

Syntheses and characterization of η^6 -hexamethylbenzeneruthenium(II)- β -diketone complexes: their reactions with mono- and bidentate neutral ligands

P. Govindaswamy^a, Shaikh M. Mobin^b, Carsten Thöne^c, Mohan Rao Kollipara^{a,*}

^a Department of Chemistry, North Eastern Hill University, Shillong 793022, India

^b National Single Crystal X-ray Diffraction Laboratory, Indian Institute of Technology, Bombay 400 076, India

^c Institut für Anorganische und Analytische Chemieder TU, Hagenring 30, 38106 Braunschweig, Germany

Received 23 September 2004; accepted 15 November 2004

Abstract

The complex $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\mu\text{-Cl})\text{Cl}]_2$ **1** react with sodium salts of β -diketonato ligands in methanol to afford the oxygen bonded neutral complexes of the type $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\kappa^2\text{-O}, O'\text{-R}^1\text{COCHCOR}^2)\text{Cl}]$ $\{\text{R}^1, \text{R}^2 = \text{CH}_3$ (**2**), $\text{CH}_3, \text{C}_6\text{H}_5$ (**3**), C_6H_5 (**4**), OCH_3 (**5**), OC_2H_5 (**6**) $\}$. Complex **4** with AgBF_4 yields the γ -carbon bonded ruthenium dimeric complex **7**. Complex **4** also reacts with tertiary phosphines and bridging ligands to yield complexes of the type $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\kappa^2\text{-O}, O'\text{-C}_6\text{H}_5\text{COCHCOC}_6\text{H}_5)(\text{L})]^+$ ($\text{L} = \text{PPh}_3$ (**8**), PMe_2Ph (**9**)) and $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\kappa^2\text{-O}, O'\text{-C}_6\text{H}_5\text{COCHCOC}_6\text{H}_5)_2(\mu\text{-L})]$ $\text{L} = 4,4'$ -bipyridine ($4,4'$ -bipy) (**11**), 1,4-dicyanobenzene (DCB) (**12**) and pyrazine (Pz) (**13**). Complexes **2–4** react with sodium azide to yield neutral complexes $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\kappa^2\text{-O}, O'\text{-R}^1\text{COCHCOR}^2)\text{N}_3]$ $\{\text{R}^1, \text{R}^2 = \text{CH}_3$ (**10a**), $\text{CH}_3, \text{C}_6\text{H}_5$ (**10b**), C_6H_5 (**10c**) $\}$. All these complexes were characterized by FT-IR and FT-NMR spectroscopy as well as analytical data. The molecular structures of complexes $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\kappa^2\text{-O}, O'\text{-CH}_3\text{COCHCOC}_6\text{H}_5)\text{Cl}]$ (**3**) and $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\kappa^2\text{-O}, O'\text{-C}_6\text{H}_5\text{COCHCOC}_6\text{H}_5)]$ (**4**) were established by single crystal X-ray diffraction studies. The complex **3** crystallizes in the triclinic space group, $P\bar{1}$ [$a = 7.9517(4)$, $b = 9.0582(4)$ and $c = 14.2373(8)$ Å, $\alpha = 88.442(3)^\circ$, $\beta = 76.68(3)^\circ$ and $\gamma = 81.715(3)^\circ$. $V = 987.17(9)$ Å³, $Z = 2$]. Complex **4** crystallizes in the monoclinic space group, $P2_1/c$ [$a = 7.5894(8)$, $b = 20.708(2)$ and $c = 29.208(3)$ Å, $\beta = 92.059(3)^\circ$ $V = 4587.5(9)$ Å³, $Z = 8$].
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Keywords: Hexamethylbenzene; β -diketones; Phosphines; Azide; Bridging ligands; Ruthenium

1. Introduction

The chemistry of half-sandwich η^6 -arene-ruthenium complexes has been widely developed in the past decade, in part due to their catalytic potential, but also due to their usefulness in the synthesis of other Ru(0) and Ru(II) complexes [1–4]. Recently, McNae et al. reported

the first half-sandwich arene ruthenium(II)-enzyme complex which was isolated by the reaction of η^6 -*p*-cymene ruthenium(II) complex with hen egg-white lysozyme [5]. The reactivity of areneruthenium(II) dimers with various ligands has been reported [6]. Only very few reports of the chemistry of areneruthenium(II) complexes containing *O, O'*-donor ligands are available, mainly examples concerned with acetylacetonato [7] and carbonylato complexes [8].

In 1979, Rigby et al. [9] reported the complex $[(\eta^5\text{-C}_5\text{Me}_5)\text{RhCl}(\text{acac})]$ obtained from the $[(\eta^5\text{-C}_5\text{Me}_5)\text{RhCl}_2]_2$ dimer with acetylacetonate salt. It was found that

* Corresponding author. Tel.: +91 364 272 2620; fax: +91 364 255 0076.

