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Synthesis of arene ruthenium triazolato complexes by cycloaddition of the corresponding arene ruthenium azido complexes with activated alkynes or with fumaronitrile

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Abstract

The neutral arene ruthenium azido complexes [(η^6-*p*-cymene)Ru(LL)(N_3)], [LL = acetylacetonato (*acac*) (**4**), benzoylacetonato (*bzac*) (**5**) diphenylbenzoyl methane (*dbzm*) (**6**)] undergo [3+2] cycloaddition reaction with a series of activated alkynes and fumaronitrile to produce the arene ruthenium triazolato complexes: [(η^6-*p*-cymene)Ru(LL){$N_3C_2(CO_2R)_2$}] [LL = (*acac*), R = Me (**7**); LL = (*bzac*), R = Me (**8**); LL = (*dbzm*), R = Me (**9**); LL = (*acac*), R = Et (**10**); LL = (*bzac*), R = Et (**11**); LL = (*dbzm*), R = Et (**12**) and [(η^6-*p*-cymene)Ru(LL)(N_3C_2HCN)]; LL = *acac* (**13**), *bzac* (**14**); *dbzm* (**15**). However, cationic azido complexes, [(η^6-*p-cymene*)Ru(*dppe*)(N_3)]$^+$ and [(η^6-*p-cymene*)Ru(*dppm*)(N_3)]$^+$ do not undergo such cycloaddition reactions. The complexes were characterized on the basis of microanalyses, FT-IR and NMR spectroscopic data. Crystal structures of representative complexes were determined by single crystal X-ray diffraction.

Keywords: *p*-Cymene; Diethylacetylenedicarboxylate; Dimethylacetylenedicarboxylate; Azide; Ruthenium; Fumaronitrile; Acetylacetonate; Benzoylacetonate; Diphenylbenzoyl methane

1. Introduction

In organic chemistry 1,3-dipolar cycloaddition reactions are common processes. The process involves the reaction between 1,3-dipoles or a propargynellyl type with dipolarophiles. One of the most useful synthetic applications of azides is the preparation of 1,2,3-triazoles via 1,3-dipolar cycloaddition reactions of azides with substituted acetylene compounds [1–4]. The dipolar cycloaddition reactions between acetylenes and azides are very important and the most efficient route to synthesize 1,2,3-triazoles [4,5]. In analogy, a coordinated azide group in metal complexes can also undergo such cycloaddition reactions [6]. Azido complexes undergo [3+2] cycloaddition reactions with nitriles [7–19] and isonitriles [7,8,20–23] to produce tetrazolato complexes. Similar reactions with alkynes produce triazolates complexes [12,24–26]; alkenes, however, react very slowly and mostly afforded mixture of products [8,12].

Although such reactions are studied extensively in synthetic organic chemistry, dipolar cycloaddition reactions of azide coordinated metal complexes are relatively unexplored. A few reports appeared on cycloaddition of alkynes to ruthenium azido complexes in recent years [27–29]. However, to the best of our knowledge cycloaddition reaction of arene ruthenium azido complexes have not been studied. Our study reveals that such cycloaddition reactions are favorable in neutral complexes, but do not occur in cationic arene ruthenium azido complexes. Bennett et al. [30] reported the synthesis of [(η^6-*arene*)Ru(*acac*)Cl] by the reaction of a arene ruthenium dimer with *acac* in presence

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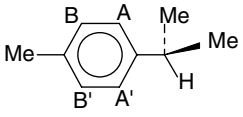
of base and its reactions with various ligands. Here, we report the preparation of *p*-cymene ruthenium β-diketonato azido complexes [(η^6-*arene*)Ru(LL)(N_3)]. These azido complexes undergo [3+2] cycloaddition reactions with a series of activated alkynes and fumaronitrile to produce *p*-cymene ruthenium triazolato complexes. The spectral and structural characterizations of these complexes are presented.

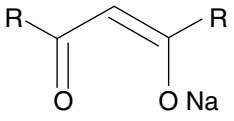
2. Experimental

Caution: All the azide reactions should perform with extreme care.

2.1. Physical methods and materials

All solvents were dried in appropriate drying agents and distilled prior to use [31]. $RuCl_3 \cdot 3H_2O$ (Arora Matthey Limited) and dimethylacetylenedicarboxylate (Aldrich) and diethylacetylenedicarboxylate (Acros) were purchased and used as received. NMR spectra were recorded on a Bruker AMX-400 MHz spectrometer at 400.13 (^{1}H), 100.61 MHz (^{13}C) with $SiMe_4$ as internal reference and coupling constants are given in hertz. Infrared spectra were recorded as a KBr pellets on a Perkin–Elmer model 983 spectrometer. Elemental analyses were carried out at the SAIF, NEHU, Shillong, using a Perkin–Elmer 2400 CHN/S analyzer. The precursor complexes [{(η^6-*p*-cymene)$RuCl_2$}$_2$] [32], [{(η^6-*p*-cymene)Ru(μ-N_3)Cl}$_2$] [33,34], [(η^6-*p*-cymene)Ru(*bzac*)Cl] (**2**) and [(η^6-*p*-cymene)Ru(*dbzm*)Cl] (**3**) were prepared by following a literature method [34]. While the complex [(η^6-*p-cymene*)Ru(*acac*)Cl] (**1**) was prepared by minor modification of reported method [35]. The following nomenclature was used in the text.





Na[*acac*]: R, R = Me,Me

Na[*bzac*]: R, R = Me, Ph

Na[*dbzm*]: R, R = Ph, Ph

2.2. Synthesis of complexes

2.2.1. Preparation of [(η^6-*p*-cymene)Ru(acac)Cl] (*1*)

The complex [{(η^6-*p*-cymene)$RuCl_2$}$_2$] (100 mg, 0.163 mmol) and Na(*acac*) (57 mg, 0.40 mmol) were stirred in dry methanol 20 ml for 3 h. The solution turned into bright yellow, the solvent was removed by rotary-evaporator and the residue was dissolved in dichloromethane and filtered to remove sodium chloride. The solution was concentrated to ca. 5 ml and excess of hexane was added and kept at room temperature. A yellow crystalline solid was precipitated out. The precipitate was collected and dried. The spectroscopic data are consisted with the reported values.

2.2.2. Preparation of [(η^6-*p*-cymene)Ru(acac)(N_3)] (*4*)

Two routes were used to prepare this complex:

Route (a): The complex [(η^6-p-cymene)Ru(acac)Cl] (100 mg, 0.270 mmol) and NaN_3 (35 mg, 0.54 mmol) were stirred in 30 ml of ethanol for 6 h. The solvent was removed on rotary-evaporator and the residue was dissolved in diethyl ether then filtered. The filtrate on evaporating at room temperature affords a bright red crystalline solid of the complex. Yield: 83 mg, 82%.

Route (b): The complex [{(η^6-*p*-cymene)Ru(μ-N_3)Cl}$_2$] (100 mg, 0.160 mmol) and [Na(*acac*) · H_2O] (56 mg, 0.40 mmol) were stirred in 30 ml of ethanol for 5 h, and then solvent was removed. The residue was dissolved in dichloromethane and then filtered. The filtrate on concentration and addition of excess hexane afford red crystalline solid of the complex.

Analytical and spectroscopic data are as follows: Anal. Calc. for $C_{15}H_{21}O_2N_3Ru$: C, 47.86; H, 5.58; N, 11.16. Found: C, 47.39; H, 5.78; N, 10.87%. IR (KBr, cm^{-1}): 2037 (ν_{N3}), 1577, 1519 ($\nu_{C=O} + \nu_{C=C}$). ^{1}H NMR ($CDCl_3$, δ): 1.31 (d, 6H, $J_{H-H} = 6.92$, $CHMe_2$), 1.98 (s, 6H, (*acac*-Me)), 2.20 (s, 3H, CH_3), 2.83 (m, 1H, $CHMe_2$), 5.11 (s, 1H, *acac*-γH), 5.13 (d, 2H, $J_{H-H} = 4.88$, C_6H_4), 5.39 (d, 2H, $J_{H-H} = 5.92$, C_6H_4). ^{13}C {^{1}H} NMR ($CDCl_3$, δ): 17.33 (s, CH_3), 22.30 (s, Me, $CHMe_2$), 27.17 (s, (*acac*-Me)), 30.62 (s, CH, $CHMe_2$), 78.87 (s, $C_{AA'}$) 82.73 (s, $C_{BB'}$), 96.91 (s, CMe), 98.63 (*acac*-γC), 99.36 (s, CPr^i), 186.93 (s, *acac*-CO).

