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# Part 1: 1,3-Dipolar addition of activated alkyne towards coordinated azido group in ruthenium(II) complexes containing $\eta^5$-cyclichydrocarbons

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**Abstract**

The indenyl and pentamethylcyclopentadienyl ruthenium(II) complexes $[(\eta^5\text{-}L_3)Ru(L_2)Cl]$ ($L_3 = C_9H_7$, $L_2 =$ dppe (**1a**), $L_2 =$ dppm (**1b**); $L_3 = C_5Me_5$, $L_2 =$ dppe (**2a**); $L_2 =$ dppm (**2b**) (where, dppe = $Ph_2PCH_2CH_2PPh_2$ and dppm = $Ph_2PCH_2PPh_2$) reacts with $NaN_3$ to yield the azido complexes $[(\eta^5\text{-}C_9H_7)Ru(L_2)N_3]$, $L_2 =$ dppe (**3a**), dppm (**3b**) and $[(\eta^5\text{-}C_5Me_5)Ru(L_2)N_3]$, $L_2 =$ dppe (**4a**), dppm (**4b**), respectively. The azido complexes undergo [3 + 2] dipolar cycloaddition reaction with dimethylacetylenedicarboxylate to yield triazole complexes $[(\eta^5\text{-}C_9H_7)Ru(L_2)(N_3C_2(CO_2Me)_2)]$, $L_2 =$ dppe (**5a**), dppm (**5b**) and $[(\eta^5\text{-}C_5Me_5)Ru(L_2)(N_3C_2\text{-}(CO_2Me)_2)]$, $L_2 =$ dppe (**6a**), dppm (**6b**), respectively. The complexes were fully characterized on the basis of microanalyses, FT-IR and NMR spectroscopy. The crystal structures of the starting complex (**1a**) and representative complexes **5a**, **5b** and **6a** have been established by single X-ray study.


*Keywords:* Indenyl; Pentamethylcyclopentadienyl; Dimethylacetylenedicarboxylate; Azide; Ruthenium; Crystal structure

## 1. Introduction

1,3-Dipolar cycloaddimbtion is a common process in organic chemistry. The process involves the reaction between 1,3-dipoles having allyl and dipolarophiles type. Among various 1,3-dipoles, organic azides are particularly known to be important for the synthesizing heterocyclic compounds [1–6]. By analogy, Dori and Ziolo [7a] and Fruhauf [7b] have reported that coordinated azide in metal complexes can also undergo cycloaddition reaction. Thus azido complexes have been reported to react with nitriles [8–14] and isonitriles [9,15–17] to produce metal–nitrogen and metal–carbon bonded tetrazoles, respectively. Interestingly it has been reported that tetrazole complexes can also be produce by the reaction of coordinated nitrile in metal complex with $NaN_3$ [18].

Literature surveys, reveals that most of the cycloaddition reactions of the azido complexes have been studied with platinum(II) [11c,16] and palladium(II) metals [14b,19] although a few have been known in compounds of other transition metals, viz., rhodium(I) iridium(I), cobalt(III) and tin(IV) [20]. However, cycloaddition reaction of coordinated azido complexes in half-sandwich systems has not been studied much except a report appeared in cyclopentadienyl ruthenium cases in recent years [21]. In contrast, to the best of our knowledge, such cycloaddition reactions of coordinated azido complexes in indenyl and pentamethylcyclopentadienyl systems have not been studied so far. It has been

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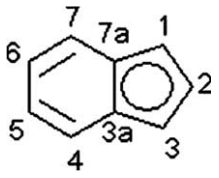
reported that the chemistry of indenyl and pentamethylcyclopentadienyl ruthenium complexes are differ from the analogous cyclopentadienyl ruthenium complex in certain aspects such as higher reactivity and labile nature of the *organic moieties*. The higher reactivity of the Cp* complexes is attributed to the sterric and inductive effect whereas in the case of indenyl complexes ring slippage nature from $\eta^5$- to $\eta^3$- and back to $\eta^5$- of the indenyl ligand is the solely responsible for the high reactivity [22]. It is noteworthy that reversible slippage of the metal across the five-membered ring can form a more reactive $\eta^3$-indenyl tautomer that has both benzenoid resonance stabilization and accesible coordination site [23]. Our current study on the reactivity of the indenyl and Cp* ruthenium bis phosphine complexes, viz., $[Cp^*Ru(PPh_3)_2Cl]$ or $[(ind)Ru(PPh_3)_2Cl]$ (where, ind = indenyl) towards N-base ligands reveals that the stability of the indenyl or Cp* ligands are largely depend on the steric nature of the incoming ligand, such that reaction of $[Cp^*Ru(PPh_3)_2(CH_3CN)]^+$ or $[(ind)Ru(PPh_3)_2(CH_3CN)]^+$ with satirically demanded multidented ligand, tetra-2-pyridyl-1,4-pyrazine (tppz), displaced the *organic moiety* and isolated the complex of the type $[Ru(tppz)(PPh_3)_2(CH_3CN)]^+$ [24]. However, the reaction with less sterric N-base ligand, the *organic moiety* remain intact to the metal and thus forming complex of the type $[\eta^5\text{-}L_3)Ru(PPh_3)(L_2)]^+$ [25] (where $L_3$ = indenyl or Cp*). In general, sterically demanded multidentate ligand displaced them from the complexes. The part 1 of this communication, we described the syntheses of azido complexes of indenyl and pentamethylcyclopentadienyl ruthenium(II) and their reactions with dimethylacetylenedicarboxylate to generate triazole complexes (**5a**,**b** and **6a**,**b**). The spectral and structural characterization of the complexes has been discussed.

## 2. Experimental

All solvents were dried in appropriate drying agents and distilled prior to use [26]. $RuCl_3 \cdot 3H_2O$ (Arora Matthey Limited) and dimethylacetylenedicarboxylate (Aldrich) were used as received. NMR spectra were recorded on an AMX-400 MHz spectrometer at 400.13 ($^1$H), 161.97 ($^{31}$P) or 100.61 MHz ($^{13}$C) with $SiMe_4$ or 85% $H_3PO_4$ as internal references and coupling constants are given in hertz. Infrared spectra were recorded as a KBr pellets on a Perkin–Elmer Model 983 spectrometer. Elemental analyses were carried out at the Regional Sophisticated Instrumentation centre (RSIC) Shillong, using a Perkin–Elmer 2400 CHN/S analyzer. Electronic spectra were recorded on a Hitachi-330 spectrophotometer in dichloromethane at ca. $10^{-4}$ M. The precursor complexes $[(\eta^5\text{-}C_9H_7)Ru(dppe)Cl]$ (**1a**) and $[(\eta^5\text{-}C_9H_7)Ru(dppm)Cl]$ (**1b**) were prepared following a literature method [27] while the complexes $[(\eta^5\text{-}C_5Me_5)Ru(dppe)Cl]$ (**2a**) and $[(\eta^5\text{-}C_5Me_5)Ru(dppm)Cl]$ (**2b**) were prepared by slight modification of the reported method [28] as described below. $^{13}C\{^1H\}$ NMR data for the indenyl complexes are presented in Table 1. The following atom labeling scheme is used for the $^1$H and $^{13}C\{^1H\}$ NMR spectroscopic data of indenyl complexes.




