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Reactivity study of arene(azido)ruthenium N∩O-base complexes with activated alkynes

Saphidabha L. Nongbri [a], Bruno Therrien [b], Kollipara Mohan Rao [a,*]

[a] Department of Chemistry, North Eastern Hill University, Shillong 793 022, India
[b] Service Analytique Facultaire, Université de Neuchâtel, Avenue de Bellevaux 51, CH-2000 Neuchâtel, Switzerland

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ABSTRACT

Substitution reaction of chloro η^6-arene ruthenium N∩O-base complexes [(η^6-arene)Ru(N∩O)Cl] [N∩O = pyrazine-2-carboxylic acid (pca-H), 8-hydroxyquinoline (hq-H); arene = *p*-^{i}PrC$_6$H$_4$Me, N∩O = hq (**1**); arene = C$_6$Me$_6$, N∩O = hq (**2**)] with NaN$_3$ yield the neutral arene ruthenium azido complexes of the general formula [(η^6-arene)Ru(N∩O)N$_3$] [N∩O = pca, arene = *p*-^{i}PrC$_6$H$_4$Me (**3**), arene = C$_6$Me$_6$ (**4**); N∩O = hq, arene = *p*-^{i}PrC$_6$H$_4$Me (**5**), arene = C$_6$Me$_6$ (**6**)]. These complexes undergo [3 + 2] dipolar cycloaddition reaction with activated alkynes dimethyl and diethyl acetylenedicarboxylates to yield the arene triazole complexes [(η^6-arene)Ru(N∩O){N$_3$C$_2$(CO$_2$R)$_2$}] [N∩O = pca, R = Me, arene = *p*-^{i}PrC$_6$H$_4$Me (**7**), C$_6$Me$_6$ (**8**); R = Et, arene = *p*-^{i}PrC$_6$H$_4$Me (**9**), C$_6$Me$_6$ (**10**); N∩O = hq, R = Me, arene = *p*-^{i}PrC$_6$H$_4$Me (**11**) C$_6$Me$_6$ (**12**); R = Et, arene = *p*-^{i}PrC$_6$H$_4$Me (**13**), C$_6$Me$_6$ (**14**)]. On the bases of proton NMR study, in the above triazole complexes N(2) isomers are assigned with dimethylacetylenedicarboxylate whereas N(1) isomers with diethylacetylenedicarboxylate. All complexes have been characterized by IR and NMR spectroscopy as well as by elemental analysis. The molecular structures of the azido complexes [(η^6-*p*-^{i}PrC$_6$H$_4$Me)Ru(pca)N$_3$] (**3**), [(η^6-*p*-^{i}PrC$_6$H$_4$Me)Ru(hq)N$_3$] (**5**) and [(η^6-C$_6$Me$_6$)Ru(hq)N$_3$] (**6**) have been established by single crystal X-ray diffraction studies.

1. Introduction

With the discovery of the click chemistry [1], the 1,3-dipolar cycloaddition of organic azides and alkynes in the presence of transition metal catalysts continue to exist as the most convincing example in this field [2]. The applications of CuAAC (Copper-catalyzed azide-alkyne cycloaddition) have been widely explored and the importance of RuAAC is only beginning to appear [3]. The advantage of RuAAC over CuAAC is that it can catalyze both terminal and internal alkynes whereas CuAAC focuses its ability to engage terminal azide only. As one can imagine from this, the scope and functional group compatibility of RuAAC are excellent [4]. The resulting triazole derivatives have become an important family of heterocycles in medicinal chemistry [5–7] and material science [8–11]. The high stability and low toxicity of 1,2,3-triazoles have allowed biological research such as development of chemically modified DNA oligonucleotides (ODNs) for biological and nano-technological applications and also syntheses of oligomers linked via 1,2,3-triazole moieties [12–16]. The growing applications of the RuAAC reaction in biological studies via click chemistry stimulated us to synthesis and study new arene ruthenium triazole complexes which may also be suitable for further researches in biological fields.

Although the isolation of the metal intermediate triazole derivatives has been relatively unexplored and only a few publications appropriately described the syntheses of isolated triazole complexes derived from arene metal azido complexes of the platinum group metals. Recent work in our group successfully synthesized and characterized a number of β-diketone triazole complexes [17–22]. The success and isolation of these complexes inspired us to synthesize and study new arene triazole complexes containing N∩O-bidentate ligand (Chart 1) as the auxiliary ligand to the arene ruthenium system.

Though extensive biological studies [23,24], catalytic activities [25] and development of structural designs [26–30] have been carried out with arene ruthenium complexes of pca-H and hq-H ligands; to the best of our knowledge, the analogous ruthenium triazole complexes of corresponding azido complexes have not yet been explored.

2. Results and discussion

2.1. Synthesis of oxinato complexes

The synthesis of the oxinato complexes [(η^6-*p*-^{i}PrC$_6$H$_4$Me)Ru(hq)Cl] (**1**) [31] and [(η^6-C$_6$Me$_6$)Ru(hq)Cl] (**2**) [25] have been

* Corresponding author. Tel.: +91 364 2620; fax: +91 364 2550 076.
E-mail address: mohanrao59@gmail.com (K.M. Rao).

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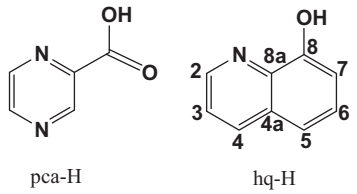


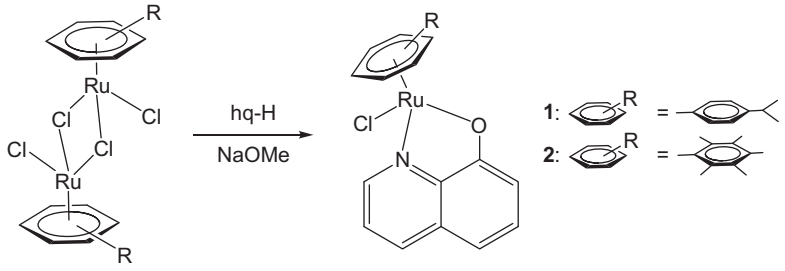
Chart 1. Ligands used in this study.

already reported. However, in this paper we report a different method of synthesis which involved treatment of the respective starting complexes $[(\eta^6\text{-arene})Ru(\mu\text{-}Cl)Cl]_2$ (arene = *p*-^{i}PrC$_6$H$_4$Me, C$_6$Me$_6$) with 2 equivalents of 8-hydroxyquinoline (hq-H) in methanol at room temperature for 4 h in the presence of NaOMe. The corresponding oxinato half-sandwich complexes **1** and **2** are precipitated during the course of the reaction in 90–95% isolated yield as orange air-stable solids (Scheme 1). Both complexes are characterized by IR, ^{1}H and ^{13}C NMR spectroscopy as well as by elemental analysis. The data are consistent with those previously reported [25,31].

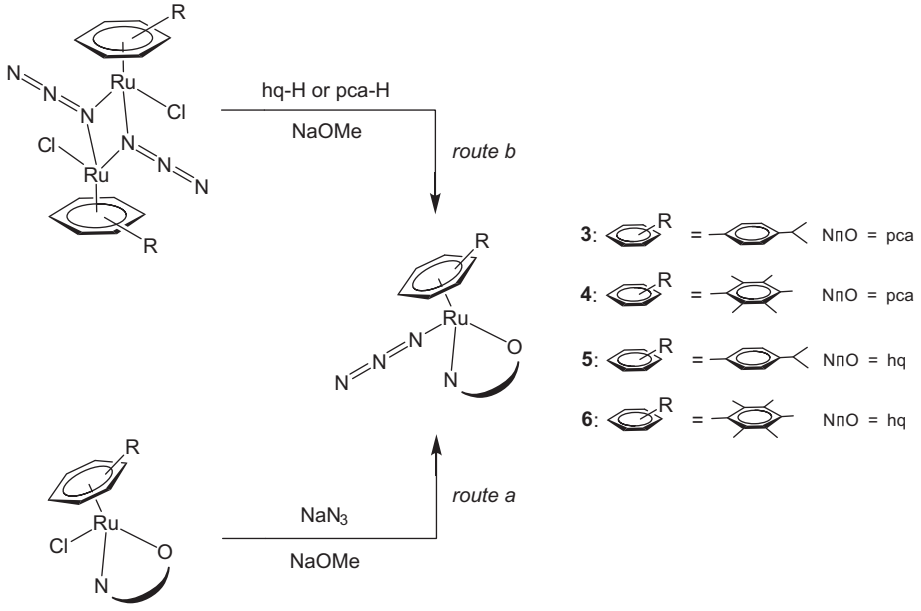
2.2. Synthesis of ruthenium azido complexes