2.2.3. Preparation of [(η^6-*p*-cymene)Ru(bzac)N_3] (*5*)

This complex was prepared by following a similar method as described in the preparation of complex **4** (route b) using [Na(*bzac*) · H_2O] instead of [Na(*acac*) · H_2O]. Yield: 82 mg, 81%.

Anal. Calc. for $C_{20}H_{23}N_3O_2Ru$: C, 54.78; H, 5.25; N, 9.58. Found: C, 54.26; H, 4.98; N, 9.27%. IR (KBr, cm^{-1}): 2015 $\nu(N_3)$, 1587, 1560, 1528 ($\nu_{C=O} + \nu_{C=C}$). ^{1}H NMR ($CDCl_3$, δ): 1.35 (d, 6H, $J_{H-H} = 6.9$, $CHMe_2$), 1.98 (s, 3H, (*bzac*-Me)), 2.24 (s, 3H, Me), 2.83 (m, 1H, $CHMe_2$), 5.21 (s, 1H, *bzac*-γH), 5.36 (d, 2H, $J_{H-H} = 5.8$), 5.52 (d, 2H, $J_{H-H} = 5.8$), 7.35 (m, 3H), 7.78 (d, 2H, $J_{H-H} = 6.8$).

2.2.4. Preparation of [(η^6-*p*-cymene)Ru(dbzm)N_3] (*6*)

This complex was prepared by following a similar method as described in the preparation of complex **4** (route b) using [Na(dbzm) · H_2O] instead of [Na(*acac*) · H_2O]. Yield: 86 mg (84%).

IR (KBr, cm^{-1}): 2030 $\nu(N_3)$, 1593, 1533 ($\nu_{C=O} + \nu_{C=C}$). ^{1}HNMR ($CDCl_3$, δ) : 1.36 (d, 6H, $J_{H-H} = 5.8$), 2.36 (s, 3H, Me), 2.89 (m, 1H, $CHMe_2$), 5.34 (d, 2H, $J_{H-H} = 6.2$), 5.56 (d, 2H, $J_{H-H} = 6.4$), 6.32 (s, 1H), 7.46 (m, 6H), 7.92 (m, 4H).

*2.2.5. Preparation of triazolato complexes [(η^6-p-cymene)Ru(LL){$N_3C_2(CO_2R)_2$}] (LL = acac, R = Me (**7**), LL = bzac, R = Me (**8**); LL = (dbzm), R = Me (**9**), LL = acac, R = Et (**10**); LL = (bzac), R = Et (**11**), LL = dbzm, R = Et (**12**))*

General procedure: A round bottom flask charged with corresponding azido complex (**4**) (100 mg, 0.26 mmol) or (**5**) (100 mg, 0.22 mmol) or (**6**) (100 mg, 0.20 mmol) was added fivefold excess of dimethylacetylenedicarboxylate/diethylacetylenedicarboxylate and CH_2Cl_2 (20 ml). The mixture was stirred at room temperature and then the solution was reduced to ca. 3 ml on rotary evaporator. To this solution was added 30 ml of hexane, whereby the compound precipitated out as a yellow solid. The solid was collected by centrifuged and washed with 2 × 20 ml of hexane and dried under vacuum to gave the triazolato complexes [(η^6-*p*-cymene)Ru(LL){$N_3C_2(CO_2R)_2$}] (**7**–**12**).

Reaction time, yield, analytical and spectroscopic data are as follows:

Complex 7. LL = (*acac*), R = Me, 12 h, 93% (128 mg). Anal. Calc. for $C_{21}H_{27}N_3O_6Ru$: C, 48.59; H, 5.21; N, 8.10. Found: C, 48.25; H, 5.16; N, 7.87%. IR (KBr, cm^{-1}): 1723 ($\nu_{C=O}$), 1579, 1560, 1517 ($\nu_{C=O} + \nu_{C=C}$). ^1H NMR ($CDCl_3$, δ): 1.21 (d, 6H, $J_{H-H} = 6.92$, $CH(CH_3)_2$), 1.91 (s, 6H, *acac*-Me), 1.94 (s, 3H), 2.75 (m, 1H, $CH(CH_3)_2$), 3.86 (s, 6H, (OCH_3)), 4.95 (s, 1H, *acac*-γH), 5.29 (m, 2H), 5.60 (m, 2H). ^{13}C {^1H} NMR ($CDCl_3$, δ): 17.65 (s, Me, CMe), 22.32 (s, Me, $CH(Me)_2$), 26.60 (s, *acac*-Me), 30.68 (s, CH, $CHMe_2$), 51.66 (s, CH_3, $CO_2(CH_3)$), 80.07 (s, $C_{AA'}$), 84.99 (s, $C_{BB'}$), 98.93 (s, CH, *acac*-γ C), 99.75 (s, C, CMe), 101.30 (s, CPr^i), 140.22 (s, $C(CO_2Me)_2$), 162.90 (s, (CO_2)), 187.12 (s, *acac*-CO).

Complex 8. LL = (*bzac*), R = Me, 18 h, 84% (112 mg). Anal. Calc. for $C_{26}H_{29}N_3O_6Ru$: C, 53.65; H, 4.98; N, 7.22. Found: C, 53.18; H, 4.73; N, 6.95%. IR (KBr, cm^{-1}): 1716 ($\nu_{C=O}$), 1578, 1552, 1517 ($\nu_{C=O} + \nu_{C=C}$). ^1H NMR ($CDCl_3$, δ): 1.24 (d, 6H, $J_{H-H} = 4$, $CH(CH_3)_2$), 1.98 (s, 3H, *bzac*-Me), 2.06 (s, 3H, *cym*), 2.79 (m, 1H, $CH(CH_3)_2$), 3.49 (s, 6H, (OCH_3)), 5.33 (m, 2H, $H_{AA'}$), 5.48 (s, 1H, *bzac*-H), 5.62 (m, 2H, $H_{BB'}$), 7.30 (m, 3H, *bzac*-Ph), 7.68 (m, 2H, *bzac*-Ph). ^{13}C {^1H} NMR ($CDCl_3$, δ): 17.67 (s, Me, CMe), 22.21 (d, Me, $J_{H-H} = 31.80$, $CHMe_2$), 27.58 (s, Me, *bzac*-Me), 30.73 (s, CH, $CHMe_2$), 51.62 (s, Me, CO_2Me), 80.30 (d, $C_{AA'}$, $J_{C-H} = 19.60$), 85.45 (d, $C_{BB'}$, $J_{C-H} = 19.60$), 96.79 (s, CH, *bzac*-γC), 99.79 (s, CMe), 101.30 (s, CPr^i), 127.12–130.81 (m, Ph), 140.05 (s, $C(CO_2Me)$), 162.99 (s, CO_2), 180.94 (s, CO), 189.13 (s, CO).