### 2.1. Synthesis of precursor complex $[(\eta^5\text{-}C_5Me_5)Ru(dppe)Cl]$ (**2a**)

A two neck round bottom flask was charged with $[(\eta^5\text{-}C_5Me_5)Ru(PPh_3)_2Cl]$ (100 mg, 0.125 mmol), dppe (60 mg, 0.150 mmol) and 50 ml of toluene was added. The mixture was heated to reflux under nitrogen atmosphere for 15 h and cooled to room temperature. The solvent was removed under reduced pressure and the solid residue was purified by column chromatography over alumina. A bright yellow band was collected when eluted with dichloromethane which on concentration

Table 1
$^{13}C\{^1H\}$ NMR data for the indenyl complexes[a,b]

| Complex | $\eta^5$-$C_9H_7$ | | | | | | Others |
|---|---|---|---|---|---|---|---|
| | C-1,3 | C-2 | C-3a,7a | $\Delta\delta$(C-3a,7a)[b] | C-4,5 | C-6,7 | |
| **3a** | 65.08 | 87.71 | 109.33 | −21.37 | 124.63 | 125.78 | 27.86 (m, $P(CH_2)_2P$), 127.66–133.73 (m, $PPh_2$) |
| **3b** | 63.09 | 87.14 | 109.07 | −21.63 | 123.20 | 125.65 | 49.40 (t, $J_{C-P}$ = 19.7, $(P(CH_2)P)$), 128.32–137.69 (m, $PPh_2$) |
| **5a** | 66.35 | 93.60 | 108.81 | −21.89 | 125.13 | 127.51 | 29.42 (m, $P(CH_2)_2P$), 51.21 (s, $(OCH_3)$), 127.66–133.73 (m, Ph), 138.12 ($C(CO_2Me)$), 167.8 (s, $(CO_2)$) |
| **5b** | 66.50 | 89.44 | 108.76 | −21.94 | 124.98 | 125.18 | 49.66 (t, $J_{C-P}$ = 21.4, $(P(CH_2)P)$), 51.11 (s, $(OCH_3)$), 127.59–134.61 (m, Ph), 138.04 ($C(CO_2Me)$), 168.72 (s, $(CO_2)$) |

[a] Spectra recorded in $CDCl_3$; $\delta$ in ppm and $J$ in Hz. Abbreviations: s, singlet; t, triplet; m, multiplet.
[b] $\Delta\delta$(C-3a,7a) = $\delta$(C-3a,7a)(η-indenyl complex) − $\delta$(C-3a,7a (sodium indenyl)), $\delta$(C-3a, 7a) for sodium indenyl, 130.70 ppm.

to ca. 5 ml and addition of excess hexane induced a bright yellow solid of the complex (**2a**). Yield: 70 mg, 83%. $^1$H NMR ($CDCl_3$, $\delta$): 7.22–7.69 (m, 20H, 4Ph); 2.34–2.04 (2m, 4H, $PCH_2CH_2P$), 1.42 (s, 15H, $C_5Me_5$). $^{31}P\{^1H\}$ ($CDCl_3$, $\delta$): 73.46.

### 2.2. Synthesis of complex [($\eta^5$-$C_5Me_5$)Ru(dppm)Cl] (**2b**)

The complex was prepared by following the same procedure as (**2a**) using dppm instead of dppe and refluxing for 18 h. Yield: 66 mg, 80%.

$^1$H NMR ($CDCl_3$, $\delta$): 7.75–7.25 (m, 20H, 4Ph); 4.92–4.02 (2m, 2H, $PCH_2P$), 1.63 (s, 15H, $C_5Me_5$). $^{31}P\{^1H\}$ ($CDCl_3$, $\delta$): 12.34.

### 2.3. Preparation of complex [($\eta^5$-$C_9H_7$)Ru(dppe)$N_3$] (**3a**)

Two routes were used to synthesize this complex.

Route (a): To a solution of [($\eta^5$-$C_9H_7$)Ru(dppe)Cl] (100 mg, 0.153 mmol) in 30 ml ethanol, was added $NaN_3$ (49 mg, 0.73 mmol). The resulting solution was refluxed for 4 h during this time the color of the solution progressively changed from yellow orange to dark red. The solution was then left at room temperature overnight. The red crystals that deposited were collected by filtration, washed with cold ethanol and air-dried. Additional product may be obtained by evaporating the filtrate under reduced pressure and extracting with $CH_2Cl_2$ and filtered (overall yield = 86 mg, 86%).

Route (b): To a solution of [($\eta^5$-$C_9H_7$)Ru(dppe)Cl] (100 mg, 0.153 mmol) in 30 ml of ethanol, was added $NaN_3$ (49 mg, 0.76mmol). The resulting solution was refluxed for 3 h. The solution was cooled to room temperature. The solvent was removed in rotary-evaporator, the solid residue was extracted with $CH_2Cl_2$ and filtered to remove NaCl and excess $NaN_3$. The filtrate on concentration to ca. 5 ml and addition of excess hexane gave a bright red crystalline solid. Yield: 83 mg, 83%. Anal. Calc. for $C_{35}H_{31}N_3P_2Ru$: C, 63.96; H, 4.72; N, 6.39. Found: C, 63.28; H, 4.03, N, 6.53%.

Spectroscopic data for the complex (**3a**) is as follows: IR (KBr, $cm^{-1}$): $\nu_{(N3)}$ 2024 (vs).

UV–Vis ($\lambda$, nm): 490.

$^1$H NMR ($CDCl_3$, $\delta$): 7.21–7.35 (m, 24H, 4Ph, H-4,7 and H-5,6, indenyl); 4.96 (br, 1H, H-2, indenyl); 4.48 (d, 2H, $J$(HH) = 3.4, H-1,3, indenyl), 2.56–2.26 (2m, 4H, $Ph_2PCH_2CH_2PPh_2$). $^{31}P\{^1H\}$ NMR ($CDCl_3$): 84.27.

### 2.4. Preparation of complex [($\eta^5$-$C_9H_7$)Ru(dppm)$N_3$] (**3b**)

A round bottom flask was charged with [($\eta^5$-$C_9H_7$)Ru(dppm)Cl] (100 mg, 0.157 mmol), $NaN_3$ (51 mg, 0.786 mmol) and 40 ml of ethanol. The resulting solution was refluxed for 5 h. The color of the solution changed from red to brick red. After the mixture was cooled, the solvent was removed by rotary evaporator, the solid residue was extracted with $CH_2Cl_2$ and the extract was filtered. The filtrate on concentration to ca. 5 ml and addition of hexane induced blood red solid. The solid was centrifuged and washed with hexane to give 89 mg, 90% yield of the complex. Anal. Calc. for $C_{34}H_{29}N_3P_2Ru$: C, 63.49; H, 4.51; N, 6.53. Found: C, 63.25; H, 4.82; N, 6.23%.

The spectroscopic data for the complex is as follows: IR (KBr, $cm^{-1}$): $\nu_{(N3)}$ 2030 (vs).

UV–Vis ($\lambda$, nm): 470.

$^1$H NMR ($CDCl_3$, $\delta$): 7.64 (dd, 2H, $J$(HH) = 6.36, $J$(HH) = 3.32, (H-5,6 or H-4,7)); 7.38–7.25 (m, 20H, 4Ph, $Ph_2PCH_2PPh_2$, H-5,6, indenyl), 4.98 (dt, 2H, $J$(HH) = 14.68, $J$(HH) = 10.48, $PCH_aCH_bP$), 4.84 (br, s, 3H, H-1,2,3), 4.12 (dt, 2H, $J$(HH) = 11.36, $J$(HH) = 11.16 Hz, $PCH_aH_bP$). $^{31}P\{^1H\}$ NMR ($CDCl_3$, $\delta$): 14.33.

