152.84, 147.50, 140.29, 140.05, 139.85, 131.85, 130.59, 129.90, 128.83, 122.64, 105.76, 101.22, 86.65, 83.89, 83.55, 81.20, 51.78, 30.86, 22.44, 21.94, 18.31.

2.3.2. Preparation of [(*p*-cymene)Ru(*quinto*){N₃C₂(CO₂Et)₂}] (**9**):

This complex was prepared following a similar procedure as described for **8** using diethylacetylenedicarboxylate.

Yield: 0.063g (91 %).

FT IR(cm⁻¹): 1728, 1658.

¹H NMR (CDCl₃, δ): 8.63 (d, 1H, *J* = 8.7), 8.28 (m, 1H), 8.13 (d, 1H, *J* = 8.1), 8.02 (d, 1H, *J* = 8.1), 7.85 (s, 1H), 7.71 (m, 1H), 5.81 (d, 2H, *J* = 5.7), 5.68 (d, 2H, *J* = 5.7), 4.21 (q, 4H, *J* = 7.2), 2.57 (m, 1H), 1.95 (s, 3H), 1.25 (t, 6H, *J* = 7.2), 1.03 (d, 3H, *J* = 6.9), 1.01 (d, 3H, *J* = 6.3).

¹³C {¹H} NMR (CDCl₃, δ): 171.93, 162.50, 153.23, 147.91, 140.22, 131.79, 131.48, 130.68, 128.60, 122.62, 105.83, 101.10, 86.52, 84.00, 81.85, 81.21, 60.63, 30.85, 22.48, 21.94, 14.07.

2.3.3. Preparation of [(*p*-cymene)Ru(*thiqc*){N₃C₂(COMe)₂}] (**10**):

This complex was prepared following a similar procedure as described for **8** using complex **2** (0.05g, 0.11 mmol) and dimethylacetylenedicarboxylate.

Yield: 0.036 g (55%).

IR (KBr, cm⁻¹): 1726, 1639.

¹H NMR (CDCl₃, δ): 7.23 (d, 1H, *J* = 7.2), 7.10 (d, 1H, *J* = 6.0), 6.9-6.77 (m, 2H), 5.78-5.46 (m, 4H), 4.31 (m, 1H), 3.87 (s, 6H, -CO₂Me), 3.47 (m, 1H), 3.05 (m, 1H), 2.83 (m, 1H), 2.69 (m, 1H), 2.19 (s, 2H), 2.08 (s, 3H), 1.31-1.14 (m, 6H).

¹³C{¹H} NMR (CDCl₃, δ): 178.12, 162.84, 140.26, 139.44, 133.20, 132.41, 129.84, 127.80, 126.74, 125.64, 105.68, 97.85, 85.46, 83.53, 82.38, 81.10, 65.81, 63.56, 58.28, 51.98, 32.41, 30.69, 22.67, 21.99, 17.96.

2.3.4. Preparation of [(*p*-cymene)Ru(*thiqc*){N₃C₂(CO₂Et)₂}] (**11**):

This complex was prepared following a similar procedure as described for **8** using complex **2** (0.05g, 0.11 mmol) and diethylacetylenedicarboxylate.

Yield: 0.04g (59%).

IR (KBr, cm⁻¹): 1732, 1651.

¹H NMR (CDCl₃, δ): 7.10 (d, 1H, *J* = 6.3), 6.94 (t, 2H, *J* = 8.7), 6.83 (d, 2H, *J* = 12), 5.71-5.47 (m, 4H, cymene), 4.29 (m, 4H), 3.10 (m, 1H), 2.75 (m, 1H), 2.60 (m, 1H), 2.08 (s, 2H), 1.96 (s, 3H), 1.36-1.28 (m, 6H), 1.23-1.10 (m, 6H).

¹³C NMR (CDCl₃, δ): 178.11, 162.63, 161.78, 140.34, 139.57, 133.31, 132.41, 129.83, 127.82, 126.74, 125.63, 103.60, 97.77, 85.13, 83.53, 82.25, 81.11, 60.89, 58.27, 54.20, 32.40, 30.50, 22.61, 22.33, 18.05, 14.18.

2.3.5. Preparation of [(*p*-cymene)Ru(*pico*){N₃C₂(CO₂Me)₂}] (**12**):

This complex was prepared following a similar procedure as described for **8** using complex **3** (0.04g, 0.1 mmol) and dimethylacetylenedicarboxylate.

Yield: 0.035g (65 %).