E-mail addresses: kmrao@nehu.ac.in, mrkollipara@yahoo.com (M.R. Kollipara).

acetylacetonate (*acac*) is bound in the usual way as a monoanionic bidentate *O,O'*-ligand. In the case of *p*-cymene ruthenium dimer only few example was available with *acac* reported by Oro and coworkers [10] and Bennett et al. [11]. Both were reported as *p*-cymene ruthenium *acac* complexes although structural characterization has not yet been carried out. Herein, we would like to report the synthesis of β -diketonato complexes of $[(\eta^6\text{-C}_6\text{Me}_6)\text{RuCl}_2]_2$ dimer, and their reactions with neutral ligands such as PPh_3 , PMe_2Ph , 4,4'-bipy, DCB and Pz. The representative complexes **3** and **4** were characterized by single crystal X-ray analyses.

2. Experimental

2.1. General considerations

Solvents obtained from commercial sources were distilled prior to use. Ketones, triphenylphosphine (Merck), PMe_2Ph , 4,4'-bipyridine, 1,4-dicyanobenzene, pyrazine (Aldrich), hexamethylbenzene (Acros Organics) and ruthenium trichloride trihydrate purchased from Arora Matthey Ltd, were used as supplied. Infrared spectra of β -diketonates and their ruthenium (II) complexes (KBr, pellets) were recorded in the 4000–400 cm^{-1} range using a Perkin–Elmer-model 983 spectrophotometer. The NMR spectra were taken on Bruker-AMX-400 (400 MHz) and Bruker-ACF-300 (300 MHz) spectrometers with tetramethylsilane as an internal standard. ^{31}P $\{^1\text{H}\}$ NMR chemical shifts were reported relative to H_3PO_4 (85%). Elemental analyses were performed in a Perkin–Elmer-2400 CHN/O analyzer. The precursor complex $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\mu\text{-Cl})\text{Cl}]_2$ **1** was prepared according to the literature method [12].

2.2. Syntheses of β -diketonato and β -dicarbonyl complexes

2.2.1. Syntheses of $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\kappa^2\text{-O},\text{O}'\text{-R}^1\text{COCHCOR}^2)\text{Cl}]$ (**2–6**) $\{R^1, R^2 = \text{CH}_3$ (**2**) [11], CH_3 , C_6H_5 (**3**), C_6H_5 (**4**)}

The following general procedure was used for the syntheses of these three complexes.

A mixture of the starting complex $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\mu\text{-Cl})\text{Cl}]_2$ **1** (100 mg, 0.149 mmol) and the appropriate sodium salt of β -diketonato ligand (0.448 mmol) in methanol (20 ml) were stirred for 3 h while the color of the solution changed red to orange. The solvent was removed in vacuo, the residue dissolved in dichloromethane (5 ml), and the solution filtered to remove sodium chloride. The orange solution was concentrated (2 ml) and an addition of excess hexane gave the orange-yellow complex, which was separated and dried under vacuum.

2 Yield: 68 mg, (53%). IR (KBr pellets, cm^{-1}): $\nu_{\text{C=O}}$ 1580s, $\nu_{\text{C=C}}$ 1520s. ^1H NMR (CDCl_3 , δ): 2.01 (s, 6H, CH₃), 2.07 (s, 18H, HMB), 5.10 (s, 1H, CH).

Elemental analysis (%) for $\text{C}_{17}\text{H}_{25}\text{O}_2\text{ClRu}$: Calculated – C 51.49, H 6.33; found – C 51.36, H 6.41.

3 Yield: 80 mg, (53%). IR (KBr pellets, cm^{-1}): $\nu_{\text{C=O}}$ 1560s, $\nu_{\text{C=C}}$ 1520s. ^1H NMR (CDCl_3 , δ): 2.12 (s, 18H, HMB), 2.15 (s, 3H, CH₃), 5.78 (s, 1H, CH), 7.34–7.42 (m, 3H, Ph), 7.89 (d, 2H, $J_{\text{H-H}}$ 7.16 Hz, Ph).

Elemental analysis (%) for $\text{C}_{22}\text{H}_{27}\text{O}_2\text{ClRu}$: Calculated – C 57.47, H 5.87; found – C 57.63, H 5.24.

4 Yield: 105 mg, (62%). IR (KBr pellets, cm^{-1}): $\nu_{\text{C=O}}$ 1593s, $\nu_{\text{C=C}}$ 1533s. ^1H NMR (CDCl_3 , δ): 2.18 (s, 18H, HMB), 6.47 (s, 1H, CH), 7.39–7.48(m, 6H, Ph), 7.99 (d, 4H, $J_{\text{H-H}}$ 7.00 Hz, Ph).

Elemental analysis (%) for $\text{C}_{27}\text{H}_{29}\text{O}_2\text{ClRu}$: Calculated – C 62.14, H 5.55; found – C 62.31, H 5.96.

2.2.2. Syntheses of β -dicarbonyl complexes

$[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\kappa^2\text{-O},\text{O}'\text{-R}^1\text{COCHCOR}^2)\text{Cl}]$ (**5–6**) $\{R^1, R^2 = \text{OCH}_3$ (**5**), OC_2H_5 (**6**)}

These two complexes were prepared by using the above method except sodium salt of dialkyl malonates used in place of sodium salt of β -diketonato ligand.