Two reaction routes (Scheme 2) have been explored for substitution of the chlorido ligand by azido group. Treatment of the half-sandwich mononuclear complexes $[(\eta^6\text{-arene})Ru(N\cap O)Cl]$ with NaN_3 in polar solvent resulted in the substitution of the chloride ligand (Scheme 2: *route a*) affording the mononuclear neutral complexes of the general formula $[(\eta^6\text{-arene})Ru(N\cap O)N_3]$ [N∩O = pca, arene = *p*-^{i}PrC$_6$H$_4$Me (**3**), C$_6$Me$_6$ (**4**); N∩O = hq, arene = *p*-^{i}PrC$_6$H$_4$Me (**5**), C$_6$Me$_6$ (**6**)]. Similarly, these terminal azido complexes **3**–**6** can be prepared from the binuclear arene ruthenium azido complexes $[(\eta^6\text{-arene})Ru(\mu\text{-}N_3)Cl]_2$ (arene = *p*-^{i}PrC$_6$H$_4$Me, C$_6$Me$_6$) [32,33] (Scheme 2: *route b*) by reacting with either pca-H or hq-H in presence of NaOMe. Only the expected arene ruthenium azido monomeric complexes are obtained by following the two reaction routes and no unexpected by-products are isolated, which is in contrast to the case observed for some arene ruthenium β-diketone azido complexes [22]. However, '*route a*' is more preferable than '*route b*' as it gives higher percentage yield of the expected complex, hence we carried out the reaction following '*route a*' and reported the yield obtained through this route in the experimental section.

The formation of these terminal azido complexes can easily be monitored by IR spectroscopy in the frequency range 2015–2036 cm^{-1} [34]. The IR spectra of the complexes show strong prominent absorption band for terminal $\nu_{(N3)}$ at frequencies 2023, 2027 and 2017 cm^{-1} for complexes **3**, **4**, **5** and **6** respectively. Complexes **3** and **4** also exhibit strong absorption frequencies at 1658 and 1656 cm^{-1} respectively for the carbonyl group of the 2-pyrazine carboxylato ligand (pca).



Scheme 1. Preparation of arene-ruthenium hq complexes.



Scheme 2. Schematic flow chart for the preparation of azido complexes (**3**–**6**).

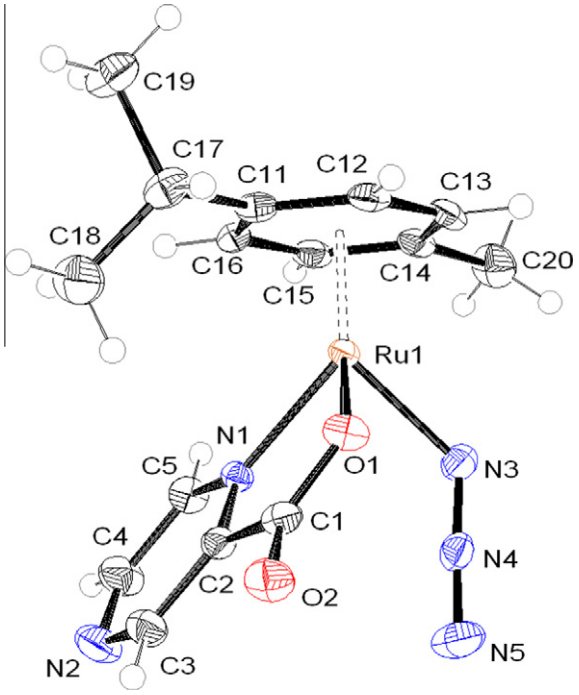


Fig. 1. ORTEP diagram of complex **3** with 50% probability thermal ellipsoids. Selected bond lengths (Å) and angles (°): Ru(1)–N(1) 2.086(3), Ru(1)–N(3) 2.104(4), Ru(1)–O(1) 2.091(3); N(1)–Ru(1)–N(3) 85.36(13), O(1)–Ru(1)–N(1) 77.51(12), O(1)–Ru(1)–N(3) 85.96(13).

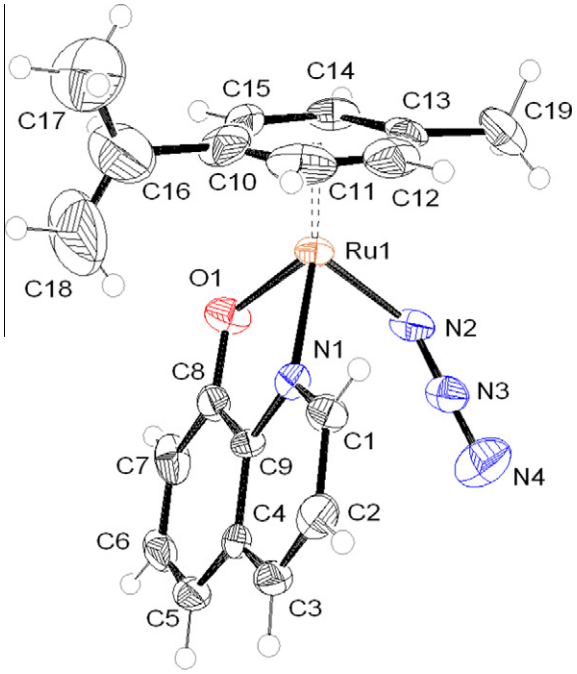


Fig. 2. ORTEP diagram of complex **5** with 50% probability thermal ellipsoids. Selected bond lengths (Å) and angles (°): Ru(1)–N(1) 2.073(7), Ru(1)–N(2) 2.124(9), Ru(1)–O(1) 2.083(6); N(1)–Ru(1)–N(2) 84.3(3), O(1)–Ru(1)–N(1) 78.8(3), O(1)–Ru(1)–N(2) 84.3(3).

The ^{1}H NMR of complex **3** displays one doublet at δ 1.29, and one singlet at δ 2.31 corresponding to methyl protons of the *p*-cymene ligand. Three distinct doublets a δ 5.38, δ 5.42, δ 5.48 and a doublet of doublet at δ 5.59 are assigned to the aromatic hydrogen atoms of the *p*-cymene ligand. Complex **4** in the ^{1}H NMR spectrum shows a singlet at δ 2.10 corresponding to the eighteen protons of the hexamethylbenzene ligand. The coordinated pyrazine carboxylato ligand in both complexes (**3**–**4**) exhibit two doublet and one singlet resonating in the region δ 8.5–9.0 analogous to the ^{1}H NMR of reported precursor mono arene ruthenium chloro complexes containing carboxylato pyrazine ligand [35]. The complexes **5** and **6** does not vary much from that of their respective arene ruthenium oxinato analog **1** and **2** in their ^{1}H NMR spectra. A noticeable feature in the ^{13}C {^{1}H} NMR of these complexes is the highly deshielded singlet of the carbonyl group located at about δ 167–170 arising from the respective N∩O – chelate ligands. It is noteworthy that the isotopic aromatic carbon of *p*-cymene in complexes **3** and **5** give rise to four distinct resonances in the expected range of δ 80.06–81.98. In addition to the signals attributed by the carbon atoms of the corresponding ligands, complexes **4** and **6** display two singlets, one in the region δ 15.18–15.33 for the methyl carbons and another at around δ 90.34–92.26 for the aromatic carbon atoms. Orange color crystals of **3**, **5** and **6** are obtained by slow diffusion of low boiling non polar solvent over solution of the respective complex in chlorinated solvent or acetone. X-ray analysis of crystals of appropriate size and shape provide complete elucidation of the detailed structures presented in Figs. 1, 2 and 3 for complexes **3**, **5** and **6**, respectively.

