

Mono and dinuclear arene ruthenium (II) triazoles by 1,3-dipolar cycloadditions to a coordinated azide in ruthenium(II) compounds

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Abstract: The dimeric η^6 -hexamethylbenzene ruthenium(II) triazole compounds of formulation $[\{(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\text{N}_3\text{C}_2(\text{CO}_2\text{R})_2)\}_2(\mu\text{C}_2\text{O}_4)]$ have been synthesized by 1,3-dipolar cycloadditions of coordinated azido compound $[\{(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\text{L}_1)\text{N}_3\}]$ (**1**) with substituted acetylene, $\text{RO}_2\text{CC}_2\text{CO}_2\text{R}$ via unexpected oxidation of coordinated ligand to oxalate (where; $\text{L}_1 = 5\text{-hydroxy-2-(hydroxymethyl)-4-pyrone}$; $\text{R} = \text{Me}$, **3** or Et , **4**). In contrast, a similar 1,3-dipolar cycloaddition reaction of $[\{(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\text{L}_2)\text{N}_3\}]$ (**2**) (where; $\text{L}_2 = \text{tropolone}$) with acetylene yielded monomeric triazole compound $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\text{L}_2)\{\text{N}_3\text{C}_2(\text{CO}_2\text{R})_2\}]$ (where; $\text{R} = \text{Me}$, **5**; Et , **6**). The compounds were characterized by spectroscopic data and structures of representative compounds **4** and **6** have been determined by single crystal X-ray diffraction. The two ruthenium centres in the compound **4**, are linked by tetra dentate oxalate group. Both the compounds **4** and **6** crystallized in a triclinic space group P-1.

Key Words: Ruthenium, triazole, cycloaddition, azide, crystallography.