5 Yield: 72 mg, (52%). IR (KBr pellets, cm^{-1}): $\nu_{\text{C=O}}$ 1593s, $\nu_{\text{C=C}}$ 1514s. ^1H NMR (CDCl_3 , δ): 2.03 (s, 18H, HMB), 3.74 (s, 6H, CH₃), 5.09 (s, 1H, CH).

Elemental analysis (%) for $\text{C}_{17}\text{H}_{25}\text{O}_4\text{ClRu}$: Calculated – C 47.49, H 5.86; found – C 47.03, H 5.98.

6 Yield: 78 mg, (53%). IR (KBr pellets, cm^{-1}): $\nu_{\text{C=O}}$ 1593s, $\nu_{\text{C=C}}$ 1520s. ^1H NMR (CDCl_3 , δ): 1.99 (t, 6H, $J_{\text{H-H}}$ 5.12 Hz, CH₃), 2.00 (s, 18H, HMB), 3.13 (b, 4H, CH₂), 5.10 (s, 1H, CH).

Elemental analysis (%) for $\text{C}_{19}\text{H}_{29}\text{O}_4\text{ClRu}$: Calculated – C 49.85, H 6.33; found – C 49.36, H 6.53.

2.3. Synthesis of $[(\eta^6\text{-C}_6\text{Me}_6)_2\text{Ru}_2(\kappa^2\text{-O},\text{O}'\text{-C}_6\text{H}_5\text{COCHCOC}_6\text{H}_5)_2](\text{BF}_4)_2$ (**7**)

A suspension of complex **4** (60 mg, 0.115 mmol) and AgBF_4 (44 mg, 0.229 mmol) in dichloromethane (15 ml) was stirred for 1 h. A white solid was precipitated which was filtered off. The solution was concentrated to 2 ml and an addition of excess hexane gave the yellow complex.

Yield: 83 mg, (63%). IR (KBr pellets, cm^{-1}): $\nu_{\text{C=O}}$ 1593s, $\nu_{\text{C=C}}$ 1527s, $\nu_{\text{B-F}}$ 1089s.

^1H NMR (CDCl_3 , δ): 2.18 (s, 36H, HMB), 5.58 (s, 2H, CH), 7.26–7.47 (m, 12H, Ph), 7.93 (d, 8H, $J_{\text{H-H}}$ 6.95 Hz, Ph).

Elemental analysis (%) for $\text{C}_{54}\text{H}_{58}\text{Ru}_2\text{O}_4\text{B}_2\text{F}_8$: Calculated – C 56.55, H 5.09; found – C 56.64, H 4.97.

2.4. Syntheses of $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\kappa^2\text{-O},\text{O}^\prime\text{-C}_6\text{H}_5\text{COCHCOC}_6\text{H}_5)(\text{L})](\text{BF}_4)\{\text{L} = \text{PPh}_3\text{ (8)}, \text{PMe}_2\text{Ph (9)}\}$ complexes

The following general procedure was used for preparing these two complexes.

A mixture of complex **4** (60 mg, 0.115 mmol), the phosphine ligand (0.344 mmol) and NH_4BF_4 (36 mg, 0.344 mmol) was stirred in acetone (15 ml) for 6 h, and the solvent was rotary evaporated. The residue was dissolved in dichloromethane and filtered through a short silica gel column to remove the insoluble material. The filtrate was concentrated to about 2 ml, whereupon addition of excess hexane gave the desired complexes (**8** and **9**) as yellow solids. The solid was washed with diethyl ether and dried under vacuum.

8 Yield: 71 mg, (75%). IR (KBr pellets, cm^{-1}): $\nu_{\text{C=O}}$ 1593s, $\nu_{\text{C=C}}$ 1533s, $\nu_{\text{B-F}}$ 1089s. ^1H NMR (CDCl_3 , δ): 1.83 (s, 18H, HMB), 6.04 (s, 1H, CH), 7.28–7.63 (m, 15H, Ph), 7.68 (d, 10H, $J_{\text{H-H}}$ 7.48 Hz, Ph). ^{31}P $\{^1\text{H}\}$ NMR (CDCl_3 , δ): 32.46 (s).

Elemental analysis (%) for $\text{C}_{45}\text{H}_{44}\text{O}_2\text{PRuBF}_4$: Calculated – C 64.67, H 5.30; found – C 64.58, H 5.15.

9 Yield: 60 mg, (74%). IR (KBr pellets, cm^{-1}): $\nu_{\text{C=O}}$ 1593s, $\nu_{\text{C=C}}$ 1527s, $\nu_{\text{B-F}}$ 1089s. ^1H NMR (CDCl_3 , δ): 1.82 (s, 6H, CH_3), 1.89 (s, 18H, HMB), 5.30 (s, 1H, CH), 7.42–7.59 (m, 9H, Ph), 7.75 (d, 2H, $J_{\text{H-H}}$ 7.37 Hz, Ph), 7.96 (d, 4H, $J_{\text{H-H}}$ 7.15 Hz, Ph). ^{31}P $\{^1\text{H}\}$ NMR (CDCl_3 , δ): 29.75 (s).

Elemental analysis (%) for $\text{C}_{35}\text{H}_{40}\text{O}_2\text{PRuBF}_4$: Calculated – C 59.08, H 5.66; found – C 59.24, H 5.38.

