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Arene ruthenium β-diketonato triazolato derivatives: Synthesis and spectral studies (β-diketones: 1-phenyl-3-methyl-4-benzoyl pyrazol-5-one, acetylacetone derivatives)

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ABSTRACT

Mononuclear neutral arene ruthenium(II) β-diketonato complexes of the general formula (η^6-arene)-Ru(LL)Cl [LL = 1-phenyl-3-methyl-4-benzoyl pyrazol-5-one (L1), arene = C_6H_6 (**1**), *p*-^{i}PrC$_6$H$_4$Me (**2**), C_6Me_6 (**3**); arene = *p*-^{i}PrC$_6$H$_4$Me, LL = 1-benzoylacetone (L3) (**8**); arene = *p*-^{i}PrC$_6$H$_4$Me, LL = dibenzoylmethane (L4) (**9**)] have been synthesized and their subsequent substitution reactions with NaN_3 in alcohol at room temperature yielded the corresponding neutral terminal azido complexes (η^6-arene)-Ru(LL)N_3 [LL = 1-phenyl-3-methyl-4-benzoyl pyrazol-5-one (L1), arene = C_6H_6 (**4**), *p*-^{i}PrC$_6$H$_4$Me (**6**), C_6Me_6 (**7**); arene = *p*-^{i}PrC$_6$H$_4$Me, LL = dibenzoylmethane (L4) (**10**)] as well as a cationic complex [(η^6-*p*-^{i}PrC$_6$H$_4$Me)Ru(L4)(PPh$_3$)]BF_4 (**12**) with PPh_3. The [3 + 2] cycloaddition reaction of selective azido complexes with the activated alkynes dimethyl and diethyl acetylenedicarboxylates produced the arene triazolato complexes [(η^6-arene)Ru(LL){$N_3C_2(CO_2R)_2$}] [arene = *p*-^{i}PrC$_6$H$_4$Me, LL = L1, R = Me (**13**); arene = C_6Me_6, LL = L1, R = Me (**14**); arene = C_6Me_6, LL = acetyl acetone (L2), R = Me (**15**); arene = C_6Me_6, LL = L3, R = Me (**16**); arene = *p*-^{i}PrC$_6$H$_4$Me, LL = L1, R = Et (**17**); arene = C_6Me_6, LL = L1, R = Et (**18**); arene = C_6Me_6, LL = L2, R = Et (**19**); arene = C_6Me_6, LL = L3, R = Et (**20**)]. With fumaronitrile the reaction yielded the triazoles [(η^6-arene)Ru(LL)(N_3C_2HCN)] [arene = *p*-^{i}PrC$_6$H$_4$Me, LL = L1 (**21**), arene = C_6Me_6, LL = L1 (**22**), arene = C_6Me_6, LL = L2 (**23**), arene = C_6Me_6, LL = L3 (**24**)]. In the above triazolato complexes only N(2) isomer was obtained. The complexes were characterized on the basis of spectroscopic data. Crystal structure of representatives complexes were determined by single crystal X-ray diffraction.

1. Introduction

The applications of half-sandwich η^6-arene ruthenium complexes are extensive, particularly in synthetic organic chemistry. These purely inorganic materials are extraordinarily robust and therefore well suited as homogenous catalysts under mild conditions [1] and also as anti-cancer drugs [2]. Only a few reports of the chemistry of arene ruthenium(II) complexes containing *O,O′*-donor ligands are available; mainly concerning acetylacetonato [3–5] and carboxylato [6,7] complexes. A new class of β-diketonate ligands – the acylpyrazolones – have been developed which possess a pyrazole ring fused to the *O,O′*- chelating fragment [8]. Marchetti et al. [R] reported extensive syntheses and studies of a series of substituted acylpyrazolone and their complexes with various transition metals. Metal derivatives of these ligands are generally considered to be more stable than the analogous acetylacetonates [9].

These β-diketonate ligands have been used commonly as monoanionic *O,O′*-chelating agents. Besides this normal chelating mode, they exhibit various other bonding modes to metal ions as neutral, di- and tri-anions [8–11]. All relevant complexes reported so far are centered on the acetylacetone ligand and its derivatives [3,12–14]. Challenges are thus still open for designing new complexes based on other functionalized β-diketonato derivatives.

Organic azides have useful applications in organic synthesis [15,16]. One of the most useful synthetic applications of azides is the preparation of 1,2,3-triazoles *via* 1,3-dipolar cycloadditions of azides with alkenes, alkynes, nitriles and isonitriles [15–18]. Such reactions give favorable results in the presence of transition metal catalysts [18–22]. The catalytic role of half-sandwich arene ruthenium complexes is also noteworthy [23–25]. Analogously, metal-coordinated azido ligands also undergo 1,3-dipolar cycloaddition reactions [26,27]. Although such reactions have so far focused on syntheses of organic triazoles, isolation of the metallacycle intermediate azide derivatives has been relatively unexplored. Recent studies reveal that dipolar cycloaddition reactions of neutral arene ruthenium azido complexes are favorable. These azido complexes

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undergo [3 + 2] cycloadditions with a series of activated alkynes and fumaronitrile to produce arene ruthenium triazolato complexes [13–14,28–31]. Cu(I) catalysts have proved considerably useful in azide–alkyne cycloadditions, but are efficient only with terminal alkyne substrates [19,24]. However, ruthenium catalysts act well with internal alkynes as well, expanding the scope of this cycloaddition process [24].

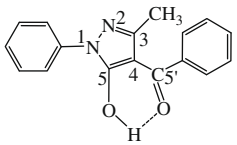
Arene ruthenium acylpyrazolate complexes and their reactions involving substitution of chloride ion by neutral and anionic ligands have already been reported [32]. However, 1,3-dipolar cycloaddition reactions of these complexes have not been reported so far to the best of our knowledge. Though the analogous triazole complexes of arene and indenyl ruthenium(II) β-diketonate have been reported in our recent papers [12–14,29–31], triazole complexes of hexamethylbenzene ruthenium(II) β-diketonate have not been reported. In continuation of earlier work, we report here the syntheses of some arene ruthenium(II) β-diketonato complexes along with their subsequent substitution reactions with monodentate ligands and the syntheses of triazolato complexes.

2. Experimental

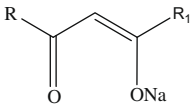
Caution: All the azide reactions should be performed with extreme care.

2.1. Physical methods and materials

All solvents were dried and purified by standard procedure. Ruthenium trichloride hydrate (Arora Matthey Ltd.), hexamethylbenzene, dibenzoylmethane and dimethyl acetylenedicarboxylate (Aldrich), benzoylacetone, diethyl acetylenedicarboxylate and fumaronitrile (Acros Organics), acetylacetone (SD Fine-Chem) and sodium azide were purchased and used as received. The compounds $[(\eta^6\text{-}C_6H_6)Ru(\mu\text{-}Cl)Cl]_2$ [33], $[(\eta^6\text{-}p\text{-}^iPrC_6H_4Me)Ru(\mu\text{-}Cl)Cl]_2$ [33,34], $[(\eta^6\text{-}C_6H_6)Ru(\mu\text{-}N_3)Cl]_2$ [14], $[(\eta^6\text{-}p\text{-}^iPrC_6H_4Me)\text{-}Ru(\mu\text{-}N_3)Cl]_2$ [35,36], $[(\eta^6\text{-}C_6Me_6)Ru(\mu\text{-}N_3)Cl]_2$ [37], $[(\eta^6\text{-}C_6Me_6)\text{-}Ru(L2)Cl]$, $[(\eta^6\text{-}C_6Me_6)Ru(L3)Cl]$, $[(\eta^6\text{-}C_6Me_6)Ru(L2)N_3]$, $[(\eta^6\text{-}C_6Me_6)Ru(L3)N_3]$ [12] and 1-phenyl-3-methyl-4-benzoyl pyrazol-5-one (L1) [38] were prepared according to the literature methods. $[(\eta^6\text{-}C_6Me_6)Ru(\mu\text{-}Cl)Cl]_2$ was prepared using a Microwave Discover CEM. NMR spectra were recorded on an AMX-400 MHz spectrometer. Infrared spectra were recorded as KBr pellets on a Perkin–Elmer 983 spectrophotometer. The following structures represent the ligands L1, L2, L3 and L4.



1-phenyl-3-methyl-4-benzoyl pyrazol-5-one (L1)



R, R_1 = Me, Me = L2
R, R_1 = Me, Ph = L3
R, R_1 = Ph, Ph = L4

2.2. Single crystal X-ray structure analyses

Crystals suitable for X-ray diffraction study for compounds **6** and **10** were grown by slow diffusion of diethyl ether into dichloromethane, while requisite size crystals of complexes **9** and **17**

Table 1
Summary of crystal structure determination and refinement parameters for complexes **6**, **9**, **10** and **17**.

	Complex **6**	Complex **9**	Complex **10**	Complex **17**
Empirical formula	$C_{27}H_{27}N_5O_2Ru$	$C_{25}H_{25}ClO_2Ru$	$C_{25}H_{25}N_3O_2Ru$	$C_{35}H_{37}N_5O_6Ru$
Formula weight	554.61	493.97	500.55	724.77
T (K)	293(2)	293(2)	293(2)	296(2)
λ (Å)	0.71073	0.70930	0.70930	0.71073
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{2}(1)/c$	$P\bar{2}(1)/c$	$P2(1)/n$
Unit cell dimensions				
a (Å)	9.0717(2)	16.4040(9)	10.6790(4)	13.9402(18)
b (Å)	10.4835(2)	7.7290(10)	11.9520(11)	13.7348(16)
c (Å)	14.0584(3)	17.2040(7)	17.7020(10)	18.065(2)
α (°)	88.7910(10)	90	90	90
β (°)	87.9000(10)	103.094(4)	90.554(4)	94.708(7)
γ (°)	73.3230(10)	90	90	90
V (Å^3)	1279.82(5)	2124.5(3)	2259.3(3)	3447.2(8)
Z	2	4	4	4
D_{calc} (Mg/m^3)	1.439	1.544	1.472	1.396
Absorption coefficient (mm^{-1})	0.645	0.882	0.720	0.506
F(0 0 0)	568	1008	1024	1496
Crystal size (mm^3)	0.50 × 0.35 × 0.24	0.25 × 0.175 × 0.20	0.35 × 0.15 × 0.10	0.38 × 0.25 × 0.16
Θ Range for data collection (°)	1.45–27.51	1.27–24.93	1.90–24.93	1.78–28.43
Index ranges	$-11 \leqslant h \leqslant 11$	$0 \leqslant h \leqslant 19$	$0 \leqslant h \leqslant 12$	$-18 \leqslant h \leqslant 18$
	$-13 \leqslant k \leqslant 13$	$0 \leqslant k \leqslant 9$	$0 \leqslant k \leqslant 14$	$-18 \leqslant k \leqslant 17$
	$-17 \leqslant l \leqslant 18$	$-20 \leqslant l \leqslant 19$	$-20 \leqslant l \leqslant 20$	$-24 \leqslant l \leqslant 24$
Reflections collected	15 326	3470	3526	45 930
Independent reflections (R_{int})	5591 (0.0142)	3470 (0.0000)	3526 (0.0000)	8533 (0.0330)
Completeness to θ (%)	27.51–96.9	24.93–85.7	24.93–84.3	28.43–98.3
Absorption correction	None	Psi-scan	Psi-scan	None
Refinement method	Full-matrix	Full-matrix	Full-matrix	Full-matrix squares on F^2
Data/restraints/parameters	559/1/321	3470/0/363	3526/0/380	8533/0/418
Goodness-of-fit on F^2	1.043	1.074	1.069	1.010
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0574,	R_1 = 0.0262	R_1 = 0.0266	R_1 = 0.0434
	wR_2 = 0.1736	wR_2 = 0.0652	wR_2 = 0.0602	wR_2 = 0.1252
R indices (all data)	R_1 = 0.0598,	R_1 = 0.0308	R_1 = 0.0369	R_1 = 0.0560
	wR_2 = 0.1773	wR_2 = 0.0684	wR_2 = 0.0658	wR_2 = 0.1357
Largest diff. peak and hole (e Å^{-3})	0.675 and -0.732	0.750 and -0.609	0.325 and -0.413	0.890 and −0.894

Table 2
Selected bond lengths (Å) for the complexes **6**, **9**, **10** and **17** with estimated standard deviations (esd's) in parentheses.