Complex 9. LL = (*dbzm*), R = Me, 18 h, 87% (111 mg). Anal. Calc. for $C_{31}H_{31}N_3O_6Ru$: C, 57.93; H, 4.82; N, 6.53. Found: C, 57.48; H, 4.66; N, 6.28%. IR (KBr, cm^{-1}): 1723 ($\nu_{C=O}$), 1579, 1560, 1517 ($\nu_{C=O} + \nu_{C=C}$). ^1H NMR ($CDCl_3$, δ): 1.29 (d, 6H, $J_{H-H} = 6.92$, $CHMe_2$), 2.17 (s, 3H, Me - *cymene*), 2.87 (m, 1H, $CHMe_2$), 3.77 (s, 6H, $(CO_2Me)_2$), 5.42 (d, 1H, $J_{H-H} = 6$), 5.46 (d, 1H, $J_{H-H} = 6$), 5.67 (d, 1H, $J_{H-H} = 6$), 5.72 (d, 1H, $J_{H-H} = 6$), 6.16 (s, 1H, *dbzm*-γH), 7.35 (m, 6H, Ph), 7.77 (m, 4H, Ph). ^{13}C {^1H} NMR ($CDCl_3$, δ): 17.79 (s, CH_3, CMe), 21.19 (s, Me, $CHMe_2$), 30.75 (s, CH, $CHMe_2$), 51.42 (d, CH_3, $J_{C-H} = 20.72$ (CO_2CH_3)$_2$), 80.63, 80.98 (s, $C_{AA'}$), 85.21, 85.54 (s, C'_{BB}), 95.87 (s, *dbzm*-γC), 98.80 (s, CPr^i), 127.34–130.93 (m, Ph), 139.30 (s, $C(CO_2Me)_2$), 153.83 (s, CO_2) 182.13, 182.78 (s, CO).

Complex 10. LL = (*acac*), R = Et, 8 h, 77% (113 mg). Anal. Calc. for $C_{23}H_{31}N_3O_6Ru$: C, 50.77; H, 5.88; N, 7.72%. Found: C, 50.25; H, 5.36; N, 7.87%. IR (KBr, cm^{-1}): 1716 ($\nu_{C=O}$), 1578, 1552, 1517 ($\nu_{C=O} + \nu_{C=C}$). ^1H NMR ($CDCl_3$, δ): 1.22 (t, 6H, $J_{H-H} = 4.8$, $CH_2(CH_3)_2$), 1.32 (t, 6H, $J_{H-H} = 4.0$, $CHMe_2$), 1.92 (s, 6H, *acac*-Me), 2.17 (s, 3H, Me (*cym*)), 2.78 (m, 1H, $CHMe_2$), 4.30 (qt, 4H, $J_{H-H} = 7.12$), 4.97 (s, 1H, *acac*-γH), 5.29 (dd, 2H, $J_{H-H} = 10.52$, $J_{H-H} = 6.04$), 5.55 (dd, 2H, $J_{H-H} = 11.28$, $J_{H-H} = 6.12$). ^{13}C {^1H} NMR ($CDCl_3$, δ): 14.21 (s, Me (–CH_2Me)), 17.68 (s, Me, CMe), 22.34 (s, Me, $CHMe_2$), 26.67 (d, $J_{C-H} = 16.50$, Me, *acac*-Me), 30.66 (s, CH, $CHMe_2$), 60.55 (s, –CH_2– (–CH_2Me)), 80.11 (s, $C_{AA'}$), 84.97 (d, $C_{BB'}$ $J_{C-H} = 24.54$), 98.98 (d, CH, *acac*-γC, $J_{C-H} = 15.59$), 99.72 (s, CMe), 101.28 (s, CPr^i), 140.26 (s, $C(CO_2Et)_2$), 162.78 (s, (CO_2)), 187.15 (s, CO).

Complex 11. LL = (*bzac*), R = Et, 10 h, 82% (114 mg). Anal. Calc. for $C_{28}H_{33}N_3O_6Ru$: C, 55.12; H, 5.41; N, 6.89. Found: C, 54.87; H, 5.23; N, 6.95%. IR (KBr, cm^{-1}): 1716 ($\nu_{C=O}$), 1578, 1552, 1517 ($\nu_{C=O} + \nu_{C=C}$). ^1H NMR ($CDCl_3$, δ): 1.26 (m, 6H, Me), 1.28 (m, 6H, $CHMe_2$), 2.07 (s, 3H (*bzac*-Me)), 2.17 (s, 3H, Me (*Cym*)), 2.82 (m, 1H, $CHMe_2$), 4.26, 4.29 (qt, 4H, $J_{H-H} = 3.2$, –CH_2– (CO_2Et)), 5.62 (d, 2H, $J_{H-H} = 8.4$), 5.65 (d, 2H, $J_{H-H} = 5.84$), 5.58 (s, 1H, γH-*bzac*), 7.31–7.35 (m, 3H), 7.71 (m, 2H). ^{13}C {^1H} NMR ($CDCl_3$, δ): 14.15 (s, Me (CO_2CH_2Me)), 17.66 (Me-*cymene*), 22.21 (d, Me $J_{C-H} = 30.28$, $CHMe_2$), 27.61 (s, Me (*bzac*-Me)), 30.68 (s, CH, $CHMe_2$), 60.45, 61.19 (s, –CH_2– (CO_2Et)), 80.30 (t, $C_{AA'}$, $J_{C-H} = 16.50$), 85.02 (d, $C_{BB'}$, $J_{C-H} = 40.34$), 96.17 (s, CH, *bzac*-γC), 99.71 (s, CMe), 101.20 (s, CPr^i), 127.10–130.84 (m, Ph), 138.90, 140.05 (s, $C(CO_2Et)$), 162.80 (s, CO_2), 180.87 (s, CO), 189.12 (s, CO).

Complex 12. LL = (*dbzm*), R = Et: 12 h, 81% (109 mg). Anal. Calc. for $C_{33}H_{35}N_3O_6Ru$: C, 59.09; H, 5.22; N, 6.26. Found: C, 58.75; H, 4.98; N, 6.12%. IR (KBr, cm^{-1}): 1723 ($\nu_{C=O}$), 1579, 1560, 1517 ($\nu_{C=O} + \nu_{C=C}$). ^1H NMR ($CDCl_3$, δ): 1.26 (m, 6H, Me, CO_2Et), 1.29 (m, 6H, $CHMe_2$), 2.17 (s, 3H, Me (Cym.)), 2.82 (m, 1H, $CHMe_2$), 4.26 (qt, 4H, $J_{H-H} = 3.2$, –CH_2– (CO_2Et)), 5.46 (d, 1H, $J_{H-H} = 6$), 5.67 (d, 1H, $J_{H-H} = 6$), 5.72 (d, 2H, $J_{H-H} = 6$), 6.18 (s, 1H, *dbzm*-γH), 7.35 (m, 6H), 7.77 (m, 4H). ^{13}C {^1H} NMR ($CDCl_3$, δ): 14.10 (s, Me ($CO_2Et)_2$), 17.72 (s, Me (*cym*)), 22.21 (d, $J_{C-H} = 30.28$, Me ($CHMe_2$)), 30.68 (s, CH, ($CHMe_2$)), 61.19 (s, –CH_2– (CO_2Et)), 80.87 (d, $C_{AA'}$, $J_{C-H} = 29.88$), 85.13 (d, $C_{BB'}$ $J_{C-H} = 30.99$), 94.85 (s, CH (*dbzm*-γC)), 99.54 (s, CMe), 101.19 (s, CPr^i), 127.34–130.98 (m, Ph), 139.91 (s, $C(CO_2Et)$), 162.81 (s, (CO_2)), 181.94, 182.58 (s, CO).

*2.2.6. [(η^6-p-cymene)Ru(acac){N_3C_2HCN}] (**13**)*

Caution: These reactions should perform under well ventilation hoods.

A round bottom flask was charged with the azido complex **4** (100 mg, 0.26 mmol) and fumaronitrile (100 mg, 1.28 mmol) and 20 ml of dichloromethane. The mixture was stirred at room temperature for 8 h. The solvent was reduced to 3 ml and added excess of *n*-pentane or *n*-hexane to give a yellow precipitate. The yellow solid was collected and washed with 2×10 ml of *n*-pentane and dried under vacuum. Yield: 81% (92 mg).