2.5. Syntheses of $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\kappa^2\text{-O},\text{O}^\prime\text{-R}^1\text{COCHCOR}^2)(\text{N}_3)]\{\text{R}^1, \text{R}^2 = \text{CH}_3\text{ (10a)}, \text{CH}_3, \text{C}_6\text{H}_5\text{ (10b)}, \text{C}_6\text{H}_5\text{ (10c)}\}$ complexes

The following general procedure was used for preparing these three complexes.

Method 1: A mixture of complexes (**2–4**) (0.115 mmol) and sodium azide (0.23 mmol) were stirred in dry acetone for 3 h at room temperature, when the orange colored suspension gradually changed to a yellow solution. The solution was concentrated under reduced pressure. The solid was dissolved in dichloromethane and then filtered. The solution was concentrated for 2 ml and an excess of hexane added for precipitation. The yellow colored product was separated out, washed with diethyl ether and dried under vacuum.

10a Yield: 45 mg, (63%). IR (KBr pellets, cm^{-1}): $\nu_{\text{C=O}}$ 1586s, $\nu_{\text{C=C}}$ 1515s, ν_{N_3} 2024s (terminal). ^1H NMR (CDCl_3 , δ): 2.01 (s, 6H, CH_3), 2.04 (s, 18H, HMB), 5.08 (s, 1H, CH).

Elemental analysis (%) for $\text{C}_{17}\text{H}_{25}\text{RuN}_3\text{O}_2$: Calculated – C 50.48, H 6.22, N 10.38; found – C 50.15, H 6.37, N 10.01.

10b Yield: 48 mg, (59%). IR (KBr pellets, cm^{-1}): $\nu_{\text{C=O}}$ 1576s, $\nu_{\text{C=C}}$ 1513s, ν_{N_3} 2026s (terminal).

^1H NMR (CDCl_3 , δ): 2.12 (s, 18H, HMB), 2.14 (s, 3H, CH_3), 5.63 (s, 1H, CH), 7.32–7.38 (m, 3H, Ph), 7.79 (d, 2H, Ph).

Elemental analysis (%) for $\text{C}_{22}\text{H}_{27}\text{RuN}_3\text{O}_2$: Calculated – C 56.63, H 5.83, N 9.00; found – C 56.42, H 5.63, N 8.91.

10c Yield: 53 mg, (57%). IR (KBr pellets, cm^{-1}): $\nu_{\text{C=O}}$ 1593s, $\nu_{\text{C=C}}$ 1533s, ν_{N_3} 2037s (terminal). ^1H NMR (CDCl_3 , δ): 2.19 (s, 18H, HMB), 6.42 (s, 1H, CH), 7.40–8.02 (m, 10H, Ph).

Elemental analysis (%) for $\text{C}_{27}\text{H}_{29}\text{RuN}_3\text{O}_2$: Calculated – C 61.34, H 5.52, N 7.94; found – C 61.06, H 5.32, N 8.03.

Method 2: The above mentioned complexes **10a–c** can be prepared by the reaction of the dimeric complex $[\{\eta^6\text{-C}_6\text{Me}_6\}\text{Ru}(\mu\text{-N}_3)\text{Cl}\}_2]$ [**12c**] (100 mg, 0.146 mmol) with sodium salt of corresponding β -diketonates (0.367 mmol) were stirred in acetone for 3 h at room temperature, while the orange colored suspension gradually changed to a yellow solution. The solution was concentrated under reduced pressure. The solid was dissolved in dichloromethane and then filtered to remove sodium chloride. The solution was concentrated for 2 ml and an excess of hexane added for precipitation. The yellow colored product was separated out, washed with diethyl ether and dried under vacuum. Yield: 55–60%.

2.6. Syntheses of $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\kappa^2\text{-O},\text{O}^\prime\text{-C}_6\text{H}_5\text{COCHCOC}_6\text{H}_5)_2(\mu\text{-L})](\text{BF}_4)_2\{\text{L} = 4,4'\text{-bipy (11)}, \text{DCB (12)}, \text{pz (13)}\}$ complexes

The following general procedure was used for preparation of these three complexes.

A mixture of complex **4** (60 mg, 0.115 mmol), ligand **L** (0.115 mmol) and AgBF_4 (89 mg, 0.46 mmol) were stirred in acetone (15 ml) for 1 h. A white solid was precipitated which was filtered off and the solution was rotary evaporated. The residue was dissolved in dichloromethane and filtered through short silica gel column to remove insoluble material. The filtrate was concentrated to about 2 ml and an addition of excess hexane gave the yellow product, which was separated and dried under vacuum.

11 Yield: 71 mg, (47%). IR (KBr pellets, cm^{-1}): $\nu_{\text{C=O}}$ 1593s, $\nu_{\text{C=C}}$ 1526s, $\nu_{\text{B-F}}$ 1075s. ^1H NMR (CDCl_3 , δ): 2.08 (s, 36H, HMB), 6.27 (s, 2H, CH), 7.44–7.50 (m, 12H, Ph), 7.68–7.89 (m, 8H, Ph), 7.97 (d, 4H, $J_{\text{H-H}}$ 5.90 Hz), 8.59 (d, 4H, $J_{\text{H-H}}$ 5.68 Hz).