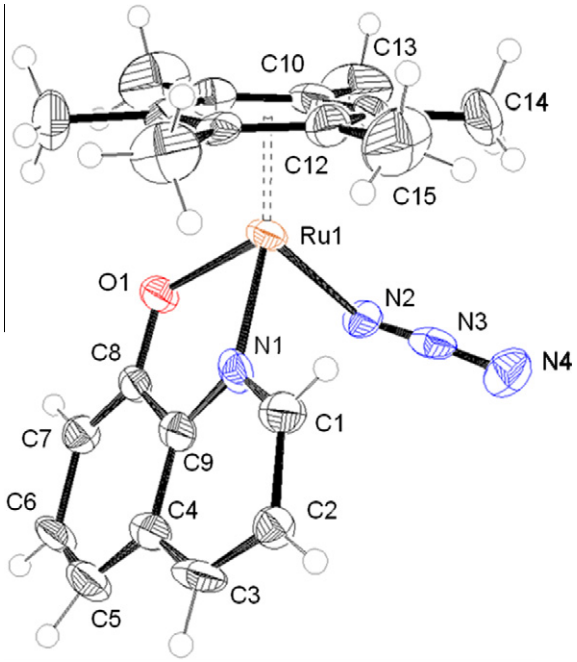
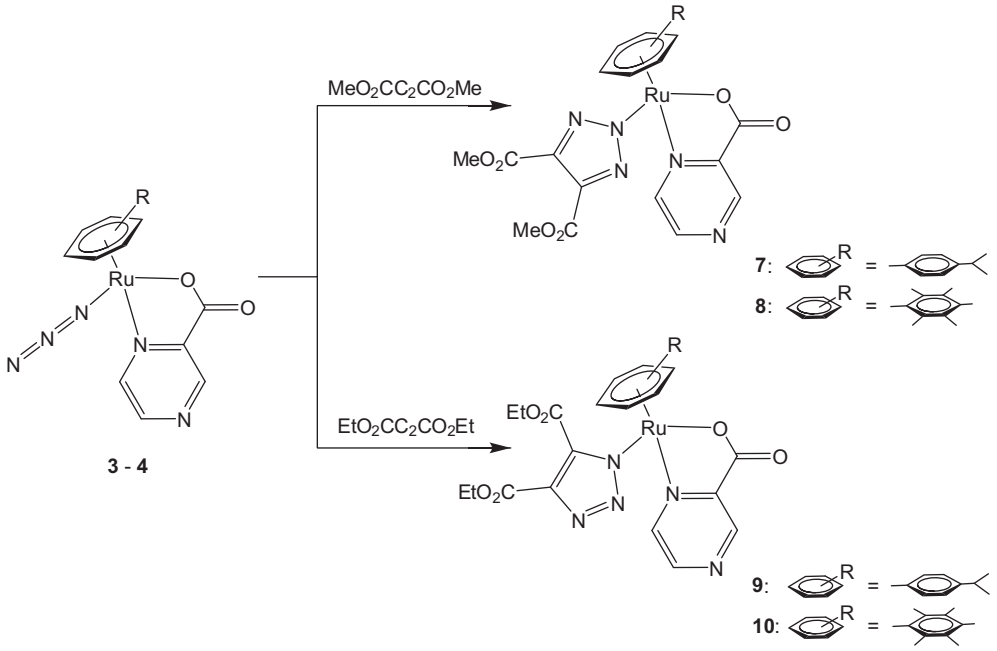


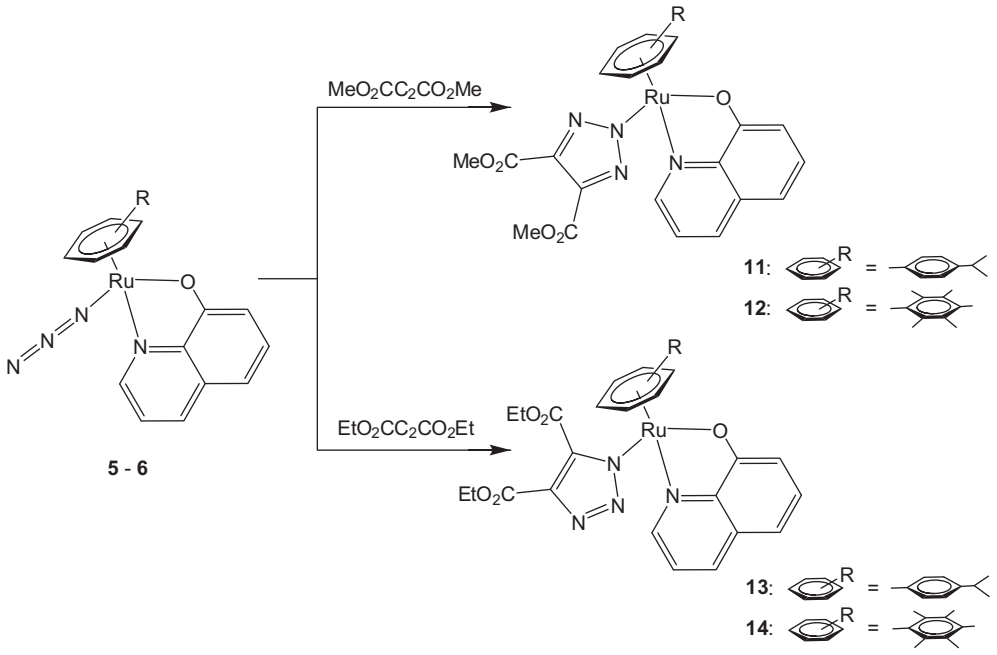
Fig. 3. ORTEP diagram of complex **6** with 50% probability thermal ellipsoids. (Symmetry code: $i = x, y, 0.5 - z$) Selected bond lengths (Å) and angles (°): Ru(1)–N(1) 2.026(8), Ru(1)–N(2) 2.143(4), Ru(1)–O(1) 2.213(6); N(1)–Ru(1)–N(2) 82.8(2), O(1)–Ru(1)–N(1) 77.9(2), O(1)–Ru(1)–N(2) 83.5(2).

2.3. Synthesis of triazolo complexes **7**–**14**

The azido complexes are further used as precursors in the synthesis of triazolo complexes. Treatment of the corresponding azido complexes **3**–**6** with fivefold excess of dimethylacetylenedicarboxylate ($MeO_2CC_2CO_2Me$) (dmd) or diethylacetylenedicarboxylate ($EtO_2CC_2CO_2Et$) (ded) in dichloromethane at room temperature affords the yellow ruthenium triazolo complexes **7**–**14** in moderate yield (Schemes 3 and 4). The formation of these triazole complexes is confirmed by the absence of the starting azide stretching frequency (2015–2036 cm^{-1}) and the appearance of a strong band



Scheme 3. Proposed scheme for the formation of triazole complexes (**7**–**10**).



Scheme 4. Proposed scheme for the formation of triazole complexes (**11**–**14**).

at around 1724–1736 cm^{-1} for the ester substituents of the triazole moiety in the IR spectra of the complexes. This new band indicates the occurrence of the 1,3-dipolar cycloaddition reaction between Ru−N_3 and the alkynyl derivative (dmd or ded).

Apart from the expected peaks of the corresponding ligand (pca/hq) and of the corresponding arene ligand with chemical shift and multiplicities in the expected range for N, O chelate coordination, the ^{1}H NMR spectra of complexes **7**, **8**, **11** and **12** exhibit singlet at *ca.* δ 3.82–4.01 related to six protons of the *methoxy* carbon group of triazolato group. This indicated the coordination of middle nitrogen (N2) of the triazole ring to the ruthenium metal in the above complexes. In contrast, the ^{1}H NMR of complexes **9**, **10**, **13** and **14** exhibit two triplets at *ca.* δ 1.25 and δ 1.41 each corresponding to three protons and two multiplets at *ca.* δ 4.22 and δ 4.41 each corresponding to methyl protons of the *ethoxy* group. Apart from the required carbon signals noticed in the ^{13}C {^{1}H} NMR spectroscopy, the most interesting signals were observed in the downfield region of the spectra of complexes **9**, **10**, **13** and **14**. The ^{13}C {^{1}H} NMR of these complexes exhibits two resonances for both carbonyls of alkoxy groups at around δ 162 and δ 163 whereas the carbonyl group of the N∩O ligand resonates downfield at around δ 168.40–171.22. This gave the inference through NMR that, either of the side nitrogen (N1) is coordinated to the ruthenium metal in the triazole ring containing *ethoxy* group

Table 1
Crystallographic and structure refinement parameters for complexes **3**, **5** and **6**.