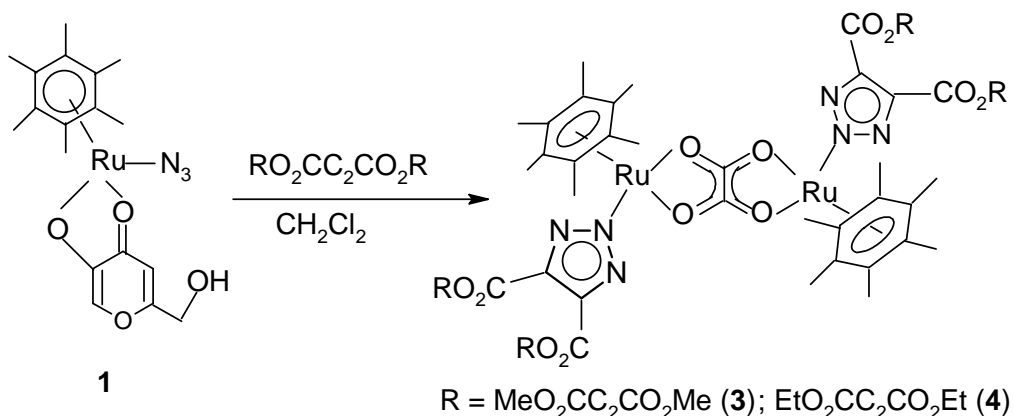
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1,3-dipolar cycloaddition is a common process in organic chemistry for synthesis of 1,2,3-triazoles compounds.¹⁻⁴ The process involves reaction between 1,3-dipoles having allyl or propargylallenyl type of zwitterionic resonating structures and multiples bonded molecules, dipolarophiles. Among the various dipolar addition reactions, organic azides are most widely studied for synthesizing heterocyclic compounds.^{1,5-7} In analogy, coordinated metal azide undergoes cycloaddition reaction with alkynes to yield triazole compounds.⁸ Our group and other have reported some example of such reaction involving metal azide and acetylenes generating triazole compounds.^{9,10} Designing of η^6 -arene ruthenium azide compounds having oxygen chelating group and their subsequent reaction to generate triazole compounds is a subject of our current interest.^{9a,11} Previously, we have reported the synthesis of η^6 -arene ruthenium azido compounds bearing oxygen chelating group such as β diketonate^{9a} and kojic acid ligands.¹¹ Ruthenium azide compound of formulation $[\{(\eta^6\text{-arene})\text{Ru}(\text{L})\text{N}_3\}]$ was readily achieved either by (i) reaction of $[\{(\eta^6\text{-}p\text{-cymene})\text{Ru}(\text{L})\text{Cl}\}]$ (where; L = β -diketonate group) with NaN_3 or (ii) more conveniently by azide cleavage reaction of $[\{(\eta^6\text{-arene})\text{Ru}(\text{N}_3)\text{Cl}\}_2]$ with β -diketonate group.^{9a} However, in our recent finding, it has shown that direct reaction of $[(\eta^6\text{-arene})\text{Ru}(\text{L}_1)\text{Cl}]$ (where; arene = *p*-cymene or C_6Me_6 ; L_1 = 5-hydroxy-2-(hydroxymethyl)-4-pyrone) with NaN_3 in ethanol yielded a tetra azido compound $[\{(\eta^6\text{-arene})\text{Ru}(\mu\text{N}_3)\text{N}_3\}_2]$ instead of the expected mono azido compound $[(\eta^6\text{-arene})\text{Ru}(\text{L}_1)\text{N}_3]$.¹¹ However, mono azido compound $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\text{L}_1)\text{N}_3]$ (**1**) was readily prepared by following the route (ii), and the compound has been fully characterized on the basis of spectroscopic data and the structure was confirmed by X-ray crystallography.¹¹ In contrast to compound **1**, synthesis of compound **2** can be achieved by following either of the two routes i.e. (i) azide cleavage reaction of $[\{(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\text{N}_3)\text{Cl}\}_2]$ with L_2 or (ii) direct reaction of $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\text{L}_2)\text{Cl}]$ with sodium azide. Notably, as mentioned earlier, a direct reaction of $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\text{L}_1)\text{Cl}]$ (**1**) with NaN_3 in ethanol yielded tetra azido compound of formulation $[\{(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\text{N}_3)(\text{N}_3)\}_2]$ but did not yield mono-azido compound $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\text{L}_1)\text{N}_3]$.¹¹ This indicates a difference in the reactivity of L_1 chelating compound $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\text{L}_1)\text{Cl}]$ to that of L_2 chelating compound $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\text{L}_2)\text{Cl}]$, towards sodium azide. As a part of our study on arene ruthenium (II) azide compounds,¹¹ herein, we would like to report, the synthesis of $(\eta^6\text{-C}_6\text{Me}_6)$ ruthenium (II) azido compound **2** and the subsequent 1,3-dipolar cycloaddition reaction of **1** and **2** with substituted alkynes generating dimeric and monomeric $(\eta^6\text{-C}_6\text{Me}_6)$ ruthenium triazole compounds **3-6**.

The synthesis of **3** and **4** were achieved by the reaction of $[\{(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\text{L}_1)\text{N}_3\}]$ (**1**), with $\text{EtO}_2\text{CC}_2\text{CO}_2\text{Et}$ or $\text{MeO}_2\text{CC}_2\text{CO}_2\text{Me}$ in dichloromethane (scheme 1). The compounds were isolated

as a yellow solid stable in air by addition of excess hexane into the reaction mixture (61-69%). We expected a monomeric compound of formulation $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\text{L}_1)\{\text{N}_3\text{C}_2(\text{CO}_2\text{R})_2\}]$, via cycloaddition of azido group with acetylenes. However, the reaction yielded an unexpected dimeric compound $[\{(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\text{N}_3\text{C}_2(\text{CO}_2\text{R})_2)_2(\mu\text{C}_2\text{O}_4)]$ bridged by oxalate group (**3** & **4**). It is believed that the compounds could be formed *via* unexpected oxidation of coordinated ligand to oxalate, during the cycloaddition reaction of azido group with alkynes. Infrared spectrum of **3** and **4** showed a complete disappearance of azide (νN_3) peak at 2030 cm^{-1} observed in the starting compound **1**. The compounds showed a strong peak appeared at 1720 cm^{-1} assignable to $\text{C}=\text{O}$ of $-\text{CO}_2\text{R}$ group. The IR spectrum of the compounds also showed absorption peaks at 1624 cm^{-1} which could be due to oxalate group. The ^1H NMR spectra of **3** and **4** are in consistent with their composition (see Notes and references). The ^1H NMR spectrum of **4** displayed one broad peak at δ 4.31 and 1.34 assignable to the methylene and methyl protons of triazole group. The methyl protons of hexamethylbenzene ring were appeared at δ 2.10. Notably, no signal was observed for alkene proton of coordinated ligand, L_1 which were observed as two doublet at δ 6.27 and 6.61 in the starting compound $[\{(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\text{L}_1)\text{N}_3\}]$ (**1**).¹¹