Elemental analysis (%) for $C_{64}H_{66}O_4N_2Ru_2B_2F_8$:
Calculated – C 58.99, H 5.10, N 2.15; found – C 58.84, H 5.17, N 2.23.

- 12** Yield: 62 mg, (43%). IR (KBr pellets, cm^{-1}): $\nu_{C=O}$ 1593s, $\nu_{C=C}$ 1533s, ν_{B-F} 1076s. 1H NMR (DMSO- d_6 , δ): 2.13 (s, 36H, HMB), 5.95 (s, 2H, CH), 6.55 (d, 2H, J_{H-H} 4.86 Hz, DCB), 7.12 (d, 2H, J_{H-H} 4.83 Hz, DCB), 7.50–7.96 (m, 12H, Ph), 8.20 (d, 8H, J_{H-H} 7.72 Hz, Ph).

Elemental analysis (%) for $C_{62}H_{62}O_4N_2Ru_2B_2F_8$:
Calculated – C 58.41, H 4.90, N 2.19; found – C 58.16, H 5.03, N 2.13.

- 13** Yield: 63 mg, (45%). IR (KBr pellets, cm^{-1}): $\nu_{C=O}$ 1593s, $\nu_{C=C}$ 1527s, ν_{B-F} 1082s. 1H NMR ($CDCl_3$, δ): 2.07 (s, 36H, HMB), 6.04 (s, 2H, CH), 7.34–7.72 (m, 20H, Ph), 7.78 (d, 2H, J_{H-H} 7.19 Hz), 8.82 (d, 2H, 6.78 Hz).

Elemental analysis (%) for $C_{58}H_{62}O_4N_2Ru_2B_2F_8$:
Calculated – C 56.53, H 5.09, N 2.28; found – C 56.34, H 5.16, N 2.32.

3. Crystallographic investigations

Crystal structure determinations of complexes **3** and **4** were performed on a Bruker SMART 1000 CCD area detector (graphite monochromated Mo $K\alpha$ radiation, $\lambda = 71.073$ pm) at -140 °C in the ω - and ϕ -scan mode. Cell parameters were refined from 7955 number of reflections in the θ -range of 2.31–30.43 for **4**, and from 15,403 number of reflections in the θ -range of 2.27–30.49 for **3**. Empirical absorption corrections were applied using the program SADABS [13]. The structures were solved by direct methods using SHELXS-86/97 [14], and subjected to full-matrix least-squares refinement on F^2 using SHELXL-93/97 [15], with anisotropic displacement parameters for non-H atoms. Methyls were treated as rigid groups. All other hydrogen atoms were included using a riding model. Figs. 1 and 2 are the ORTEP [16] representations of the molecules with 50% probability thermal ellipsoids displayed. Refinement converged at a final R_1 value of 0.0238 for complex **3** and 0.0410 for complex **4** (for observed data F), and wR_2 values of 0.0617 and 0.0826 for complex **3** and **4**, respectively (for unique data F^2).

4. Results and discussion

4.1. β -Diketonato and β -dicarbonyl complexes

The reaction of $[(\eta^6-C_6Me_6)Ru(\mu-Cl)Cl]_2$ **1** with sodium salts of β -diketonates in methanol at room temperature results in the cleavage of the halide bridges of the starting dimer (Fig. 1). The orange-yellow complexes are

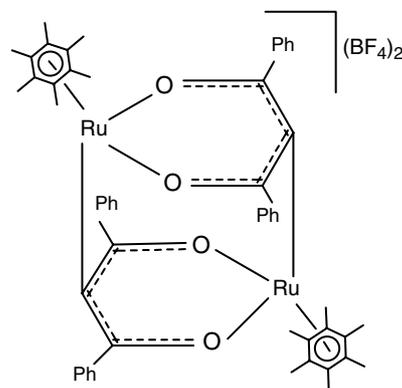


Fig. 1. Complex 7.