	3	**5**	**6**
Chemical formula	$C_{15}H_{17}N_5O_2Ru$	$C_{19}H_{20}N_4ORu$	$C_{21}H_{24}N_4ORu$
Formula weight	400.41	421.46	449.51
Crystal system	monoclinic	tetragonal	orthorhombic
Space group	$P2_17c$ (no. 14)	$P\bar{4}2_1c$ (No. 114)	*Pbcm* (no. 57)
Crystal color and shape	orange block	orange block	orange block
Crystal size	0.22 × 0.21 × 0.17	0.17 × 0.15 × 0.15	0.22 × 0.20 × 0.17
a (Å)	12.7912(13)	17.9051(9)	7.4970(10)
b (Å)	9.2088(8)	17.9051(9)	16.735(3)
c (Å)	13.2206(12)	11.7463(6)	14.976(3)
α (°)	90	90	90
β (°)	90.712(12)	90	90
γ (°)	90	90	90
V (Å^3)	1557.2(3)	3765.8(3)	1878.9(6)
Z	4	8	4
T (K)	203(2)	203(2)	173(2)
D_{calc} (g cm^{-3})	1.708	1.487	1.589
μ (mm^{-1})	1.024	0.846	0.853
Scan range (°)	2.70 < θ < 26.16	1.61 < θ < 29.18	2.43 < θ < 26.06
Unique reflections	2956	5083	1938
Reflections used [$I > 2\sigma(I)$]	2411	3231	1366
R_{int}	0.0401	0.1693	0.1053
Final *R* indices [$I > 2\sigma(I)$][a]	0.0245, wR_2 0.0541	0.0816, wR_2 0.1534	0.0357, wR_2 0.0848
R indices (all data)	0.0398, wR_2 0.0846	0.1351, wR_2 0.1737	0.0594, wR_2 0.0981
Goodness-of-fit (GOF)	1.193	1.057	1.043
Maximum, Minimum $\delta\rho$ (e Å^{-3})	1.382, −1.676	1.319, −0.833	0.860, −0.856

[a] Structures were refined on F_0^2: $wR_2 = [\Sigma[w(F_0^2 - F_c^2)^2]/\Sigma w(F_0^2)^2]^{1/2}$, where $w^{-1} = [\Sigma(F_0^2) + (aP)^2 + bP]$ and $P = [\max(F_0^2, 0) + 2F_c^2]/3$.

substituents in complexes **9**, **10**, **13** and **14**. Due to lack of single crystal study of these complexes, analysis of triazole bonded ruthenium is provided through spectroscopy techniques.

Previous results reveal that the triazole anion can be coordinated by a metal through either its N(1) or N(2) nitrogen atoms [36,37], which are essentially isoenergetic as indicated by molecular orbital calculations [37,38]. Evidence obtained to date indicates that both isomers [corresponding to coordination at N(1) and N(2)] are formed simultaneously [18,39,37,38] or else only the N(2) bound isomer is produced exclusively [17,20–22,36,40,41]. Ellis and Purcell have reported the initial formation of N(1) bonded complex via azide attack on the coordinated nitrile carbon of pentamethylamine cobalt complexes which slowly isomerized to the N(2) bonded complex [42]. It is believed that the triazolato complexes initially forms the N(1) bonded. Published results confirm that N(1) isomers is surely the kinetic product of these reactions, the isolated thermodynamically stable product being the N(2) isomer. Isomerization from N(1) to N(2) bound triazole is most likely sterically promoted as it has been found for the analogous tetrazolato complexes [43], while electronic factors favor no isomerization. It has been reported that electronic factor such as nucleophilicity of the triazole anion favors N(1) isomers. Thus, accordingly the N(1) isomers will prevail in the *ethoxy* substituted triazolato complexes which was also observed in the previous result reported in our laboratory [17,20,21]. As supported by previous discussions and by spectroscopic data, this present work confirms formation of N(2) isomers with *methoxy* substituted triazolo complexes and N(1) bonded isomers with *ethoxy* groups. However, these observations are contradictory to the case of β-diketone triazole complexes in which steric factor of chelating β-diketone ligand favor N(2) triazolato complexes [21,22].

3. Molecular structures

The molecular structure of the mononuclear complexes **3**, **5** and **6** has been established by single-crystal X-ray structure analysis. All complexes show typical piano-stool geometry with the metal center coordinated by the arene ligand, a terminal azido and the chelating N∩O-ligand (see Figs. 1, 2 and 3). The distances between the Ru atom and the center of the C_6-aromatic ring of the η^6-*p*-Pr^{i}C$_6$H$_4$Me ligand in **3** and **5** at 1.657 and 1.663 Å, respectively, and of the hexamethylbenzene ligand in **6** at 1.665 Å are all normal. The Ru(1)–N(1) bond distance [2.073(7) Å] in **5** is longer to that in **6** [2.026(8) Å] whereas the Ru(1)–O(1) bond distance [2.083(6) Å] in **5** is shorter to the one observed in **6** [2.213(6) Å]. These differences are due to the presence of a more electron rich arene in **6** as compare to **5**. Otherwise the bond lengths and angles observed in **3**, **5** and **6** are comparable to those in related N∩O arene ruthenium complexes [24,35]. In the mononuclear complexes **3**, **5** and **6**, the metal center is stereogenic. However, since none of the ligands contain chiral information, these complexes crystallized as racemic mixtures. Data collected are presented in Table 1.

4. Experimental

Caution: All the azide reaction should be performed with extreme care.

4.1. Physical methods and materials

All solvents were dried and purified according to standard procedure. Ruthenium trichloride hydrate (Arora Matthey Ltd.), hexamethylbenzene, pyrazine-2-carboxylic acid (pca-H), dimethylacetylenedicarboxylate (Aldrich), diethylacetylenedicarboxylate, 8-hydoxy quinoline(hq-H) (Acros Organic) and NaN_3 all of standard reagent grade were purchased and used without further purification. The compounds [(η^6-*p*-^{i}PrC$_6$H$_4$Me)Ru(μ-Cl)Cl]$_2$ [44,45], [(η^6-C$_6$Me$_6$)Ru(μ-Cl)Cl]$_2$ [22], [(η^6-*p*-^{i}PrC$_6$H$_4$Me)Ru(μ-N$_3$)Cl]$_2$ [32], [(η^6-C$_6$Me$_6$)Ru(μ-N$_3$)Cl]$_2$ [33], [(η^6-*p*-^{i}PrC$_6$H$_4$Me)Ru(pca)Cl], [(η^6-C$_6$Me$_6$)Ru(pca)Cl] [35] were prepared according to literature methods. NMR spectra were recorded on AMX-400 MHz spectrometer. Infrared spectra were recorded as KBr pellets on a Perkin-Elmer 983 spectrophotometer. Elemental analyses were performed in Perkin-Elmer-2400 CHNS analyzer.

4.2. Single-crystal X-ray structures analyses

The orange crystals of complexes **3**, **5** and **6** were obtained by slow diffusion of non polar solvent over dichloromethane or acetone solution of the corresponding complexes. Crystals of complexes [(η^6-*p*-^{i}PrC$_6$H$_4$Me)Ru(pca)N$_3$] (**3**), [(η^6-*p*-^{i}PrC$_6$H$_4$Me)Ru(hq)N$_3$] (**5**) and [(η^6-C$_6$Me$_6$)Ru(hq)N$_3$] (**6**) were mounted on a Stoe Image Plate Diffraction system equipped with a ϕ circle goniometer, using Mo Kα graphite monochromated radiation (λ = 0.71073 Å) with range 0–200°. The structures were solved by direct methods using the program SHELXS-97. Refinement and all further calculations were carried out using SHELXL-97 [46]. In **5**, the crystal used for data collection was a racemic twin, and consequently twinned refinement was applied with a domain ratio of 0.5. In **6**, the hq ligand was disordered over two positions by symmetry. In **3** and **5**, the residual electron densities greater than 1 e Å^{-3} are located at less than 1 Å from the Ru atom. The H-atoms were included in calculated positions and treated as riding atoms using the SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-square on F^2. Crystallographic details are summarized in Table 1. Figures **1**–**3** were drawn with ORTEP-32 [47].

4.3. Synthesis of complexes

4.3.1. Preparation of [(η^6-arene)Ru(hq)Cl] (arene = *p*-^{i}PrC$_6$H$_4$Me (**1**), C$_6$Me$_6$ (**2**))

To a solution of either of the complex [(η^6-*p*-^{i}PrC$_6$H$_4$Me)Ru(μ-Cl)Cl]$_2$ (100 mg, 0.16 mmol) or [(η^6-C$_6$Me$_6$)Ru(μ-Cl)Cl]$_2$ (100 mg, 0.15 mmol) in dry methanol, hq-H (47 mg, 0.33 mmol) or (43 mg, 0.30 mmol) and NaOMe (16 mg, 0.33 mmol) or (17 mg, 0.30 mmol) were added in 1:2 ratio with respect to the corresponding dimer. The resulting solution was stirred whereby the respective product **1** or **2** started precipitating out after 30 min. Reaction was continued for 4 h to ensure completeness. The orange precipitate was filtered and washed with diethyl ether. The filtrate was dried under vacuum, the residue extracted with dichloromethane and filtered to remove NaCl. The solution was concentrated to 2 ml, whereupon addition of excess diethyl ether precipitated the additional complex which was centrifuged, separated and dried under vacuum.