IR (KBr, cm⁻¹): 1732, 1651.

¹H NMR (CDCl₃, δ): 9.01 (s, 1H), 7.96 (m, 2H), 7.51 (s, 1H), 5.77 (br, 2H), 5.63 (m, 2H), 3.77 (s, 6H), 2.80 (m, 1H), 2.10 (s, 3H), 1.14 (s, 6H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , δ): 171.71, 163.00, 154.04, 153.04, 139.90, 139.59, 128.32, 128.16, 126.91, 104.77, 100.53, 84.86, 83.86, 83.24, 82.00, 51.86, 30.89, 22.28, 18.41.

2.3.6. Preparation of $[(p\text{-cymene})\text{Ru}(\text{pico})\{\text{N}_3\text{C}_2(\text{CO}_2\text{Et})_2\}]$ (**13**):

This complex was prepared following a similar procedure as described for **8** using complex **3** (0.04g, 0.1 mmol) and diethylacetylenedicarboxylate.

Yield: 0.032 g (56%).

^1H NMR (CDCl_3 , δ): 9.01 (s, 1H), 7.95 (m, 2H), 7.50 (s, 1H), 5.78 (m, 2H), 5.64 (d, 2H, $J = 10$), 4.22 (m, 4H), 2.78 (m, 1H), 2.14 (s, 3H), 1.25-1.13 (m, 12H, CH_3 , $p\text{-Cym}$ & CO_2Et).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , δ): 171.63, 162.35, 153.98, 152.72, 139.90, 139.52, 128.12, 127.75, 126.63, 104.82, 100.55, 84.79, 84.75, 83.75, 83.05, 60.67, 30.86, 22.39, 22.27, 18.23, 14.10.

2.3.7. Preparation of $[(p\text{-cymene})\text{Ru}(\text{Gly})\{\text{N}_3\text{C}_2(\text{CO}_2\text{Me})_2\}]$ (**14**) :

This complex was prepared following a similar procedure as described for **8** using complex **5** (0.04g, 0.113 mmol) and dimethylacetylenedicarboxylate.

Yield: 0.031g (55%).

IR (KBr, cm^{-1}): 1732, 1653, 1628.

^1H NMR (CDCl_3 , δ): 5.76 (d, 2H, $J = 10$), 5.53 (d, 2H, $J = 9.0$), 3.84 (s, 6H), 3.53-3.25 (m, 2H), 2.82 (m, 1H), 1.99 (s, 3H), 1.06 (s, 6H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): 182.18, 162.49, 139.85, 101.87, 98.45, 85.89, 82.47, 82.02, 81.41, 52.10, 46.60, 30.63, 22.48, 22.14, 17.92.

2.3.8 .Preparation of $[(p\text{-cymene})\text{Ru}(\text{Gly})\{\text{N}_3\text{C}_2(\text{CO}_2\text{Et})_2\}]$ (**15**):

This complex was prepared following a similar procedure as described for **8** using complex **5** (0.04g, 0.113 mmol) and diethylacetylenedicarboxylate.

Yield: 0.028 g (47 %).

IR (KBr, cm^{-1}): 1726, 1650, 1610.

^1H NMR (CDCl_3 , δ): 5.83 (m, 2H), 5.62 (m, 2H), 4.41 (q, 4H, $J = 7.2$), 3.21 (m, 2H), 2.85 (m, 1H), 2.16 (s, 3H), 1.33 (t, 6H, $J = 6.9$), 1.25 (s, 6H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): 181.99, 162.39, 139.98, 101.86, 99.16, 82.41, 81.48, 61.00, 30.64, 22.56, 22.27, 46.53, 18.56, 14.21.