Anal. Calc. for $C_{18}H_{22}N_4O_2Ru$: C, 50.57; H, 5.15; N, 13.11. Found: C, 50.26; H, 4.93; N, 12.87%. IR (KBr, cm^{-1}): 2223 ($\nu_{C\equiv N}$), 1571, 1520 ($\nu_{C=O} + \nu_{C=C}$). ^1H NMR ($CDCl_3$, δ): 1.23 (d, 6H, Me, $CHMe_2$), 1.94 (d, 6H, $J_{H-H} = 2.92$), 2.08 (s, 3H, Me, CMe), 2.79 (m, 1H), 5.19 (s, 1H, *acac*-γH), 5.27 (d, 1H, $J_{H-H} = 5.92$), 5.34 (d, 1H, $J_{H-H} = 5.92$), 5.57 (d, 1H, $J_{H-H} = 5.92$), 5.61 (d, 1H, $J_{H-H} = 5.96$), 6.92 (s, 1H, CH). ^{13}C {^1H} NMR ($CDCl_3$, δ): 17.25 (d, Me, CMe), 22.09 (d, Me, CMe_2, $J_{C-H} = 13.88$), 26.94 (d, $J_{C-H} = 22.13$, CMe), 30.49 (s, CH, $CHMe_2$), 80.64 (s, $C_{AA'}$), 81.24 (s, $C_{BB'}$), 83.15 (s), 84.34 (s), 84.77 (s), 99.04 (d, $J_{C-H} = 26.35$, *acac*-γCH), 100.08 (s, CPr^i), 114.88 (s, CN), 128.93 (s), 134.91 (s, CH), 138.56 (s, C(CN)), 187.50 (s, CO).

2.2.7. [(η^6-*p*-cymene)Ru(*bzac*){N_3 C_2HCN}] (**14**)

Caution: These reactions should perform under well ventilation hoods.

This compound was prepared in analogy to that of (**13**) using the compound (**5**) instead of (**4**). Yield: 78% (90 mg).

Anal. Calc. for $C_{23}H_{24}N_4O_2Ru$: C, 56.43; H, 4.90; N, 11.45. Found: C, 56.17; H, 4.69; N, 11.27%. IR (KBr, cm^{-1}): 2220 ($\nu_{C\equiv N}$), 1571, 1520 ($\nu_{C=O} + \nu_{C=C}$). ^1H NMR ($CDCl_3$, δ): 1.26 (d, 6H, Me, $CHMe_2$), 2.12 (s, 3H (*bzac*-Me)), 2.18 (s, 3H, Me (*cym*)), 2.84 (m, 1H, $CHMe_2$), 5.60 (d, 2H, $J_{H-H} = 8.2$), 5.64 (d, 2H, $J_{H-H} = 8.4$), 5.72 (s, 1H, γH-*bzac*), 6.98 (s, 1H, CH), 7.26–7.68 (m, 5H). ^{13}C {^1H} NMR ($CDCl_3$, δ): 18.26 Me (*cymene*), 22.28 (d, Me $J_{C-H} = 30.28$, ($CHMe_2$)), 27.73 (s, Me (*bzac*-Me)), 30.68 (s, CH, ($CHMe_2$)), 82.30 (t, $C_{AA'}$), 84.02 (d, $C_{BB'}$), 97.13 (s, CH, *bzac*-γC), 99.21 (s, CMe), 101.28 (s, CPr^i), 114.38 (s, CN), 127.10–132.84 (Ph), 138.90 (s, C(CN)), 180.67 (s, CO), 189.32 (s, CO).

2.2.8. [(η^6-*p*-cymene)(*dbzm*)Ru{N_3C_2HCN}] (**15**)

Caution: These reactions should perform under well ventilation hoods.

This complex was prepared by adopting a similar method as described in the preparation of (**13**) using the compound (**6**) instead of (**4**). Yield: 77% (85 mg, 0.185 mmol).

Anal. Calc. for $C_{28}H_{26}N_4O_2Ru$: C, 60.97; H, 4.71; N, 10.16. Found: C, 60.58; H, 4.39; N, 9.87%. IR (KBr, cm^{-1}): 2220 ($\nu_{C\equiv N}$), 1571, 1520 ($\nu_{C=O} + \nu_{C=C}$). ^1H NMR ($CDCl_3$, δ): 1.31 (d, 6H, $J_{H-H} = 6.92$), 2.17 (s, 3H), 2.87 (m, 1H), 5.54 (d, 1H, $J_{H-H} = 6.38$), 5.61 (d, 1H, $J_{H-H} = 6.42$), 5.67 (d, 1H, $J_{H-H} = 6$), 5.72 (d, 1H, $J_{H-H} = 6$), 6.16 (s, 1H, *dbzm*-γH), 6.89 (s, 1H), 7.25 (m, 6H), 7.48 (m, 4H). ^{13}C {^1H} NMR ($CDCl_3$, δ): 17.48 (s, CH_3 (*cymene*)), 21.36 (s, CH_3, $CHMe_2$), 30.76 (s, CH, $CHMe_2$), 80.63, 80.98 (s, $C_{AA'}$), 85.21, 85.54 (s, $C_{BB'}$), 94.87 (s, *dbzm*-γC), 98.80 (s, CPr^i), 114.27 (s, CN) 128.74–132.53 (m, Ph), 139.30 (s, C(CN)), 183.58 (s, CO).

3. Structural analysis and refinement

X-ray quality crystals of complex **4** were grown by slow evaporation of diethyl ether solution of complex **4** at room temperature while the crystals of **7**, **11**, **12** and **13** were obtained by diffusion of hexane into acetone solution of the complexes. X-ray diffraction data were measured at 120(2) K on a Bruker AXS Apex CCD area detector employing graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Absorption correction were made by modeling a transmission surface by spherical harmonics employing equivalent reflections with $I > 2\sigma(I)$ (SADBAS) [36]. The structures were solved by direct methods and refined by full matrix least squares base on F^2 [37,38]. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a "riding" model. The selected bond lengths and angles are tabulated in Tables 1, 2 and summary of collection parameters and refinement data is presented in Table 3 respectively.

4. Result and discussions

4.1. Synthesis of arene ruthenium azido complexes

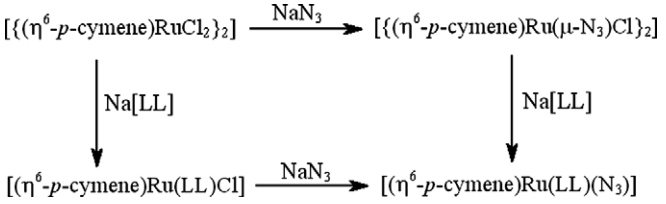
Treatment of the complexes [(η^6-*p*-cymene)Ru(LL)Cl] with NaN_3 in ethanol afforded the azido complexes [(η^6-*p*-cymene)Ru(LL)(N_3)] in fairly good yield (Scheme 1). The formation of the azido complexes can be readily confirmed by the appearance of a strong characteristic band of the terminal azide stretching frequency at around 2015–2036 cm^{-1}. Alternatively, the azido complexes can also be prepared by the reaction of azide dimer [{(η^6-*p*-cymene)Ru(μ-N_3)Cl}$_2$] with sodium salts of β-diketonate. The absence of the bridging azido band at 2057 cm^{-1} of the starting complex and appearance of a new band in

Table 1
Selected bond lengths (Å) and bond angles (°) for the complex **4** with estimated standard deviations (esds) in parenthesis

