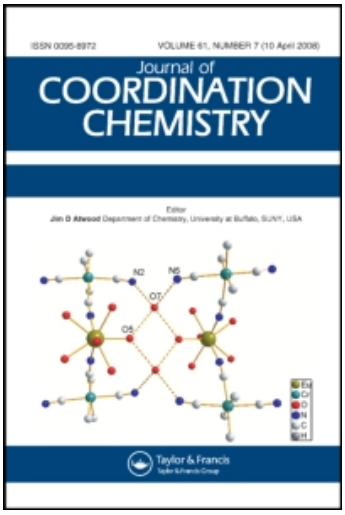

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Synthesis of indenyl ruthenium triazolato complexes by [3 + 2] cycloaddition of activated nitrile and alkynes to indenyl ruthenium azido complexes: crystal structures of $[(\eta^5\text{-}C_9H_7)Ru(PMe_2Ph)_2\{N_3C_2(CO_2Me)_2\}]$ and $[(\eta^5\text{-}C_9H_7)Ru(dppe)\{N_3C_2H(CN)\}]$

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The indenyl ruthenium(II) azide complexes $[(\eta^5\text{-}C_9H_7)Ru(L_2)N_3]$, $L_2 = (PMe_2Ph)_2$ (**1**), dppe (**2**) and dppm (**3**), (where dppe = $Ph_2PCH_2CH_2PPh_2$ and dppm = $PPh_2CH_2PPh_2$) were readily prepared by the reaction of NaN_3 with corresponding chloro complexes $[(\eta^5\text{-}C_9H_7)Ru(L_2)Cl]$. The azido complexes undergo [3 + 2] dipolar cycloaddition reactions with activated alkynes and nitrile (NCCH = CHCN) to yield new indenyl ruthenium triazolato complexes $[(\eta^5\text{-}C_9H_7)Ru(L_2)(N_3C_2(CO_2R)_2)]$, $L_2 = (PMe_2Ph)_2$, R = Me (**4**), Et (**5**); L_2 = dppe, R = Et (**6**), L_2 = dppm, R = Et (**7**) and $[(\eta^5\text{-}C_9H_7)Ru(L_2)(N_3C_2HCN)]$, $L_2 = (PMe_2Ph)_2$ (**8**), L_2 = dppe (**9**), L_2 = dppm (**10**). The complexes were fully characterized on the basis of microanalyses, IR and NMR spectroscopy. The structures of representative complexes **4** and **9** have been determined by single-crystal X-ray methods.

Keywords: Indenyl; Dimethylacetylenedicarboxylate; Diethylacetylenedicarboxylate; Dimethylphenylphosphine; Azide; Ruthenium; Fumaronitrile; Cycloaddition; X-ray structure

1. Introduction

The chemistry of azides has attracted the attention of many chemists, since they play an important role in organic chemistry [1–6]. One of the most useful synthetic applications of azides is the preparation of 1,2,3-triazoles *via* 1,3-dipolar cycloaddition reactions of azides with substituted acetylene compounds. Organic azides are particularly important for synthesizing heterocyclic compounds [3, 7]. By analogy, coordinated azide groups in metal azides have been reported to undergo cycloaddition reactions [8, 9]. Azido complexes react with nitriles [10–22] and isonitriles [11, 12, 23–25] to produce metal-nitrogen and metal-carbon bonded tetrazolates, respectively. Similar reactions with alkynes produce triazolates [10, 15, 19–21]; alkenes, however, react very slowly and mostly afford decomposition products [10, 20].