3. Structure analysis and refinement

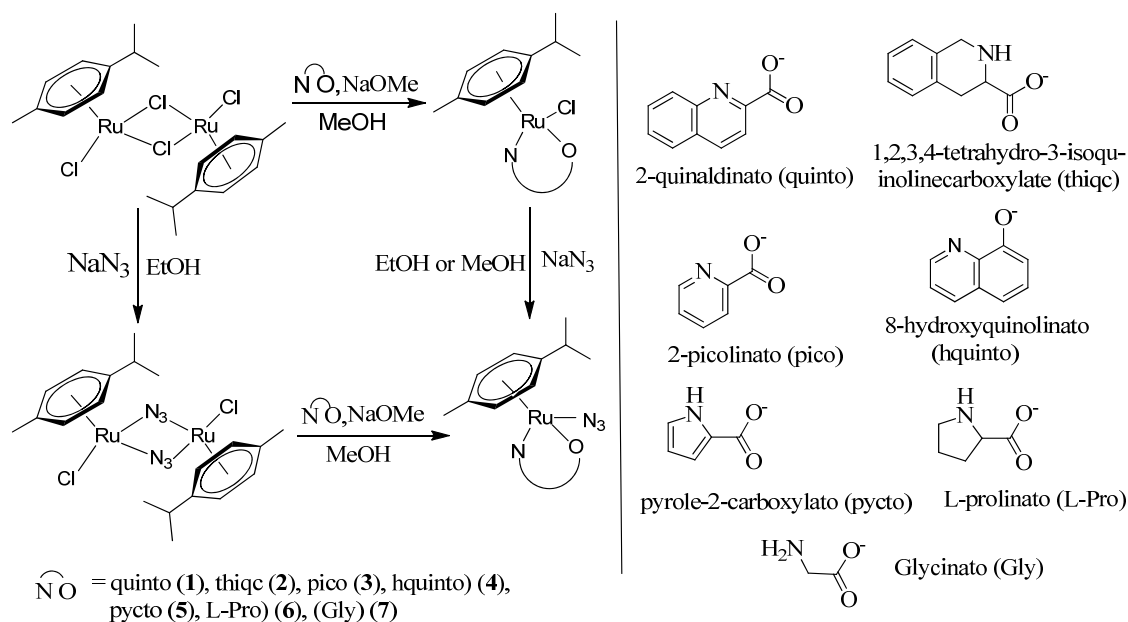
X-ray quality crystals of the complex **9** were grown by slow diffusion of hexane into a dichloromethane solution of **9**. The X-ray diffraction data was collected at 296°K on a Nonius Kappa CCD FR590 single crystal X-ray diffractometer, using MoK α radiation ($\lambda = 0.71073 \text{ \AA}$). Crystal-to-detector distance was 30 mm and exposure time was 20 seconds per degree. Data collection was 99.5% complete to 25° in θ . The data was integrated and scaled using hkl-SCALEPACK [35]. The structure was solved by direct methods (SHELXS, SIR97) [36] and refined by full matrix least squares base on F^2 using (SHELXL 97) [37]. The weighting scheme used was $W = 1/[\sigma^2(F_o^2) + 0.0490P^2 + 0.0000P]$ where $P = (F_o^2 + 2F_c^2)/3$. All non-hydrogen atoms were refined anisotropically while hydrogen atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms with C-H distances in the range 0.95-1.0 Å. Refinement converged at a final $R = 0.0402$ (for observed data F), and $wR_2 = 0.0984$ (for unique data F^2). The data collection parameters, selected bond lengths and angles are presented in Tables 1 and 2, respectively. Figure 3 shows an ORTEP diagram [38] of the compound **9**.

4. Results and Discussion:

The reaction of [$\{(p\text{-cymene})\text{Ru}(\mu\text{N}_3)\text{Cl}\}_2$] with two equivalents of the ligands in the presence of NaOMe yielded a series of ($\eta^6\text{-arene}$)ruthenium (II) azido compounds of general formula [$\{(p\text{-cymene})\text{Ru}(\text{N}^{\wedge}\text{O})\text{N}_3\}$] (**1-6**) in fairly good yield (44-72%). Compound **7** was obtained by the reaction of sodium salt of glycine with [$(p\text{-cymene})\text{Ru}(\mu\text{N}_3)(\text{Cl})_2$] (Scheme 1). The formation of these complexes is readily followed from the IR spectrum by the complete disappearance of the starting compound azide peak at 2057 cm^{-1} (bridging νN_3) and appearance of a strong peak at around 2030 cm^{-1} corresponding to terminal azide (νN_3). Alternatively, the complexes can also be prepared by the direct reaction of chloro analogue [$(p\text{-cymene})\text{Ru}(\text{N}^{\wedge}\text{O})\text{Cl}$] with NaN_3 in methanol or ethanol.