Complex **6**		Complex **9**		Complex **10**		Complex **17**	
Selected bonds	Bond lengths (Å)	Selected bonds	Bond lengths (Å)	Selected bonds	Bond lengths (Å)	Selected bonds	Bond lengths (Å)
Ru(1)–cent	1.645	Ru(1)–cent	1.656	Ru(1)–cent	1.654	Ru(1)–cent	1.652
Ru(1)–O(1)	2.094(3)	Ru(1)–O–(1)	2.0683(18)	Ru(1)–O(1)	2.0795(19)	Ru(1)–O(1)	2.082(19)
Ru(1)–O(2)	2.092(3)	Ru(1)–O(2)	2.0675(17)	Ru(1)–O(2)	2.0652(19)	Ru(1)–O(2)	2.093(19)
Ru(1)–N(3)	2.210(7)	Ru(1)–Cl(1)	2.4173(8)	Ru(1)–N(1)	2.155(3)	Ru(1)–N(1)	2.074(2)
O(1)–C(9)	1.262(5)	O(1)–C(14)	1.272(3)	O(1)–C(11)	1.279(3)	O(1)–C(20)	1.267(4)
O(2)–C(11)	1.273(5)	O(2)–C(12)	1.277(3)	O(2)–C(19)	1.279(3)	O(2)–C(11)	1.268(3)
C(9)–C(8)	1.422(6)	C(14)–C(13)	1.391(4)	C(11)–C(18)	1.392(4)	C(20)–C(18)	1.427(4)
C(11)–C(8)	1.404(5)	C(12)–C(13)	1.389(4)	C(19)–C(18)	1.392(4)	C(11)–C(18)	1.401(4)
N(2)–C(7)	1.320(6)			N(1)–N(2)	1.038	N(4)–C(20)	1.369(4)
N(1)–C(9)	1.355(3)			N(2)–N(3)	1.227	N(5)–C(19)	1.314(4)
N(4)–N(3)	0.843(11)					N(2)–C(29)	1.334(4)
N(4)–N(5)	1.462(15)					N(3)–C(28)	1.341(3)
						N(4)–N(5)	1.391(4)
						N(1)–N(3)	1.338(3)
						N(1)–N(2)	1.340(3)

Table 3
Selected bond angles (°) for the complexes **6**, **9**, **10** and **17** with estimated standard deviations (esd's) in parentheses.

Complex **6**		Complex **9**		Complex **10**		Complex **17**	
Selected bond angles	Bond angles (°)	Selected bond angles	Bond angles (°)	Selected bond angles	Bond angles (°)	Selected bond angles	Bond angles (°)
O(2)–Ru(1)–O(1)	88.20(12)	O(2)–Ru(1)–O(1)	87.59(7)	O(2)–Ru(1)–O(1)	87.21(8)	O(2)–Ru(1)–O(1)	88.80(8)
O(2)–Ru(1)–N(3)	82.34(17)	O(2)–Ru(1)–Cl(1)	84.87(6)	O(2)–Ru(1)–N(1)	80.26(10)	O(2)–Ru(1)–N(1)	82.99(8)
O(1)–Ru(1)–N(3)	82.68(19)	O(1)–Ru(1)–Cl(1)	85.46(6)	O(1)–Ru(1)–N(1)	83.41(10)	O(1)–Ru(1)–N(1)	85.81(9)
Ru(1)–N(3)–N(4)	116.5(7)			Ru(1)–N(1)–N(2)	127.7(3)	Ru(1)–N(1)–N(2)	123.81(18)
N(3)–N(4)–N(5)	169.6(11)			N(1)–N(2)–N(3)	174.2(4)	Ru(1)–N(1)–N(3)	122.73(17)
						N(3)–N(1)–N(2)	113.3(2)

were obtained by diffusion of hexane into chloroform or dichloromethane. The red colored crystal of compound **6** and the bright orange crystal of **17** 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 a ϕ range of 0–200° in increments of 1.2°, and $D_{max} - D_{min}$ = 12.45–0.81 Å. X-ray intensity data were collected with Mo Kα graphite monochromatic radiation at 293(2) K, with a 0.3° ω scan mode and 10 s per frame. However, the orange-red crystals of the complexes **9** and **10** were mounted on the end of the glass fibre on a Nonius MACH3 diffractometer with graphite monochromatized Mo Kα (λ = 0.70930 Å) radiation at 293 K for cell determination and intensity data collection. The intensity data were corrected for Lorenz and polarization effects. The structures were solved by direct methods using the program SHELXS-97 [39]. Refinement and all further calculations

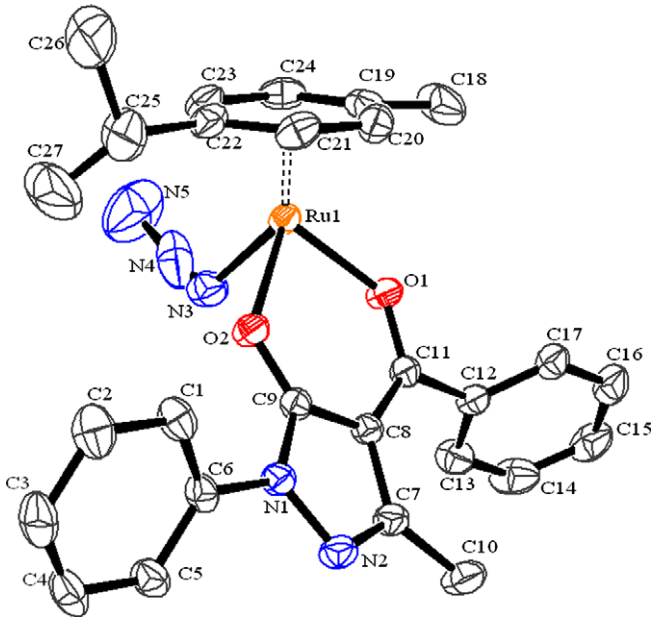


Fig. 1. Molecular structure of complex [(η^6-*p*-^{i}PrC$_6$H$_4$Me)Ru(L1)N$_3$] (**6**) with atom numbering scheme. Thermal ellipsoids are depicted with 35% probability level. Hydrogen atoms are omitted for clarity.

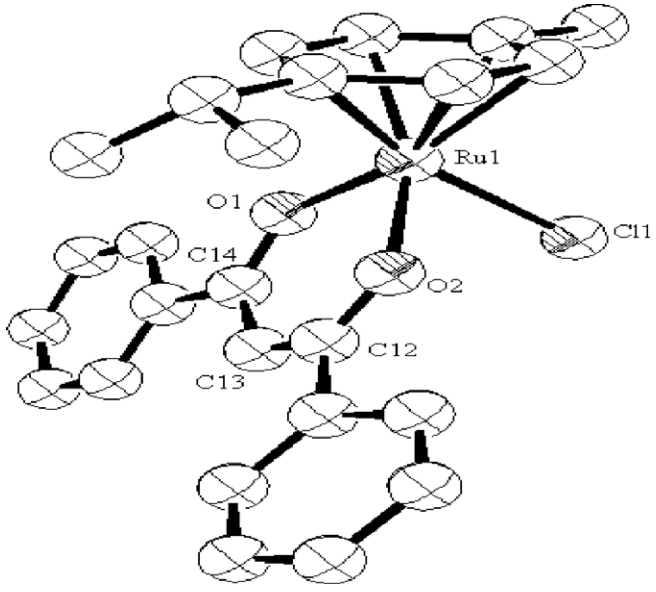


Fig. 2. Molecular structure of complex [(η^6-*p*-^{i}PrC$_6$H$_4$Me)Ru(L4)Cl] (**9**) with atom numbering scheme. Thermal ellipsoids are depicted with 50% probability level. Hydrogen atoms are omitted for clarity.

were carried out using SHELXL-97 [40]. 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-squares on F^2. The data collection parameters, selective bond lengths and bond angles are presented in Tables 1–3, respectively. Figs. 1–4 are the ORTEP [41] representation of the molecules with 35% (Figs. 1, 3 and 4) and 50% (Fig. 2) probability thermal ellipsoids displayed.

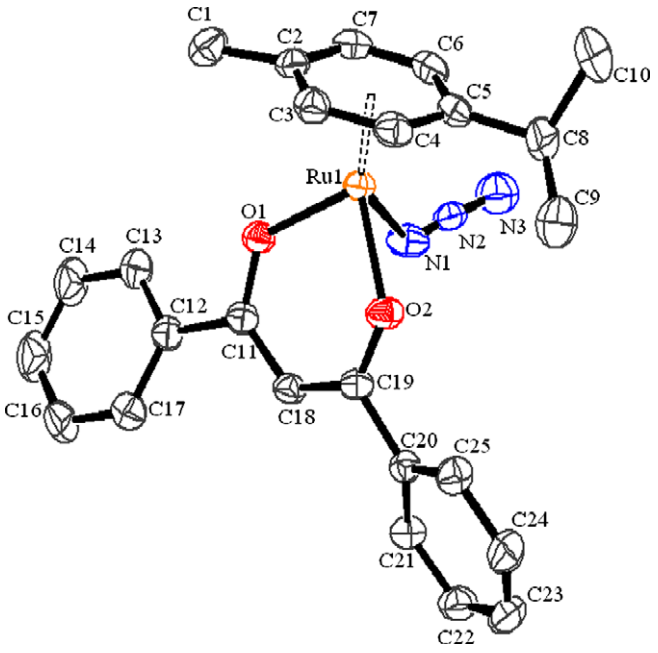


Fig. 3. Molecular structure of complex [(η^6-*p*-^{i}PrC$_6$H$_4$Me)Ru(L4)(N$_3$)] (**10**) with atom numbering scheme. Thermal ellipsoids are depicted with 35% probability level. Hydrogen atoms are omitted for clarity.