Scheme 1

The single crystals of **4** suitable for X-ray analysis were obtained by slow diffusion of diethyl ether into dichloromethane solution of **4** over a period of several days. The structure is centrosymmetric and possesses a crystallographic inversion centre at the mid point of C01-C01A vector of the oxalate (figure 1). The compound crystallized in triclinic space group P-1. The distance between the centroid of the C_6Me_6 ring to ruthenium is 1.650 \AA . Both the ruthenium atoms are bounded to the triazole ring through N-(2). The selected bond lengths and bond angles are presented in Table 1. In the structure, the bond distance $\text{Ru}(1)\text{-N}(32)$ is $2.104(5)\text{ \AA}$, which is slightly longer

than that of Ru-N bond distance of 2.099 (2) Å reported in other *p*-cymene ruthenium triazole compounds.^{9a} The C-C bond length of the oxalate group is 1.520 (11) Å, which is comparable to the reported distance in the related *p*-cymene oxalate complex.¹²

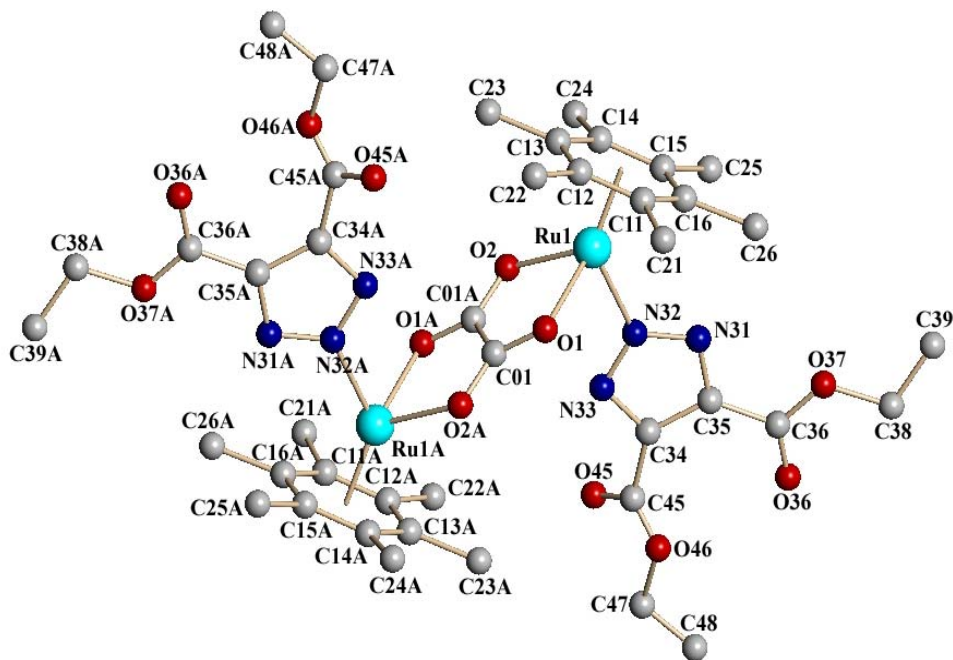


Figure 1. Crystal structure of **4** showing atoms numbering scheme. Hydrogen atoms have been omitted for clarity.