In a previous study, the direct reaction of NaN_3 with [$\{(p\text{-cymene})\text{Ru}(\text{KA})\text{Cl}\}$] or [$\{(p\text{-cymene})\text{Ru}(\text{ox})\text{Cl}\}_2$] resulted in the formation of dimeric azido complexes [$\{(p\text{-cymene})\text{Ru}(\mu\text{N}_3)\}_2$] [13] and [$\{(p\text{-cymene})\text{Ru}(\mu\text{N}_3)\text{Cl}\}_2$] [39], respectively (KA = kojic acidate, ox = oxalate). Thus, we could demonstrate with the azide dimer complex [$\{(p\text{-cymene})\text{Ru}(\mu\text{N}_3)\text{Cl}\}_2$] as precursor, a more convenient pathway for the preparation of terminal azide complex, because i) the complete conversion of starting azide complexes to terminal azide complexes can be readily followed from the inspection of their IR spectra and ii) this pathway can avoid displacement of labile ligand such as

kojic acidate or oxalate from the ruthenium complexes that were observed during the direct reaction of NaN_3 with $[\{(p\text{-cymene})\text{Ru}(\text{KA})\text{Cl}\}]$ [13] or $[\{(p\text{-cymene})\text{Ru}(\text{ox})\text{Cl}\}_2]$ [39].



Scheme 1

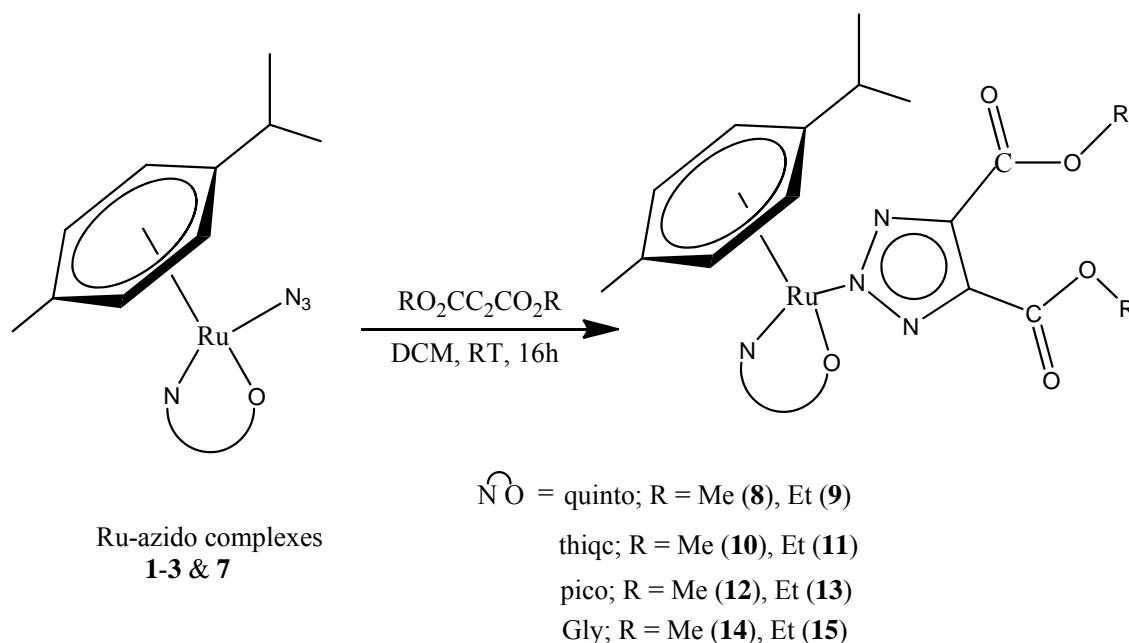
The complexes **5** and **6** are air and moisture sensitive solids whereas, the rest of the complexes are stable in air. All these complexes are partially or completely soluble in water and the complexes were characterized on the basis of FT-IR and NMR spectroscopic data (^1H , ^{13}C).

The NMR spectrum of complex **1** and **4** showed a slightly different spectra pattern for *p*-cymene ligand as compared to the rest of the complexes. For instant, the complex **1** exhibits two doublets for diastereotopic methyl protons of the isopropyl group at around δ 1.12-0.99 (Fig. 1). Likewise, the aromatic proton of the *p*-cymene ligand displayed four doublets due to the coupling of the diastereotopic CH proton with the aromatic ring protons. This spectra patterned arises due to diastereotopic nature of isopropyl group [41]. The different in NMR spectrum pattern of *p*-cymene group is also seen in the ^{13}C NMR spectrum for both the complexes **1** and **4**. The four distinct signals were observed in the region of δ 83 to 80 instead of usually two signals observed for aromatic carbon of *p*-cymene group. The similar spectra patterned of *p*-cymene ligand have been reported elsewhere in other *p*-cymene complexes [40-43].