### 2.5. Preparation of complex [($\eta^5$-$C_5Me_5$)Ru(dppe)$N_3$] (**4a**)

A 100 ml round bottom flask was charged with [($\eta^5$-$C_5Me_5$)Ru(dppe)Cl] (100 mg, 0.149 mmol), $NaN_3$ (48 mg, 0.745 mmol) and ethanol (40 ml). The yellow orange suspension was refluxed for 4 h during this time solution became bright yellow. The reaction mixture was cooled to room temperature and the solvent was removed by rotary evaporator. The solid residue was extracted with 5 ml dichloromethane and filtered to remove NaCl and excess $NaN_3$. The filtrate was concentrated to ca. 5 ml and excess of hexane was added. On reduction the volume of the solution in rotary evaporator a yellow crystalline solid was separated out. The solid was collected and dried in vacuum. Yield: 88 mg, 87%. Anal. Calc. for $C_{36}H_{39}N_3P_2Ru$: C, 63.89; H, 5.76; N, 6.21. Found: C, 63.28, H, 5.17; N, 5.98%.

Spectroscopic data for the complex **4a** are as follows: IR (KBr, $cm^{-1}$): $\nu_{(N3)}$ 2030 (vs).

$^1$H NMR ($CDCl_3$, $\delta$): 7.69–7.20 (m, 20H, 4Ph, $Ph_2PCH_2CH_2PPh_2$), 2.52–2.41 (m, 2H, $Ph_2P(CH_2)_2PPh_2$), 2.13–2.04 (m, 2H, $Ph_2P(CH_2)_2PPh_2$), 1.45 (s, 15H, $C_5Me_5$).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, $\delta$): 138.04–127.79 (m, Ph), 89.67 (s, $C_5Me_5$ (ring C)), 28.67 (t, $P(CH_2)_2P$, $J_{C-P}$ = 21.5), 9.66 (s, $C_5Me_5$, ($CH_3$)). $^{31}P\{^1H\}$ ($CDCl_3$, $\delta$): 75.74.

### 2.6. Preparation of the complex [($\eta^5$-$C_5Me_5$)-Ru(dppm)$N_3$] (**4b**)

This complex was prepared in analogy to the complex (**4a**), [($\eta^5$-$C_5Me_5$)Ru(dppm)Cl] (200 mg, 0.3 mmol), $NaN_3$ (99 mg, 1.5 mmol) EtOH (40 ml) were used. Recrystallization from dichloromethane and hexane gave yellow crystals of complex **4b**. Yield: 87%, 176 mg. Anal. Calc. for $C_{35}H_{37}N_3P_2Ru$: C, 63.43; H, 5.58; N, 6.34. Found: C, 63.98; H, 5.36; N, 6.12%.

IR (KBr, $cm^{-1}$): $\nu_{(N3)}$ 2037 (vs).

$^1H$ NMR ($CDCl_3$, $\delta$): 7.75–7.28 (m, 20H, 4Ph, $Ph_2CH_2Ph_2$), 4.92–4.83 (dt, 1H, $J(HH) = 14.84$, $J(HH) = 9.64$ Hz, $PCH_aCH_bP$), 4.12–4.02 (dt, 1H, $J(HH) = 14.88$, $J(HH) = 10.84$, $PCH_aCH_bP$), 1.68(s, 15H, $C_5Me_5$).

$^{13}C$ $\{^1H\}$($CDCl_3$, $\delta$): 136.32–128.01 (m, Ph), 88.89 (s, $C_5Me_5$(ring)), 49.59 (t, $J_{C-P} = 18.9$, $P(CH_2)P$), 10.36 (s, $C_5Me_5(CH_3)$). $^{31}P\{^1H\}$ ($CDCl_3$, $\delta$): 12.44.

### 2.7. Preparation of indenyl triazole complexes $[(\eta^5\text{-}C_9H_7)Ru(L_2)(N_3C_2(CO_2Me)_2)]$, $L_2$ = dppe (**5a**), dppm (**5b**)

General procedure: To a round bottom flask charged with corresponding azido complex (**3a**) (164 mg, 0.25 mmol) or (**3b**) (160 mg, 0.25 mmol) was added dimethylacetylene-dicarboxylate (177 mg, 1.25 mmol) and $CH_2Cl_2$ (20 ml). The mixture was stirred at room temperature then the solution was reduced to ca. 3 ml in rotary evaporator. To this solution was added 30 ml of hexane, whereby the compound precipitated out as a yellow solid. The solid was collected by centrifuged and washed with $2 \times 20$ ml of hexane and dried under vacuum to gave the N(2)-bound triazole complex $[(\eta^5\text{-}C_9H_7)Ru(L_2)$–$(N_3C_2(CO_2Me)_2)]$ (**5a**) and (**5b**). Yield (%), reaction time, color, analytical and spectroscopic data are as follows: $L_2$ = dppe (**5a**): 92, (183 mg, 0.229 mmol); 8 h, yellow, Anal. Calc. for $C_{41}H_{37}N_3O_4P_2Ru$: C, 61.59; H, 4.63; N, 5.25. Found: C, 61.24; H, 4.23; N, 5.38%. IR (KBr, $cm^{-1}$): $\nu_{(C=O)}$ 1732 (vs), $\nu_{(N=N)}$ 1438(s), $\nu_{(CO)}$ 1295 (m).

UV–Vis ($\lambda$, nm): 423.

$^1H$ NMR ($CDCl_3$, $\delta$): 7.40–6.67 (m, 24H, 4Ph, $Ph_2P(CH_2)_2PPh_2$, H-5,6 and H-4,7, indenyl), 4.87 (t, 1H, J(HH) = 3.8, indenyl), 4.72 (d, 2H, $J(HH) = 3.62$, indenyl), 3.62 (s, 6H, $OCH_3$), 3.14–3.11 (m, 2H, $P(CH_2)_2P$), 2.46–2.44 (m, 2H, $P(CH_2)_2P$).

$^{31}P\{^1H\}$ NMR ($CDCl_3$, $\delta$): 91.16.

$L_2$ = dppm (**5b**): 89 (174 mg, 0.221 mmol), 15 h, yellow orange. Anal. Calc. for $C_{40}H_{35}N_3O_4P_2Ru$: C, 61.16; H, 4.46; N, 5.35. Found: C, 60.87; H, 4.25; N, 5.12%.

IR (KBr, $cm^{-1}$): $\nu_{(C=O)}$ 1725, $\nu_{(N=N)}$ 1440 (m), $\nu_{(CO)}$ 1275 (m).

UV–Vis ($\lambda$, nm): 425.

$^1H$ NMR ($CDCl_3$, $\delta$): 7.59–7.01 (m, 24H, Ph, $Ph_2P(CH_2)PPh_2$, H-5,6, H-4,7, indenyl), 5.29–5.19 (m, 1H, $PCH_aCH_bP$), 4.96–4.87 (br, s, 3H, H-1,2,3, indenyl), 3.91–3.75 (m, 1H, $PCH_aCH_bP$), 3.63 (s, 6H, $2(OCH_3)$).$^{31}P\{^1H\}$ NMR ($CDCl_3$, $\delta$): 14.56.

### 2.8. Preparation of pentamethylcyclopentadienyl N(2)-bound triazole complexes $[(\eta^5\text{-}C_5Me_5)Ru(L_2)$-$(N_3C_2(CO_2Me)_2)]$, $L_2$ = dppe (**6a**), dppm (**6b**)

General procedure: To a round bottom flask charged with corresponding azido complexes (**4a**) (150 mg, 0.221 mmol) or (**4b**) (146 mg, 0.220 mmol) was added dimethylacetylenedicarboxylate (155 mg, 1.10 mmol) and $CH_2Cl_2$ (20 ml). The mixture was stirred at room temperature then the solution was reduced to 3 ml under reduce pressure. To this solution was added excess of hexane. The volume of the resulting solution was reduced in rotary evaporator giving a yellow solid. The yellow solid was collected, washed with hexane $2 \times 10$ ml and dried under vacuum to give triazole complexes (**6a**) and (**6b**). Yield (%), reaction time, color, analytical and spectroscopic data are as follows: $L_2$ = dppe (**6a**): 89 (161 mg, 0.196 mmol), 14 h, yellow.