	Molecule 1	Molecule 2	
Bond lengths (Å)			
Ru(1)–Cent	1.652 (4)	Ru(2)–Cent	1.657 (5)
Ru(1)–O(1)	2.077(3)	Ru(2)–O(3)	2.066(3)
Ru(1)–O(2)	2.057(3)	Ru(2)–O(4)	2.071(3)
Ru(1)–N(1)	2.102(4)	Ru(2)–N(4)	2.095(4)
N(1)–N(2)	1.151(5)	N(4)–N(5)	1.162(5)
N(2)–N(3)	1.153(6)	N(5)–N(6)	1.134(6)
Bond angles (°)			
O(1)–Ru(1)–O(2)	88.56(12)	O(3)–Ru(2)–O(4)	85.96(15)
Ru(1)–N(1)–N(2)	131.0(3)	Ru(2)–N(4)–N(5)	124.1(3)
O(1)–Ru(1)–N(1)	80.33(15)	O(3)–Ru(2)–N(4)	85.96(15)
O(2)–Ru(1)–N(1)	84.86(18)	O(4)–Ru(2)–N(4)	85.74(14)

Table 2
Selected bond lengths (Å) and bond angles (°) for the complexes **7**, **11**, **12** and **13** with estimated standard deviations (esd's) in parenthesis

	Complex **7**	Complex **11**	Complex **12**	Complex **13**
Bond lengths (Å)				
Ru–Cent	1.660(3)	1.667(4)	1.670 (2)	1.656(5)
Ru–N(1)		2.101(4)	2.0969(19)	
Ru–N(2)	2.099(2)			2.091(3)
Ru–O(1)	2.0627(18)	2.068(3)	2.0642(16)	2.074(3)
Ru–O(2)	2.0581(18)	2.063(3)	2.0647(16)	2.079(3)
N(1)–N(2)	1.338(3)	1.356(4)	1.364(2)	1.353(6)
N(2)–N(3)	1.334(3)	1.314(4)	1.320(3)	1.330(6)
Bond angles (°)				
O(1)–Ru–O(2)	88.81(8)	88.32(11)	88.89(6)	87.93(14)
N(1)–N(2)–N(3)	113.46(19)	109.5(3)	109.23(17)	108.4(4)
O(2)–Ru–N(2)	83.69(7)			85.64(15)
O(1)–Ru–N(2)	86.68(7)			83.86(15)
O(1)–Ru–N(1)		84.97(11)	84.45(7)	
O(2)–Ru–N(1)		83.44(11)	85.11(7)	



Scheme 1. Reaction pathway of starting materials.

the region 2015–2030 cm^{-1} confirmed the formation of the azido complexes [(η^6-*p*-cymene)Ru(LL)(N_3)].

4.2. Reaction of ruthenium azido complexes with DMD or DED

The reaction of azido complexes **4**–**6** with a fivefold excess of the substituted acetylenes dimethylacetylene-

Table 3
Summary of crystal structure determination and refinement parameters for complexes **4**, **7**, **11**, **12** and **13**

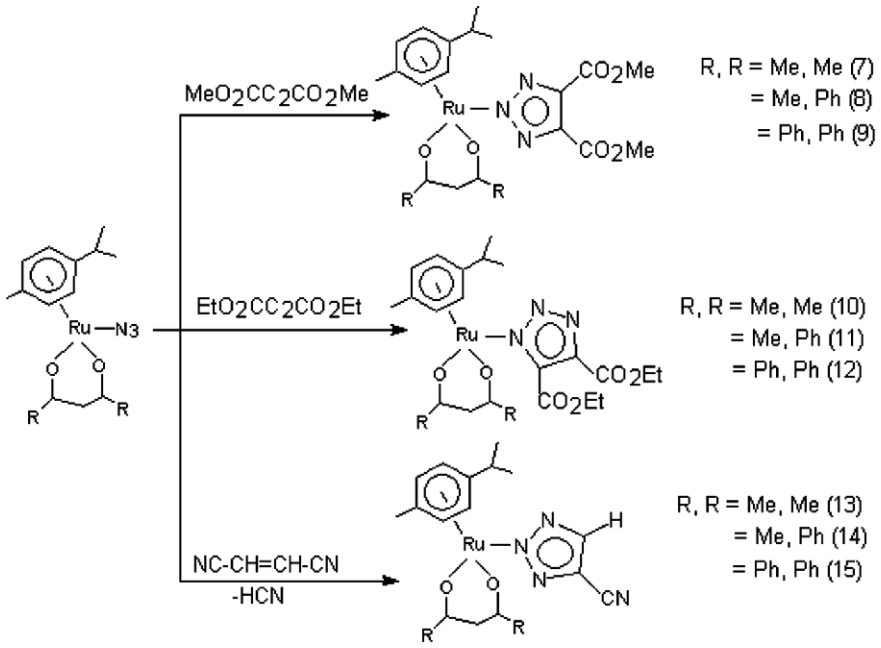
	Complex **4**	Complex **7**	Complex **11**	Complex **12**	Complex **13**
Empirical formula	$C_{15}H_{21}N_3O_2Ru$	$C_{21}H_{27}N_3O_6Ru$	$C_{28}H_{33}N_3O_6Ru$	$C_{33}H_{35}N_3O_6Ru$	$C_{18}H_{22}N_4O_2Ru$
Formula weight	376.42	519.53	608.64	670.71	427.47
Temperature (K)	298(2)	120(2)	120(2)	120(2)	298(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic	Orthorhombic	Monoclinic
Space group	*P*2(1)/*c*	*P*2(1)/*c*	*P*2(1)/*c*	*P*2(1)2(1)2(1)	*P*2(1)/*n*
Unit cell dimensions					
a (Å)	20.110(18)	8.500(3)	10.060(9)	11.221(6)	9.964(4)
b (Å)	9.192(8)	11.099(4)	13.284(12)	11.300(6)	12.378(5)
c (Å)	19.953(18)	23.147(9)	19.707(18)	23.783(12)	15.629(6)
α (°)				90	
β (°)	117.246(13)	91.109(4)	100.273(15)	90	103.848(6)
γ (°)				90	
Volume ($Å^3$)	3279(5)	2183.2(15)	2591(4)	3016(3)	1871.6(12)
Z	8	4	4	4	4
Calculated density (Mg/m^3)	1.525	1.581	1.560	1.477	1.517
Absorption coefficient (mm^{-1})	0.964	0.761	0.654	0.570	0.856
F(000)	1536	1068	1256	1384	872
Crystal size (mm)	$0.21 \times 0.15 \times 0.10$	$0.41 \times 0.36 \times 0.18$	$0.34 \times 0.26 \times 0.19$	$0.38 \times 0.31 \times 0.27$	$0.19 \times 0.12 \times 0.06$
θ Range for data collection (°)	2.04–28.48	1.76–28.32	1.86–28.32	1.71–28.26	2.12–28.22
Limiting indices	$-25 \leqslant h \leqslant 26$, $-11 \leqslant k \leqslant 12$, $-25 \leqslant l \leqslant 26$	$-10 \leqslant h \leqslant 10$, $-14 \leqslant k \leqslant 14$, $-29 \leqslant l \leqslant 29$	$-13 \leqslant h \leqslant 12$, $-16 \leqslant k \leqslant 17$, $-26 \leqslant l \leqslant 26$	$-14 \leqslant h \leqslant 14$, $-14 \leqslant k \leqslant 14$, $-30 \leqslant l \leqslant 31$	$-12 \leqslant h \leqslant 11$, $-15 \leqslant k \leqslant 14$, $-20 \leqslant l \leqslant 20$
Reflections collected/ unique [R_{int}]	34013/7729 [0.0681]	11902/4819 [0.0370]	25517/6076 [0.0953]	28487/6897 [0.0530]	10451/4178 [0.0691]
Completeness to θ (%)	28.48–93.0	28.32–88.6	28.32–94.0	28.26–95.2	28.22–90.5
Absorption correction	Semi-empirical equivalents				
Refinement method	Full-matrix least squares on F^2				
Data/restraints/parameters	7729/3/405	4819/0/287	6076/0/349	6897/0/393	4178/0/231
Goodness-of-fit on F^2	1.032	1.044	1.055	1.034	1.027
Final *R* indices [$I > 2$sigma(I)]	$R_1 = 0.0497$, $wR_2 = 0.1199$	$R_1 = 0.0343$, $wR_2 = 0.0852$	$R_1 = 0.0666$, $wR_2 = 0.1704$	$R_1 = 0.0277$ $wR_2 = 0.0667$	$R_1 = 0.0572$, $wR_2 = 0.1306$
R indices (all data)	$R_1 = 0.0632$, $wR_2 = 0.1304$	$R_1 = 0.0404$, $wR_2 = 0.0895$	$R_1 = 0.0714$, $wR_2 = 0.1752$	$R_1 = 0.0302$ $wR_2 = 0.0680$	$R_1 = 0.0834$ $wR_2 = 0.1482$
Largest difference peak and hole (e $Å^{-3}$)	1.663 and −0.377	0.876 and −0.861	1.988 and −2.236	0.670 and −0.319	0.826 and −0.482