The azido complexes **1-3** and **7** were studied for 1,3-dipolar cycloaddition reaction with alkynes. As usual, we conducted the reaction in dichloromethane using ruthenium azido complexes (**1-3** & **7**) and 4 fold excess of alkynes at room temperature to give a series of ruthenium (II)

triazolato complexes **8-15** (Scheme 2). The complexes **8-13** were stable and readily isolable but complex **14 & 15** are hygroscopic, and prolong exposure to air resulted in oily solid. The formation of the complexes was readily confirmed by the inspection of their IR spectra. The IR spectrum of complex **8-15** showed a complete disappearance of the azide peak at around 2030 cm^{-1} observed in the starting complexes and the new peaks have appeared at 1732 cm^{-1} corresponding to the C=O of carboxylate group (A representative IR spectra of the starting complex **1** and product **9** is shown in Fig. 2). The proton NMR spectra of all the complexes exhibit two doublets (occasionally unresolved) at around δ 5.42-5.78 for aromatic proton of *p*-cymene ring while proton of isopropyl methyl group appeared as doublet δ 0.96-1.32. In the case of complex **8** and **9**, the isopropyl methyl group was observed as two doublets similar to that observed in the starting ruthenium azido complex **1**. The complexes **8** and **9** also displayed a singlet at δ 3.76 and quartet at δ 4.21 assignable to the methoxy (CO₂Me) and ethoxy (CO₂Et) groups of the triazole ring. The signals for quinaldinato ring and *p*-cymene ligands were observed in the usual range and the values are comparable to that of starting azido complex **1**. The spectroscopic data of all these triazolato complexes **8-15** are well matched with their composition and the proposed structure were supported by solid state structure determination of the representative complex **9**.

Notably, triazole anions could be coordinated to a metal through either N-1 or N-2 nitrogen atoms [21, 25, 37] which are isoenergetics as indicated by molecular orbital calculations [44, 45]. It is believed that triazolato complexes may initially formed *N(1)* bonded complexes which then isomerized to the sterically more favour *N-2* bonded complexes. In our cases, the triazolato complexes formed are exclusively *N(2)* bound isomer which is supported by their NMR spectral data. For instant, the proton NMR spectrum of **8** displayed a, singlet at δ 3.75 assignable to the protons of a methoxy carbonyl group while for complex **9** a quartet was observed at δ 4.29 assignable to the -CH₂- protons of an ethoxycarbonyl group (-CO₂Et). One would expect that the *N(1)* bound isomer would exhibit two resonances for its anisochronous methoxy or ethoxycarbonyl group [25, 29]. These spectra suggest that the triazolato complexes formed are *N(2)* bound isomers and the structure was unambiguously confirmed by single X-ray analysis of representative compound **9**.



Scheme 2

We have extended this reaction to the other neutral ruthenium (II) azido complex [$\{(p\text{-cymene})\text{Ru}(\text{PTA})\text{N}_3\text{Cl}\}$] (PTA = 1,3,5-triazo-7-phosphaadamantane). However, the reaction did not proceed to the non-chelated complex [$\{(p\text{-cymene})\text{Ru}(\text{PTA})(\text{N}_3)\text{Cl}\}$]. This result suggests that neutral and chelated ($\eta^6\text{-arene}$) ruthenium (II) complexes favour cycloaddition reaction but non-chelated complexes do not favour the reaction. The reason could be the flexibility nature of coordinated azide bonds arising from free movement of the azide around the ruthenium centre. Further work is underway in our laboratory to achieve the cycloaddition reaction of alkynes with non-chelated ($\eta^6\text{-arene}$) ruthenium (II) azido complexes containing a bulky ligand that might cause to a more rigid azide bond.

5. Crystal Structure:

The molecular structure of representative compound **9** has been established by single X-ray crystallography (Fig 3). The complex crystallizes in a triclinic space group P-1. The geometry around the ruthenium atom can be regarded as pseudooctahedral with the *p*-cymene ligands occupying the three coordination sites while the remaining coordination sites are occupied by the N and O atoms of the quinaldinato group and the N-2 atom of the triazolato ring. The average bond distance of ruthenium to *p*-cymene ring carbons is 2.188 Å. The ruthenium atom is not in equidistant to the six coordinated *p*-cymene ring carbons but slightly twisted as evident by the longer ruthenium to carbon

bond distances for Ru-C4 (2.220(3) Å) and Ru-C5 (2.205(3) Å), compared to the ruthenium-carbon bond distances for the rest of ring carbons which have a bond distances in the range of 2.149-2.189 Å (Table 2).