Anal. Calc. for $C_{42}H_{45}N_3O_4P_2Ru$: C, 61.55; H, 5.49; N, 5.12. Found: C, 60.94; H, 5.28; N, 5.26%. IR (KBr, $cm^{-1}$): $\nu_{(C=O)}$ 1732 (vs), $\nu_{(N=N)}$ 1438(s), $\nu_{(C-O)}$ 1295 (m).

$^1H$ NMR ($CDCl_3$, $\delta$): 7.69–7.07 (m, 20H, 4Ph, $Ph_2P(CH_2)_2PPh_2$), 3.60 (s, 6H, $2CH_3$), 3.53–2.51 (2m, 4H, $P(CH_2)_2P$), 1.43 (s, 15H, $C_5Me_5$).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, $\delta$): 162.13($CO_2$), 138.19 ($C(CO_2Me)$, 134.79–127.44(Ph), 91.70 (ring C ($C_5Me_5$)), 51.01 ($OCH_3$), 31.27 (t, $P(CH_2)_2P$, $J_{C-P} = 33.7$), 9.64 (s, $CH_3$ ($C_5Me_5$)). $^{31}P\{^1H\}$ NMR ($CDCl_3$, $\delta$): 87.32.

$L_2$ = dppm (**6b**): 87 (154 mg, 0.191 mmol), 18 h, yellow, Anal. Calc. for $C_{41}H_{43}N_3O_4P_2Ru$: C, 61.13; H, 5.34; N, 5.21. Found: C, 60.82; H, 5.14; N, 4.98%.

IR (KBr, $cm^{-1}$): $\nu_{(C=O)}$ 1732 (vs), $\nu_{(N=N)}$ 1440(s), $\nu_{(C-O)}$ 1268 (m).

$^1H$ NMR ($CDCl_3$, $\delta$): 7.69–7.11 (m, 20H, Ph), 5.35–5.26 (dt, 1H, $J(HH) = 14.6$Hz, $J(HH) = 11.6$, $PCH_aCH_bP$), 4.99–4.93 (dt, 1H, $J(HH) = 14.68$, $J(HH) = 9.44$, $PCH_aCH_bP$), 3.60 (s, 6H, $2(OCH_3)$), 1.65 (s, 15H, ($C_5Me_5$)).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, $\delta$): 162.49 ($CO_2$), 138.42 ($C(CO_2Me)$), 137.15–127.50 (Ph), 90.66 (ring $C(C_5Me_5)$), 51.48 (t, $J_{C-H} = 21.5$, ($OCH_3$)), 30.88 ($PCH_2P$), 10.31 ($CH_3(C_5Me_5)$). $^{31}P\{^1H\}$ ($CDCl_3$, $\delta$): 15.46.

## 3. Structure analysis and refinement

X-ray quality crystals of all the four complexes **1a**, **5a**, **5b** and **6a** were grown by slow diffusion of hexane into dichloromethane solution of the complexes. The X-ray intensity data were measured at 133(2) K for complexes **1a**, **5a**, **5b** and **6a** on a Bruker Smart 1000 CCD diffractometer, using graphite monochromated Mo K$\alpha$ radiation ($\lambda = 0.71073$ Å). Intensity data were corrected for Lorentz and polarization effects and absorption correction [29] The structures were solved by direct methods (SHELXS-97) [30] and refined by full-matrix least-squares base on $F^2$ using SHELXL-97 [31]. The weighting scheme used $w = 1/[\sigma_2(F_o^2) + aP^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined

using a ''riding'' model or as rigid groups (methyls). Refinement converged at a final $R = 0.0235$, 0.0366, 0.0240 and 0.0331 for complex **1a**, **5a**, **5b** and **6a**, respectively, (for observed data $F$), and $wR_2 = 0.0639$, 0.0998, 0.0626 and 0.0814 for complex **1a**, **5a**, **5b** and **6a**, respectively, (all data on $F^2$). Summary of crystal structures data collection and refinement parameters are given in Table 7 and selected bond lengths and angles have been given in Tables 2–5.

Table 2
Selected bond lengths (Å), angles (°) and slip parameter $\Delta$[a] for the compound **1a**

| | | | |
|---|---|---|---|
| Ru–C[b] | 1.8960(6) | C(12)–C(13) | 1.375(2) |
| Ru–Cl | 2.4331(4) | C(10)–C(11) | 1.368(2) |
| Ru–P(1) | 2.2314(4) | C(2)–P(2) | 1.8353(14) |
| Ru–P(2) | 2.2970(4) | C(1)–P(1) | 1.8590(14) |
| $\Delta_{M-C}$ | 0.158 | | |
| P(1)–Ru–P(2) | 82.171(13) | Ru–P(1)–C(1) | 112.30(5) |
| P(1)–Ru–Cl | 91.509(13) | Ru–P(2)–C(2) | 106.83(4) |
| P(2)–Ru–Cl | 84.087(13) | | |

[a] $\Delta = d_{avg}$ (Ru–C(14), C(18)) − $d_{avg}$ (Ru–C(15), C(17)).
[b] Centroid of C(14), C(15), C(16), C(17), C(18).

Table 3
Selected bond lengths (Å), angles (°), torsion angles (°) and slip parameter $\Delta$[a] for the compound **5a**

| | | | |
|---|---|---|---|
| Ru–C[b] | 1.888(1) | Ru–N(1) | 2.0904(18) |
| Ru–P(1) | 2.2396(6) | Ru–P(2) | 2.2720(6) |
| N(1)–N(2) | 1.336(3) | N(1)–N(3) | 1.336(3) |
| N(2)–C(6) | 1.348(3) | N(3)–C(3) | 1.351(3) |
| C(7)–O(3) | 1.205(3) | C(4)–O(1) | 1.200(3) |
| $\Delta_{M-C}$ | 0.175 | C(3)–C(6) | 1.395(3) |
| P(1)–Ru–P(2) | 84.92(2) | N(2)–N(1)–N(3) | 112.95(17) |
| N(1)–N(2)–C(6) | 105.83(18)[a] | N(1)–N(3)–C(3) | 108.29(19)[a] |
| N(1)–Ru–P(1) | 86.38(5) | N(1)–Ru–P(2) | 89.73(5) |
| N(2)–C(6)–C(3) | 107.67(19) | N(3)–C(3)–C(6) | 108.29(19) |
| N(3)–C(3)–C(4) | 120.7(2) | N(2)–C(6)–C(7) | 121.2(2) |
| P(2)–C(2)–C(1) | 111.1(3) | P(1)–C(1)–C(2) | 108.9(3) |

[a] $\Delta = d_{avg}$(Ru–C(13),C(17)) − $d_{avg}$(Ru–C(14),C(16)).
[b] Centroid of C(13), C(14), C(15), C(16), C(17).

Table 4
Selected bond lengths (Å), angles (°) and slip parameter $\Delta$[a] for the compound **5b**

| | | | |
|---|---|---|---|
| Ru–C[b] | 1.8837(6) | Ru–N(1) | 2.0893(10) |
| Ru–P(1) | 2.3229(3) | Ru–P(2) | 2.2427(3) |
| N(1)–N(2) | 1.3362(15) | N(1)–N(3) | 1.3380(14) |
| N(2)–C(11) | 1.3467(15) | N(3)–C(14) | 1.3493(16) |
| C(12)–O(2) | 1.3369(16) | C(15)–O(3) | 1.2026(16) |
| C(11)–C(14) | 1.3989(17) | $\Delta_{M-C}$ | 0.123 |
| P(1)–Ru–P(2) | 72.003(12) | N(2)–N(1)–N(3) | 113.03(10) |
| Ru–P(1)–P(2) | 52.614(10) | Ru–P(2)–P(1) | 55.384(10) |
| N(1)–N(2)–C(11) | 105.67(10) | N(1)–N(3)–C(14) | 105.37(10) |
| N(1)–Ru–P(1) | 90.46(3) | N(1)–Ru–P(2) | 90.22(3) |
| Ru–P(1)–C(10) | 95.09 (4) | Ru–P(2)–C(10) | 98.04(4) |
| P(1)–C(10)–P(2) | 93.16(6) | | |

[a] $\Delta = d_{avg}$ (Ru–C(5),C(9)) − $d_{avg}$ (Ru–C(6),C(8)).
[b] Centroid of C(5), C(6), C(7), C(8), C(9).