4.3.1.1. Complex ***1*** *[(η^6-*p*-^{i}PrC$_6$H$_4$Me)Ru(hq)Cl].* Yield = 128 mg (87%). Elemental *Anal.* Calc. for C$_{19}$H$_{20}$NOClRu: C, 57.66; H, 4.81; N, 3.54. Found: C, 58.10; H, 5.01; N, 3.28%. IR (KBr, cm^{-1}): 1461 $\nu_{(C-O)}$.

^{1}H NMR (CDCl$_3$, δ): 1.16 (d, 6H, J_{H-H} = 6.2, CH(C$\underline{H}_3$)$_2$), 2.29 (s, 3H, C$\underline{H}_{3cym}$), 2.89 (sept, 1H, C$\underline{H}$(CH$_3$)$_2$), 5.38 (d, 1H, J_{H-H} = 6, C$_6\underline{H}_{4cym}$), 5.41 (d, 1H, J_{H-H} = 6, C$_6\underline{H}_{4cym}$), 5.48 (d, 1H, J_{H-H} = 5.6, C$_6\underline{H}_{4cym}$), 5.57 (d, 1H, J_{H-H} = 6, C$_6\underline{H}_{4cym}$), 6.85 (d, 1H, J_{H-H} = 7.6, HC^7-hq), 7.05 (d, 1H, J_{H-H} = 8, HC^5-hq), 7.34 (s, 1H, HC^3-hq), 7.36–7.41 (m, 1H, HC^6-hq), 8.13 (d, 1H, J_{H-H} = 8, HC^4-hq), 8.91 (d, 1H, J_{H-H} = 5, HC^2-hq).

^{13}C {^{1}H} NMR (CDCl$_3$, δ): 17.85 (s, C$\underline{H}_{3cym}$), 22.31 (s, CH(C$\underline{H}_3$)$_2$), 31.62 (s, C$\underline{H}$(CH$_3$)$_2$), 80.02, 80.15, 80.57, 80.65 (C$_6$H$_{4cym}$), 110.82 (s, C^7-hq), 115.05 (s, C^5-hq), 121.81 (s, C^3-hq), 130.41 (s, C^{4a}-hq), 131.06 (s, C^6-hq), 137.86 (s, C^4-hq), 145.98 (s, C^{8a}-hq), 150.75 (s, C^2-hq), 170.60 (s, C^{8}O-hq).

4.3.1.2. Complex ***2*** *[(η^6-C$_6$Me$_6$)Ru(hq)Cl].* Yield = 129 mg (86%). Elemental *Anal.* Calc. for C$_{21}$H$_{24}$NOClRu: C, 57.28; H, 3.02; N, 3.34. Found: C, 57.78; H, 3.37; N, 3.17%. IR (KBr, cm^{-1}): 1461 $\nu_{(C-O)}$.

^{1}H NMR (CDCl$_3$, δ): 1.65 (s, 18H, C$_6$Me$_6$), 6.75 (d, 1H, J_{H-H} = 8, HC^7-hq), 6.89 (d, 1H, J_{H-H} = 8, HC^5-hq), 7.30 (s, 1H, HC^3-hq), 7.34–7.41 (m, 1H, HC^6-hq), 7.98 (d, 1H, J_{H-H} = 8, HC^4-hq), 8.85 (d, 1H, J_{H-H} = 4.4, HC^2-hq).

^{13}C {^{1}H} NMR (CDCl$_3$, δ): 15.28 (s, Me (C$_6$Me$_6$)), 91.81 (s, C (C$_6$Me$_6$)), 110.62 (s, C^7-hq), 114.95 (s, C^5-hq), 122.33 (s, C^3-hq), 130.41 (s, C^{4a}-hq), 130.98 (s, C^6-hq), 138.05 (s, C^4-hq), 145.23 (s, C^{8a}-hq), 149.86 (s, C^2-hq), 172.93 (s, C^{8}O-hq).

4.3.2. Preparation of [(η^6-arene)Ru(pca)N$_3$] (arene = *p*-^{i}PrC$_6$H$_4$Me (**3**), C$_6$Me$_6$ (**4**))

Route (a): A suspension of the required starting complex [(η^6-arene)Ru(pca)Cl] [(arene = *p*-^{i}PrC$_6$H$_4$Me (100 mg, 0.25 mmol), C$_6$Me$_6$ (100 mg, 0.23 mmol)] and NaN$_3$ (0.50 mmol or 0.47 mmol) in 1:2 ratio in dry ethanol (25 ml) was stirred at room temperature for 6 h. The solvent was removed to dryness using rotary evaporator. The residue was extracted with dichloromethane, filtered and precipitated with diethyl ether.

Route (b): Corresponding azido dimer [(η^6-*p*-^{i}PrC$_6$H$_4$Me)Ru(μ-N$_3$)Cl]$_2$ (100 mg, 0.16 mmol) or [(η^6-C$_6$Me$_6$)Ru(μ-N$_3$)Cl]$_2$ (100 mg, 0.15 mmol) was treated in 1:2 ratio with pca-H (39 mg, 0.32 mmol) in dry methanol in the presence of NaOMe (17 mg, 0.32 mmol) or (15 mg, 0.30 mmol) respectively. The resulting mixture was stirred for 5 h at room temperature. After completion of the reaction, the solvent was removed to dryness by aid of a rotary evaporator; the expected complex was extracted with dichloromethane, filtered, precipitated with diethyl ether and dried in vacuum.

4.3.2.1. Complex ***3*** *[(η^6-*p*-^{i}PrC$_6$H$_4$Me)Ru(pca)N$_3$].* Yield = 76 mg (78%). Elemental *Anal.* Calc. for C$_{14}$H$_{17}$N$_5$O$_2$Ru: C, 42.29; H, 4.41; N, 18.03. Found: C, 42.51; H, 4.82; N, 17.78%. IR (KBr, cm^{-1}): 2023 $\nu_{(N3)}$, 1658 $\nu_{(C=O)}$.

^{1}H NMR (CDCl$_3$, δ): 1.29 (d, 6H, J_{H-H} = 6.2, CH(C$\underline{H}_3$)$_2$), 2.31 (s, 3H, C$\underline{H}_{3cym}$), 2.89 (sept, 1H, C$\underline{H}$(CH$_3$)$_2$), 5.38 (d, 1H, J_{H-H} = 6, C$_6\underline{H}_{4cym}$), 5.42 (d, 1H, J_{H-H} = 8, C$_6\underline{H}_{4cym}$), 5.48 (d, 1H, J_{H-H} = 5.6, C$_6\underline{H}_{4cym}$), 5.59 (dd, 2H, J_{H-H} = 6.4, C$_6\underline{H}_{4cym}$), 8.80 (d, 1H, J_{H-H} = 4, pca-H$_\alpha$), 8.85 (d, 1H, J_{H-H} = 2.8, pca-H$_\beta$), 9.27 (s, 1H, pca-H$_{\beta'}$).

^{13}C {^{1}H} NMR (CDCl$_3$, δ): 17.87 (s, C$\underline{H}_{3cym}$), 22.21 (s, CH(C$\underline{H}_3$)$_2$), 30.7 (s, C$\underline{H}$(CH$_3$)$_2$), 80.06, 80.12, 80.77, 81.03 (C$_6$H$_{4cym}$), 143.61–147.11 (pca), 168.02 (s, CO (pca)).

4.3.2.2. Complex ***4*** *[(η^6-C$_6$Me$_6$)Ru(pca)N$_3$].* Yield = 75 mg (77%). Elemental *Anal.* Calc. for C$_{17}$H$_{21}$N$_5$O$_2$Ru: C, 47.66; H, 4.94; N, 16.35. Found: C, 48.01; H, 4.76; N, 16.11%. IR (KBr, cm^{-1}): 2027 $\nu_{(N3)}$, 1656 $\nu_{(C=O)}$.

^{1}H NMR (CDCl$_3$, δ): 2.10 (s, 18H, C$_6$Me$_6$), 8.51 (d, 1H, J_{H-H} = 2.8, pca-H$_\alpha$), 8.71 (d, 1H, J_{H-H} = 2.8, pca-H$_\beta$), 9.08 (s, 1H, pca-H $_{\beta'}$).