The C-C bond distances of the five membered heterocyclic ring are comparable suggesting a significant delocalization of electrons. The bite angle, N4-Ru1-O1 is 77.66 (8) Å which is very close to that observed in the related compounds [40]. The C-O bond distances 1.215 (4) and 1.282 (4) Å are comparable with the values reported in the related compounds [40, 41]. The bond distances of Ru-O (2.056 (19) Å) and Ru-N4 (2.099(2) Å) are slightly shorter than the previously reported values of a ruthenium (II) quinaldinato complexes [34], while Ru-N1 bond length (2.099(2) Å) is equal to the Ru-N bond length of the related (η^6 -arene) ruthenium triazolato complexes [27]. In the structure, a true hydrogen bonding interaction was not noticed. However, we observed a weak van der Waals interactions between O2 of the carboxylate group and a neighboring C-18 hydrogen by inversion-symmetric related complex, which leads to a dimeric $R_2^2(10)$ ring configuration of the type -H-C-C=O (Fig. 4) [46]. The quinaldinato moieties pack as antiparallel pairs at a plane to plane distance of 3.364(6) Å which is driven by pi-pi interactions, stacked throughout the lattice roughly along the [0-1 1] direction.

Table 1. Summary of structure determination and refinement for complex **9**

Empirical formula	C ₂₈ H ₃₀ N ₄ O ₆ Ru
Formula Weight	619.63
Temperature (K)	292(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	
<i>a</i> (Å)	10.2660(10)
<i>b</i> (Å)	12.2220(10)
<i>c</i> (Å)	12.5780(10)
α (°)	64.904(10)
β (°)	79.670(10)
γ (°)	75.593(10)
Volume (Å ³)	1379.3(2)
<i>Z</i>	2
Density (calculated) (Mg/m ³)	1.492 Mg/m ³
Absorption coefficient (mm ⁻¹)	0.617 mm ⁻¹
F(000)	636
θ range for data collection (°)	2.06 to 28.28
index ranges	-13 ≤ <i>h</i> ≤ 13, -16 ≤ <i>k</i> ≤ 12, -15 ≤ <i>l</i> ≤ 16
Reflection collected/unique	9167
Completeness to theta	25.0° to 99.5%
Refinement method	Full-matrix least squares on F^2
Data/restraints/parameters	6359 /26 /384
Goodness-of-fit on F^2	1.146
Final <i>R</i> indices	R ₁ = 0.0402, wR ₂ = 0.0984
[<i>I</i> > 2σ(<i>I</i>)]	
<i>R</i> indices (all data)	R ₁ = 0.0525, wR ₂ = 0.1046
Largest different peak and hole (eÅ ⁻³)	0.767 and -0.805

Table 2: Selected bond lengths (Å) and angles (°)

<i>Bond lengths (Å)</i>			
Ru-N1	2.099(2)	Ru-N4	2.126(2)
Ru-O1	2.0567(19)	C21-C22	1.387(4)
N1-N2	1.326(3)	N2-N3	1.329(3)
N2-C21	1.345(4)	N3-C22	1.345(4)
C20-O1	1.282(4)	C20-O2	1.215(4)
Ru1-C1	2.189(3)	Ru1-C2	2.149(2)
Ru1-C3	2.188(3)	Ru1-C4	2.220(3)
R1-C5	2.205(3)	Ru1-C6	2.178(3)
<i>Bond angles (°)</i>			
N4-Ru1-O1	77.66(8)	N1-Ru1-O1	86.10(9)
N2-N1-N3	113.4(2)	C20-O1-Ru1	117.64(19)
C22-C21-C26	131.9(3)	C21-C22-C23	132.9(3)

5. Concluding Remarks:

This paper describes the synthesis of a series of (*p*-cymene) ruthenium (II) azido complexes bearing N,O-chelate ligands. The complexes of general formula [(*p*-cymene)Ru(N[∘]O)N₃] (**1-7**) were prepared by azide cleavage reaction of [(*p*-cymene)Ru(N₃)Cl]₂ with N,O ligands or alternatively by direct reaction of [(*p*-cymene)Ru(N[∘]O)Cl] with NaN₃. It was found that the former method is more convenient not only in terms of product yield but it also allows ready characterization of the product formed by inspection of IR-data. Complexes **1-3** and **7** undergoes 1,3-dipolar cycloaddition reactions with substituted alkynes such as DMD or DED to give triazolato complexes **8-15**. The cycloaddition reaction readily undergoes in neutral chelated complexes such as [(η⁶-arene)Ru(N[∘]O)N₃] but fails to proceed in non-chelated complex [(η⁶-arene)Ru(PTA)N₃Cl]. Study on cycloaddition reaction of non-chelated complexes using more ‘bulky’ ligands as well as dipolar cycloaddition reaction of coordinated metal azides with alkynes in water is under way in our laboratory.