Table 5
Selected bond lengths (Å) and angles (°) for the compound **6a**

| | | | |
|---|---|---|---|
| Ru–C[a] | 1.8798(8) | Ru–N(2) | 2.1010(16) |
| Ru–P(1) | 2.2923(5) | Ru–P(2) | 2.2993(5) |
| N(1)–N(2) | 1.332(2) | N(2)–N(3) | 1.344(2) |
| N(1)–C(15) | 1.350(3) | N(3)–C(16) | 1.340(3) |
| C(14)–O(1) | 1.196(3) | C(17)–O(3) | 1.202(3) |
| C(15)–C(16) | 1.392(3) | C(11)–C(12) | 1.532(3) |
| P(1)–Ru–P(2) | 84.294(18) | N(1)–N(2)–N(3) | 112.45(15) |
| Ru–N(2)–N(1) | 122.97(12) | Ru–N(2)–N(3) | 124.1(2) |
| N(2)–N(1)–C(15) | 105.92(16) | N(2)–N(3)–C(16) | 105.63(16) |
| N(3)–C(16)–C(15) | 108.33(17) | C(15)–C(16)–C(17) | 130.09(19) |

[a] Centroid of C(1), C(2), C(3), C(4), C(5).

Table 6
Hydrogen bonds (Å) and (°) for compounds **5b** and **6a**

| D–H···A | $d$(D–H) | $d$(H···A) | $d$(D···A) | ∠(DHA) |
|---|---|---|---|---|
| *Compound **5b*** | | | | |
| C(45)–H(45)···O(3)#1 | 0.95 | 2.43 | 3.2141(18) | 139.8 |
| C(22)–H(22)···O(3)#2 | 0.95 | 2.68 | 3.4030(17) | 133.9 |
| C(13)–H(13C)···O(2)#3 | 0.98 | 2.62 | 3.3703(19) | 133.2 |
| C(3)–H(3)···O(4)#4 | 0.95 | 2.60 | 3.453(2) | 149.4 |
| C(33)–H(33)···O(3)#4 | 0.95 | 2.64 | 3.510(2) | 152.7 |
| C(2)–H(2)···O(2)#4 | 0.95 | 2.66 | 3.4837(18) | 145.2 |
| C(16)–H(16C)···O(1)#5 | 0.98 | 2.58 | 3.536(3) | 163.8 |
| *Compound **6a*** | | | | |
| C(26)–H(26)···O(1)#6 | 0.95 | 2.41 | 3.122(3) | 131.2 |
| C(43)–H(43)···O(3)#6 | 0.95 | 2.64 | 3.267(3) | 123.9 |

Symmetry transformations used to generate equivalent atoms: #1: $-x$, $-y$, $-z$; #2: $x+1$, $y$, $z$; # 3: $-x+1$, $-y$, $-z+1$; #4: $-x+1$, $-y+1$, $-z+1$; #5: $-x$, $-y$, $-z+1$; #6: $x$, $-y+1/2$, $z-1/2$.

## 4. Results and discussion

### 4.1. Synthetic considerations and spectral studies

#### 4.1.1. Preparation of azido complexes $[(\eta^5\text{-}C_9H_7)Ru(L_2)N_3]$ and $[(\eta^5\text{-}C_5Me_5)Ru(L_2)N_3]$

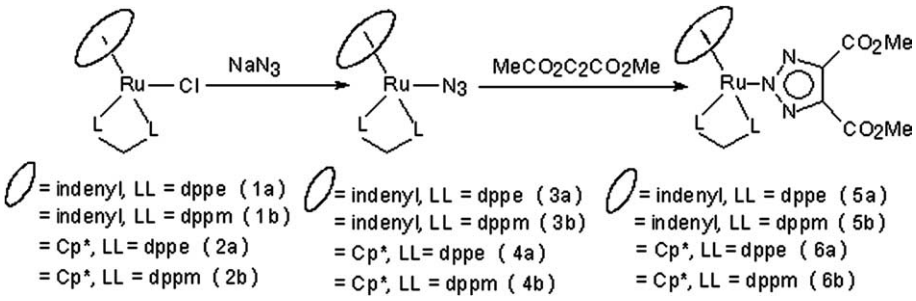
The reaction of $[(\eta^5\text{-}C_9H_7)Ru(L_2)Cl]$ ($L_2$ = dppe(**1a**), dppm(**1b**)) with fivefold excess of $NaN_3$ in refluxing ethanol gives indenyl azido complexes **3a** and **3b** in good yield (86% and 90%) (Scheme 1). Under similar reaction conditions, $[(\eta^5\text{-}C_5Me_5)Ru(L_2)Cl]$ {$L_2$ = dppe (**2a**), dppm (**2b**)} reacts with excess of $NaN_3$ affords corresponding azido complexes **4a** and **4b** (87%) (Scheme 1). All these azido complexes are air stable and soluble in chlorinated solvents. The complexes have been characterized by microanalyses, infrared and NMR ($^1$H), $^{31}$P{$^1$H}, $^{13}$C{$^1$H} spectroscopy (details are given in Section 2). The formation of azido complexes is confirmed by the appearance of strong

Table 7
Summary of crystal structure determination and refinement for complexes **1a**, **5a**, **5b** and **6a**