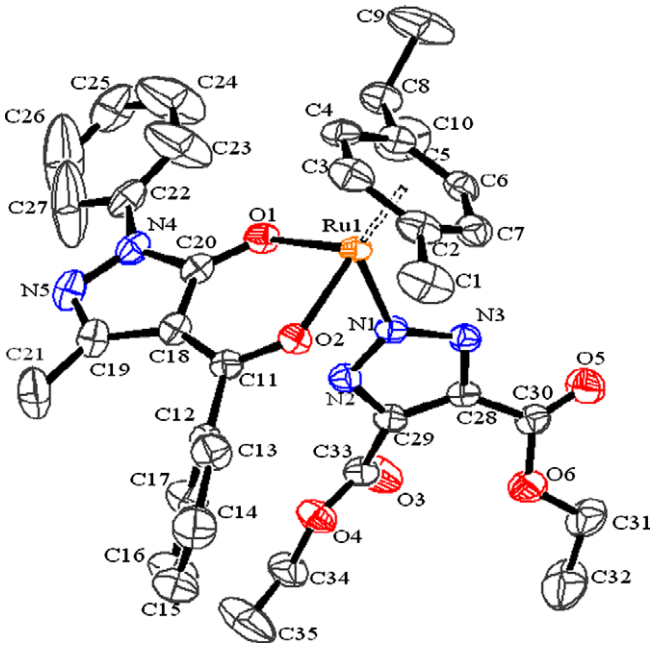


Fig. 4. Molecular structure of complex [(η^6-*p*-^{i}PrC$_6$H$_4$Me)Ru(L1){N$_3$C$_2$(CO$_2$Et)$_2$}] (**17**) with atom numbering scheme. Thermal ellipsoids are depicted with 35% probability level. Hydrogen atoms are omitted for clarity.

2.3. Synthesis of complexes

2.3.1. Preparation of [(η^6-C$_6$Me$_6$)Ru(-Cl)Cl]$_2$

To the dimer [(η^6-*p*-^{i}PrC$_6$H$_4$Me)Ru(μ-Cl)Cl]$_2$ (200 mg, 0.33 mmol) taken in a sealed glass vial of 5 ml capacity, a threefold excess of hexamethylbenzene (0.98 mmol) was added and mixed properly. The reaction was carried out fixing the microwave at 170 °C and a pressure of 5 bar. With the 200 W microwave system, this temperature was reached within a few minutes, and the reaction completed in 10 min. Excess hexamethylbenzene was recovered by washing with hexane through a silica gel column using hexane as eluant. The orange-red band [(η^6-C$_6$Me$_6$)Ru(μ-Cl)Cl]$_2$ was collected by passing a mixture of methanol–acetone in 1:1 ratio. The solvent was removed on a rotary evaporator. The resulting complex was washed with hexane and diethyl ether and dried in vacuum.

Yield = 175 mg (96%); M.pt. = 270 °C; ^{1}H NMR (CDCl$_3$, δ): 2.06 (s, 36H, C$_6$Me$_6$).

2.3.2. Preparation of [(η^6-C$_6$H$_6$)Ru(L1)Cl] (**1**)

To a solution of the complex [(η^6ÙC$_6$H$_6$)Ru(μ-Cl)Cl]$_2$ (450 mg, 0.9 mmol) in acetonitrile, the ligand L1 (500 mg, 1.8 mmol) and NaOMe (97 mg, 1.8 mmol) were added. The resulting solution was stirred whereby compound **1** started precipitating after 5 min. Stirring was continued further to complete the reaction. The precipitate was filtered and washed with diethyl ether. The filtrate was dried under vacuum, the residue dissolved in dichloromethane (10 ml) and the solution filtered to remove sodium chloride. The solution was concentrated to 2 ml, whereupon addition of excess diethyl ether precipitated the additional complex which was separated and dried under vacuum.

Yield = 550 mg (60.1%); IR (KBr, cm^{-1}): 1603 $\nu_{(C=O)}$, 1585, 1575 $\nu_{(C=O\ +\ C=C)}$ ^{1}H NMR (CDCl$_3$, δ): 2.27 (s, 3H, CH$_3$), 5.8 (s, 6H, C$_6$H$_6$), 7.38–7.5 (m, 8H, C$_6$H$_5$ and N1–C$_6$H$_5$), 7.92 (d, 2H, J_{H-H} = 8, N1–C$_6$H$_5$).

2.3.3. Preparation of [(η^6-*p*-^{i}PrC$_6$H$_4$Me)Ru(L1)Cl] (**2**)

Complex **2** was prepared following a method similar to that described for complex **1**. Reaction of [(η^6-*p*-^{i}PrC$_6$H$_4$Me)Ru(μ-Cl)Cl]$_2$ (500 mg, 0.82 mmol) with ligand L1 (454 mg, 1.63 mmol) in 1:2 ratio in the presence of NaOMe (88 mg, 1.63 mmol) in methanol yielded complex **2**.

Yield = 880 mg (78.8%); IR (KBr, cm^{-1}): 1601 $\nu_{(C=O)}$, 1591, 1576 $\nu_{(C=O+C=C)}$. ^{1}H NMR (CDCl$_3$, δ): 1.3 (d, 6H, J_{H-H} = 2.8, CH(C*H*$_3$)$_2$), 1.6 (s, 3H, C*H*$_{3cym}$), 2.2 (s, 3H, CH$_3$), 2.9 (m, 1H, C*H*(CH$_3$)$_2$), 5.2 (d, 2H, J_{H-H} = 5.6, C$_6$H$_{4cym}$), 5.5 (d, 2H, J_{H-H} = 4.8, C$_6$H$_{4cym}$), 7.2–7.4 (m, 8H, C$_6$H$_5$ and N1–C$_6$H$_5$), 7.8 (d, 2H, J_{H-H} = 7.6, N1–C$_6$H$_5$).

2.3.4. Preparation of [(η^6-C$_6$Me$_6$)Ru(L1)Cl] (**3**)

Following a method similar to that described for the preparation of complex **1**, complex **3** was prepared by the reaction of [(η^6-C$_6$Me$_6$)Ru(μ-Cl)Cl]$_2$ (500 mg, 0.75 mmol) with ligand L1 (80 mg, 1.5 mmol) in 1:2 ratio in the presence of NaOMe (80 mg, 1.5 mmol), using methanol instead of acetonitrile.

Yield = 760 mg (88.37%); IR (KBr, cm^{-1}): 1600 $\nu_{(C=O)}$, 1582, 1573 $\nu_{(C=O+C=C)}$. ^{1}H NMR (CDCl$_3$, δ): 2.09 (s, 18H, C$_6$Me$_6$), 2.17 (s, 3H, CH$_3$), 7.35–7.5 (m, 8H, C$_6$H$_5$ and N1–C$_6$H$_5$), 7.95 (d, 2H, J_{H-H} = 8, N1–C$_6$H$_5$).

^{13}C {^{1}H} NMR (CDCl$_3$, δ): 15.27 (s, Me (C$_6$Me$_6$)), 16.38 (s, CH$_3$ (C3–CH$_3$)), 89.79 (s, C (C$_6$Me$_6$)), 106 (s, C4), 138.76 (s, C3), 120.73–148.89 (N1–C$_6$H$_5$), 127.56–139.49 (Ph (C5′-Ph)), 163.23 (s, C5), 188.15(s, CO (C5′-CO)).

2.3.5. Preparation of [(η^6-C$_6$H$_6$)Ru(L1)N$_3$] (**4**)

Route (a): A suspension of complex **1** (250 mg, 0.5 mmol) and NaN$_3$ (66 mg, 1.016 mmol) in 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 diffused with diethyl ether. On slow evaporation, the compound was obtained as red crystals. [The remaining ether-insoluble red-brown residue was extracted with acetone, filtered and concentrated. On addition of excess hexane, an orange-red solid precipitated out. It was ambiguously characterized to be $[(\eta^6\text{ÙC}_6\text{H}_6)\text{Ru}(\mu\text{-N}_3)\text{Cl}]_2$ (**5**)].

Route (b): The benzene ruthenium azido bridge dimer $[(\eta^6\text{ÙC}_6\text{H}_6)\text{Ru}(\mu\text{-N}_3)\text{Cl}]_2$ (250 mg, 0.49 mmol) was added to a methanolic solution of L1 (270 mg, 0.97 mmol) and NaOMe (50 mg, 0.96 mmol). The mixture was stirred at room temperature; within 30 min, the color of solution changed from reddish-brown to brown while stirring was continued for 6 h. The solvent was removed in vacuum; the residue was dissolved in dichloromethane and filtered. The filtrate was concentrated and the excess diethyl ether was added for precipitation. The product was separated, washed with diethyl ether and dried in vacuum.

Yield = 115 mg (46.74%); IR (KBr, cm^{-1}): 2026 $\nu_{(N3terminal)}$, 1603 $\nu_{(C=O)}$, 1591, 1575 $\nu_{(C=O+C=C)}$. ^{1}H NMR ($CDCl_3$, δ): 2.27 (s, 3H, CH_3), 5.77 (s, 6H, C_6H_6), 7.2–7.35 (m, 8H, C_6H_5 and N1–C_6H_5) 7.96 (d, 2H, J_{H-H} = 8, N1–C_6H_5).

2.3.6. Preparation of $[(\eta\text{-}^6p\text{-}^i\text{PrC}_6\text{H}_4\text{Me})\text{Ru(L1)N}_3]$ (**6**)

The required starting complexes (**2** and $[(\eta^6\text{-}p\text{-}^i\text{PrC}_6\text{H}_4\text{Me})\text{Ru}(\mu\text{-N}_3)\text{Cl}]_2$) were treated with sodium azide and L1, respectively, in appropriate ratio, yielding complex **6** by following the methods (*route a*/*route b*) described above for the preparation of complex **4**. [No by-product $[(\eta^6\text{-}p\text{-}^i\text{PrC}_6\text{H}_4\text{Me})\text{Ru}(\mu\text{-N}_3)\text{Cl}]_2$ was obtained in this case *via* either route.]

Yield = 245 mg (74.2%); IR (KBr, cm^{-1}): 2035 $\nu_{(N3terminal)}$, 1605 $\nu_{(C=O)}$, 1598, 1583 $\nu_{(C=O+C=C)}$. ^{1}H NMR ($CDCl_3$, δ): 1.36 (d, 6H, J_{H-H} = 2.8 $CH(CH_3)_2$), 1.66 (s, 3H, CH_{3cym}), 2.23 (s, 3H, CH_3), 2.9 (m, 1H, $CH(CH_3)_2$), 5.28 (d, 2H, J_{H-H} = 4.8, C_6H_{4cym}), 5.5 (d, 2H, J_{H-H} = 5.2, C_6H_{4cym}), 7.35–7.5 (m, 8H, C_6H_5 and N1–C_6H_5), 7.93 (d, 2H, J_{H-H} = 7.8, N1–C_6H_5).

2.3.7. Preparation of $[(\eta^6\text{-}C_6Me_6)\text{Ru(L1)N}_3]$ (**7**)

Complex **7** was prepared by either of the methods (*route a*/*route b*) described for the preparation of complex **4** by reacting the required starting complexes (**3** and $[(\eta^6\text{-}C_6Me_6)\text{Ru}(\mu\text{-N}_3)\text{Cl}]_2$) with sodium azide and L1, respectively, in appropriate ratio. [No by-product $[(\eta^6\text{-}C_6Me_6)\text{Ru}(\mu\text{-N}_3)\text{Cl}]_2$ was obtained in this case *via* either route.]

Yield = 285 mg (81.42%); IR (KBr, cm^{-1}): 2027 $\nu_{(N3terminal)}$, 1593 $\nu_{(C=O)}$, 1582, 1573 $\nu_{(C=O+C=C)}$. ^{1}H NMR ($CDCl_3$, δ): 2.06 (s, 18H, C_6Me_6), 2.1 (s, 3H, CH_3), 7.2–7.5 (m, 8H, C_6H_5 and N1–C_6H_5), 7.96 (d, 2H, J_{H-H} = 8, N1–C_6H_5).