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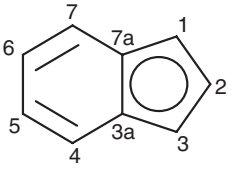
A survey of the literature indicated that cycloaddition reactions have been mostly reported for nickel(II) [10], palladium(II) [26] and platinum(II) [18], although a few reports are available for other transition metals like rhodium(I) and iridium(I) [20, 27, 28]. Cycloaddition of coordinated azide in half sandwich complexes remain unexplored except for a few recent reports on chelating phosphine complexes [29, 30]. However, to the best of our knowledge, such reactions have not been studied in indenyl ruthenium bisphosphine complexes. This article describes some studies on cycloadditions of half sandwich ruthenium azido complexes. The study reveals that the reaction is favourable in neutral rather than cationic complexes. Reactions with varying bulkiness of the phosphine coordinated to the metal have been carried out. Cycloaddition readily takes place with $[(\eta^5\text{-}C_9H_7)Ru(PMe_2Ph)_2N_3]$ but with the more sterically bulky complex $[(\eta^5\text{-}C_9H_7)Ru(PPh_3)_2N_3]$ cycloaddition does not occur. Thus, cycloaddition reactions of azides depend on the charge and steric bulkiness of the phosphines. Here, we report the synthesis of a series of indenyl triazolato complexes *via* [3 + 2] cycloaddition reactions of activated nitrile and alkynes with the indenyl ruthenium azido complexes $[(\eta^5\text{-}C_9H_7)Ru(L_2)N_3]$ where $L_2 = (PMe_2Ph)_2$ (**1**), dppe (**2**) and dppm (**3**). The reactions gave $[(\eta^5\text{-}C_9H_7)Ru(L_2)(N_3C_2(CO_2R)_2)]$, $L_2 = (PMe_2Ph)_2$, R = Me (**4**), Et (**5**); L_2 = dppe, R = Et (**6**), L_2 = dppm, R = Et (**7**) and $[(\eta^5\text{-}C_9H_7)Ru(L_2)(N_3C_2HCN)]$, $L_2 = (PMe_2Ph)_2$ (**8**), L_2 = dppe (**9**), L_2 = dppm (**10**). The complexes were characterized analytically and spectroscopically. The structures of the representative complexes **4** and **9** have been established by single crystal X-ray methods.

2. Experimental

All solvents were dried and distilled prior to use [31]. $RuCl_3 \cdot 3H_2O$, dimethylacetylenedicarboxylate, diethylacetylenedicarboxylate and fumaronitrile were commercially available and used as received. NMR spectra were recorded on Bruker 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; coupling constants are given in Hz. IR spectra (KBr pellets) were recorded on a Perkin Elmer 983 spectrophotometer. Elemental analyses were carried out at the SAIF Shillong, using a Perkin Elmer 2400 CHN/S system. Precursor complexes $[(\eta^5\text{-}C_9H_7)Ru(PMe_2Ph)_2Cl]$ [32], $[(\eta^5\text{-}C_9H_7)Ru(dppe)N_3]$ [29] and $[(\eta^5\text{-}C_9H_7)Ru(dppm)N_3]$ [29] were prepared following literature methods. The following atom labelling scheme is used for ^{1}H and ^{13}C $\{^1H\}$ NMR spectroscopic data.



The parameter $\Delta\delta$(C-3a,7a) has been used to correlate $^{13}C\{^1H\}$ chemical shifts and capacity of indenyl complexes. $\Delta\delta$(C-3a,7a) is defined as the difference between δ(C-3a,7a) of the indenyl complex and $\Delta\delta$(C-3a,7a) of sodium indenyl ($\delta = 130.70$ ppm) [33].