| Complex | **1a** | **5a** | **5b** | **6a** |
|---|---|---|---|---|
| Empirical formula | $C_{35}H_{37}ClP_2Ru$ | $C_{41}H_{37}N_3O_4P_2Ru$ | $C_{40}H_{35}N_3O_4P_2Ru$ | $C_{42}H_{45}N_3O_4P_2Ru$ |
| Formula weight | 650.06 | 798.75 | 784.72 | 818.82 |
| $T$ (K) | 133(2) | 133(2) | 133(2) | 133(2) |
| $\lambda$ (Å) | 0.71073 | 0.71073 | 0.71073 | 0.71073 |
| Crystal system | Monoclinic | Monoclinic | Triclinic | Monoclinic |
| Space group | $P2_1/c$ | $P2_1/c$ | $P\bar{1}$ | $P2_1/c$ |
| Unit cell dimensions | | | | |
| $a$ (Å) | 13.2690(8) | 13.0622(8) | 11.5173(6) | 12.5815(8) |
| $b$ (Å) | 10.6998(6) | 12.2684(8) | 12.6026(8) | 13.5221(8) |
| $c$ (Å) | 21.0635(12) | 23.3982(14) | 14.3999(8) | 22.3516(14) |
| $\alpha$ (°) | | | 91.852(3) | |
| $\beta$ (°) | 107.947(3) | 104.963(3) | 109.856(3) | 97.701(3) |
| $\gamma$ (°) | | | 114.218(3) | |
| $V$ (Å$^3$) | 2845.0(3) | 3622.5(4) | 1756.58(17) | |
| $Z$ | 4 | 4 | 2 | 4 |
| $Dcal$ (Mg/m$^3$) | 1.518 | 1.465 | 1.484 | 1.443 |
| Absorption coefficient (mm$^{-1}$) | 0.782 | 0.568 | 0.584 | 0.548 |
| $F$(000) | 1328 | 1640 | 804 | 1696 |
| Crystal size (mm$^3$) | $0.38 \times 0.34 \times 0.21$ | $0.25 \times 0.19 \times 0.18$ | $0.39 \times 0.38 \times 0.18$ | $0.28 \times 0.22 \times 0.17$ |
| $\theta$ Range for data collection (°) | 1.61–30.03 | 1.80–30.03 | 1.53–30.03 | 1.63–30.03 |
| Index ranges | $-18 \leqslant h \leqslant 18$, $-15 \leqslant k \leqslant 15$, $-29 \leqslant l \leqslant 29$ | $-18 \leqslant h \leqslant 18$, $-17 \leqslant k \leqslant 17$, $-32 \leqslant l \leqslant 32$ | $-16 \leqslant h \leqslant 16$, $-17 \leqslant k \leqslant 17$, $-20 \leqslant l \leqslant 20$ | $-17 \leqslant h \leqslant 17$, $-19 \leqslant k \leqslant 19$, $-31 \leqslant l \leqslant 31$ |
| Reflections collected | 59146 | 75429 | 35066 | 78441 |
| Independent reflections ($R_{int}$) | 8313 (0.0246) | 10589 (0.0470) | 10230 (0.0185) | 11011 (0.0549) |
| Completeness to $\theta$ (°) | 30.00 | 30.00 | 30.00 | 30.00 |
| Absorption correction | Semi-empirical from equivalents | | | |
| Maximum and minimum transmission | 0.8530 and 0.7452 | 0.9047 and 0.7965 | 0.9021 and 0.7326 | 0.9126 and 0.7896 |
| Refinement method | Full-matrix least-squares on $F^2$ | | | |
| Data/restraints/parameters | 8313/0/352 | 10589/21/481 | 10230/0/453 | 11011/0/476 |
| Goodness-of-fit on $F^2$ | 1.068 | 1.063 | 1.023 | 1.056 |
| Final $R$ indices [$I > 2\sigma(I)$] | $R_1 = 0.0235$, $wR_2 = 0.0598$ | $R_1 = 0.0366$, $wR_2 = 0.0882$ | $R_1 = 0.0240$, $wR_2 = 0.0602$ | $R_1 = 0.0331$, $wR_2 = 0.0718$ |
| $R$ indices (all data) | $R_1 = 0.0291$, $wR_2 = 0.0639$ | $R_1 = 0.0562$, $wR_2 = 0.0998$ | $R_1 = 0.0275$, $wR_2 = 0.0626$ | $R_1 = 0.0539$, $wR_2 = 0.0814$ |
| Largest difference in peak and hole (e Å$^{-3}$) | 0.654 and −0.309 | 1.681 and −0.539 | 0.683 and −0.404 | 0.700 and −0.284 |

absorption band corresponding to the asymmetric $\nu_{(N3)}$ in the region 2024–2037 cm$^{-1}$ in the FT-IR spectra of the complexes. The UV–Vis spectra for the azido complexes under investigation were measured in dichloromethane at ca. $10^{-4}$ M. The broad band were observed in the range $\lambda_{max} = 470$–490 nm which are assignable to the low energy transition (MLCT) band. The $^{31}P\{^1H\}$ spectra of the indenyl as well as pentamethylcyclopentadienyl complexes show a single resonance at $\delta$ 84.27 (**3a**), 14.33 (**3b**), 75.74 (**4a**) and 12.44 (**4b**) which is consistent with the chemical equivalence of both the phosphorous atoms. It is notable that the $^{31}P\{^1H\}$ spectra of the dppe in the complexes were resonance at low field while that of dppm in the upfield region in both indenyl and Cp* complexes which are comparable with those of reported values [27,32,33]. The proton NMR spectra of the complexes are well consisted with the proposed structures. In the $^1H$ NMR spectra of the indenyl complexe (**3a**) the resonance for the H-2 proton of the indenyl appeared in the downfield region at $\delta$ 4.96 while that of H-1,3 resonate at $\delta$ 4.48 as doublet ($J$(HH) = 3.4 Hz). However, in the case of **3b** the resonance of these protons appeared as unresolved signal at $\delta$ 4.84. The –$CH_2$– protons of dppe in the complexes **3a** and **4a** exhibited two multiplets in the range of $\delta$ 2.26–2.56 (**3a**) and $\delta$ 1.04–2.52 (**4a**), respectively. While $CH_2$ of dppm protons in the complexes **3b** and **4b** resonate as doublet of triplet at $\delta$ 4.98 ($J_{HH} = 10.32$, $J_{H-P} = 10.48$ Hz) and 4.02 [$J_{(HH)} = 14.88$, $J_{(HP)} = 10.84$ Hz], respectively. A multiplet in the region $\delta$ 7.21–7.38 was observed in the spectra of the complexes **3a** and **3b** corresponding to the protons of phenyl and H-5, 6 and H-4, 7 of the indenyl group. As expected the $^{13}C$ NMR of the complexes displayed a triplet, occasionally as unresolved peak for the $CH_2$ carbon of dppe at ca. $\delta$ 27.86 and 28.67 for **3a** and **4a** while that of dppm appeared as triplet at $\delta$ ca. 49.40 (**3b**) [$J_{C-P} = 19.7$ Hz] and 49.59 (**4b**) [$J_{C-P} = 21.4$ Hz], respectively.

Indenyl carbon resonances (Table 1) have also been assigned; they are in accordance with the proposed $\eta^5$-coordination [34]. As have been proven previously, the parameter $\Delta\delta$(C-3a, 7a) = $\delta$(C-3a, 7a) ($\eta$-indenyl




Scheme 1.

complex) – $\delta$(C-3a, 7a-sodium indenyl) can be used as indication of the indenyl distortion [35]. The calculated values of $\Delta\delta$(C-3a, 7a) are given in Table 1. The calculated values for the complexes **3a** and **3b** are $\delta$ −21.37 and −21.63, respectively and the values are indicative of a slight distortion of the indenyl ring.

*4.1.2. Preparation of triazole complexes, [($\eta^5$-$C_9H_7$)-Ru($L_2$)$N_3C_2(CO_2Me)_2$)] and [($\eta^5$-$C_9H_7$)Ru($L_2$)-($N_3C_2(CO_2Me)_2$)]*

N(2)-bound 4,5-bis(methoxycarbonyl)-1,2,3-triazole complexes, [($\eta^5$-$C_9H_7$)Ru($L_2$)($N_3C_2(CO_2Me)_2$)], $L_2$ = dppe (**5a**), dppm (**5b**) and [($\eta^5$-Cp*)Ru($L_2$)($N_3C_2$-($CO_2Me)_2$)], $L_2$ = dppe (**6a**), dppm = **6b**, respectively, are readily prepared in quantitatively good yield (87–92%) by the treatment of complexes (**3a-b**) or (**4a-b**) with sixfold excess of dimethylacetylenedicarboxylate in $CH_2Cl_2$ at room temperature. But attempt to syntheses corresponding triazole complexes of bis triphenyl phosphine [($\eta^5$-$L_3$)Ru($PPh_3$)$_2$($N_3C_2(CO_2Me)_2$)], $L_3 = C_9H_7$ or $C_5Me_5$, were not successful so far. It is possible that the more satirically demanding bis triphenylphosphine group compared to chelating dppe or dppm may prevent cycloaddition at terminal azide around the ruthenium center. However, the reaction readily undergo with the analogous complexes of less steric bis phosphine such as bis dimethylphenylphosphine ($PMe_2Ph$), the work is in due course. Further, our current study on the azido complexes of arene ruthenium with various activated acetylenes reveals that such triazole complexes are readily generate from the neutral ruthenium azido complexes, but the reaction did not undergo in cationic ruthenium azido complexes. The work is in under progress. The complexes were characterized by FT-IR, NMR ($^1$H, $^{31}$P{$^1$H}, $^{13}$C {$^1$H}) spectroscopy (details are given in Section 2). Thus, the IR spectra (KBr) of the complexes show strong absorption band characteristic of $\nu_{(C=O)}$ at 1732 while $\nu_{(C-O)}$ and $\nu_{(N=N)}$ were observed in the range 1268–1295 and 1438–1440 cm$^{-1}$, respectively. The UV–Vis spectra of the complexes **5a** and **5b** show absorption band in the region 423–425 nm which is blue shift relative to the starting azido complexes. The complexes are N(2)-bound triazole as evidence from the appearance of a singlet resonance at ca. $\delta$ 3.62 for the six methoxycarbonyl protons the $^1$H NMR spectra of the complexes (Fig. 1).