dicarboxylate ($MeO_2CC_2CO_2Me$) (DMD) or diethylacetylenedicarboxylate ($EtO_2CC_2CO_2Et$) (DED) in dichloromethane at room temperature afforded the yellow ruthenium triazolato complexes in good yield (Scheme 2). The formation of the triazolato complexes can be readily confirmed by observing the disappearance of azide band and the appearance of new bands due to C=O stretching frequencies at 1726 cm^{-1}. In addition to the C=O stretching frequencies, the IR spectra of these complexes showed a pair of strong bands at around 1517–1578 cm^{-1} which are assignable to coupled (C=O) + (C=C) modes of the β-*diketonate* [39,40]. Surprisingly, the triazolato complexes formed from the two acetylenes differ in their mode of bonding. The dimethylacetylenedicarboxylate exclusively produced N(2) bonded triazolato complexes while diethylacetylenedicarboxylate produced exclusively N(1) bonded triazolato complexes. This has been confirmed by the X-ray analysis of the complexes **7**, **11** and **12**.

It should be noted that the triazole anion could be coordinated by a metal through either its N(1) or N(2) nitrogen atoms [7,26] which are essentially isoenergetic as indicated by molecular orbital calculations [26,27]. Evidence obtained to date indicates that either of the two isomers N(1) and N(2)-bonded are formed simultaneously [7,12,16,26,27] or only the N(2) bound isomer is produced exclusively [7,12,16,17]. In our cases both the N(1) and N(2) bonded isomers are formed depending on the substituents of the triazolato ring. Thus, *methoxy*-substituted acetylene produced exclusively N(2) bonded isomer while *ethoxy*-substituted acetylene exclusively produced N(1) isomer. Ellis et al. 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 [41]. It is believed that the triazolato complexes initially form the N(1) bonded complexes which then isomerize to the N(2) bonded complexes. Isomerization from N(1) to N(2) is favored as far as steric factors are concerned while electronic factors favor no isomerization.

It has been reported that the N(1) nitrogens of the triazolato anions are more nucleophilic than the N(2) nitrogens [27]. The N(1) to N(2) linkage isomerization reaction appears to be driven by the steric congestion between the triazole ring substituents. An inspection of molecular models of the linkage isomers indicates that this congestion would be totally relieved in the N(2) bonding isomer. Thus, formation of exclusively N(1) bonded triazolato complexes **10**–**12** could not be due to steric factors but it is believed that it is due to electronic factors. As mentioned previously, a consideration of ring nitrogen nucleophilicity favors N(1) coordination for substituted triazolato complexes [27]. Thus, in the case of the *ethoxy* substituted triazolato complexes (**10**–**12**) no isomerization takes place from the N(1) to N(2) bonded complexes due to the high inductive effect of the *ethoxy* group which favors the N(1) bonded triazolato complexes. But the methoxy substituted triazolato complexes isomerize from the N(1) to N(2) bonded isomers and produce exclusively the N(2) bonded triazolato complexes (**7**–**9**). In order to confirm the mode of bonding, the crystal structures of the representative complexes have been determined. On the basis of spectroscopic data and X-ray analysis, the *methoxy*-substituted triazolato complex has been proposed N(2) bonded while *ethoxy*-substituted triazolato complexes are proposed to be N(1) bonded triazolato complexes.

The ^1H NMR spectrum of complex **7** is shown in Fig. 1. The ^1H NMR spectra of the complexes **7**–**9** exhibit, in addition to the *p*-cymene resonances, singlet resonances



Scheme 2. Synthetic pathway of complexes.

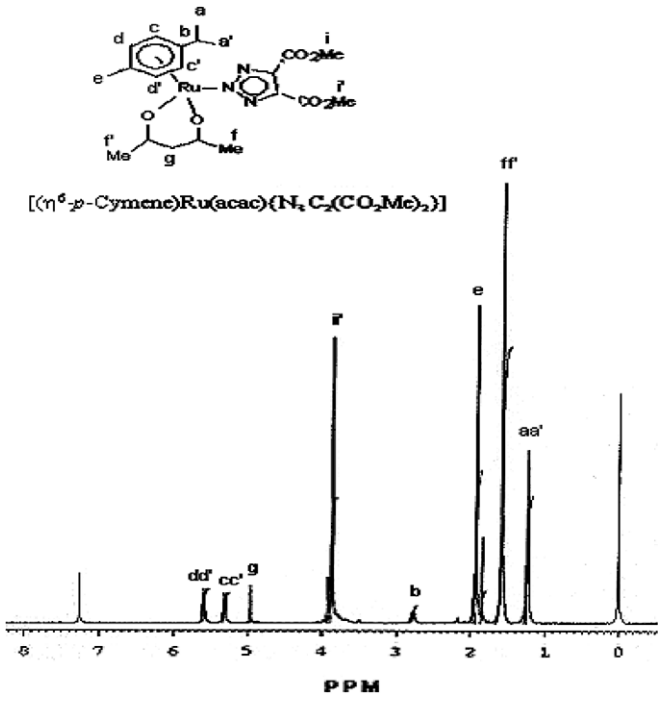


Fig. 1. ^{1}H NMR Spectrum of complex [(η^6-*p*-cymene)Ru(*acac*)-{$N_3C_2(CO_2Me)_2$}] (**7**).

corresponding to the β-diketonate ligand in the region δ 4.9–6.2 for γ-proton and a singlet at ca. δ 3.8 assignable to the methoxy carbonyl group protons of the triazolato group.

The ^{1}H NMR spectra of complexes **10**–**12** exhibited a quartet at ca. δ 4.29 and a triplet ca. δ 1.28 due to the methylene and methyl protons of the ethoxy carbonyl group. The ^{13}C {^{1}H} NMR of these complexes exhibited a single resonance at δ 162 due to carbon of CO_2 group while the carbons of the β-diketonate group appear at δ 183–189.

4.3. Reaction of ruthenium azido complexes with fumaronitrile

The reaction of the azido complexes **4**–**6** with excess fumaronitrile at room temperature for 10–15 h affords the N(2) bound 4-cyano-1,2,3-triazolato complexes (**13**–**15**) in good yield. The formation of the triazolato complexes is readily confirmed by the absence of the starting azide stretching frequency and the appearance of a strong band at around 2220 cm^{-1} corresponding to the stretching frequency of the C≡N group of the coordinated triazolato group. The ^{1}H NMR spectra of these complexes showed characteristic singlet resonances at δ 6.9 assigned to the CH group of the triazolato ring proton and a singlet in the region δ 5.19–6.16 attributed to γ-proton of the β-diketonato group. In addition, the ^{1}H NMR spectra contains doublet resonances corresponding to the *p*-cymene group in the region δ 5.3 arising from the protons of the arene ring, a multiplet at ca. δ 2.87 due to C$\underline{\underline{H}}Me_2$, a singlet at δ 2 for methyl group and a doublet at δ 1.2 for the methyl protons of isopropyl group. In principle, the cycloaddition of fumaronitrile to the coordinated azide can take place via C=C or C≡N. The reaction of coordinated azide in Ni(II) with CH_2=CHCN gave a triazolinato complex [7]. A pathway via direct cyclization of HC≡CCN with azide resulting in the formation of triazolato has also occurred [27,42]. Complexes **13**–**15** are clearly formed by [3+2] cyclization between the azido ligand and the C=C double bond following removal of a HCN molecule. The proposed structures of the complexes are confirmed by a determination of molecular structure of representative complex **13** by single crystal X-ray diffraction.