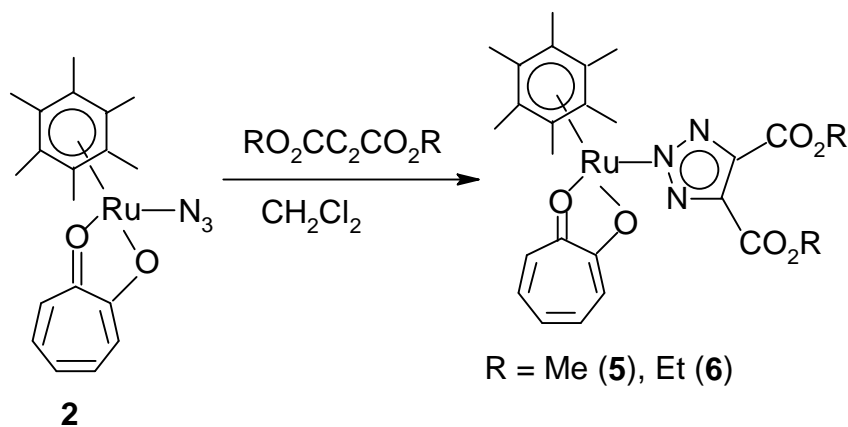
Table1. Selected bond lengths (Å) and bond angles (°) for **4** with esd's

Ru(1)-C*	1.650	Ru(1)-N (32)	2.104 (5)
N(32)-N(33)	1.305 (6)	N(31)-N (32)	1.300 (7)
Ru(1)-O(1)	2.134 (3)	Ru(1)-O(2)	2.123 (4)
C(01A)-O(2)	1.262 (6)	C(01)-O(1)	1.271 (6)
C(01A)-C(01)	1.520 (11)	C(34)-C(35)	1.405 (8)
C(45)-O(45)	1.222 (14)	C(36)-(O36)	1.207 (7)
N33-C34	1.349 (7)	N31-C35	1.349 (7)
C(01)-O1-Ru(1)	112.6 (3)	C(01A)-O2-Ru(1)	112.9 (4)
N(31)-N(32)-N(33)	114.4 (5)	N(32)-N(31)-C(35)	106.2 (5)

O(1)-Ru(1)-O(2)	78.66 (14)	N(32)-N(33)-C(34)	105.5 (5)
O(1)-C(01)-C(01A)	117.6 (6)	O(2A)-C(01)-O(1)	124.5 (5)

C* = Centroid of hexamethylbenzene (C₆Me₆) ring carbons

In order to understand the influence of coordinated ligand in the formation of these dimeric compounds, we have extended our study by choosing another ruthenium azido compound **2**. The compound **2** was fully characterized by FTIR, ¹H and ¹³C{¹H} NMR spectroscopic data. The IR spectrum of compound **2** showed absorption peak at 2029 cm⁻¹ due to νN₃. The ¹³C{¹H} NMR spectrum of **2** showed a singlet at δ 184.71 due to C=O group of L₂. But there is no signal for carbon of C-O, suggesting a delocalisation of C=O in compound **2**, this is contrast to localize C=O bond observed in the related *p*-cymene kojic acid compound.¹¹ Surprisingly, reaction of [(η⁶-C₆Me₆)Ru(L₂)N₃] (**2**) with acetylenes yielded a monomeric triazole compound [(η⁶-C₆Me₆)Ru(L₂){N₃C₂(CO₂R)₂] (where; R = Me (**5**) or Et (**6**)) instead of a dimeric compound analogous to **3** or **4** (Scheme 2). This observation is in support of our assumption that oxalate group of **3&4** could be stem from the oxidation of 5-hydroxy-2-(hydroxymethyl)-4-pyrone (L₁). The compounds **5** and **6** were obtained as yellow solid in good yield (85-87%) by stirring compound **2** with the corresponding acetylenes. The formation of these compounds was readily confirmed by complete disappearance of azide peak at 2029 cm⁻¹, observed in the starting azide compound **2** and appearance of peak at 1730 cm⁻¹ corresponding to -CO₂R group of the coordinated triazole group. Further, the IR spectrum also showed absorption peak at 1590 cm⁻¹ due to C=O group of the coordinated ligand, L₂.