It is noteworthy that for the N(1) bound isomer the spectra would exhibit two resonances for its anisochronous methoxycarbonyl groups. Further the complexes are N(2) bound isomer was confirmed from the crystal structure of the representative complexes. The most remarkable feature of the $^1$H NMR spectra of the complexes **5b** and **6b** are the presence of a doublet of triplet at ca. $\delta$ 4.93 and 5.26 assigned to the $(Ph_2P)_2CH_2$

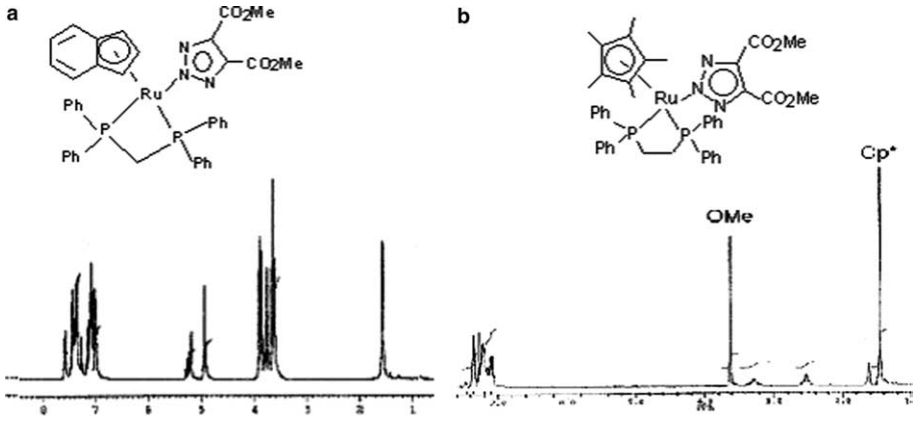



Fig. 1. (a) Proton NMR spectrum of **5b** and (b) proton NMR spectrum of **6a** in $CDCl_3$.

proton and appearance of unresolved resonance for the protons of indenyl ligand (H-1,2,3). As expected the $^{31}P\{^1H\}$ spectra of the indenyl as well as pentamethylcyclopentadienyl complexes display a single resonance at $\delta$ 91.16 (**5a**), 14.56 (**3b**), 87.32 (**4a**) and 15.46 (**4b**) which is consistent with the chemical equivalence of both the phosphorous atoms. The $^{13}C\{^1H\}$ NMR spectra of these complexes exhibit multiplet signals at $\delta$ 127.59-134.61 for the carbon of the phenyl group. $^{13}C$ $\{^1H\}$ NMR of the indenyl triazole complexes were also studied. Kohler [35b] proposed a correlation between $^{13}C\{^1H\}$ chemical shift of indenyl ring junction carbons, C(3a)–(7a) and hapacity of the coordinated ligand. The indenyl carbon resonances and the calculated parameter $\Delta\delta$(C-3a, 7a) of the complexes **5a** and **5b** are listed in Table 1. Thus, up field shift of signals for C(3a)–(7a) relative to indene were indication of $\eta^5$-coordination. The calculated values of $\Delta\delta$(C-3a, 7a) for the complexes **5a** and **5b** are $\delta$ −21.89 and −21.94, respectively, which are slightly lower than that of the starting azido complexes **3a** and **3b**. These values are indicative of a slight distortion of the indenyl ring [35a] and they are consistent with the X-ray diffraction studies for complexes **5a** and **5b**.

## 5. Crystal structures

### *5.1. [($\eta^5$-$C_9H_7$)Ru(dppe)Cl] (**1a**), [($\eta^5$-$C_9H_7$)-Ru(dppe)($N_3C_2(CO_2Me)_2$)] (**5a**) and [($\eta^5$-$C_9H_7$)-Ru(dppm)($N_3C_2(CO_2Me)_2$)] (**5b**)*

The compounds **1a** and **5a** are crystallizes in $P2_1/c$ space group in monoclinic unit cell while that of **5b** in $P\bar{1}$ space group in triclinic unit cell. Ortep drawing with the atoms labeling scheme for the compounds are shown in Figs. 2–4. The selected bond lengths and angles with esd's are given in Tables 2–4. The ruthenium atom is coordinated by the indenyl ligand in $\eta^5$-fashion and displays the asymmetric coordination generally observed with this ligand [36]. Thus, ruthenium to ring junction carbon bond distances is longer than the bond distances between ruthenium to the adjacent carbon atom of the five-membered ring. The ruthenium to ring junction bond distances in the complexes falls within 2.314–2.3767 Å while ruthenium to the rest of the three carbon of five-membered ring falls in the range of 2.1821–2.2096 Å in the complexes **1a**, **5a** and **5b** which are comparable to that of other indenyl complexes [33,37]. The asymmetric is explained on the basis of slippage of $\eta^5$-coordination towards $\eta^3$-coordination [38]. Although the indenyl ligand is $\eta^5$-bonded to the ruthenium atom, the structures show slight distortions of five carbons ring from planarity.

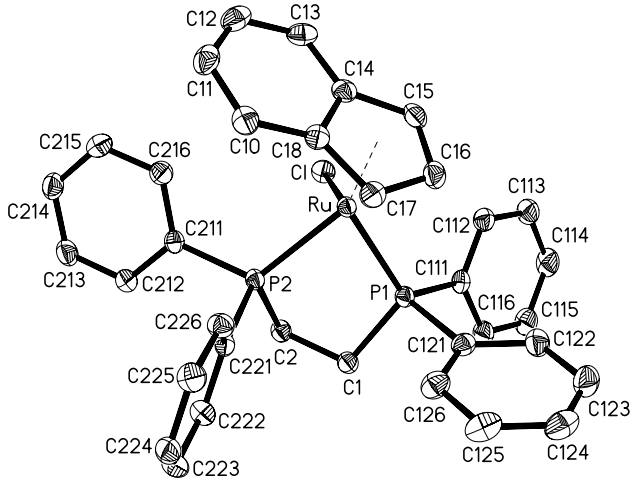



Fig. 2. Molecular structure of the complex [($\eta^5$-$C_9H_7$)Ru(dppe)Cl] (**1a**) showing 50% probable thermal ellipsoids.

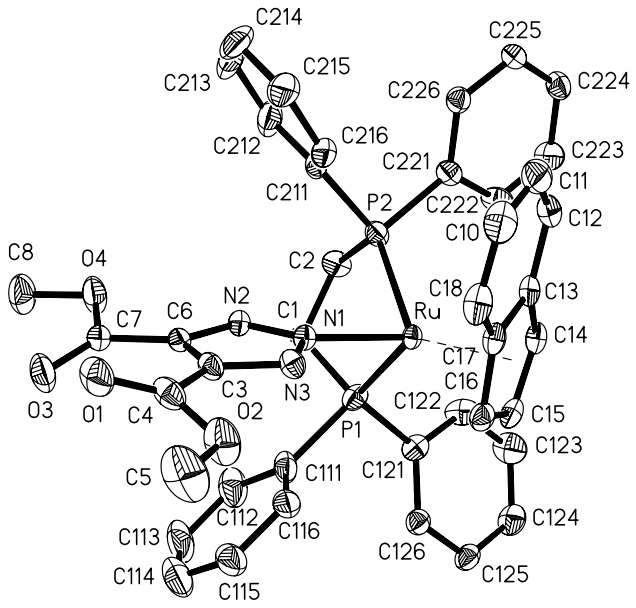



Fig. 3. Molecular structure of the complex [($\eta^5$-$C_9H_7$)Ru(dppe)-($N_3C_2(CO_2Me)_2$)] (**5a**) showing 50% probable thermal ellipsoids.