^{13}C {^{1}H} NMR (CDCl$_3$, δ): 15.18 (s, Me (C$_6$Me$_6$)), 90.34 (s, C (C$_6$Me$_6$)), 144.08–147.23 (pca), 167.5 (s, CO (pca)).

4.3.3. Preparation of [(η^6-arene)Ru(hq)N$_3$] (arene = *p*-^{i}PrC$_6$H$_4$Me (**5**),C$_6$Me$_6$ (**6**))

The complexes **5** and **6** were prepared by reacting the required complexes **1** or [(η^6-*p*-^{i}PrC$_6$H$_4$Me)Ru(μ-N$_3$)Cl]$_2$; **2** or [(η^6-C$_6$Me$_6$)Ru(μ-N$_3$)Cl]$_2$ with NaN$_3$ or hq-H respectively in appropriate ratio. Following either of the methods (*route a/route b*) described for the preparation of complexes **3** and **4**.

*4.3.3.1. Complex 5 [(η^6-*p*-^{i}PrC$_6$H$_4$Me)Ru(hq)N$_3$].* Yield = 79 mg (80%). Elemental *Anal.* Calc. for C$_{19}$H$_{20}$N$_4$ORu: C, 54.15; H, 4.74; N, 13.29. Found: C, 54.41; H, 4.99; N, 13.07%. IR (KBr, cm^{-1}): 2027 $\nu_{(N3)}$, 1464 $\nu_{(C-O)}$.

^{1}H NMR (CDCl$_3$, δ): 1.15 (dd, 6H, J_{H-H} = 7.2, CH(C$\underline{H}_3$)$_2$), 2.31 (s, 3H, C$\underline{H}_{3cym}$), 2.72 (sept, 1H, C$\underline{H}$(CH$_3$)$_2$), 5.27 (d, 1H, J_{H-H} = 6, C$_6\underline{H}_{4cym}$), 5.38 (d, 1H, J_{H-H} = 5.6, C$_6\underline{H}_{4cym}$), 5.49 (d, 1H, J_{H-H} = 5.6, C$_6\underline{H}_{4cym}$), 5.57 (d, 1H, J_{H-H} = 6, C$_6\underline{H}_{4cym}$), 6.86 (d, 1H, J_{H-H} = 7.6, HC^7-hq), 7.02 (d, 1H, J_{H-H} = 8, HC^5-hq), 7.33 (s, 1H, HC^3-hq), 7.36–7.39 (m, 1H, HC^6-hq), 8.11 (d, 1H, J_{H-H} = 9.2, HC^4-hq), 8.87 (d, 1H, J_{H-H} = 5.2, HC^2-hq).

^{13}C {^{1}H} NMR ($CDCl_3$, δ): 17.88 (s, $\underline{C}H_{3cym}$), 21.98 (s, CH($\underline{C}H_3$)$_2$), 31.02 (s, $\underline{C}H(CH_3)_2$), 80.09, 80.15, 81.66, 81.98 (C_6H_{4cym}), 110.82 (s, C^7-hq), 115.11 (s, C^5-hq), 121.83 (s, C^3-hq), 130.39 (s, C^{4a}-hq), 131.16 (s, C^6-hq), 138.16 (s, C^4-hq), 144.87 (s, C^{8a}-hq), 150.55 (s, C^2-hq), 169.52 (s, C^8O-hq).

4.3.3.2. Complex ***6*** *[(η^6-C_6Me_6)Ru(hq)N_3].* Yield = 80 mg (81.21%). Elemental *Anal.* Calc. for $C_{21}H_{24}N_4ORu$: C, 56.11; H, 5.38; N, 12.46. Found: C, 56.31; H, 5.52; N, 12.21. IR (KBr, cm^{-1}): 2017 $\nu_{(N3)}$, 1454 $\nu_{(C-O)}$.

^{1}H NMR ($CDCl_3$, δ): 1.65 (s, 18H, C_6Me_6), 6.75 (d, 1H, J_{H-H} = 8, HC^7-hq), 6.99 (d, 1H, J_{H-H} = 8, HC^5-hq), 7.30 (s, 1H, HC^3-hq), 7.34–7.41(m, 1H, HC^6-hq), 7.98 (d, 1H, J_{H-H} = 8, HC^4-hq), 8.59 (d, 1H, J_{H-H} = 4.4, HC^2-hq).

^{13}C {^{1}H} NMR ($CDCl_3$, δ): 15.33 (s, Me (C_6Me_6)), 92.26 (s, C (C_6Me_6)), 110.62 (s, C^7-hq), 115.11 (s, C^5-hq), 122.50 (s, C^3-hq), 129.99 (s, C^{4a}-hq), 131.12 (s, C^6-hq), 137.98 (s, C^4-hq), 144.75 (s, C^{8a}-hq), 149.93 (s, C^2-hq), 171.03 (s, C^8O-hq).

4.3.4. General procedure for the preparation of [(η^6-arene)Ru(N∩O){$N_3C_2(CO_2R)_2$}]

(arene = *p*-^{i}PrC_6H_4Me, N∩O = pca, R = Me (**7**); arene = C_6Me_6, N∩O = pca, R = Me (**8**); arene = *p*-^{i}PrC_6H_4Me, N∩O = pca, R = Et (**9**); arene = C_6Me_6, N∩O = pca, R = Et (**10**), arene = *p*-^{i}PrC_6H_4Me, N∩O = hq, R = Me (**11**), arene = C_6Me_6, N∩O = hq, R = Me (**12**), arene = *p*-^{i}PrC_6H_4Me, N∩O = hq, R = Et (**13**); arene = C_6Me_6, N∩O = hq, R = Et (**14**).

Into a round bottom flask, charged with the corresponding azido complex **3** (55 mg, 0.14 mmol) or **4** (55 mg, 0.13 mmol) or **5** (55 mg, 0.13 mmol) or **6** (55 mg, 0.12 mmol), fivefold excess of dimethylacetylenedicarboxylate/diethylacetylenedicarboxylate correspondingly and dichloromethane (20 ml) was added. The mixture was stirred at room temperature for 24 h. The solution was reduced to *ca.* 3 ml on rotary evaporator. To this solution, 30 ml of hexane was added whereby the compound precipitate out as a yellow solid. The solid was collected by centrifuge and washed with hexane (2 × 20 ml) and dried under vacuum.

4.3.4.1. Complex ***7*** *[(η^6-p- ^{i}PrC_6H_4Me)Ru(pca){$N_3C_2(CO_2Me)_2$}].* Yield = 31 mg (76%). Elemental *Anal.* Calc. for $C_{21}H_{23}N_5O_6Ru$: C, 46.49; H, 4.27; N, 12.91. Found: C, 46.76; H, 4.58; N, 12.72%. IR (KBr, cm^{-1}): 1734 $\nu_{(C=O}$ of ester group), 1663 $\nu_{(C=O)}$, 1446 $\nu_{(C-N)}$, 775 of triazole ring.

^{1}H NMR ($CDCl_3$, δ): 1.18 (dd, 6H, J_{H-H} = 6.92, CH($C\underline{H}_3$)$_2$), 2.19 (s, 3H,$C\underline{H}_{3cym}$), 2.88 (sept, 1H, $C\underline{H}(CH_3)_2$), 3.82 (s, 6H, CO_2CH_3), 5.57 (bd, 1H, J_{H-H} = 6, C_6H_{4cym}), 5.65 (bq, 1H, J_{H-H} = 6,C_6H_{4cym}), 5.71 (bt, 1H,J_{H-H} = 8, C_6H_{4cym}), 5.81 (t, 1H, J_{H-H} = 6, C_6H_{4cym}), 8.82 (d, 1H, J_{H-H} = 4, pca-H_α), 8.88 (d, 1H, J_{H-H} = 4, pca-H_β), 9.12 (s, 1H, pca-$H_{\beta'}$).

^{13}C {^{1}H} NMR ($CDCl_3$, δ): 18.07 (s, $\underline{C}H_{3cym}$), 22.28 (s, CH($\underline{C}H_3$)$_2$), 30.98 (s, $\underline{C}H(CH_3)_2$), 61.32 (s, $CO_2\underline{C}H_3$), 80.09, 80.61, 82.36, 83.11 (C_6H_{4cym}), 140.12 (s, $\underline{C}CO_2CH_3$), 143.25–148.02 (pca), 160.74 (s, $\underline{C}O_2CH_3$), 171.26 (s, CO (pca)).