^{13}C {^{1}H} NMR ($CDCl_3$, δ): 15.18 (s, Me (C_6Me_6)), 16.3 (s, CH_3 (C3–CH_3)), 90.34 (s, C (C_6Me_6)), 106.01(s, C4), 138.67 (s, C3), 120.71–149.3 (N1–C_6H_5), 127.61–139.3 (Ph (C5′-Ph)), 163.4 (s, C5), 188.75 (s, CO (C5′-CO)).

2.3.8. Preparation of $[(\eta^6\text{-}p\text{-}^i\text{PrC}_6\text{H}_4\text{Me})\text{Ru(LL)Cl}]$; LL = L3 (**8**); LL = L4 (**9**)

A suspension of $[(\eta^6\text{-}p\text{-}^i\text{PrC}_6\text{H}_4\text{Me})\text{Ru}(\mu\text{-Cl})\text{Cl}]_2$ (285 mg, 0.45 mmol) and sodium salt of L3/L4 (1.13 mmol) in methanol (50 ml) was stirred at room temperature for 2 h. Solvent was removed on a rotary evaporator; the residue was extracted with chloroform and filtered to remove any insoluble materials. Addition of excess hexane resulted in precipitation of the desired compound as an orange-red microcrystalline solid.

Complex **8** $[(\eta^6\text{-}p\text{-}^i\text{PrC}_6\text{H}_4\text{Me})\text{Ru(L3)Cl}]$: Yield = 365 mg (90%); IR (KBr, cm^{-1}): 1589 $\nu_{(C=O)}$, 1556, 1518 $\nu_{(C=O+C=C)}$. ^{1}H NMR ($CDCl_3$, δ): 1.36 (d, 6H, J_{H-H} = 7, $CH(CH_3)_2$), 2.11 (s, 3H, L3-CH_3), 2.28 (s, 3H, CH_{3cym}), 2.94 (sept, 1H, $CH(CH_3)_2$), 5.24 (d, 2H, J_{H-H} = 5, C_6H_{4cym}), 5.51 (d, 2H, J_{H-H} = 5.5, C_6H_{4cym}), 5.78 (s, 1H, L3-γH), 7.31–7.42 (m, 3H, *p*,*m*-Ph), 7.81 (d, 2H, J_{H-H} = 7.2, *o*-Ph).

Complex **9** $[(\eta^6\text{-}p\text{-}^i\text{PrC}_6\text{H}_4\text{Me})\text{Ru(L4)Cl}]$: Yield = 400 mg (87%); IR (KBr, cm^{-1}): 1592 $\nu_{(C=O)}$, 1543, 1520 $\nu_{(C=O+C=C)}$. ^{1}H NMR ($CDCl_3$, δ): 1.42 (d, 6H, J_{H-H} = 6, $CH(CH_3)_2$), 2.34 (s, 3H, CH_{3cym}), 3.02 (sept, 1H, $CH(CH_3)_2$), 5.32 (d, 2H, J_{H-H} = 6, C_6H_{4cym}), 5.58 (d, 2H, J_{H-H} = 6, C_6H_{4cym}), 6.38 (s, 1H, L4–γH), 7.38 (m, 6H, Ph), 7.90 (m, 4H, Ph).

2.3.9. Preparation of $[(\eta^6\text{-}p\text{-}^i\text{PrC}_6\text{H}_4\text{Me})\text{Ru(L4)(N}_3)]$ (**10**)

A suspension of complex **9** (100 mg, 0.2 mmol) and NaN_3 (13 mg, 0.2 mmol) in ethanol (15 ml) was stirred at room temperature for 1 h. Solvent was dried on a rotary evaporator and the residue dissolved in dichloromethane, filtered, diffused with diethyl ether and on slow evaporation, the compound **10** was obtained as red crystals. [The remaining ether-insoluble red-brown residue was extracted with acetone, filtered through silica gel and concentrated. On addition of excess hexane, an orange-red solid precipitated out and was ambiguously characterized as $[(\eta^6\text{-}p\text{-}^i\text{PrC}_6\text{H}_4\text{Me})\text{Ru}(\mu\text{-N}_3)\text{Cl}]_2$ (**11**)].

Complex **10** $[(\eta^6\text{-}p\text{-}^i\text{PrC}_6\text{H}_4\text{Me})\text{Ru(L4)(N}_3)]$: Yield = 65 mg (64%); IR (KBr, cm^{-1}): 2030 $\nu_{(N3terminal)}$ 1593 $\nu_{(C=O)}$, 1543, 1533 $\nu_{(C=O+C=C)}$. ^{1}H NMR ($CDCl_3$, δ): 1.32 (d, 6H, J_{H-H} = 6, $CH(CH_3)_2$), 2.32 (s, 3H, CH_{3cym}), 3.02 (sept, 1H, $CH(CH_3)_2$), 5.32 (d, 2H, J_{H-H} = 6, C_6H_{4cym}), 5.58 (d, 2H, J_{H-H} = 6, C_6H_{4cym}), 6.41 (s, 1H, L4–γH), 7.42–7.87 (m, 10H, Ph).

2.3.10. Preparation of $[(\eta^6\text{-}p\text{-}^i\text{PrC}_6\text{H}_4\text{Me})\text{Ru(L4)(PPh}_3)]\text{BF}_4$ (**12**)

A suspension of complex **9** (100 mg, 0.2 mmol), PPh_3 (51 mg, 0.2 mmol) and NH_4BF_4 (40 mg, 0.39 mmol) in methanol (10 ml) was refluxed for 2 h. Solvent was removed to dryness on vacuum; the residue extracted with chloroform and filtered. Addition of excess hexane to the concentrated solution afforded compound **12** as a yellow solid.

Yield = 75 mg (80%); IR (KBr, cm^{-1}): 1593 $\nu_{(C=O)}$, 1543, 1533 $\nu_{(C=O+C=C)}$, 1081 $\nu_{(B-F)}$. ^{1}H NMR ($CDCl_3$, δ): 1.32 (d, 6H, J_{H-H} = 6, $CH(CH_3)_2$), 2.32 (s, 3H, CH_{3cym}), 3.02 (sept, 1H, $CH(CH_3)_2$), 5.32 (d, 2H, J_{H-H} = 6, C_6H_{4cym}), 5.58 (d, 2H, J_{H-H} = 6, C_6H_{4cym}), 6.41 (s, 1H, L4–γH), 7.42–7.87 (m, 25H, Ph).

2.3.11. General procedure for preparation of $[(\eta^6\text{-arene})\text{Ru(L)-}\{N_3C_2(CO_2R)_2\}]$

(arene = p-^{i}PrC$_6$H$_4$Me, LL = L1, R = Me (**13**); arene = C_6Me_6, LL = L1, R = Me (**14**); arene = C_6Me_6, LL = L2, R = Me (**15**); arene = C_6Me_6, LL = L3, R = Me (**16**); arene = p-^{i}PrC$_6$H$_4$Me, LL = L1, R = Et (**17**); arene = C_6Me_6, LL = L1, R = Et (**18**); arene = C_6Me_6, LL = L2, R = Et (**19**); arene = C_6Me_6, LL = L3, R = Et (**20**)).

Into a round-bottomed flask charged with the azido complex **6** (100 mg, 0.18 mmol) or **7** (100 mg, 0.17 mmol) or $[(\eta^6\text{-}C_6Me_6)\text{Ru(L2)N}_3]$ (100 mg, 0.25 mmol) or $[(\eta^6\text{-}C_6Me_6)\text{Ru (L3)N}_3]$ (100 mg, 0.17 mmol), a fivefold excess of dimethyl acetylenedicarboxylate/diethyl acetylenedicarboxylate and dichloromethane (20 ml) was added. The mixture was stirred at room temperature for 15 h. The solution was reduced to *ca.* 2 ml on rotary evaporator. To this solution, 30 ml of hexane was added whereupon the compound precipitated out as a yellow solid. The solid was collected by centrifuge, washed with hexane (2 × 20 ml) and dried under vacuum.

Complex **13** $[(\eta^6\text{-}p\text{-}^i\text{PrC}_6\text{H}_4\text{Me})\text{Ru(L1)}\{N_3C_2(CO_2Me)_2\}]$: Yield = 71 mg (89.87%); IR (KBr, cm^{-1}): 1724 $\nu_{(C=O}$ of ester group), 1603 $\nu_{(C=O)}$, 1584, 1575 $\nu_{(C=O+C=C)}$, 1476 $\nu_{(C-H\ def)}$, 1440 $\nu_{(C-N)}$, 771 of triazole ring. ^{1}H NMR ($CDCl_3$, δ): 1.23 (d, 6H, J_{H-H} = 6.92, $CH(CH_3)_2$), 2.075 (s, 3H, CH_{3cym}), 2.76 (sept, 1H, $CH(CH_3)_2$), 3.04 (s, 3H, CH_3), 3.76 (s, 6H, CO_2CH_3), 5.57 (d, 2H, J_{H-H} = 8, C_6H_{4cym}), 5.68 (d, 2H, J_{H-H} = 6, C_6H_{4cym}), 7.2–7.5 (m, 8H, C_6H_5 and N1–C_6H_5), 7.79 (d, 2H, J_{H-H} = 7.6, N1–C_6H_5).

^{13}C {^{1}H} NMR ($CDCl_3$, δ): 15.9 (s, CH_3 (C3–CH_3)), 17.87 (s, Me (CMe)), 22.21 (s, Me ($CHMe_2$)), 30.7 (s, CH ($CHMe_2$)), 51.64 (s,

CH_3 (CO_2CH_3)), 80.31–100.73 (C_6H_{4cym}), 106.04 (s, C4), 138.38 (s, C3), 120.47–149.17 (N1–C_6H_5), 127.52–138.34 (Ph (C5′-Ph)), 139.77 (s, C (C–CO_2CH_3)), 162.6 (s, CO_2 (CO_2CH_3)), 163.7 (s, C5), 190.062 (s, CO (C5′-CO)).

Complex **14** [(η^6-C_6Me_6)Ru(L1){$N_3C_2(CO_2Me)_2$}]: Yield = 62 mg (77%); IR (KBr, cm^{-1}): 1734 $\nu_{(C=O\ of\ ester\ group)}$, 1593 $\nu_{(C=O)}$, 1575, 1568 $\nu_{(C=O+C=C)}$, 1474 $\nu_{(C-H\ def)}$, 1441 $\nu_{(C-N)}$, 765 of triazole ring. ^{1}H NMR ($CDCl_3$, δ): 2.07 (s, 18H, C_6Me_6), 2.18 (s, 3H, CH_3), 3.81 (s, 6H, CO_2CH_3), 7.31–7.45 (m, 8H, C_6H_5 and N1–C_6H_5), 7.8 (d, 2H, J_{H-H} = 8, N1–C_6H_5).

^{13}C {^{1}H} NMR ($CDCl_3$, δ): 15.23 (s, Me (C_6Me_6)), 16.28 (s, CH_3 (C3–CH_3), 51.57 (s, CH_3 (CO_2CH_3)), 92.04 (s, C (C_6Me_6)), 106.04 (s, C4), 138.52 (s, C3), 120.35–148.95 (N1–C_6H_5), 127.59–139.5 (Ph (C5′-Ph)), 140.06 (s, C (C–CO_2CH_3)), 162.6 (s, CO_2 (CO_2CH_3)), 163.17 (s, C5), 188.48 (s, CO (C5′-CO)).