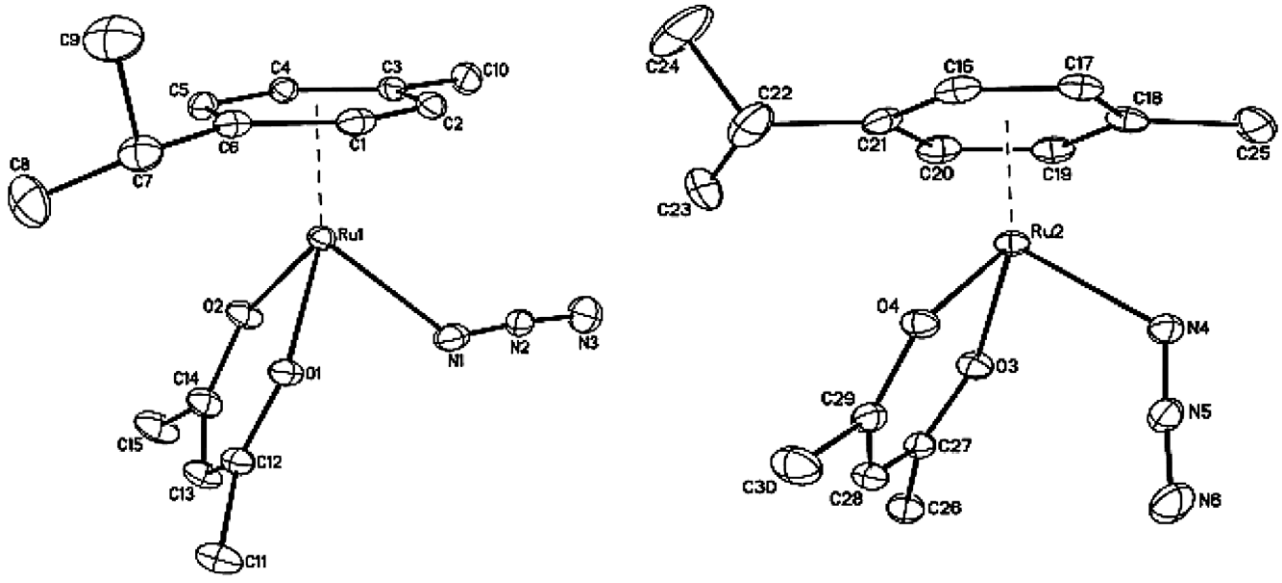


Fig. 2. Molecular structure of complex [{(η^6-*p*-cymene)Ru(*acac*)N_3}] (**4**). Thermal ellipsoids are depicted with 30% probability level.

5. Crystal structures

5.1. Crystal structure of $[(\eta^6\text{-}p\text{-cymene})Ru(acac)N_3]$ (4)

The ORTEP drawing of complex **4** with the atom labeling scheme is shown in Fig. 2. The selected bond lengths and angles are listed in Table 1.

The complex crystallizes in the $P2(1)/c$ space group. The ruthenium atom is coordinated by a *p*-cymene ligand in η^6-fashion occupying three facile coordination sites. The remaining coordination sites are occupied by the O-atoms of the acetylacetonate ligand and azide group. The unit cell consists of two molecules. The two molecules differ only in the orientation of the azide groups. In one molecule

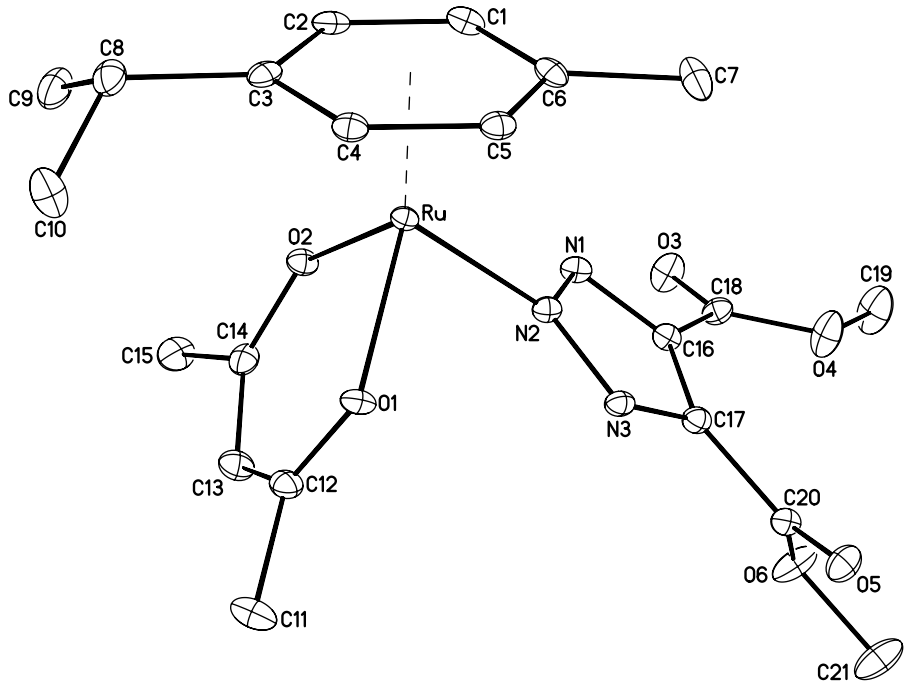


Fig. 3. Molecular structure of $[(\eta^6\text{-}p\text{-cymene})Ru(acac)\{N_3C_2(CO_2Me)_2\}]$ (**7**). Thermal ellipsoids are depicted with 30% probability level.

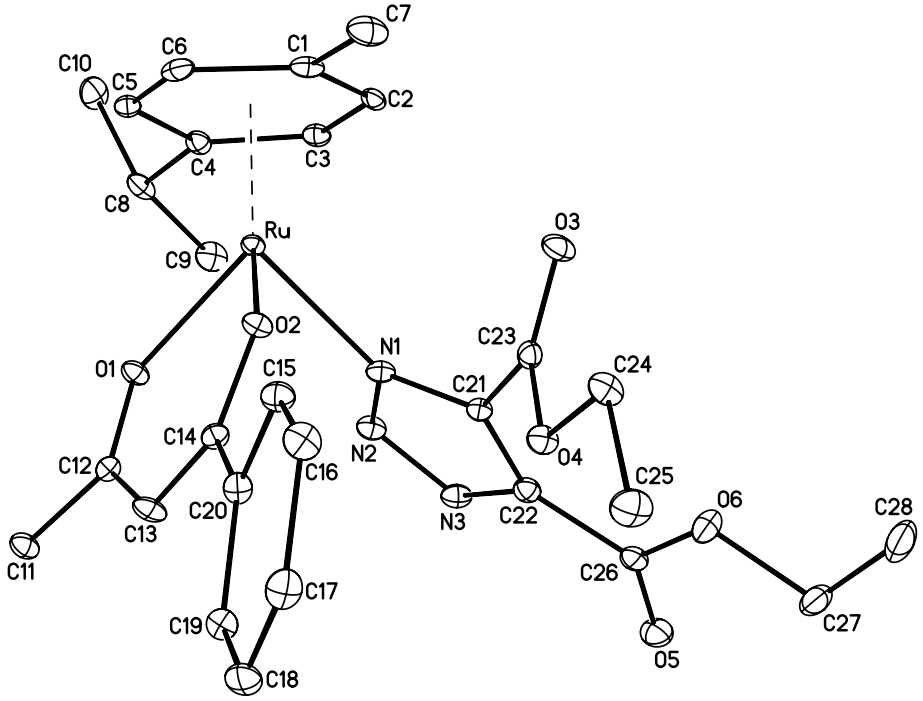


Fig. 4. Molecular structure of $[(\eta^6\text{-}p\text{-cymene})Ru(bzac)\{N_3C_2(CO_2Et)_2\}]$ (**11**). Thermal ellipsoids are depicted with 30% probability level.

the –N=N=N group is directed horizontally while in the other it directed vertically. The distance between the ruthenium and the centroid of the *p*-cymene ligand in both molecules is comparable, the values being 1.652(4) Å (Ru1–Cent) and 1.657(5) Å, (Ru2–Cent). The Ru1–O(1) [2.077(3) Å] and Ru1–O(2) [2.057(3) Å], in one of the molecules is comparable to that of the other and the values are in the range of reported Ru–O bond lengths of other ruthenium β-diketnoate systems [43].