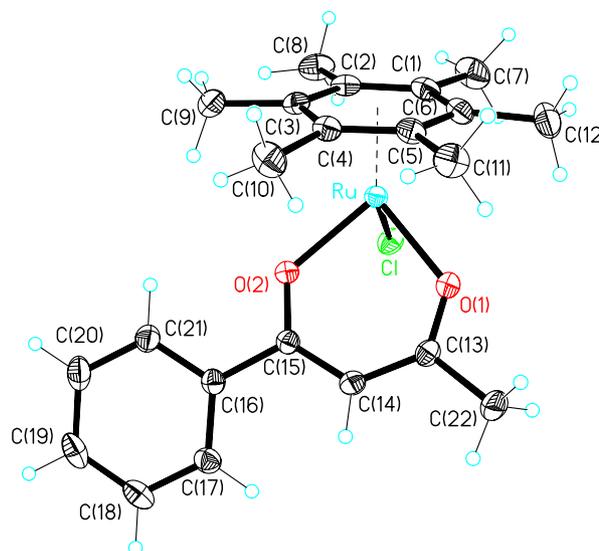
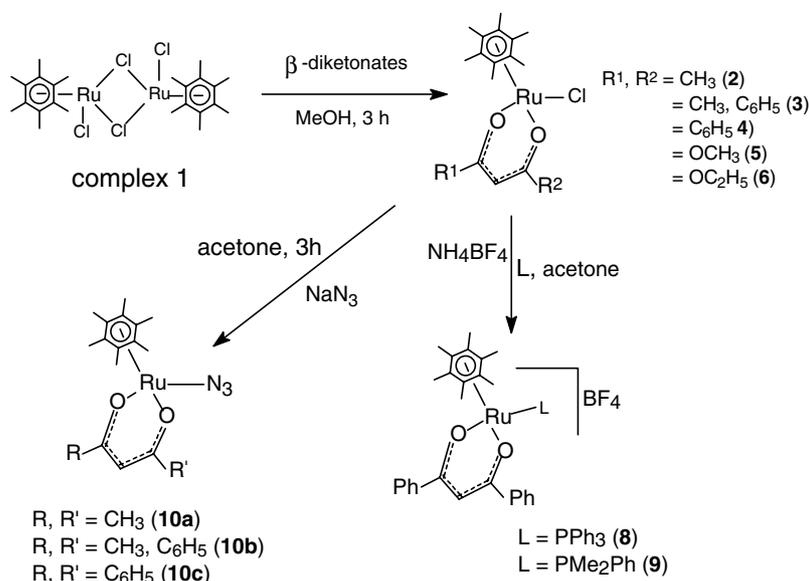


Fig. 2. ORTEP diagram of the complex **3** with 50% probability thermal ellipsoids.

air-stable microcrystalline solids, soluble in chloroform and dichloromethane and partially soluble in benzene or diethylether. These complexes were characterized on the basis of elemental analysis and 1H NMR and IR spectroscopy. The IR spectra show the presence of two ν_{CO} bands in the range 1560–1593 cm^{-1} and $\nu_{C=C}$ bands in the range 1514–1533 cm^{-1} [17–19]. The 1H NMR spectra of these complexes exhibit a strong peak at 2.00–2.12 ppm for hexamethylbenzene, which is slightly shifted downfield in comparison to the starting complex **1**, which exhibits it at 2.02 ppm. Resonance of the C–H proton of the β -diketonato ligands is observed as a singlet in the range 5.10–6.47 ppm in these complexes.

The β -diketonato ruthenium(II) complexes **2–4** undergo substitution reactions with excess of sodium azide in acetone, giving the neutral complexes (**10a–c**) (Fig. 1). The infrared spectra of the complexes **10a–c** show a strong band around 2037 cm^{-1} due to the terminal azide group [12c,20] along with other strong bands due to the



Scheme 1.

ν_{CO} and $\nu_{\text{C}=\text{C}}$ groups of the β -diketonato ligands. The ^1H NMR spectra of these complexes exhibit a strong peak for hexamethylbenzene at 2.04–2.19 ppm.

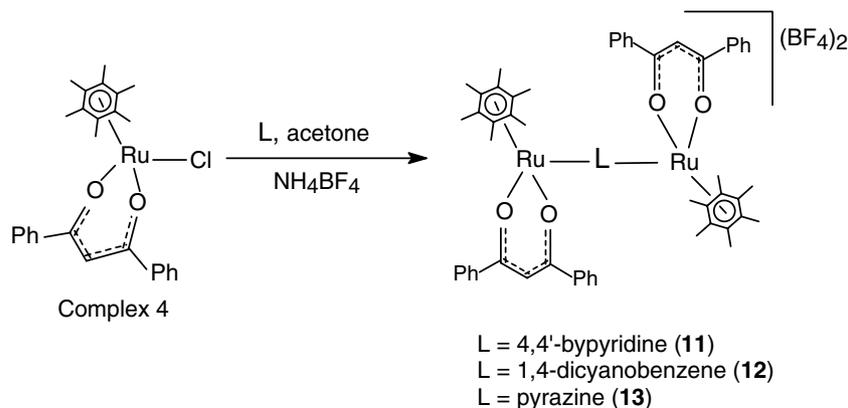
4.2. Cationic complexes

The complex **7** was obtained when the β -diketonato complex **4** was treated with AgBF_4 in dichloromethane. The IR spectra show a strong ν_{CO} band at 1593 cm^{-1} and a $\nu_{\text{C}=\text{C}}$ band at 1527 cm^{-1} . In addition, a strong band appears at 1089 cm^{-1} due to the $\nu_{\text{B-F}}$ mode of the BF_4 group. The elemental analysis and ^1H NMR spectra suggest that the complex **7** is binuclear (Fig. 1) containing a bridging ($\kappa^2\text{-O, O', C-C}_6\text{H}_5\text{COCHCOC}_6\text{H}_5$) group.

This type of bonding (Fig. 1) was also observed in the case of β -diketonato complexes of Cp^*Rh [9] and *p*-cymene osmium [11], where the γ -carbon proton is removed and a metal–carbon bond is formed [21]. The

^1H NMR spectrum of the complex shows a singlet at 2.18 ppm for HMB, and a multiplet for the phenyl groups in the region at 7.26–7.93 ppm.