2.1. *Synthesis*

2.2.1. Preparation of $[(\eta^5\text{-}C_9H_7)Ru(PMe_2Ph)_2N_3]$ (1). To a solution of $[(\eta^5\text{-}C_9H_7)Ru(PMe_2Ph)_2Cl]$ (100 mg, 0.153 mmol) in 30 cm^3 of ethanol, was added NaN_3 (49 mg, 0.76 mmol). The resulting solution was refluxed for 3 h; the colour of the solution changed from orange to bright red as the reaction progressed. The solution was cooled to room temperature then the solvent removed using a rotary evaporator. The residue was extracted with CH_2Cl_2, filtered to remove NaCl and excess NaN_3, and concentrated to ca 5 cm^3. Addition of excess hexane gave red crystals that were collected and washed with hexane. Yield 87%. Anal. Calcd for $C_{25}H_{29}N_3P_2Ru$ (%): C, 56.87; H, 5.42; N, 7.86. Found: C, 55.87; H, 5.16; N, 8.12. IR (cm^{-1}): $\nu_{(N_3)}$ 2015 (vs). ^{1}H NMR ($CDCl_3$): δ 1.32 (vt, 6H, $|^2J_{P-H} + {}^4J_{P-H}| = 9.0$ Hz, $PMe_a + P'Me_{a'}$), 1.50 (vt, 6H, $|^2J_{P-H} + {}^4J_{P-H}| = 9.1$ Hz, $PMe_b + P'Me_{b'}$), 4.48 (d, 2H, $^3J_{HH} = 3.4$, H-1,3, indenyl), 4.56 (t, 1H, $^3J_{HH} = 2.2$, H-2, indenyl), 7.08–7.52 (m, 4H, H-4,7 & H-5,6), 7.25–7.52 (m, 10H, 2Ph).$^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 16.19 (vt, $|^1J_{P-C} + {}^3J_{P-C}| = 28.87$, $PMe_a + P'Me_{a'}$), 18.82 (vt, $|^1J_{P-C} + {}^3J_{P-C}| = 28.47$ Hz, $PMe_b + P'Me_{b'}$), 62.21 (s, C-1,3, indenyl), 87.07 (s, C-2, indenyl), 109.07 (s, C-3a,7a, indenyl), 122.94–129.85 (m, Ph). $\Delta\delta$(C-3a,7a) = −21.63.$^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 22.91.

2.1.2. Preparation of $[(\eta^5\text{-}C_9H_7)Ru(L_2)\{N_3C_2(CO_2R)_2\}]$; $L_2 = (PMe_2Ph)_2$, R = Me (4); $L_2 = (PMe_2Ph)_2$, R = Et (5); L_2 = dppe, R = Et (6); L_2 = dppm, R = Et (7). *General procedure*: To a round bottomed flask charged with the corresponding azido complex (**1**) (133 mg, 0.25 mmol), (**2**) (164 mg, 0.25 mmol) or (**3**) (160 mg, 0.25 mmol) was added dimethylacetylenedicarboxylate (177 mg, 1.25 mmol) or diethylacetylenedicarboxylate (212 mg, 1.25 mmol) and CH_2Cl_2 (20 cm^3). The mixture was stirred at room temperature for 12 h, and then the solution reduced to ca 3 cm^3 using a rotary evaporator. To this solution 40 cm^3 of hexane was added and then the solution was reduced to 10 cm^3. Resulting yellow to orange solids were centrifuged, washed with hexane (2 × 20 cm^3) and dried under vacuum to give the *N*(2)-bound triazole complexes **4**–**7**.

For $L_2 = PMe_2Ph$, R = Me (**4**), yield = 91%. Anal. Calcd for $C_{31}H_{35}N_3O_4P_2Ru$ (%): C, 54.97; H, 5.17; N, 6.20. Found: C, 55.23; H, 4.98; N, 5.86. IR (cm^{-1}): $\nu_{(C=O)}$ 1732 (vs), $\nu_{(N=N)}$ 1438(s), $\nu_{(CO)}$ 1295 (m). ^{1}H NMR ($CDCl_3$): δ 1.12 (t, 12H, $J_{HH} = 4.64$), 3.89 (s, 6H, $(CO_2Me)_2$), 4.67 (d, 2H, $J_{HH} = 2.28$), 4.95 (br, 1H, unresolved), 6.94 (m, 2H, H-4,7), 7.15 (m, 2H, H-5,6), 7.25–7.40 (m, 10H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 15.36 (vt, $|^1J_{P-C} + {}^3J_{P-C}| = 29.8$ Hz), 19.22 (vt, $|^1J_{P-C} + {}^3J_{P-C}| = 29.7$ Hz), 51.58 (s, (OCH_3)), 64.27 (s, (C-1,3)), 89.85 (s, C-2), 109.06 (s, C-3a,7a), 124.07 (s, C-4,7), 125.93 (s, C-5,6), 127.88–130.47 (m, Ph), 139.81 (s, $C(CO_2Me)$), 141.18 (s), 162.98 (s, (CO_2)). $\Delta\delta$(C-3a,7a) = −21.64.