Supplementary Materials

CCDC No. 942548 contains the supplementary crystallography data for this paper. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> or from the

Cambridge Crystallography Data Centre, 12 Union Road, Cambridge CB21 2E2, UK; fax : (+ 44) 1223-336-033; or e-mail:deposit@ccdc.cam.ac.uk.

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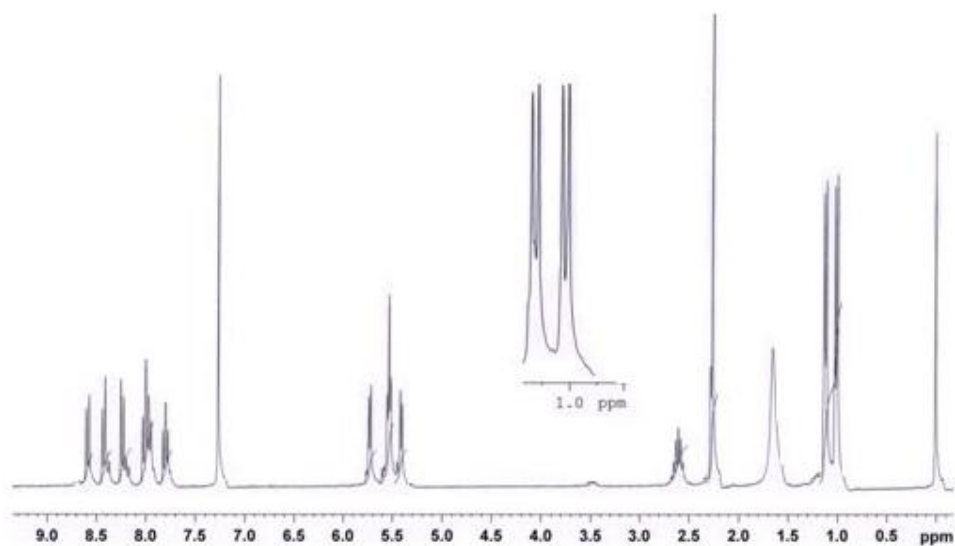
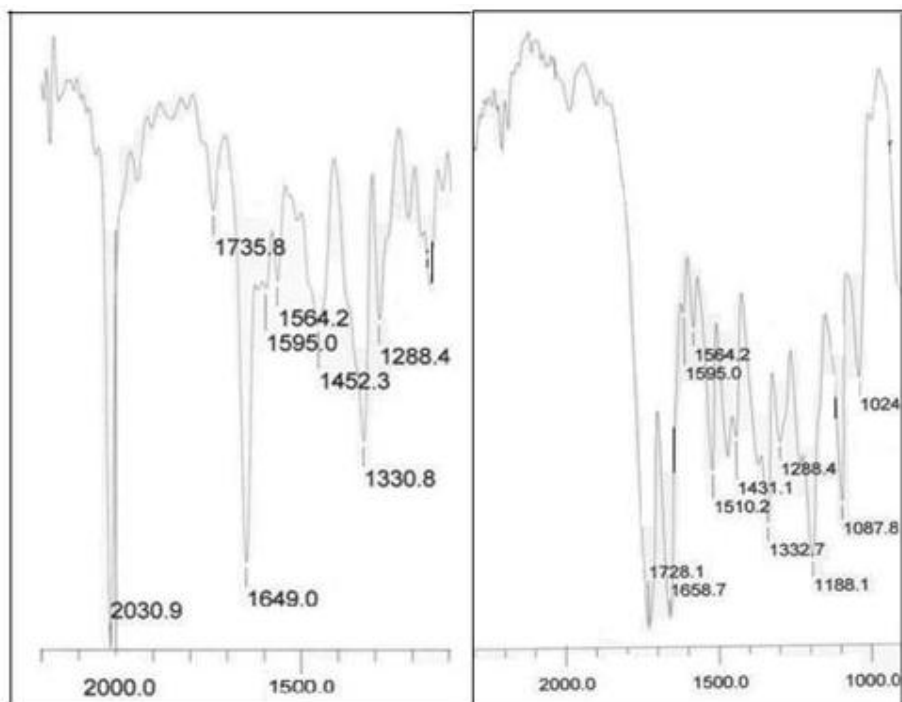
Fig 1: ^1H NMR Spectrum of complex 1