Complex **15** [(η^6-C_6Me_6)Ru(L2){$N_3C_2(CO_2Me)_2$}]: Yield = 60 mg (82%); IR (KBr, cm^{-1}): 1736 $\nu_{(C=O}$ of ester group), 1601 $\nu_{(C=O)}$, 1577, 1568 $\nu_{(C=O+C=C)}$, 1474 $\nu_{(C-H\ def)}$, 1440 $\nu_{(C-N)}$, 786 of triazole ring. ^{1}H NMR ($CDCl_3$, δ): 1.95 (s, 6H, L2-CH_3), 2.05 (s, 18H, C_6Me_6), 3.75 (s, 6H, CO_2CH_3), 5.08 (s, 1H, L2-γH).

^{13}C {^{1}H} NMR ($CDCl_3$, δ): 15.05 (s, Me (C_6Me_6)), 27.94 (s, CH_3 (L2-CH_3)), 51.32 (s, CH_3 (CO_2CH_3)), 89.93 (s, C (C_6Me_6)), 98.27 (s, γC (L2-γC)), 140.06 (s, C (C–CO_2CH_3)), 162.86 (s, CO_2(CO_2CH_3)), 182.92 (s, CO (L2-CO).

Complex **16** [(η^6-C_6Me_6)Ru(L3){$N_3C_2(CO_2Me)_2$}]: IR (KBr, cm^{-1}): 1726 $\nu_{(C=O}$ of ester group), 1600 $\nu_{(C=O)}$, 1578, 1575, 1568 $\nu_{(C=O+C=C)}$, 1464 $\nu_{(C-H\ def)}$, 1442 $\nu_{(C-N)}$, 786 of triazole ring. ^{1}H NMR ($CDCl_3$, δ): 1.9 (s, 3H, L3-CH_3), 2.06 (s, 18H, C_6Me_6), 3.5 (s, 6H, CO_2CH_3), 5.5 (s, 1H, L3-γH), 7.1 (m, 3H, L3-Ph), 7.4 (m, 2H, L3-Ph).

^{13}C {^{1}H} NMR ($CDCl_3$, δ): 15.27 (s, Me (C_6Me_6)), 27.58 (s, CH_3 (L3-CH_3)), 51.62 (s, CH_3 (CO_2CH_3)), 92.19 (s, C (C_6Me_6)), 98.7 (s, γC (L3-γC)), 127.12–130.18 (Ph), 140.22 (s, C (C–CO_2CH_3)), 162.98 (s, CO_2 (CO_2CH_3)), 180.86 (s, CO (L3-CO)), 188.13 (s, CO (L3-CO)).

Complex **17** [(η^6-*p*-^{i}PrC_6H_4Me)Ru(L1){$N_3C_2(CO_2Et)_2$}]: Yield = 71 mg (88.4%); IR (KBr, cm^{-1}): 1724 $\nu_{(C=O}$ of ester group), 1605 $\nu_{(C=O)}$, 1594, 1583, 1575 $\nu_{(C=O+C=C)}$, 1474 $\nu_{(C-H\ def)}$, 1440 $\nu_{(C-N)}$, 786 of triazole ring. ^{1}H NMR ($CDCl_3$, δ): 1.2 (d, 6H, J_{H-H} = 7, CH(CH_3)$_2$), 1.3 (t, 6H, OCH$_2$CH_3), 1.9 (s, 3H, CH_{3cym}), 2.2 (s, 3H, CH_3), 2.8 (m, 1H, CH(CH_3)$_2$), 4.3 (q, 4H, OCH_2CH$_3$), 5.6 (d, 2H, J_{H-H} = 6, C_6H_{4cym}), 5.7 (d, 2H, J_{H-H} = 5.6, C_6H_{4cym}), 7.2–7.4 (m, 8H, C_6H_5 and N1–C_6H_5), 7.8 (d, 2H, J_{H-H} = 8, N1–C_6H_5).

^{13}C {^{1}H} NMR ($CDCl_3$, δ): 14.15 (s, CH_3 ($CO_2CH_2CH_3$)), 16.32 (s, CH_3 (C3–CH_3), 18.2 (s, Me (CMe)), 22.24 (s, Me ($CHMe_2$)), 31.02 (s, CH ($CHMe_2$)), 80.09–101.31 (C_6H_{4cym}), 61.21 (s, CH_2 ($CO_2CH_2CH_3$)), 106.06 (s, C4), 138.54 (s, C3), 140.1 (s, C (C–$CO_2CH_2CH_3$)), 120.36–150.0 (N1–C_6H_5), 127.67–139.45 (Ph (C5′-Ph)). 163.25 (s, C5), 162.12 (s, CO_2 (C–$CO_2CH_2CH_3$)), 189.56 (s, CO (C5′–CO)).

Complex **18** [(η^6-C_6Me_6)Ru(L1){$N_3C_2(CO_2Et)_2$}]: Yield = 69 mg (89.6%); IR (KBr, cm^{-1}): 1736 $\nu_{(C=O}$ of ester group), 1601 $\nu_{(C=O)}$, 1594, 1577, 1568 $\nu_{(C=O+C=C)}$, 1474 $\nu_{(C-H\ def)}$, 1440 $\nu_{(C-N)}$, 786 of triazole ring. ^{1}H NMR ($CDCl_3$, δ): 1.23 (t, 6H, OCH$_2$CH_3), 2.07 (s, 18H, C_6Me_6), 2.1 (s, 3H, CH_3), 4.3 (q, 4H, OCH_2CH$_3$), 7.31–7.56 (m, 6H, C_6H_5 and N1–C_6H_5), 7.8 (d, 2H, J_{H-H} = 8, N1–C_6H_5).

^{13}C {^{1}H} NMR ($CDCl_3$, δ): 14.15 (s, CH_3 ($CO_2CH_2CH_3$)), 15.23 (s, Me (C_6Me_6)), 16.32 (s, CH_3 (C3–CH_3), 61.19 (s, CH_2 ($CO_2CH_2CH_3$)), 92.045 (s, C (C_6Me_6)), 106.03 (s, C4), 138.66 (s, C3), 140.05 (s, C (C–$CO_2CH_2CH_3$)), 120.4–148.9 (N1–C_6H_5), 127.56–139.45 (Ph (C5′-Ph)). 163.14 (s, C5), 162.8 (s, CO_2 (C–$CO_2CH_2CH_3$)), 188.61 (s, CO (C5′–CO)).

Complex **19** [(η^6-C_6Me_6)Ru(L2){$N_3C_2(CO_2Et)_2$}]: Yield = 55 mg (78.5%); IR (KBr, cm^{-1}): 1734 $\nu_{(C=O\ of\ ester\ group)}$, 1584, 1571, 1568 $\nu_{(C=O+C=C)}$, 1477 $\nu_{(C-H\ def)}$, 1438 $\nu_{(C-N)}$, 782 of triazole ring. ^{1}H NMR ($CDCl_3$, δ): 1.26 (t, 6H, OCH$_2$CH$_3$), 1.96 (s, 6H, L2-CH_3), 2.05 (s, 18H, C_6Me_6), 4.45 (q, 4H, OCH$_2$CH$_3$), 4.98 (s, 1H, L2-γH).

^{13}C {^{1}H} NMR ($CDCl_3$, δ): 14.17 (s, CH_3 ($CO_2CH_2CH_3$)), 15.36 (s, Me (C_6Me_6)), 28.1 (s, CH_3 (L2-CH_3)), 60.45 (s, CH_2 ($CO_2CH_2CH_3$)), 90.16 (s, C (C_6Me_6)), 96.27 (s, γC (L2-γC)), 141.06 (s, C (C–$CO_2CH_2CH_3$)$_2$), 163.6 (s, CO_2 ($CO_2CH_2CH_3$)), 190.1 (s, CO (L2-CO).

Complex **20** [(η^6-C_6Me_6)Ru(L3){$N_3C_2(CO_2Et)_2$}]: Yield = 68 mg (93%); IR (KBr, cm^{-1}): 1736 $\nu_{(C=O}$ of ester group), 1601 $\nu_{(C=O)}$, 1585, 1577 $\nu_{(C=O+C=C)}$, 1474 $\nu_{(C-H\ def)}$, 1446 $\nu_{(C-N)}$, 790 of triazole ring. ^{1}H NMR ($CDCl_3$, δ): 1.22 (t, 6H, OCH$_2$CH$_3$), 1.95 (s, 3H, L3-CH_3), 2.06 (s, 18H, C_6Me_6), 4.2 (q, 4H, OCH$_2$CH$_3$), 5.32 (s, 1H, L3-γH), 7.4 (m, 3H, L3-Ph), 7.6 (m, 2H, L3-Ph).

^{13}C {^{1}H} NMR ($CDCl_3$, δ): 14.2 (s, CH_3 ($CO_2CH_2CH_3$)), 15.11 (s, Me (C_6Me_6)), 27.58 (s, CH_3 (L3-CH_3)), 60.6 (s, CH_2 ($CO_2CH_2CH_3$)), 91 (s, C (C_6Me_6)), 98.1 (s, γC (L3-γC)), 128.12-130.5 (Ph (L3-Ph)), 140.8 (s, C (C–CO_2CH_3)), 162.86 (s, CO_2 ($CO_2CH_2CH_3$)), 181.6 (s, CO (L3-CO)), 189.03 (s, CO (L3-CO)).

*2.3.12. Preparation of [(η^6-p-^{i}PrC_6H_4Me)Ru(L1)(N_3C_2HCN)] (**21**)*

A round-bottomed flask was charged with the azido complex **6** (100 mg, 0.18 mmol) and fumaronitrile (70 mg, 0.9 mmol) and 20 ml of methanol was added. The mixture was refluxed for 3 h. The solvent was removed by rotary evaporation, the residue dissolved in dichloromethane and concentrated to 2 ml. Addition of excess of hexane gave a chocolate brown precipitate. The chocolate brown solid was collected by centrifuging, washed with hexane (2 × 20 ml) and dried under vacuum.

Yield = 82 mg (89.7%); IR (KBr, cm^{-1}): 2239 $\nu_{CN,}$ 1602 $\nu_{C=O}$, 1593, 1571 $\nu_{(C=O+C=C)}$, 1475 $\nu_{(C-H\ def)}$, 1446 $\nu_{(C-N)}$, 790 for the triazole ring. ^{1}H NMR ($CDCl_3$, δ): 1.3 (d, 6H, J_{H-H} = 6, CH(CH_3)$_2$), 1.6 (s, 3H, CH_{3cym}), 1.8 (m, 1H, CH(CH_3)$_2$), 2.18 (s, 3H, CH_3), 5.2 (d, 2H, J_{H-H} = 4.8, C_6H_{4cym}), 5.4 (d, 2H, J_{H-H} = 5, C_6H_{4cym}), 6.9 (s, 1H, CH), 7.3–7.4 (m, 8H, C_6H_5 and N1–C_6H_5), 7.9 (d, 2H, N1–C_6H_5).

^{13}C {^{1}H} NMR ($CDCl_3$, δ): 16.02 (s, CH_3 (C3–CH_3)), 17.9 (s, Me (CMe)), 22.23 (s, Me ($CHMe_2$)), 31.02 (s, CH ($CHMe_2$)), 80.11–101.28 (C_6H_{4cym}), 106.22 (s, C4), 114.81 (s, C≡N) 134.91 (s, CH), 138.56 (s, C (C≡N)), 138.7 (s, C3), 120.62–150.11 (N1–C_6H_5), 128.11–140.5 (Ph (C5′-Ph)), 164.2 (s, C5), 190.05 (s, CO (C5′–CO)).