$^{31}P\{^1H\}$ NMR: ($CDCl_3$): δ 22.835.

For $L_2 = (PMe_2Ph)_2$, R = Et (**5**), yield = 89%. Anal. Calcd for $C_{33}H_{39}N_3O_4P_2Ru$ (%): C, 56.19; H, 5.53; N, 5.96. Found: C, 55.84; H, 5.53; N, 5.96. IR (cm^{-1}): $\nu_{(C=O)}$ 1732 (vs), $\nu_{(N=N)}$ 1438(s), $\nu_{(CO)}$ 1295 (m). ^{1}H NMR ($CDCl_3$): 1.13 (vt, 6H, $^3J_{HH} = 9.16$ Hz, $PMe_a + P'Me_{a'}$), 1.35 (vt, 6H, $|^2J_{P-H} + {}^4J_{P-H}| = 14.24$, $PMe_b + P'Me_{b'}$), 1.57 (t, 6H, $J_{H-H} = 4.68$, Me, $(CO_2Et)_2$) 4.32 (qt, 4H, $^3J_{H-H} = 7.12$ Hz, –CH_2–, $(CO_2Et)_2$), 4.67 (d, 2H, $J_{H-H} = 2.24$, H-1,3) 4.9 (br, 1H, H-3), 6.94 (m, 2H, H-4,7) 7.15 (m, 2H, H-5,6), 7.21–7.51 (m, 10H, Ph).

$^{13}C\{^1H\}$ NMR: ($CDCl_3$): δ 14,29 (s, CH_3), 15.30 (vt, $|^1J_{P-C} + {}^3J_{P-C}| = 13{,}88$, $PMe_a + P'Me_{a'}$), 19.34 (vt, $|^1J_{P-C} + {}^3J_{P-C}| = 14.48$, $PMe_b + P'Me_{b'}$), 60.34 (s, $-CH_2-$, $(CO_2Et)_2$), 64.24 (s, C-1,3-indenyl), 89.82 (s, C-2, indenyl), 109.08 (s, C-3a,7a, indenyl), 124.11 (s, C-4,7), 125.93 (s, C-5,6), 127.89–130.53 (m, Ph), 140.0 (s, $C(CO_2Et)$), 141.01 (t, $^1J_{P-C} + {}^3J_{P-C} = 20.6$ Hz, Ph), 162.64 (s, (CO_2)). $\Delta\delta$(C-3a,7a) = −21.62. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 22.85.

For L_2 = dppe, R = Et (**6**), yield = 84%. Anal. Calcd for $C_{43}H_{41}N_3O_4P_2Ru$ (%): C, 62.46; H, 4.96; N, 5.08. Found: C, 62.98; H, 5.16; N, 5.36. IR (cm^{-1}): $\nu_{(C=O)}$ 1732 (vs), $\nu_{(N=N)}$ 1438(s), $\nu_{(CO)}$ 1295 (m). ^1H NMR ($CDCl_3$): δ 1.18 (t, 6H, $J_{H-H} = 7.12$, $2CH_3$), 2.39–2.48 (m, 2H, $P(CH_2)_2P$), 3.10–3.19 (m, 2H, $P(CH_2)_2P$), 4.05 (qt, 4H, $J_{H-H} = 7.12$), 4.72 (d, 2H, $J_{HH} = 1.92$), 4.88 (br, 1H, unresolved), 6.86 (m, 4H, C-4,7 and C-5,6), 7.01–7.40 (m, 20H, Ph). $^{13}C\{^1H\}$ NMR: ($CDCl_3$): δ 13.78 (s, CH_3), 28.81 (t, $J_{P-C} = 22.73$ Hz, $P(CH_2)_2P$), 59.58 (s, $-CH_2-$, (CO_2Et)), 66.41 (s, C-1,3, indenyl), 108.90 (s, C-3a,7a), 125.11 (s, C-4,7), 127.58 (s, C-5,6), 129.31–133.31 (m, Ph), 141.16 (t, $C(CO_2Et)$), 161.91 (s, (CO_2)). $\Delta\delta$ (C-3a,7a) = −21.80. $^{31}P\{^1H\}$ NMR: ($CDCl_3$): δ 91.16.