Figure 2: IR Spectra of complex 1 (left) and complex 9 (Right)

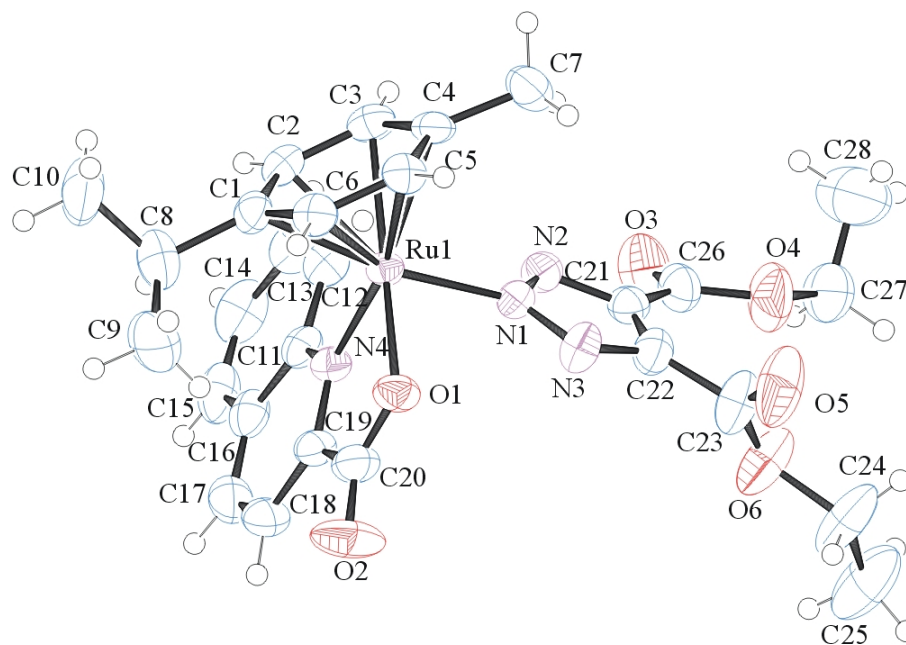


Figure 3: ORTEP diagram of $[(p\text{-cymene})\text{Ru}(\text{quinto})(\text{N}_3\text{C}_2(\text{CO}_2\text{Et})_2)]$ (**9**) with thermal ellipsoid at the 50% of probability level.

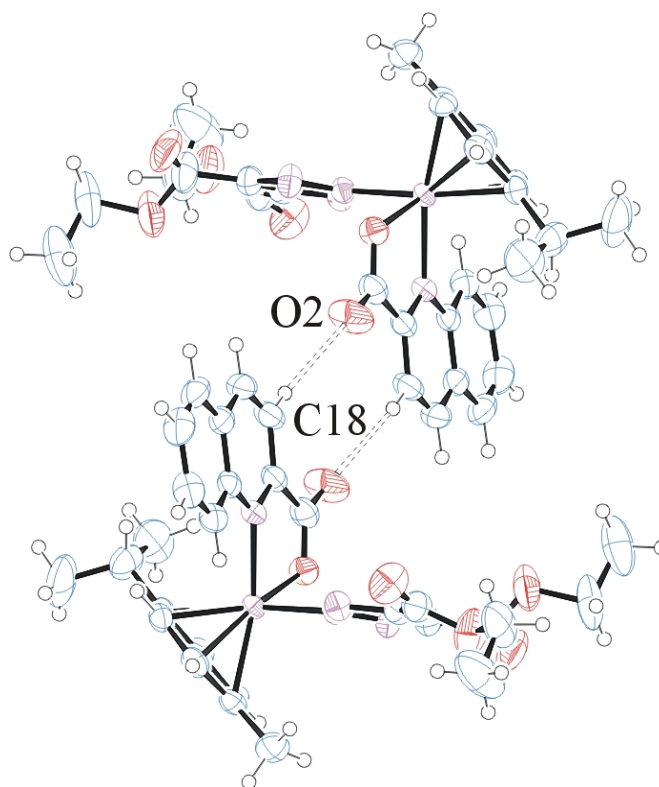


Figure 4. Intermolecular R_2^2 (10) dimeric ring configuration induced via weak van der Waals interactions C18-H...O2.