Scheme 2

The ^1H NMR spectrum of compound **6** showed quartet and triplet at δ 4.23 and 1.25 assignable to the methylene and methyl protons of triazole groups. In addition to the signal observed for C_6Me_6 protons at δ 15.2, the ^1H NMR spectra of compounds **5** and **6** also displayed a triplet and multiplet peaks at δ 6.69 and 7.01 assignable to the aromatic protons of coordinating ligand, L_2 . The spectroscopic data are in well agreement with the proposed structures of compounds **5** and **6** and this has been further confirmed by X-ray structure analysis of compound **6** (figure 2). A significant delocalization of bond in the triazole ring of compound **6** is evident from the comparable bond length of the ring atoms. The average bond distance of atoms in the triazole ring is 1.345 (4) Å, this value is comparable to that for compound **4**. Another feature of the structure is comparable bond lengths of C(31)-O(1) and C(32)-O(2) (Table 2), thus suggesting a delocalization of C=O bond in the structure. However, ^{13}C $\{^1\text{H}\}$ NMR of compounds **5** & **6** showed peaks at δ 185.11 and 184.70 assignable to the C=O and C-O group of the coordinated ligand, L_2^{13} and thus, proposed a localised C-O and C=O bond for L_2 in compounds **5**&**6**.

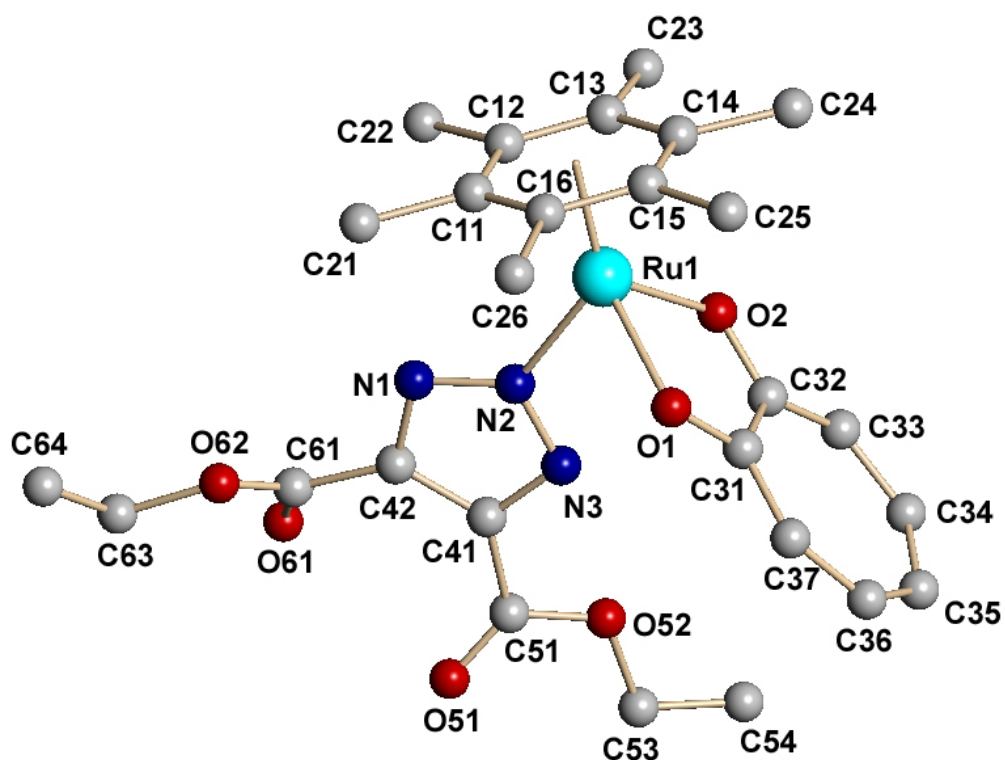


Figure 2. Crystal structure of **6** showing atoms numbering scheme. Hydrogen atoms have been omitted for clarity.

Table 2. Selected bond lengths (Å) and bond angles (°) of **6** with esd's.