4.3.4.2. Complex ***8*** *[(η^6-C_6Me_6)Ru(pca){$N_3C_2(CO_2Me)_2$}].* Yield = 24 mg (59%). Elemental *Anal.* Calc. for $C_{23}H_{27}N_5O_6Ru$: C, 48.42; H, 4.77; N, 12.27. Found: C, 48.69; H, 4.85; N, 12.13%. IR (KBr, cm^{-1}): 1734 $\nu_{(C=O}$ of ester group), 1663 $\nu_{(C=O)}$, 1446 $\nu_{(C-N)}$, 776 of triazole ring.

^{1}H NMR ($CDCl_3$, δ): 2.09 (s, 18H, C_6Me_6), 4.10 (s, 6H, CO_2CH_3), 8.52 (d, 1H, J_{H-H} = 2.8, pca-H_α), 8.71 (d, 1H, J_{H-H} = 2.8, pca-H_β), 9.21 (s, 1H, pca-$H_{\beta'}$).

^{13}C {^{1}H} NMR ($CDCl_3$, δ): 15.22 (s, Me (C_6Me_6)), 51.42 (s, $CO_2\underline{C}H_3$), 93.06 (s, C (C_6Me_6)), 139.32 (s, $\underline{C}CO_2CH_3$), 143.55–147.61 (pca), 164.33 (s, $\underline{C}O_2CH_3$), 170.43 (s, CO (pca)).

4.3.4.3. Complex ***9*** *[(η^6-p-^{i}PrC_6H_4Me)Ru(pca){$N_3C_2(CO_2Et)_2$}].* Yield = 25 mg (65%). Elemental *Anal.* Calc. for $C_{23}H_{27}N_5O_6Ru$: C, 48.42; H, 4.77; N, 12.27. Found: C, 48.71; H, 4.81; N, 12.35%. IR (KBr, cm^{-1}): 1736 $\nu_{(C=O}$ of ester group), 1660 $\nu_{(C=O)}$, 1446 $\nu_{(C-N)}$, 775 of triazole ring.

^{1}H NMR ($CDCl_3$, δ): 1.21 (dd, 6H, CH($C\underline{H}_3$)$_2$), 1.25 (t, 3H, $OCH_2C\underline{H}_3$), 1.41 (t, 3H, $OCH_2C\underline{H}_3$), 2.20 (s, 3H, $C\underline{H}_{3cym}$), 2.82 (sept, 1H, $C\underline{H}(CH_3)_2$), 4.22 (q, 4H, $OC\underline{H}_2CH_3$), 4.42 (t, 4H, $OC\underline{H}_2CH_3$), 5.56 (bq, 1H, J_{H-H} = 6,C_6H_{4cym}), 5.64 (quin, 2H, J_{H-H} = 8, C_6H_{4cym}), 5.81 (t, 1H, J_{H-H} = 6.4, C_6H_{4cym}), 8.79 (d, 1H, J_{H-H} = 2.8, pca-H_α), 8.86 (d, 1H, J_{H-H} = 2, pca-H_β), 9.12 (s, 1H, pca-$H_{\beta'}$).

^{13}C {^{1}H} NMR ($CDCl_3$, δ): 14.26 (s, $CO_2CH_2\underline{C}H_3$), 18.06 (s, $\underline{C}H_{3cym}$), 22.42 (s, CH($\underline{C}H_3$)$_2$), 31.11 (s, $\underline{C}H(CH_3)_2$), 61.33, 62.26 (s, $CO_2\underline{C}H_2CH_3$), 80.08, 80.6, 82.36, 83.05 (C_6H_{4cym}), 140.12, 140.35 (s, $\underline{C}CO_2CH_2CH_3$), 144.06–148.31 (pca), 162.72, 163.81 (s, $\underline{C}O_2CH_2CH_3$), 168.43 (s, CO (pca)).

4.3.4.4. Complex ***10*** *[(η^6-C_6Me_6)Ru(pca){$N_3C_2(CO_2Et)_2$}].* Yield = 28 mg (72%). Elemental *Anal.* Calc. for $C_{25}H_{31}N_5O_6Ru$: C, 50.16; H, 5.22; N, 11.70. Found: C, 50.48; H, 5.65; N, 11.51%. IR (KBr, cm^{-1}): 1735 $\nu_{(C=O}$ of ester group), 1656 $\nu_{(C=O)}$, 1445 $\nu_{(C-N)}$, 775 of triazole ring.

^{1}H NMR ($CDCl_3$, δ): 1.23 (t, 3H, $OCH_2C\underline{H}_3$), 1.25 (t, 3H, $OCH_2C\underline{H}_3$), 2.10 (s, 18H, C_6Me_6), 3.81 (q, 4H, $OC\underline{H}_2CH_3$), 4.01 (t, 4H, $OC\underline{H}_2CH_3$), 8.55 (d, 1H, J_{H-H} = 2.8, pca-H_α), 8.71 (d, 1H, J_{H-H} = 2, pca-H_β), 9.27 (s, 1H, pca-$H_{\beta'}$).

^{13}C {^{1}H} NMR ($CDCl_3$, δ): 14.22, 14.31 (s, $CO_2CH_2\underline{C}H_3$), 15.27 (s, Me (C_6Me_6)), 61.45, 62.19 (s, $CO_2\underline{C}H_2CH_3$), 93.06 (s, C (C_6Me_6)), 140.14, 140.23 (s, $\underline{C}CO_2CH_2CH_3$), 143.85–148.01 (pca), 161.88, 163.71 (s, $\underline{C}O_2CH_2CH_3$), 169.16 (s, CO (pca)).

4.3.4.5. Complex ***11*** *[(η^6-p-^{i}PrC_6H_4Me)Ru(hq){$N_3C_2(CO_2Me)_2$}].* Yield = 32 mg (78%). Elemental *Anal.* Calc. for $C_{25}H_{26}N_4O_5Ru$: C, 53.28; H, 4.65; N, 9.94. Found: C, 53.71; H, 4.72; N, 9.68%. IR (KBr, cm^{-1}): 1734 $\nu_{(C=O}$ of ester group), 1446 $\nu_{(C-N)}$, 775 of triazole ring.

^{1}H NMR ($CDCl_3$, δ): 1.18 (d, 3H, J_{H-H} = 6.3, CH($C\underline{H}_3$)$_2$), 1.38 (d, 3H, J_{H-H} = 6, CH($C\underline{H}_3$)$_2$), 2.33 (s, 3H,$C\underline{H}_{3cym}$), 3.23 (sept, 1H, $C\underline{H}(CH_3)_2$), 4.12 (s, 6H, CO_2CH_3), 5.56 (d, 1H, J_{H-H} = 6, C_6H_{4cym}), 5.62 (d, 1H, J_{H-H} = 8, C_6H_{4cym}), 5.73 (d, 1H, J_{H-H} = 6, C_6H_{4cym}), 5.86 (d, 1H, J_{H-H} = 6, C_6H_{4cym}), 6.82 (d, 1H, J_{H-H} = 7.6, HC^7-hq), 7.10 (d, 1H, J_{H-H} = 8, HC^5-hq), 7.31 (s, 1H, HC^3-hq), 7.33–7.39 (m, 1H, HC^3-hq and HC^6-hq), 8.13 (d, 1H, J_{H-H} = 8, HC^4-hq), 9.12 (d, 1H, J_{H-H} = 4.8, HC^2-hq).

^{13}C {^{1}H} NMR ($CDCl_3$, δ): 17.92 (s, $\underline{C}H_{3cym}$), 22.23 (s, CH($\underline{C}H_3$)$_2$), 30.70 (s, $\underline{C}H(CH_3)_2$), 51.66 (s, CH_3 (CO_2CH_3)), 80.09, 80.61, 82.36, 83.12 (C_6H_{4cym}), 111.73 (s, C^7-hq), 114.65 (s, C^5-hq), 123.42 (s, C^3-hq), 130.56 (s, C^{4a}-hq), 131.24 (s, C^6-hq), 137.92 (s, C^4-hq), 140.22 (s, C ($\underline{C}CO_2CH_3$)), 146.02 (s, C^{8a}-hq), 151.32 (s, C^2-hq), 162.91 (s, CO_2 (CO_2CH_3)), 169.83 (s, C^8O-hq).