For L_2 = dppm, R = Et (**7**), yield = 86%. Anal. Calcd for $C_{42}H_{39}N_3O_4P_2Ru$ (%): C, 62.06; H, 4.80; N, 5.17. Found: C, 61.84; H, 4.533; N, 4.78. IR (cm^{-1}): $\nu_{(C=O)}$ 1732 (vs), $\nu_{(N=N)}$ 1438(s), $\nu_{(CO)}$ 1295 (m). ^1H NMR ($CDCl_3$): δ 1.89 (t, 6H, $J_{H-H} = 7.08$, $2CH_3$), 4.06 (qt, 4H, $J_{H-H} = 7.08$), 4.87 (m, 3H, indenyl), 5.18–5.32 (m, 2H, $P(CH_2)P$), 6.98–7.81 (m, 24H, Ph). $^{13}C\{^1H\}$ NMR: ($CDCl_3$): δ 14.21 (s, CH_3), 49.57 (t, $J_{C-P} = 21.53$, $P(CH_2)P$), 59.64 (s, $-CH_2-$, (CO_2Et)), 65.40 (s, C-1,3), 89.42 (s, C-2), 108.75 (s, C-3a,7a), 124.91 (s, C-4,7), 125.18 (s, C-5,6), 127.57–136.34 (m, Ph), 139.11 (s, $C(CO_2Et)$), 161.96 (s, (CO_2)). $\Delta\delta$(C-3a,7a) = −21.95. $^{31}P\{^1H\}$ NMR: ($CDCl_3$): δ 14.64.

2.1.3. Preparation of [(η^5-C_9H_7)Ru(L_2){(N_3C_2HCN)}]; L_2 = PMe_2Ph, (8); dppe (9); dppm (10). To a round bottomed flask charged with the corresponding azido complex **1** (133 mg, 0.25 mmol), **2** (164 mg, 0.25 mmol) or **3** (160 mg, 0.25 mmol) was added fumaronitrile (160 mg, 1.25 mmol) and CH_2Cl_2 (20 cm^3). The mixture was stirred at room temperature for 16 to 18 h and reduced to ca 5 cm^3 using a rotary evaporator. To this solution 40 cm^3 of *n*-pentane was added and then the solution reduced to 10 cm^3. Resulting yellow solids were centrifuged and washed with pentane (2 × 20 cm^3) and dried under vacuum to gave the *N*(2)-bound triazole complexes **8**–**10**. Yield (%), reaction time, colour, analytical and spectroscopic data are as follows:

For L_2 = PMe_2Ph (**8**), yield = 83%. Anal. Calcd for $C_{28}H_{30}N_4P_2Ru$ (%): C, 57.42; H, 5.12; N, 9.57. Found: C, 57.16, H, 4.87; N, 9.86. IR (cm^{-1}): $\nu_{(C=N)}$ 2220 (vs). ^1H NMR ($CDCl_3$): δ 1.19 (vt, 6H $|^2J_{P-H} + {}^4J_{P-H}| = 9.08$ Hz, $PMe_a + P'Me_{a'}$), 1.55 (vt, 6H $|^2J_{P-H} + {}^4J_{P-H}| = 9.28$ Hz, $PMe_b + P'Me_{b'}$), 4.58 (d, 2H, $J_{H-H} = 2.24$), 4.90 (br, 1H, indenyl), 6.93 (m, 4H, H-4,7 & H-5,6), 6.96–7.99 (m, 11H, CH & Ph). $^{13}C\{^1H\}$ NMR: ($CDCl_3$): δ 16.20 (vt, $^1J_{P-C} + {}^3J_{P-C} = 28$ Hz, $PMe_a + P'Me_{a'}$), 18.91 (vt, $|^1J_{P-C} + {}^3J_{P-C}| = 28.8$ Hz, $PMe_b + P'Me_{b'}$), 64.34 (s, C-1,3), 89.82 (s, C-2), 109.28 (s, C-3a,7a), 113.87 (s, (CN)), 119.08 (s, C-4,7), 123.91 (s, C-5,6), 126.05–130.21 (m, Ph), 135.24 9s, CH), 138.75 (s, C(CN)). $\Delta\delta$(C-3a,7a) = −21.42. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 23.21.