Ru(1)-C**	1.663	N(1)-N(2)	1.338(4)
Ru(1)-O(1)	2.084(2)	N(2)-N(3)	1.327(4)
Ru(1)-O(2)	2.077(2)	Ru(1)-N(2)	2.102(3)
N(1)-C(42)	1.340(4)	N(3)-C(41)	1.343(4)
C(41)-C(42)	1.379(5)	C(31)-C(32)	1.454(4)
C(32)-O(2)	1.292(3)	C(31)-O(1)	1.290(4)
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N(1)-N(2)-N(3)	112.9(2)	O(1)-Ru(1)-O(2)	76.73(8)
N(2)-N(1)-C(42)	105.0(3)	N(2)-N(3)-C(41)	105.5(3)
N(1)-C(42)-C(61)	123.0(3)	N(3)-C(41)-C(51)	121.4(3)

C** = Centroid distance of hexamethylbenzene (C₆Me₆) ring carbons

In conclusion, we have demonstrated that η^6 -hexamethylbenzene ruthenium azido compound **2** could be prepared either by (i) azide cleavage reaction of [$\{(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\text{N}_3)\text{Cl}\}_2$] with tropolone (L₂) in the presence of sodium methoxide or (ii) direct reaction of chloro analogue [$\{(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\text{L}_2)\text{Cl}\}$] with NaN₃. The dimeric compounds **3** and **4** were formed when **1** undergoes [3+2] cycloaddition reaction with acetylenes such as EtO₂CC₂CO₂Et or MeO₂CC₂CO₂Me, but a similar cycloaddition reaction of compound **2** yielded monomeric triazole compounds **5&6**.

KSS gratefully acknowledges the Council of Scientific and Industrial Research (CSIR) and the Ministry of Earth Sciences (MoES), India for financial support. We also thank the reviewers for valuable comments.

Notes and references

1 was prepared in 72% yield and fully characterized by spectroscopy and X-ray crystallography.¹¹ **2** was prepared following a similar method reported for **1**, as delineated here. A mixture of **L**₂ (0.019g, 0.16 mmol) and NaOMe (0.0087g, 0.16 mmol) was stirred in MeOH till all the components are completely dissolved. To this solution, the complex [$\{\eta^6\text{-C}_6\text{Me}_6\text{Ru}(\text{N}_3)\text{Cl}\}_2$] (0.05g, 0.073 mmol) was added and the mixture was stirred for 6 hrs. After which the solvent was removed in a rotary evaporator and the residue was extracted with dichloromethane then filtered. Addition of excess hexane to this filtrate afforded red crystals of **2**, after leaving the solution for 2 hrs at room temperature (0.042g, 68% yield). IR (KBr, cm^{-1}): 1124, 1352 ν (C-O), 1504 ν (C=C), 1587 ν (C=O), 2029 ν (N₃); ¹HNMR (CDCl₃, δ): 2.17 (s, 18H), 6.69 (m, 1H), 7.12–7.17(m, 4H). ¹³C{¹H}NMR (CDCl₃, δ): 15.29, 89.79, 125.32, 126.78, 126.87, 137.14, 184.71.

3 was prepared by stirring **1** (0.05g, 0.122mmol) with MeO₂CC₂CO₂Me (0.086g, 0.61mmol) in dichloromethane for 21 hrs. After the solution was reduced to *ca* 3ml excess hexane was added resulting in precipitation of yellow solid (0.08g, 69%).

FTIR (KBr, cm^{-1}): 1506 ν (C=C), 1624 ν (C=O), 1733 (C=O); ¹HNMR (CDCl₃, δ): 2.10 (br s, 36H, C₆Me₆), 3.82 (br s, 12H, Me).

4 was synthesized by following a similar procedure described for **3** using EtO₂CC₂CO₂Et (0.672 mmol) instead of MeO₂CC₂CO₂Me.

Yield: (0.074g, 61%); IR (KBr, cm^{-1}): 1506 ν (C=C), 1633 ν (C=O), 1737 ν (C=O); ¹HNMR (CDCl₃, δ): 1.34 (br s, 12H), 2.10 (br m, 36H, C₆Me₆), 4.31(m, 8H).