*2.3.13. Preparation of [(η^6-C_6Me_6)Ru(L1)(N_3C_2HCN)] (**22**)*

Employing a procedure similar to that described for complex **21**, complex **22** was prepared using complex **7** (100 mg, 0.171 mmol) with a fivefold excess of fumaronitrile (66 mg, 0.855 mmol).

Yield = 71 mg (78%); IR (KBr, cm^{-1}): 2226 $\nu_{CN,}$ 1594, 1577, 1568 $\nu_{(C=O+C=C)}$, 1474 $\nu_{(C-H\ def)}$, 1440 $\nu_{(C-N)}$, 781 for the triazole ring. ^{1}H NMR ($CDCl_3$, δ): 2.072 (s, 18H, C_6Me_6), 2.17 (s, 3H, CH_3), 6.97 (s, 1H, CH), 7.2–7.5 (m, 8H, C_6H_5 and N1–C_6H_5), 7.94 (d, 2H, J_{H-H} = 8, N1–C_6H_5).

^{13}C {^{1}H} NMR ($CDCl_3$, δ): 15.178 (s, Me (C_6Me_6)), 17.02 (s, CH_3 (C3–CH_3), 89.82 (s, C (C_6Me_6)), 106.12 (s, C4), 114.79 (s, C≡N), 135.13 (s, CH), 138.62 (s, C (C≡N)), 138.72 (s, C3), 120.66–150.07 (N1–C_6H_5), 127.621–140.01 (Ph (C5′-Ph), 163.4 (s,C5), 188.83 (s, CO (C5′–CO)).

*2.3.14. Preparation of [(η^6-C_6Me_6)Ru(L2)(N_3C_2HCN)] (**23**)*

A round-bottomed flask was charged with the azido complex [(η^6-C_6Me_6)Ru(L2)N_3] (100 mg, 0.247 mmol), fumaronitrile (96 mg, 1.235 mmol) and 20 ml of dichloromethane. The mixture was stirred for 8 h. The solution was concentrated to 2 ml and excess of hexane was added to give a yellow microcrystalline precipitate. The precipitate was collected by centrifuging, washed with hexane (2×20 ml) and dried under vacuum.

Yield = 69 mg (78.4%); IR (KBr, cm^{-1}): 2229 $\nu_{(C\equiv N),}$ 1577, 1518 $\nu_{(C=O+C=C)}$, 1471 $\nu_{(C-H\ def)}$, 1438 $\nu_{(C-N)}$, 781 for the triazole ring. ^{1}H NMR ($CDCl_3$, δ): 2.07 (s, 18H, C_6Me_6), 2.01 (s, 6H, CH_3), 5.17 (s, 1H, L2-γH), 7.1 (s, 1H, CH).

^{13}C {^1H} NMR ($CDCl_3$, δ): 15.025 (s, Me (C_6Me_6)), 27.85 (s, CH_3 (L2-CH_3)), 92.26 (s, C (C_6Me_6)), 98.862 (s, γC (L2-γC)), 114.91 (s, C≡N), 134.91 (s, CH), 138.56 (s, C (C≡N)), 185.93 (s, CO (L2-CO)).

*2.3.15. Preparation of [(η^6-C_6Me_6)Ru(L3)(N_3C_2HCN)] (**24**)*

Employing a procedure similar to that described above for complex **23**, complex **24** was prepared using [(η^6-C_6Me_6)Ru(L3)N_3] (100 mg, 0.171 mmol) with a fivefold excess of fumaronitrile (66 mg, 0.855 mmol).

Yield = 61 mg (68%); IR (KBr, cm^{-1}): 2239 $\nu_{(C\equiv N)}$, 1584, 1515 $\nu_{(C=O+C=C)}$, 1469 $\nu_{(C-H\ def)}$, 1442 $\nu_{(C-N)}$, 779 for the triazole ring. ^1H NMR ($CDCl_3$, δ): 2.07 (s, 18H, C_6Me_6), 2.01 (s, 3H, CH_3), 5.73 (s, 1H, L3-γH), 7.11 (s, 1H, CH), 7.2–7.9 (m, 5H, L3-Ph).

^{13}C {^1H} NMR ($CDCl_3$, δ): 15.19 (s, Me (C_6Me_6)), 27.94 (s, CH_3 (L3-CH_3)), 91.3 (s, C (C_6Me_6)), 98.062 (s, γC (L3-γC)), 114.45 (s, C≡N), 126.92–132.34 (Ph (L3-Ph)), 139.23 (s, C (C≡N)), 182.3 (s, CO (L3-CO)), 187.32 (s, CO (L3-CO).

3. Results and discussion

3.1. Synthesis of hexamethylbenzene ruthenium (II) chloro bridged dimer

Although most of the early pioneering experiments were performed by conventional methods, in this paper we report a more convenient microwave synthetic method using optimized molar ratios from 1:10 to 1:3 for the reactants and reduced the duration of the preparation from 2 h to 10 min. Moreover, it produced better yields of [(η^6-C_6Me_6)Ru(μ-Cl)Cl]$_2$ in comparison to the conventional method [34]. ^1H NMR spectrum of the complex shows a singlet at δ 2.06 for the methyl protons which is in agreement with the reported result in the literature [34].

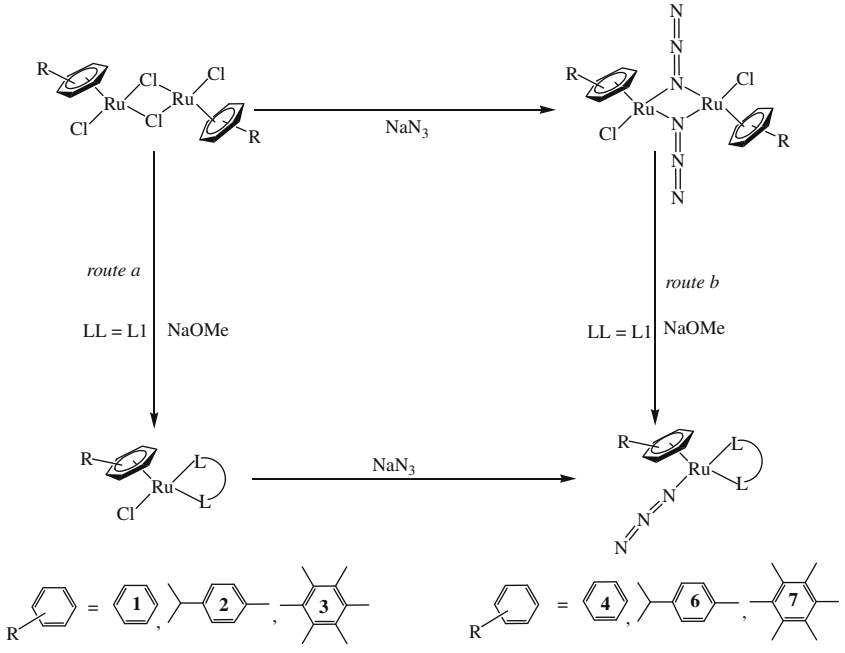
3.2. Synthesis of ligand L1

The ligand L1 was prepared as per the methods reported in the literature [38] and its structure was confirmed by melting point, infrared, mass and NMR spectroscopy. Acylation easily occurs at the C4 position of the pyrazole ring. The neutral ligand L1 is coordinated in O_2-chelating bidentate keto-amino tautomeric form to the metal. The IR spectrum of L1 showed a broad band at 3000 cm^{-1}, a medium peak at 1758 cm^{-1} due to $\nu_{C=O}$ and a $\nu_{C=O}$+$\nu_{C=C}$ conjugated peak at 1508 cm^{-1}. The presence of a strong broad band around 3000 cm^{-1} arises from intra-molecular O–H···O bonding, indicating that L1 exist in the enol form. The disappearance of this band upon complexation indicates presence of the deprotonated L1 ligand in the complexes **1–3**. The melting point recorded at 120 °C is in agreement with the reported result, and indicates intra-molecular O–H···O bonding in this ligand [38]. The ^1H NMR spectrum of the ligand exhibits a singlet at δ 2.0 for methyl protons, multiplets in the aromatic region at δ 7.3–7.4 and a doublet at δ 7.8 for the two phenyl groups. The increasing number of signals in the multiplet aromatic region and the absence of a singlet at the region *ca.* δ 3–3.5 confirmed acylation at the C4 position. The calculated mass of L1 is 278.29 and the MS recorded *m*/*z* is 279.0. The increase in *m*/*z* ratio from 174.9 of phenyl pyrazole moiety to 279.0 in the acyl pyrazolone ligand L1 also confirmed bonding of the acyl group to the pyrazole ring.

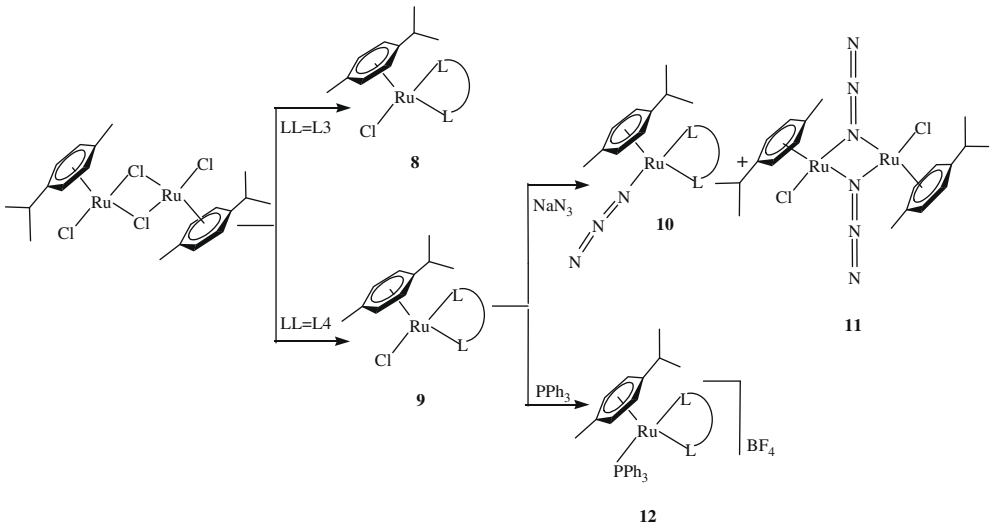
3.3. Syntheses of ruthenium β-diketonato complexes

The precursor complexes [(η^6-arene)Ru(μ-Cl)Cl]$_2$ (arene = C_6H_6, *p*-^{i}PrC_6H_4Me, C_6Me_6) undergo a bridged cleavage reaction in 1:2 molar ratio with the ligand L1 in methanol and in the presence of a base such as sodium methoxide, giving the mononuclear complexes **1–3** (Scheme 1). In these reactions, the products **1–3** are precipitated during the course of reaction. The compounds **1–3** are air stable and soluble in most organic solvents, but complexes **2** and **3** are more soluble in almost all polar solvents compared to complex **1**.