For L_2 = dppe (**9**), yield = 90%. Anal. Calcd for $C_{38}H_{32}N_4P_2Ru$ (%): C, 64.43; H, 4.52; N, 7.91. Found: C, 63.96; H, 4.25; N, 7.68. IR (cm^{-1}): $\nu_{(C=N)}$ 2220 (vs). ^1H NMR ($CDCl_3$): δ 2.47–2.99 (m, 2H, $P(CH_2)_2P$), 3.02–3.11 (m, 2H, $P(CH_2)_2P$), 4.55 (d, 2H, $J_{H-H} = 2.28$), 4.62 (br, 1H, unresolved), 6.97 (s, 1H, CH), 6.84 (m, 4H, H-4,7 & H-5,6),

7.04–7.41 (m, 20, Ph). $^{13}C\{^1H\}$ NMR: ($CDCl_3$): δ 29.14 (t, $J_{C-P} = 22.73$, $P(CH_2)_2P$), 66.33 (s, C-1,3, indenyl), 92.91 (s, C-2, indenyl), 108.96 (s, C-3a,7a), 115.16 (s, (CN)), 124.09 (s), 124.98 (s, C-4, 7), 125.99 (s, C-5,6), 127.62–132.699 (m, Ph), 134.20 (s, CH), 137.72 (s, C(CN)). $\Delta\delta$(C-3a,7a) = −21.74. $^{31}P\{^1H\}$ NMR: ($CDCl_3$): δ 92.07.

For L_2 = dppm (**10**), yield = 89%. Anal. Calcd for $C_{37}H_{30}N_4P_2Ru$ (%): C, 64.00; H, 4.32; N, 8.07. Found: C, 63.87; H, 3.98; N, 7.83. IR (cm^{-1}): $\nu_{(C=N)}$ 2224 (vs).

^1H NMR ($CDCl_3$, 400.13 MHz): δ 4.83 (br, 3H, H-2, H-1,3, indenyl), 4.90–4.99 (m, 2H, $P(CH_2)P$), 6.94–7.38 (m, 25H, CH, H-5,6, H-4,7, Ph). $^{13}C\{^1H\}$ NMR: ($CDCl_3$): δ 49.59 (t, $J_{C-P} = 21.3$ Hz, $P(CH_2)P$), 65.27 (s, C-1,3), 89.80 (s, C-2, indenyl), 109.42 (s, C-3a,7a), 115.10 (s, (CN)), 124.18 (s, C-4,7), 125.70 (s, C-5,6), 127.69–131.21 (m, Ph), 134.21 (s, CH), 138.04 (s, C(CN)). $\Delta\delta$(C-3a,7a) = −21.28. $^{31}P\{^1H\}$ NMR: ($CDCl_3$): δ 15.08.

2.2. *Crystallography*

X-ray quality crystals were grown by slow diffusion of hexane into an acetone solution of **4** and by diffusion of hexane into a dichloromethane solution of **9**. X-ray diffraction data were measured at 120(2) K on a Bruker AXS Apex CCD area detector employing graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Absorption correction were made by modelLing a transmission surface by spherical harmonics employing equivalent reflections with $I > 2\sigma(I)$ (SADABS) [34]. The structures were solved by direct methods and refined by full-matrix least-squares procedures based on F^2 [35, 36]. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a riding model. A summary of crystallographic parameters and refinement details is given in table 1 and selected bond lengths and angles are tabulated in table 2.