The N–N bond lengths in the molecules are in the range of 1.134 (6)–1.162 (5) Å, which are comparable to other reported N–N bond lengths. However, the ruthenium and nitrogen of the azide bond distance, 2.102(4) Å, is slightly longer than that of other reported complexes such as rhodium [44] and copper [6b] complexes.

5.2. Crystal structures of [(η⁶-p-cymene)Ru(acac){N₃C₂(CO₂Me)₂}] (7); [(η⁶-p-cymene)Ru(bzac){N₃C₂(CO₂Et)₂}] (11); [(η⁶-p-cymene)Ru(dbzm){N₃C₂(CO₂Et)₂}] (12) and [(η⁶-p-cymene)Ru(acac){N₃C₂(H)(CN)}] (13)

The structure of the compounds **7**, **11**, **12** and **13** consists of a neutral arene ring bonded to the ruthenium, along with anionic β-diketonato and triazolato ligands. The molecular structures of complexes **7**, **11**, **12** and **13** with atom labeling scheme are shown in Figs. 3–6. Selected bond lengths and angles are presented in Table 2. The complexes **7**, **11** and **13** crystallized in the *P*2(1)/*c* space group while complex **12** crystallized in the *P*2(1)2(1)2(1) space group. The *p*-cymene ligand is bonded to the ruthenium atom in η⁶-fashion with ruthenium to centroid of the ring being 1.660 (3), 1.667 (4), 1.670 (2) and 1.656 (5) Å, for complex **7**, **11**, **12** and **13**, respectively. The complexes adopt a typical three-legged piano stool conformation with the N and the two O-atoms as the legs. The Ru–O(1) and Ru–O(2) bond distances of the triazolato complexes **7**, **13** are comparable to the starting azido complex **4**. The remarkable difference in the structure between the *methoxy* substituted complex **7** and that of *ethoxy* substituted complexes **11** and **12** is the mode of coordination of the triazolato unit to the ruthenium atom. In complex **7**, the triazolato group is bonded to the metal through N(2) – while in complexes **11** and **12**, it is bonded through N(1) – atom of the triazolato group. It is notable that most cycloaddition reactions of coordinated azide with acetylenes to produce triazoles exclusively form the N(2)-isomer. To the best of our knowledge, complexes **11** and **12** represent first structurally characterized N(1)-bound isomer obtained from such cycloaddition reaction. There is no significant difference in the bond distances of the heterocyclic ring indicating delocalization of electrons in the ring. The Ru–O (1) and Ru–O(2) bond distances in the complexes range from 2.0581 to 2.079 Å which is comparable to those of the reported Ru–O bond lengths [43]. The O(1)–Ru–O(2) bond angles of the complex **7** (88.81(8) Å) are comparable to that of complexes **11** (88.32(11) Å) and **12** (88.89(6) Å).

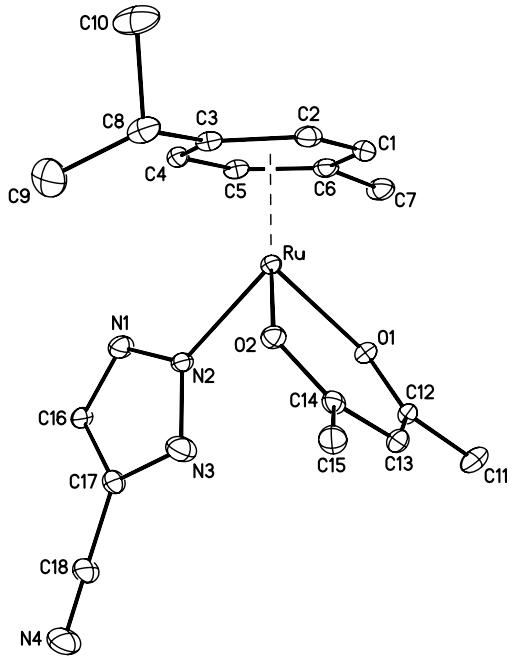


Fig. 6. Molecular structure of [(η⁶-*p*-cymene)Ru(*acac*){N_3C_2(H)(CN)}] (**13**). Thermal ellipsoids are depicted with 30% probability level.

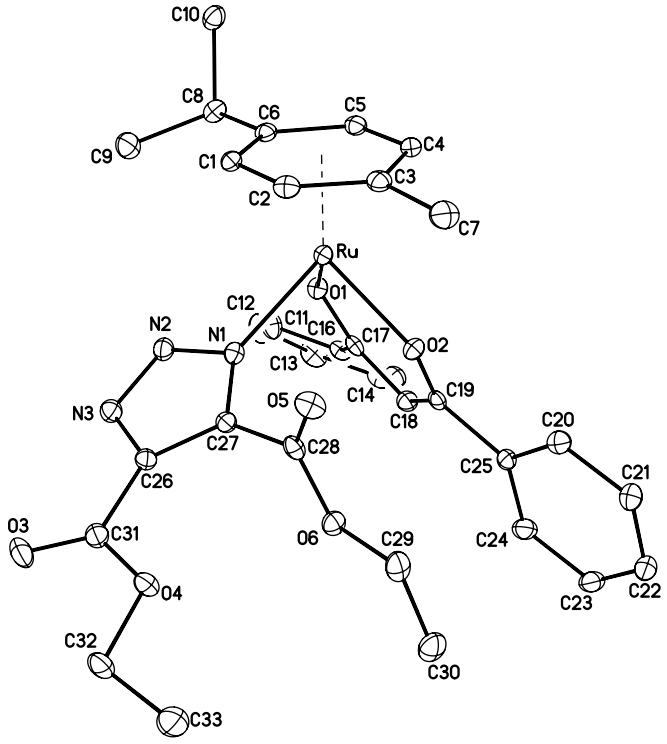


Fig. 5. Molecular structure of [(η⁶-*p*-cymene)Ru(*dbzm*){$N_3C_2(CO_2Et)_2$}] (**12**). Thermal ellipsoids are depicted with 30% probability level.

6. Conclusions

Previously, we reported the syntheses of indenyl ruthenium triazolato complexes. In these complexes the

triazolato ligand binds to the metal through the N(2) atom irrespective of acetylenes are used. Where as in the present study the bonding depend on the acetylene. In the case of dimethylacetylenedicarboxylate the bonding is through N(2) whereas in the case of diethylacetylenedicarboxylate the bonding is through N(1). Even though we expected the chemistry to be similar to indenyl ruthenium systems, we observed the formation of new bonding modes in the arene ruthenium system. Complexes **11** and **12** are the first examples of structurally characterized N(1)-bound isomers obtained from such cycloaddition reactions.

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Appendix A. Supplementary material

Crystallographic data for the structural analysis have been deposited at the Cambridge Crystallographic Data Centre (CCDC), CCDC No. 287034 for complex **4**, CCDC No. 287035 for complex **7**, CCDC No. 287036 for complex **11**, CCDC No. 287037 for complex **13** and CCDC No. 290263 for complex **12**, respectively. Copies of this information may be obtained free of charge from the director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336 033; e mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.05.001.

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