IR spectra show a typical low frequency shift of $\nu_{C=O}$ from 1683 cm^{-1} in the ligand to 1600–1603 cm^{-1} in these complexes upon coordination of the chelating bidentate acyl pyrazolone to the metal. The ^1H NMR spectrum of **1** shows a singlet at δ 5.8 assignable to the six arene protons of the monomer. The ^1H NMR spectrum of complex **2** exhibits two doublets at δ 5.2 and δ 5.5 corresponding to two protons each, a singlet at δ 1.6 for the three methyl group protons, a multiplet at δ 2.9 and a doublet at δ 1.3 for one methylene and six methyl protons, respectively. Similarly, the ^1H NMR spectrum of complex **3** shows a downfield shift of the



Scheme 1.



Scheme 2.

arene methyl protons from δ 2.06 in the starting dimer to δ 2.09. The ^{13}C {^1H} NMR spectra also show singlets at δ 15.27 and δ 89.79 corresponding to the carbons of the hexamethylbenzene ring, along with a singlet for the carbonyl group at δ 188.15. Apart from these, in the ^1H NMR spectra of these complexes, the methyl group of the pyrazolate ligand exhibit singlets at δ 2.2–2.5 and a range of multiplets from δ 7.2–7.5 and a doublet at δ 7.8–7.9 for the aromatic protons. These spectroscopic data confirmed the formation of these complexes.

The reaction of $[(\eta^6\text{-}p\text{-}^i\text{PrC}_6\text{H}_4\text{Me})\text{Ru}(\mu\text{-Cl})\text{Cl}]_2$ with 2 equiv. of the sodium salt of 1-benzoylacetone (L3) or dibenzoylmethane (L4) at ambient temperature in methanol for 2 h afforded orange-red colored compounds of the formula $[(\eta^6\text{-}p\text{-}^i\text{PrC}_6\text{H}_4\text{Me})\text{Ru(LL)Cl}]$ [LL = L3 (**8**); LL = L4 (**9**)] as shown in Scheme 2. The sodium salts were prepared by reacting equimolar amounts of NaOH and the free β-diketones in ethanol at ambient temperature. It was observed that no reactions took place when the free ligands were used. Moreover, attempts to prepare the analogous complexes from the sodium salt of dimethyl or diethylmalonate were unsuccessful, probably due to easy hydrolysis of these ligands.

The IR spectra of both complexes showed bands at *ca.* 1590, 1550, 1520 cm^{-1} which were assigned to the $\nu_{(C=O+C=C)}$ modes of the bidentate *O,O′*-donor ligands.

These complexes are highly soluble in polar solvents. The ^1H NMR spectrum of the complex $[(\eta^6\text{-}p\text{-}^i\text{PrC}_6\text{H}_4\text{Me})\text{Ru(L3)Cl}]$ (**8**) in $CDCl_3$ shows (beside the characteristic peaks corresponding to the *p*-cymene ligand) a singlet for the γ-hydrogen resonating at δ 5.78. This compound also shows two singlets corresponding to the methyl protons at δ 2.28 and δ 2.11. In comparison with the spectrum of the starting dimeric complex, the latter chemical shift may be assigned to the methyl proton of the L3 ligand. The ^1H NMR spectrum of the complex $[(\eta^6\text{-}p\text{-}^i\text{PrC}_6\text{H}_4\text{Me})\text{Ru(L4)Cl}]$ (**9**) is also essentially similar, except that the γ-hydrogens resonate at a relatively lower field (δ 6.38) while 10 multiplets in the aromatic region are observed due to the phenyl groups of the L4 ligand.

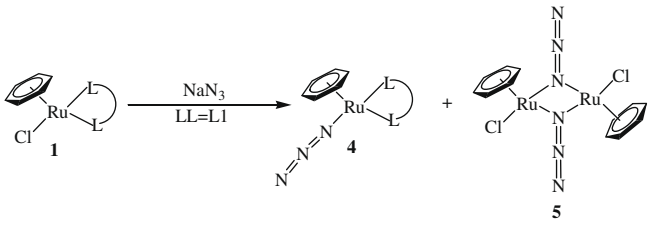
Single crystal X-ray studies of complex **9** confirmed the spectroscopic formulation, and the geometry of the compound can be described as a piano-stool distorted octahedron with the *O,O′* and Cl acting as the legs (Fig 2).

3.4. Syntheses of ruthenium azido complexes

Some initial studies of the reactivity of $[(\eta^6\text{-arene})\text{Ru(L1)Cl}]$ (arene = C_6H_6 (**1**), $p\text{-}^i\text{PrC}_6\text{H}_4\text{Me}$ (**2**), C_6Me_6(**3**)) or $[(\eta^6\text{-}p\text{-}^i\text{PrC}_6\text{H}_4\text{Me})\text{Ru(L4)Cl}]$ (**9**) with azide ion have also been carried out. Treatment of these complexes with mono-dentate ligands such as NaN_3 in polar solvent resulted in substitution of the chloride ligand (Schemes 1 and 2), affording the mononuclear neutral complexes **4**, **6**, **7** and **10** and the azido bridged binuclear complexes **5** and **11**.

One interesting observation is the unexpected formation of the ether-insoluble by-products **5** and **11** during the preparation of **4** and **10**, respectively (Schemes 2 and 3). These complexes show strong characteristic IR absorption bands assigned to the bridged azido ligand, but no bands assignable to $\nu_{C=O}$ (as must be associated with the L1 or L4 ligands) was observed. The ^1H NMR spectra show peaks corresponding to resonance of the protons of the arene ligand but none for the L1 or L4 ligand. We unambiguously propose the formulae $[(\eta^6\text{-}C_6H_6)\text{Ru}(\mu\text{-}N_3)\text{Cl}]_2$ and $[(\eta^6\text{-}p\text{-}^i\text{PrC}_6\text{H}_4\text{Me})\text{Ru}(\mu\text{-}N_3)\text{Cl}]_2$ for **5** and **11**, respectively. It is somewhat difficult to explain how complexes **5** and **11** were generated, which should essentially proceed *via* displacement of the L1 and L4 ligands, respectively. It is probably due to generation of hydrazoic acid (HN_3) under the reaction conditions which would lead to protonation of the β-diketonate ligand and hence result in de-coordination. Repetition of the preparation of **4** and **10** invariably give these by-products **5** and **11**. However, we made no extra efforts to improve the synthetic procedures for the preparation of **5** and **11** as these compounds can be prepared in high yield starting from $[(\eta^6\text{-}C_6H_6)\text{Ru}(\mu\text{-Cl})\text{Cl}]_2$ or $[(\eta^6\text{-}p\text{-}^i\text{PrC}_6\text{H}_4\text{Me})\text{Ru}(\mu\text{-Cl})\text{Cl}]_2$ and trimethylsilyl azide [35] or sodium azide [36]. The IR spectra of complexes **4**, **6**, **7** and **10** show characteristic bands at 2026–2035 cm^{-1} due to the terminally bound azido ligands.

In addition, the terminal azido complexes **4**, **6** and **7** have also been prepared from arene ruthenium azide dimers (Scheme 1: *route b*). Treatment of $[(\eta^6\text{-arene})\text{Ru}(\mu\text{-}N_3)\text{Cl}]_2$ (arene = C_6H_6, $p\text{-}^i\text{PrC}_6\text{H}_4\text{Me}$, C_6Me_6) with ligand L1 in the presence of the proton



Scheme 3.

scavenger sodium methoxide yielded complexes **4**, **6** and **7**. The IR spectra of these complexes show absence of the bridging azido band in the range 2045–2065 cm^{-1} and the appearance of new bands in the range 2026–2035 cm^{-1}. This leads us to infer the formation of terminal azido complexes. Note that this synthetic route does not give the by-product **5**. This accounts for the higher yield of the complexes **4** by this route as compared to that obtained by the previous route (*route a*). Attempts to synthesize $[(\eta^6\text{-}p\text{-}^i PrC_6H_4\text{-}Me)Ru(\mu\text{-}N_3)N_3]_2$ from *p*-cymene ruthenium β-diketone complexes by reacting with NaN_3 have been carried out, but invariably only the azido bridging dimer $[(\eta^6\text{-}p\text{-}^i PrC_6H_4Me)Ru(\mu\text{-}N_3)Cl]_2$ (**10**) was reported, showing the characteristic bridging νN_3 IR band at 2056 cm^{-1} [35]. Structures of the complexes **6** and **10** are further confirmed by single crystal X-ray studies (Figs. 1 and 3).

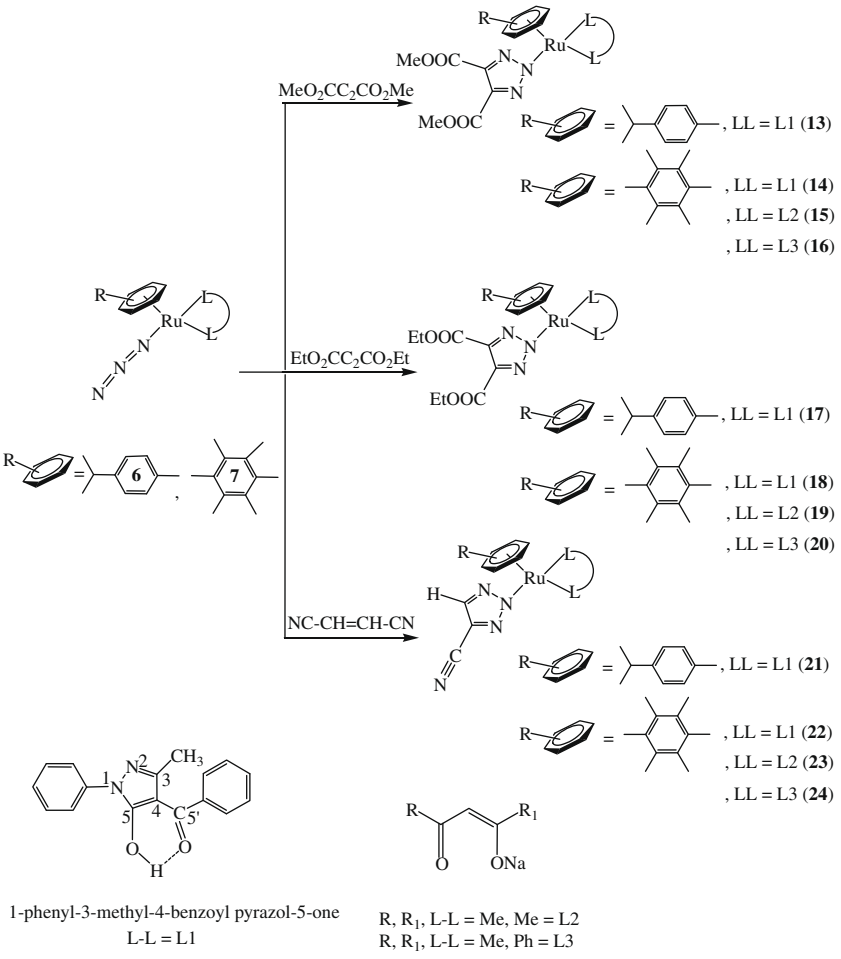
3.5. Synthesis of cationic complex

Treatment of the complex $[(\eta^6\text{-}p\text{-}^i PrC_6H_4Me)Ru(L4)Cl]$ (**9**) with phosphine generates the cationic complex **12** which was isolated in good yield (80%) as the BF_4 salt. Formation of the cationic complex is confirmed by the appearance of the $\nu_{C=O}$ absorption band at 1593 cm^{-1} and of the strong $\nu_{(B-F)}$ absorption band at 1081 cm^{-1}.