3. Results and discussion

3.1. *Reaction of ruthenium azido complexes with dimethylacetylenedicarboxylate or diethylacetylenedicarboxylate*

Reaction of [(η^5-C_9H_7)Ru(PMe_2Ph)$_2$Cl] with sodium azide in refluxing ethanol for 2–3 h gave the red azido complex [(η^5-C_9H_7)Ru(PMe_2Ph)$_2N_3$] (**1**). The IR spectrum shows a strong stretch at 2015 cm^{-1} corresponding to ν_{N_3}. Treatment of **1** with excess dimethylacetylenedicarboxylate in dichloromethane or acetone at room temperature for 12–15 h gave the *N*(2)-bound 4,5-bis-(methoxycarbonyl)-1,2,3-triazolato complex [(η^5-C_9H_7)Ru(PMe_2Ph)$_2${$N_3C_2(CO_2Me)_2$}] (**4**) in good yield (scheme 1). Under similar conditions, treatment of azido complexes **1**–**3** with diethylacetylenedicarboxylate afforded corresponding *N*(2)-bound 4,5-bis-(ethoxycarbonyl)-1,2,3-triazolato complexes [(η^5-C_9H_7)Ru(L)$_2${$N_3C_2(CO_2Et)_2$}] [L_2 = 2PMe_2Ph (**5**), dppe (**6**), dppm (**7**)] in 84–91% yield (scheme 1). The complexes are soluble in chlorinated solvents but insoluble in non-polar solvents and are stable in air.

It has thus been shown that cycloadditions can be extended to indenyl ruthenium bisphosphine complexes. Although the triazolato complexes [(η^5-C_9H_7)Ru(PMe_2Ph)$_2$ {$N_3C_2(CO_2R)_2$}] were readily generated from **1** and acetylenes, attempts to synthesize the corresponding triazolato complexes of bis(triphenylphosphine) have been unsuccessful. This may be due to the bulky nature of triphenylphosphine.

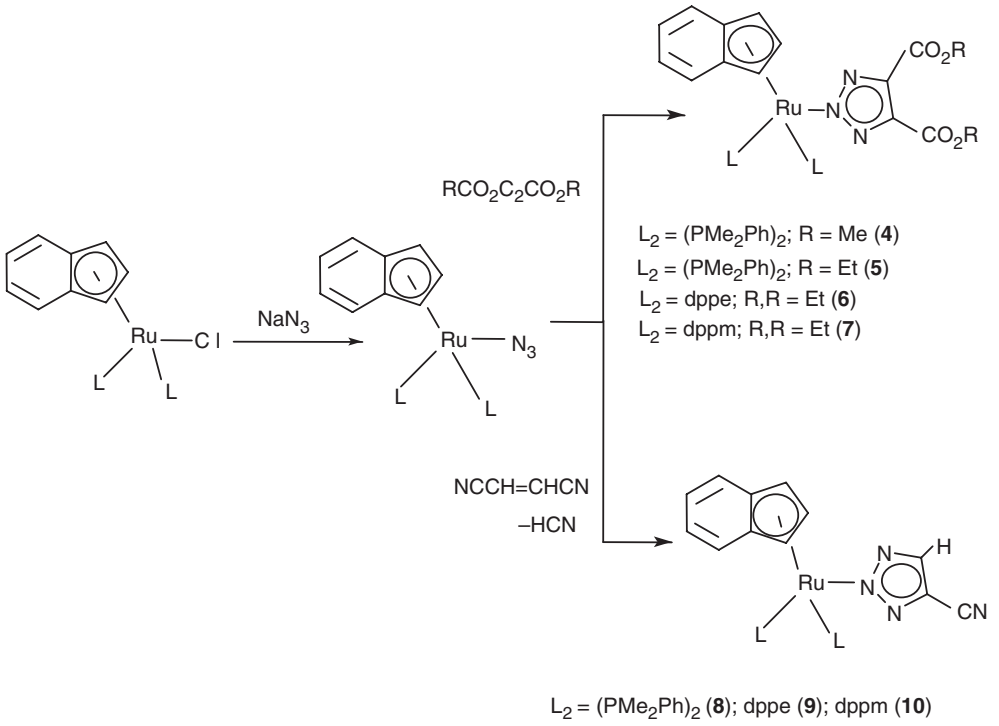
Table 1. Summary of crystal data and refinement details.