4.3.4.6. Complex ***12*** *[(η^6-C_6Me_6)Ru(hq){$N_3C_2(CO_2Me)_2$}].* Yield = 27 mg (69%). Elemental *Anal.* Calc. for $C_{27}H_{30}N_4O_5Ru$: C, 54.81; H, 5.11; N, 9.47. Found: C, 55.06; H, 5.36; N, 9.22%. IR (KBr, cm^{-1}): 1734 $\nu_{(C=O}$ of ester group), 1446 $\nu_{(C-N)}$, 775 of triazole ring.

^{1}H NMR ($CDCl_3$, δ): 2.05 (s, 18H, C_6Me_6), 3.78 (s, 6H, CO_2CH_3), 6.66–6.79 (3d, 1H, J_{H-H} = 8, HC^7-hq), 6.99 (d, 1H, J_{H-H} = 4.4, HC^5-hq), 7.34–7.38 (m, 2H, HC^3-hq and HC^6-hq), 7.89–7.99 (2d, 1H, J_{H-H} = 8, HC^4-hq), 8.79–8.91 (2d, 1H, J_{H-H} = 4, HC^2-hq).

^{13}C {^{1}H} NMR ($CDCl_3$, δ): 15.21 (s, Me (C_6Me_6)), 51.74 (s, $CO_2\underline{C}H_3$), 92.19 (s, C (C_6Me_6)), 110.23 (s, C^7-hq), 114.56 (s, C^5-hq), 121.51 (s, C^3-hq), 129.71 (s, C^{4a}-hq), 131.14 (s, C^6-hq), 137.54 (s, C^4-hq), 140.28 (s, $\underline{C}CO_2CH_3$), 147.64 (s, C^{8a}-hq), 148.97 (s, C^2-hq), 163.23 (s, CO_2 (CO_2CH_3)), 170.11 (s, C^8O-hq).

4.3.4.7. Complex ***13*** *[(η^6 -p-^{i}PrC_6H_4Me)Ru(hq){$N_3C_2(CO_2Et)_2$}].* Yield = 25 mg (64%). Elemental *Anal.* Calc. for $C_{27}H_{30}N_4O_5Ru$: C, 54.81; H, 5.11; N, 9.47. Found: C, 54.99; H, 5.40; N, 9.12%. IR

(KBr, cm^{-1}): 1736 $\nu_{(C=O}$ of ester group), 1446 $\nu_{(C-N)}$, 775 of triazole ring.

^1H NMR ($CDCl_3$, δ): 1.18 (d, 3H, J_{H-H} = 6, $CH(C\underline{H}_3)_2$), 1.25 (t, 3H, $OCH_2C\underline{H}_3$), 1.38 (t, 3H, $OCH_2C\underline{H}_3$), 2.26 (s, 3H, CH_{3cym}), 2.90 (sept, 1H, $C\underline{H}(CH_3)_2$), 4.22 (q, 4H, $OC\underline{H}_2CH_3$), 4.45 (q, 4H, $OC\underline{H}_2CH_3$), 5.58 (d, 1H, J_{H-H} = 6, C_6H_{4cym}), 5.64 (d, 2H, J_{H-H} = 8, C_6H_{4cym}), 5.71 (d, 2H, J_{H-H} = 7.4, C_6H_{4cym}), 5.84 (t, 1H, J_{H-H} = 6.4, C_6H_{4cym}), 6.77 (d, 1H, J_{H-H} = 7, HC^7-hq), 7.1 (d, 1H, J_{H-H} = 8, HC^5-hq), 7.34–7.39 (m, 2H, HC^3-hq and HC^6-hq), 8.11 (d, 1H, J_{H-H} = 8, HC^4-hq), 8.85 (d, 1H, J_{H-H} = 4.8, HC^2-hq).

^{13}C {^1H} NMR ($CDCl_3$, δ): 14.21 (s, $CO_2CH_2\underline{C}H_3$), 17.98 (s, CH_{3cym}), 22.26 (s, $CH(\underline{C}H_3)_2$), 30.71 (s, $\underline{C}H(CH_3)_2$), 60.45, 61.19 (s, $\underline{C}H_2$ ($CO_2CH_2CH_3$), 79.96, 80.06, 81.88, 82.13 (C_6H_{4cym}), 110.38 (s, C^7-hq), 114.46 (s, C^5-hq), 122.62 (s, C^3-hq), 130.56 (s, C^{4a}-hq), 130.87 (s, C^6-hq), 138.06 (s, C^4-hq), 140.14, 140.23 (s, $\underline{C}CO_2CH_2CH_3$), 147.76 (s, C^{8a}-hq), 150.27 (s, C^2-hq), 162.08, 163.11 (s, $\underline{C}O_2CH_2CH_3$), 170.43 (s, C^8O-hq).

4.3.4.8. Complex ***14*** *[(η^6-C_6Me_6)Ru(hq){$N_3C_2(CO_2Et)_2$}].* Yield = 29 mg (78%). Elemental *Anal.* Calc. for $C_{29}H_{34}N_5O_5Ru$: C, 56.21; H, 5.53; N, 9.04. Found: C, 56.39; H, 5.71; N, 8.86%. IR (KBr, cm^{-1}): 1734 $\nu_{(C=O}$ of ester group), 1446 $\nu_{(C-N)}$, 775 of triazole ring.

^1H NMR ($CDCl_3$, δ): 2.09 (s, 18H, C_6Me_6), 1.26 (t, 3H, $OCH_2C\underline{H}_3$), 1.45 (t, 3H, $OCH_2C\underline{H}_3$), 4.32 (q, 4H, $OC\underline{H}_2CH_3$), 4.46 (q, 4H, $OC\underline{H}_2CH_3$), 6.78 (d, 1H, J_{H-H} = 7.4, HC^7-hq), 7.15 (d, 1H, J_{H-H} = 8, HC^5-hq), 7.34–7.41 (m, 2H, HC^3-hq and HC^6-hq), 8.21 (d, 1H, J_{H-H} = 7.8, HC^4-hq), 8.89 (d, 1H, J_{H-H} = 4.8, HC^2-hq).

^{13}C {^1H} NMR ($CDCl_3$, δ): 14.21 (s, $CO_2CH_2\underline{C}H_3$), 15.31 (s, Me (C_6Me_6)), 60.55, 61.21 (s, $CO_2\underline{C}H_2CH_3$), 92.36 (s, C (C_6Me_6)), 110.88 (s, C^7-hq), 115.06 (s, C^5-hq), 121.62 (s, C^3-hq), 130.11 (s, C^{4a}-hq), 130.76 (s, C^6-hq), 138.02 (s, C^4-hq), 140.11, 140.26 (s, $\underline{C}CO_2CH_2CH_3$), 148.03 (s, C^{8a}-hq), 148.33 (s, C^2-hq), 162.86, 164.02 (s, $\underline{C}O_2CH_2CH_3$), 171.22 (s, C^8O-hq).

5. Conclusion

Previously, we reported the syntheses of indenyl [17] and benzene [20] ruthenium triazolo complexes as well as the intermediate ruthenium β-diketone triazolo complexes having a pyrazole group fused to the O∩O-chelating moiety [22]. In these complexes the triazolo ligand binds to the metal through the N(2) atom irrespective of the acetylene used. However, in the present study, for different substituted acetylenes, a different mode of bonding is observed. In the case of dimethylacetylenedicarboxylate the bonding is through the N(2) whereas in the case of diethylacetylenedicarboxylate the bonding is through N(1). These results are similar to the reported observation in *p*-cymene ruthenium triazolo complexes containing acetylacetone or its analog with O∩O-chelating groups [18]. Though publications from our group reported isolation of the triazoles and tetrazoles metallacycle complexes derived from substituted nitrile [18,20–22]; but we were not successful in isolating these complexes in the present work. This maybe attributed by the presence of the coordinated hetero atoms in the respective azido precursors. In view of previous publications and discussion, the steric factor due to bulkiness of the auxiliary ligand also play an important role in the formation of either N(1) or N(2) isomers. In the presence of bulky groups the N(2) bound isomer complexes dominate whereas in the case where the auxiliary ligands are less bulky, though both N(1) and N(2) isomers are reported as well as observed in the present work, however, their formation of either of the two isomers depends on the substituted acetylene used as mentioned earlier. We conclude here that, in addition to the effect peculiar to each substituted acetylene ligand used; the nature and type of the hetero ligand coordinated to the ruthenium center also plays a significant role in the formation of isomerized triazoles by 1,3-dipolar cycloaddition reactions studied.

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Appendix A

CCDC 803369, 803370 and 803371 contain the supplementary crystallographic data for complexes **3**, **5** and **6**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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