3.6. Reaction of ruthenium azido complexes with DMD or DED

The reaction of terminal azido complexes with a fivefold excess of dimethyl acetylenedicarboxylate ($MeO_2CC_2CO_2Me$) (DMD) or diethyl acetylenedicarboxylate ($EtO_2CC_2CO_2Et$) (DED) in dichloromethane at room temperature afforded the yellow ruthenium triazolato complexes in good yield (Scheme 4). The absence of a νN_3 terminal absorption band at 2026–2035 cm^{-1} and the presence of a strong $\nu_{C=O}$ absorption band (for the ester group of the triazole moiety at around 1724–1736 cm^{-1}) in the IR spectra of complexes **13–20** indicate the occurrence of 1,3-dipolar cycloaddition between $Ru\text{–}N_3$ and the substituted alkyne (DMD or DED). In addition to the C=O stretching frequencies, the IR spectra of these complexes show a pair of strong bands at around 1568–1585 cm^{-1} which are assignable to coupled (C=O) + (C=C) modes of β-diketonate [42,43].

The 1,3-dipolar cycloaddition of complex azides and non-terminal alkynes, a direct route to 1,2,3-triazoles, is usually slow, not regioselective and concerted [24,27]. The nature of the substituent/group(s) influences the regioselectivity of these reactions. Depending on the nature of the alkyne employed here (dialkylacetylenedicarboxylate), the regioselectivity seems to be governed primarily by the electronic, and, possibly, the steric factor. Reactivity of the dipolarophile increases with increased electron-withdrawing power of its substituents and the reaction rate is also influenced by the electron-releasing power of the terminal nitrogen atom of the azide ligand [26]. It had been considered in the case of cobalt chelate complexes that the scope of cycloaddition reactions of azido complexes can be considerably widened by including metal chelates that provide substantial electron delocalization in the chelate ring and a suitable steric environment for uninhibited approach of a dipolarophile toward the azide [26]. The same



Scheme 4.

situation probably prevails here for these cases of ruthenium chelate diketone complexes.

Previous results revealed that the triazole anion could be coordinated by a metal through either its N(1) or N(2) nitrogen atoms [27,44] which are essentially isoenergetic as indicated by molecular orbital calculations [28,44]. Evidence obtained to date indicated that both the two isomers [corresponding to coordination at N(1) and at N(2)] were formed simultaneously [26–28,44], or else only the N(2) bound isomer was produced exclusively [27,26,45,46]. In contrast to the result published earlier by our group [13], we here obtain only the N(2) bound isomers for both alkoxy substituted acetylenes. Ellis et al. have reported the initial formation of the 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 [47]. It is believed that the triazolato complexes initially form the N(1) bonded complexes. Published results have confirmed that the N(1) bound isomers are definitely the kinetic product of these reactions; the isolated thermodynamically stable product is the N(2) bound isomer. Isomerization from N(1) to N(2) bound triazole is most likely sterically promoted, as has been found for the analogous tetrazolato complexes [48], while electronic factors favor no isomerization at all.

It has been reported that electronic factors such as nucleophilicity of the triazole anion would favor N(1) bound isomers. Accordingly, formation of the N(1) bound isomers would be expected to prevail in the *ethoxy* substituted triazolato complexes, as has been observed in previous work reported from our laboratory [13]. However, supporting data in this present work confirms the formation of only the N(2) bonded complexes for both type of *alkoxy* substituted triazole. As supported by previous discussions, the steric factor involved in the chelating β-diketone ligand would favor formation of the N(2) bound triazolato complexes. On the basis of spectroscopic data and X-ray analysis, both the *methoxy* and the *ethoxy* substituted triazolato complexes are confirmed to be N(2) bonded triazolato complexes.

The ^{1}H NMR spectra of complexes **13–16** exhibit a singlet at *ca.* δ 3.5–3.8, assigned to the methoxy carbonyl group protons of the triazolato group. Likewise, the ^{1}H NMR spectra of complexes **17–20** exhibit a quartet at *ca.* δ 4.5 and a triplet at *ca.* δ 1.2–1.3 due to methylene and methyl protons of the ethoxy carbonyl group. In addition, the ^{1}H NMR spectra of complexes **13**, **14**, **17** and **18** exhibit characteristic peaks corresponding to the ligand L1. Similarly, the singlets observed in the region δ 4.9–5.1 for the γ protons indicate coordination of the β-diketone ligand L2 in complexes **15** and **19**, and of L3 in complexes **16** and **20**, respectively. Apart from these, complexes **13** and **17** show peaks for the *p*-cymene moiety, whereas complexes **14–16** and **18–20** exhibit prominent singlet at *ca.* δ 2.07 corresponding to the protons of the methyl groups of the hexamethylbenzene ring. The ^{13}C {^{1}H} NMR of complexes **14–16** and **18–20** exhibit a single resonance at *ca.* δ 162 due to the carbon of the CO_2 group, while the carbons of the β-diketonate group appear at δ 182–190.

3.7. Reaction of ruthenium azido complexes with fumaronitrile

The reaction of ruthenium(II) terminal azido complexes with excess of fumaronitrile at room temperature for 10–15 h affords the N(2) bound 4-cyano-1,2,3-triazole complexes **21–24**. Formation of these triazolato complexes is readily confirmed by the absence of the starting azide stretching frequency and the appearance of a strong band at around 2226–2239 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 show characteristic singlet resonances at around δ 6.9–7.1, assigned to the CH group protons of the triazole ring. Complexes **21** and **22** show a characteristic signal corresponding to the pyrazolone ligand, whereas complexes **23** and **24** exhibit a singlet in the region δ 5.1–5.7 attributed to the γ-proton of the β-diketonato group. In addition, the ^{1}H NMR spectrum of complex **21** contains doublet resonances in the region δ 5.4 corresponding to the *p*-cymene group and arising from the arene ring protons. A multiplet at *ca.* δ 1.8 is due to the C*H*Me group, a singlet at δ 1.6 to the methyl group and a doublet at δ 1.3 to the methyl protons of the isopropyl group. The ^{1}H NMR spectra of complexes **22–24** also show singlets in the region around δ 2.06–2.07 pertaining to the methyl group protons of the hexamethylbenzene ring. Apart from this, the ^{13}C {^{1}H} NMR of these complexes exhibit single resonances at around δ 114–115 due to the C≡N moiety, while the carbon of the β-diketone group appears at δ 185–187. The 1,3-dipolar cycloaddition of coordinated azide to fumaronitrile may take place *via* the C=C or C≡N functionalities. In continuation of our work on other related complexes [13–15,30], we herein report the formation of the triazolato complexes **21–24** by [3 + 2] cyclization between the azido ligand and the C=C double bond following removal of an HCN molecule.

3.8. Molecular structures

Molecular structures of the mononuclear neutral complexes **6**, **9**, **10** and **17** are drawn in ORTEP with atom-labeling schemes as depicted in Figs. 1–4, respectively. The data collection parameters are listed in Table 1, and selected bond lengths and bond angles in Tables 2 and 3, respectively. Complex **6** crystallized in the $P\bar{1}$ space group while complexes **9**, **10** and **17** crystallized in the *P2(1)/c* space group. The *p*-cymene ligand is bonded to the ruthenium atom in η^6-fashion with a Ru(1)–centroid distance of 1.655 Å [13,32]; these complexes adopt a typical three-legged piano-stool conformation with N (or Cl in complex **9**) and the two O-atoms as the legs. Moreover, complexes **6** and **17** acquire quasi-octahedral geometry [32]. The Ru(1)–O(1) and Ru(1)–O(2) bond distances in these complexes range from 2.0652 to 2.093 Å, which is comparable to other reported Ru–O bond lengths [49]. In complex **9**, the Ru(1)–Cl(1) bond length is 2.4173(8) Å, while the Ru(1)–O(1) and Ru(1)–O(2) bond distances are almost the same, being 2.0683(18) and 2.0675(17) Å, respectively. In comparison to **9**, complex **10** possesses a Ru(1)–O(1) bond length of 2.0795(19) Å which is slightly but significantly longer than the reported Ru(1)–O(2) distance of 2.0652(19) Å [13]. The Ru(1)–O(1) and Ru(1)–O(2) bond distances in complex **6** are 2.094(3) Å and 2.092(3) Å, respectively, while for complex **17** these respective bond lengths are 2.0819(19) Å and 2.0937(19) Å, which are comparable to those in the starting azido complex **6**. In comparison to the ruthenium–oxygen bond distances of complexes **9** and **10**, the complexes **6** and **17** possess longer ruthenium–oxygen bond length; this may be attributed to bonding by the pyrozolate ligand. The bond distance between the Ru atom and the ligating nitrogen of the azide group in complex **10** is 2.155(3) Å. The N(1)–N(2)–N(3) bond angle is 174.2(4)° [35], showing a slight deviation from perfectly linear geometry. In comparison to **10**, complex **6** possesses a Ru(1)–N(3) bond length of 2.210(7) Å and the N(3)–N(4)–N(5) bond angle is 169.6(11)°. The bond distances N(1)–N(2) (1.038 Å) and N(2)–N(3) (1.227 Å) in complex **10** differ by only *ca.* 0.2 Å, whereas in complex **6** the bond distances N(4)–N(3) (0.843(11) Å) and N(4)–N(5) (1.462(15) Å) exhibit a larger difference of *ca.* 1.4 Å. Similar results are also observed when complex **6** is compared to other reported complexes [12,13,32]. With respect to the starting azido complex **6**, the Ru(1)–N(1) length in the triazole complex **17** is 2.074(2) Å. It appears that, after undergoing reductive elimination reaction during the course of the 1,3-dipolar cycloaddition reaction [25], the Ru(1)–N(3) bond in the starting azido complex **6** gets converted to a Ru(1)–N(1) bond in the ruthenacycle complex **17**. The N(3)–N(1)–N(2) bond angle in the triazole ring of complex **17** is

113.3(2)°. The triazolato ligand is bonded to the metal through the middle nitrogen with regard to the N(2) isomers in complex **17**, which is different from previously reported results [13], but is in agreement with the results on benzene ruthenium triazolato complexes [14].

4. Conclusions

As a consequence of our quest for the synthesis of new compounds, we have reported herein the synthesis of a few new complexes, and confirmed their formation through various analyses. Apart from acetylacetone derivatives, we have used functionalized β-diketones and 1-phenyl-3-methyl-4-benzoyl pyrazol-5-one in this present work, thereby extending the scope for development of new intermediate ruthenacycle triazole complexes having a pyrazole group fused to the *O,O′*-chelating moiety. In this work, only N(2) bound isomers were formed with dimethyl and diethyl acetylenedicarboxylate ligands, as is the case with benzene [14,30] and indenyl systems [31]. The X-ray crystal structure of complex **17** supports formation of the N(2) bound isomer with diethyl acetylenedicarboxylate, which is not in agreement with previous work on *p*-cymene ruthenium systems [13], where formation of N(1) bound isomers was reported. We conclude here that, in addition to the effects peculiar to each substituted acetylene ligand used; the nature and type of the β-diketone ligand coordinated to the ruthenium center also plays a significantly important role in the formation of isomerized triazoles in the 1,3-dipolar cycloaddition reactions studied here.

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Appendix A. Supplementary data

CCDC 735478, 627022, 627023 and 735479 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.08.006.

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