5 and **6** were prepared by following a similar method described for **3** and **4** using **2** (0.05g, 0.122mmol) and MeO₂CC₂CO₂Me or EtO₂CC₂CO₂Et (0.67 mmol). The reaction mixture was stirred for 15 hrs.

Yield and spectroscopic data are as follows:

5: (0.056g, 85%); IR (KBr, cm^{-1}): 1182, 1218 ν (C-O), 1509 ν (C=C), 1580 ν (C=O), 1731 ν (C=O); ¹HNMR (CDCl₃, δ): 2.10 (s, 18H), 3.92 (m, 6H), 6.49 (t, 1H, $J_{\text{H-H}} = 5.8$), 7.49 (m, 4H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , δ): 15.23 (CH₃, C₆Me₆), 51.36 (s, CH₃, CO₂(CH₃)), 91.64 (s, ring carbon, C₆Me₆), 125.68 (s), 126.69 (s), 126.97, 137.07 (d, L₂), 140.16 (s, C(CO₂Me)), 162.99 (s, CO₂), 184.70 (s, C-O, L₂), 184.86 (s, C=O, L₂).

6: (0.06g, 87%); IR (KBr, cm^{-1}): 1190, 1224 ν (C-O), 1512 ν (C=C), 1589 ν (C=O), 1732 ν (C=O); ^1H NMR (CDCl_3 , δ): 1.26 (t, 6H), 2.12 (d, 18H, $J_{\text{H-H}} = 6.3$), 4.24 (qt, 4H, $J_{\text{H-H}} = 7.2$), 6.69 (t, 1H, $J_{\text{H-H}} = 6.9$), 7.01 (m, 4H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , δ): 14.17 (s, CH₃, (CO₂CH₂CH₃)), 15.28 (s, CH₃, C₆Me₆), 60.15 (s, CH₂, CO₂CH₂CH₃), 91.64 (s, ring carbon, (C₆Me₆)), 125.44 (s), 126.61 (s), 126.89 (s), 136.49 (s), 140.11 (s, C(CO₂Et)), 162.79 (s, (CO₂)), 184.74 (s, C-O, L₂), 185.11 (s, C=O, L₂).

X-ray data for 4: C₄₂H₅₆N₆O₁₂Ru₂, $M = 1039.08$, transparent plate, triclinic, space group P-1, $a = 8.5202$ (10) Å, $b = 11.2899$ (12) Å, $c = 12.7502$ (14) Å, $\alpha = 95.894$ (9)°, $\beta = 102.640$ (9)°, $\gamma = 109.373$ (9)°, $V = 1108.3$ (2) Å³, $Z = 2$, $D_{\text{calc}} = 1.557$ Mgm⁻³, $T = 293$ (2)° K, with MoK α ($\lambda = 0.71073$ Å), 21097 reflections collected, 5995 unique ($R_{\text{int}} = 0.1771$), $R_1[\text{I} > 2 \sigma (\text{I})] = 0.0536$, wR_2 (F, all data) = 0.0653, GoF = 0.664. CCDC 777765.

X-ray data for 6: C₂₇H₃₃N₃O₆Ru, $M = 596.63$, yellow bar, triclinic, space group P-1, $a = 9.4032$ (4) Å, $b = 11.5596$ (5) Å, $c = 14.4230$ (6) Å, $\alpha = 111.292$ (3)°, $\beta = 92.407$ (4)°, $\gamma = 109.007$ (3)°, $V = 1358.04$ (10) Å³, $Z = 2$, $D_{\text{calc}} = 1.459$ Mgm⁻³, $T = 293$ (2)° K, with MoK α ($\lambda = 0.71073$ Å), 51183 reflections collected, 7374 unique ($R_{\text{int}} = 0.0614$), $R_1[\text{I} > 2 \sigma (\text{I})] = 0.0442$, wR_2 (F, all data) = 0.0867, GoF = 0.919. CCDC 777766.

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