Treatment of the complex $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\kappa^2\text{-O, O'-C}_6\text{H}_5\text{COCHCOC}_6\text{H}_5)\text{Cl}]$ **4** with phosphine ligands generates the cationic complexes **8** and **9** (Fig. 1), which can be isolated in good yield as their BF_4 salts. The formation of the cationic complexes **8** and **9** is confirmed by the appearance of the ν_{CO} absorption band at 1593 cm^{-1} and $\nu_{\text{B-F}}$ absorption as a strong band at 1089 cm^{-1} . The ^1H NMR spectrum of the complexes shows a singlet for the hexamethylbenzene protons at 1.83 and 1.89 ppm, while the phenyl protons appear in the aromatic region in the range of 7.28–7.96 ppm for both the complexes. The methine (C–H) proton is observed at 6.04 ppm for complex **8** and 5.30 ppm for complex **9**. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of these complexes exhibit a sharp peak at 32.46 ppm for complex **8** and 29.75 ppm for complex **9**.



Scheme 2.

4.3. Binuclear bridging complexes

The reaction of the complex **4** with bridging nitrogen donor ligands in presence of silver tetrafluoroborate in acetone resulted in the formation of yellow-colored and air-stable binuclear complexes **11–13** (Fig. 2), respectively. The formation of these complexes is confirmed by their ^1H NMR spectra. The IR spectra of these complexes show a strong band in the range 1075–1082 cm^{-1} due to the $\nu_{(\text{B-F})}$ mode of the BF_4 group. The ^1H NMR spectra of these complexes exhibit a strong peak for hexamethylbenzene protons as a singlet in the range 2.07–2.13 ppm. The aromatic protons of the ligand L appear as multiplets around 6.55–8.50 ppm for these complexes. The singlet in the range 5.95–6.27 ppm is observed due to the C–H proton of the β -diketonato ligands.

5. Molecular structures

Single-crystal X-ray structure determinations were carried out for complexes **3** and **4** for confirmation of the formulation. Crystals **3** and **4** were grown by slow diffusion of hexane into dichloromethane solution of the complexes. The ruthenium atom is coordinated to two oxygen atoms of the β -diketonato ligand, one chloride ligand and the hexamethylbenzene molecule in η^6 -fashion leading to the usual ‘three-legged piano stool’ structures. The geometry around the metal atom can be regarded as distorted octahedral if the η^6 -hexamethylbenzene moieties are assumed to occupy three facial-coordinated positions. The summary of the single-crystal X-ray structure analyses is shown in Table 1. Selected bond lengths and bond angles are given in Tables 2 and 3. The ORTEP drawings of complexes **3** and **4** are shown in Figs. 2 and 3, respectively.

The complex $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\kappa^2\text{-O, O'}\text{-CH}_3\text{COCHCO}_6\text{H}_5\text{Cl})]$ **3** crystallizes in the triclinic space group $P2_1/c$ (Fig. 2) where as the complex $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\kappa^2\text{-O, O'}\text{-C}_6\text{H}_5\text{COCHCO}_6\text{H}_5\text{Cl})]$ **4** crystallizes in the monoclinic space group $P2_1/c$ (Fig. 3). The distance be-

Table 1
Crystal data and structure refinement parameters for complexes **3** and **4**

	3	4
Formula	$\text{C}_{22}\text{H}_{27}\text{ClO}_2\text{Ru}$	$\text{C}_{27}\text{H}_{29}\text{ClO}_2\text{Ru}$
M_r	459.96	522.02
T (K)	133 (2)	133 (2)
Wavelength (\AA)	0.71073	0.71073
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a (\AA)	7.9517(4)	7.5894(8)
b (\AA)	9.0582(4)	20.708(2)
c (\AA)	14.2373(8)	29.208(3)
α ($^\circ$)	88.442(3)	90
β ($^\circ$)	76.608(3)	92.059(3)
γ ($^\circ$)	81.715(3)	90
V (\AA^3)	987.17(2)	4587.5(9)
Z	2	8
Crystal size (mm^3)	$0.27 \times 0.25 \times 0.16$	$0.18 \times 0.17 \times 0.12$
D_{calc} (g cm^{-3})	1.547	1.512
$F(0\ 0\ 0)$	472	2144
θ ($^\circ$)	1.47–30.03.	1.40–28.00
Reflections collected	21,112	83,882
Independent reflections (R_{int})	5748 (0.0198)	11,040 (0.0887)
Completeness to θ	30.00° – 99.5%	28.00° – 100.0%
Data/parameters	5748/0/242	11,040/0/571
Goodness-of-fit on F^2	1.025	1.037
R_1 [$I > 2\sigma(I)$], wR_2	0.0238, 0.0617	0.0410, 0.0826
R_1 , R_2 (all data)	0.0261, 0.0632	0.0791, 0.0975
Largest differential peak and hole (e \AA^{-3})	1.488 and -0.481	0.784 and -0.563

tween the ruthenium atom and the centroid of ring is 1.648 (1) \AA in complex **3** whereas 1.653 (1) \AA in complex **4**, respectively. These bond lengths are closely related to those in other reported complexes [22]. The Ru–O bond lengths involving in bonding to the -diketonates are 2.0793(11), 2.0749(10) \AA for complex **3** and 2.083(2) and 2.094(2) \AA for complex **4**, respectively, well in accord with the literature values [23]. The Ru–Cl bond length is 2.4197(4) \AA for complex **3** and (2.4199(9) \AA) for complex **4** slightly longer than the other reported Ru–Cl bond distances (2.39 \AA) [24]. The geometry of the complexes is octahedral with a piano-stool structure, and is marked by nearly 90° values for the bond angles between the non-hexamethylbenzene ligands.