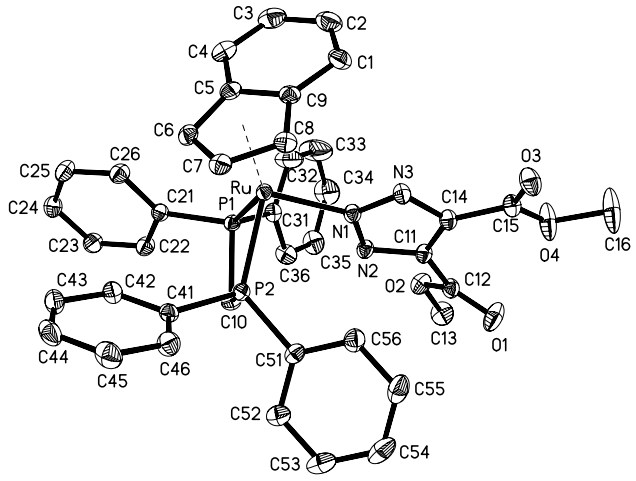



Fig. 4. Molecular structure of the complex [($\eta^5$-$C_9H_7$)Ru(dppm)-($N_3C_2(CO_2Me)_2$)] (**5b**) showing 50% probable thermal ellipsoids.

The characteristic slippage of the indenyl ring is also observed with slip-fold (Δ) values of 0.158(14) (**1a**), 0.175(2) (**5a**) and 0.123(13) (**5b**), which are comparable to those shown, by indenyl allenylidene complexes [33] and indenyl azine [37] complexes. These $\Delta_{M-C}$ values are indicative of slight distortion of $\eta^5$-indenyl ligand. The result is consistent with the solution $^{13}C\{^1H\}$ NMR data for the complexes (**5a**) and (**5b**). For a true $\eta^5$-indenyl ligand Δ should be ca. 0 Å [22a]. As previously found in other indenyl complexes [22a,34], there is significant localization of double bond at C(12)–C(13) and C(10)–C(11) (**1a**), C(11)–C(12) and C(10)–C(18) (**5a**) and C(1)–C(2) and C(3)–C(4) (**5b**) of the benzo ring of the indenyl moiety. These bond lengths falls in the range 1.363(4)–1.375(2) Å. Both these bond lengths are significantly shorter than other C–C bond distances of the benzo ring of which the bond lengths falls in the range 1.414(4)–1.438(3) Å. In contrast, the five-membered indenyl ring show considerable delocalization of double bond as evident from the nearly equal C–C bond distances in the ring, the bond lengths falling within the range 1.433(2)–1.453(2) (**1a**), 1.419(4)–1.438(3) (**5a**) and 1.4254(18)–1.4552(18) Å (**5b**).

The N–N bond distances, viz., N(1)–N(2) and N(1)–N(3) (Tables 3 and 4) in both the complexes **5a** and **5b** are comparatively longer than those of terminal N–N azide bond distances (1.170(8) and 1.146 (10) Å) [39] indicating delocalization of π electron in the heterocyclic ring. Further there is no significant difference in the Ru–N1, and bond distances of atoms in the heterocyclic ring in both the complexes **5a** and **5b**.The crystal structure of compound **5b** show existence of a number of intra molecular hydrogen bonding. The bond lengths and angles of the hydrogen bonds are listed in Table 6.

### 5.2. *[($\eta^5$-$C_5Me_5$)Ru(dppe)($N_3C_2(CO_2Me)_2$)] (**6a**)*

The compound crystallizes in $P2_1/c$ space group in a monoclinic unit cell. An ortep drawing with the atoms labeling scheme is shown in Fig. 5. Selected bond lengths and angles are presented in Table 5. The ruthenium atom is coordinated to $C_5Me_5$ ligand in $\eta^5$-fashion and displays planarity of the five member Cp* ring as evident from nearly equal bond distances between ruthenium and carbons of the ring, the bond distances falls within the range 2.2335(18) to 2.284 (18) Å. Further, there is significant delocalization of π-electron in the Cp* ring as evident by the nearly equal bond lengths of C–C atoms in the ring. The bond lengths falls within the range of 1.417(3)–1.448 (3) Å. The Ru–N bond distance in the compound is 2.1010(16) Å which is about 0.031 Å shorter than a Ru–$N_3$ bond length 2.132(5) Å [40]. This suggests a stronger bond for Ru–N bond of triazole compound as compared to Ru–$N_3$ bond. Interestingly, the five member heterocyclic triazole ring has equal bond lengths suggesting a considerable delocalization of π-electron in the ring. The Ru–P1 (2.2923(5) Å), Ru–P2 (2.2993 (5) Å) and Ru–N (2.1010(16) Å) bond distances are comparable to those of indenyl triazole complexes **5a** and **5b**. As in compound **5b** the molecule show the presence of hydrogen bonding between the hydrogen of phenyl ring C(26)–H(26) and oxygen O(1); hydrogen of phenyl ring C(43)–H(43) and oxygen O(3) of the $CO_2Me$ groups.

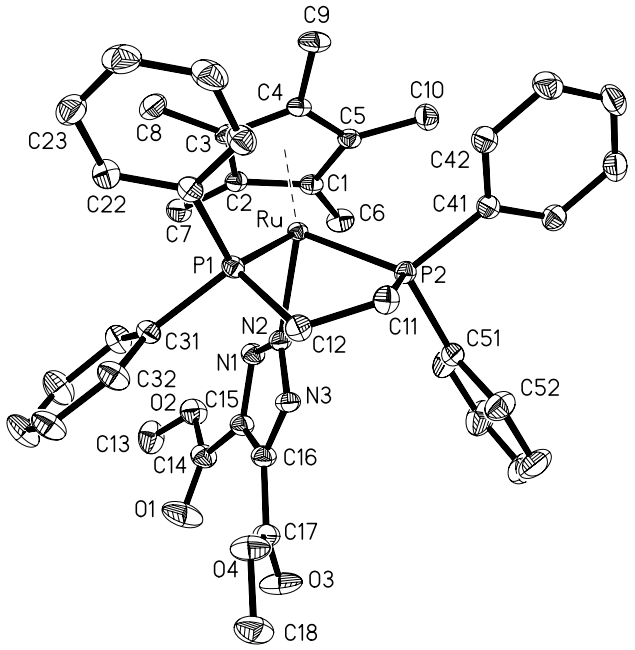



Fig. 5. Molecular structure of the complex [($\eta^5$-$C_5Me_5$)Ru(dppe)-($N_3C_2(CO_2Me)_2$)] (**6a**) showing 50% probable thermal ellipsoids.

## 6. Conclusions

The present study describe the syntheses of four new triazole complexes containing $\eta^5$-indenyl and $\eta^5$-Cp* through 1,3-dipolar cycloaddition of dimethylacetylene dicarboxylate to their corresponding ruthenium azido complexes. Syntheses of such triazole complexes with less steric bis phosphine and analogous triazole complexes of arene are under progress.

## 7. Supplementary material

Crystallographic data for the structural analysis have been deposited at the Cambridge Crystallographic Data Centre (CCDC), CCDC No. 267912 for complex **1a**, CCDC No. 267913 for complex **5a**, CCDC No. 267914 for complex **5b** and CCDC No. 267915 for complex **6a**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44

1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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