Table 2
Selected bond lengths (\AA) and bond angles ($^\circ$) for $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\kappa^2\text{-O, O'}\text{-CH}_3\text{COCHCO}_6\text{H}_5\text{Cl})]$ (**3**)

Bond lengths					
Ru–C(1)	2.1881(15)	Ru–C(2)	2.1937(15)	Ru–C(3)	2.1888(15)
Ru–C(4)	2.1624(15)	Ru–C(5)	2.1808(15)	Ru–C(6)	2.1846(15)
Ru–O(1)	2.0793(11)	Ru–O(2)	2.0749(10)	Ru–Cl	2.4197(4)
O(1)–C(13)	1.2693(19)	O(2)–C(15)	1.2696(18)	Ru–C*	1.648(1)
Bond angles					
O(2)–Ru–O(1)	88.06(4)	O(2)–Ru–Cl	84.63(3)		
O(1)–Ru–Cl	87.07(3)				

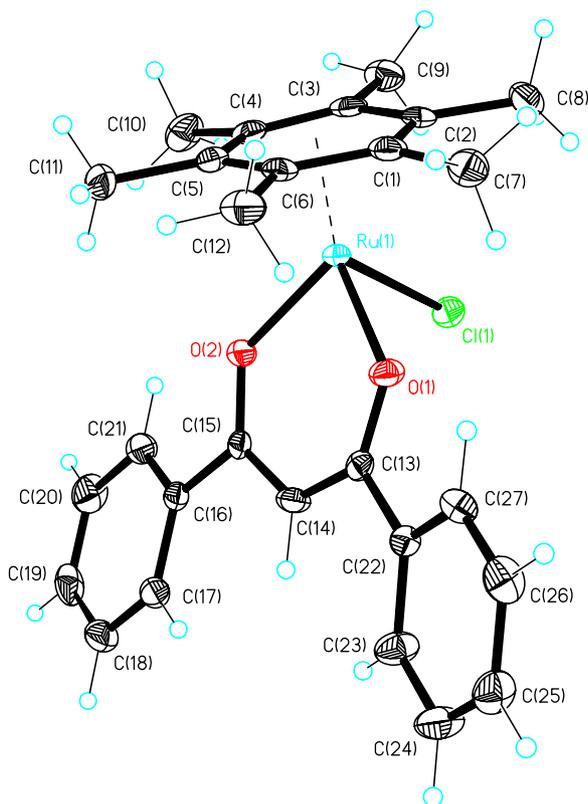
* Ruthenium to centroid of HMB.

Table 3

Selected bond lengths (Å) and bond angles (°) for $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\kappa^2\text{-O, O}'\text{-C}_6\text{H}_5\text{COCHCOC}_6\text{H}_5)\text{Cl}]$ (**4**)

Bond lengths					
Ru(1)–C(1)	2.172(4)	Ru(1)–C(2)	2.172(3)	Ru(1)–C(3)	2.202(4)
Ru(1)–C(4)	2.164(4)	Ru(1)–C(5)	2.197(3)	Ru(1)–C(6)	2.196(4)
Ru(1)–O(1)	2.083(2)	Ru(1)–O(2)	2.094(2)	Ru(1)–Cl(1)	2.4199(9)
O(1)–C(13)	1.276(4)	O(2)–C(15)	1.274(4)	Ru(1)–C*	1.653(1)
Bond angles					
O(1)–Ru(1)–O(2)	88.40(9)	O(2)–Ru(1)–Cl(1)		84.60(7)	
O(1)–Ru(1)–Cl(1)	87.20(7)				

* Ruthenium to centroid of HMB.

Fig. 3. ORTEP diagram of the complex **4** with 50% probability thermal ellipsoids.

Acknowledgements

K.M.R. and P.G. thanks the Sophisticated Instruments Facility (SIF), Indian Institute of Science, Bangalore, for providing the NMR facility. We are grateful to Professor Pradeep Mathur of the National Single Crystal X-ray Facility at the Indian Institute of Technology, Bombay. We also thank Professor R.H. Duncan Lyndogh for his help in preparing the manuscript.

Appendix A. Supplementary data

Crystallographic data (excluding structure factors) for the structures reported in this paper have been

deposited with the Cambridge Crystallographic Data Centre as supplementary Publication Nos. CCDC 246136 for complex **3** and CCDC 246137 for complex **4**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: Int. code +(44) 1223/336033; 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.2004.11.036](https://doi.org/10.1016/j.jorganchem.2004.11.036).

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