	4	**9**
Empirical formula	$C_{31}H_{35}N_3O_4P_2Ru$	$C_{38}H_{32}N_4P_2Ru$
Formula weight	676.63	707.69
Space group	$P\bar{1}$	$R\bar{3}$
Unit cell dimensions (Å, °)		
a	10.723(7)	38.649(3)
b	11.445(7)	
c	14.349(9)	11.4503(19)
α	69.535(6)	90
β	72.113(6)	90
γ	68.407(6)	120
V (Å^3)	1501.4 (16)	14813 (3)
Z	2	18
Calculated density (Mg m^{-3})	1.497	1.428
Absorption coefficient (mm^{-1})	0.670	0.607
$F(000)$	696	6516
Crystal size (mm^3)	$0.41 \times 0.37 \times 0.22$	$0.39 \times 0.31 \times 0.20$
θ range for collection (°)	1.99 to 28.17	1.83 to 24.99
Limiting indices	$-14 \le h \le 13$; $-14 \le k \le 15$; $-18 \le l \le 18$	$-45 \le h \le 45$; $-45 \le k \le 45$; $-13 \le l \le 13$
Reflections collected/unique	16785/6790 [R(int) = 0.0561]	46738/5787 [R(int) = 0.0573]
Completeness to θ (%)	92.1	99.9
Max. and min. transmission	0.8667 and 0.7709	0.8882 and 0.7977
Data/restraints/parameters	6790/0/376	5787/0/406
Goodness-of-fit on F^2	1.053	1.027
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0436$, $wR_2 = 0.1160$	$R_1 = 0.0303$, $wR_2 = 0.0996$
R indices (all data)	$R_1 = 0.0476$, $wR_2 = 0.1193$	$R_1 = 0.0329$, $wR_2 = 0.1021$
Largest diff. peak and hole (e A^{-3})	1.223 and −1.047	1.599 and −0.274

Table 2. Selected bond lengths (Å), angles (°) and slip parameter Δ^a (Å) for **4** and **9**.

	Complex **4**	Complex **9**
Ru–CENT	1.897(3)	1.903(3)
Ru–P(1)	2.3171(13)	2.2406(7)
Ru–P(2)	2.2495(12)	2.2831(7)
Ru–N(2)	2.095(3)	2.093(2)
N(1)–N(2)	1.335(3)	1.327(3)
N(2)–N(3)	1.341(3)	1.346(3)
C(10)–C(11)	1.398(4)	1.379(4)
C(14)–O(3)	1.186(4)	
C(12)–O(2)	1.180(4)	
C(12)–N(4)		1.147(4)
Δ	0.1235	0.1120
N(2)–Ru–P(1)	92.12(7)	87.48(6)
P(1)–Ru–P(2)	94.95(6)	84.11(3)
N(2)–Ru–P(2)	89.23(7)	91.63(6)
N(1)–N(2)–N(3)	112.2(2)	112.8(2)
N(1)–C(10)–C(11)	107.5(2)	108.4(2)
N(3)–C(11)–C(10)	108.0(2)	108.1(2)

$\Delta^a = d_{avg}$ (Ru–C(4), C(5)) − d_{avg} (Ru–C(1), C(3)).



Scheme 1. Synthetic pathways.

Further, cycloaddition reactions are favoured with neutral azido complexes but reaction with cationic arene ruthenium azido complexes was unsuccessful under variable reaction conditions. The formation of the yellow triazolato complexes is readily confirmed by the disappearance of the azido stretch and appearance of a $\nu_{(C=O)}$ stretch at 1726 cm^{-1}. Apart from $\nu_{(C=O)}$, IR spectra show medium stretches in the regions 1238–1286 and 1437–1446 cm^{-1} due to $\nu_{(C-O)}$ and $\nu_{(N=N)}$, respectively.

^{1}H NMR spectra of all complexes exhibit a doublet for H-1,3 and a triplet for H-2 (occasionally unresolved) of the indenyl ligand. In the case of **4** and **5** protons of PMe_2Ph appear around δ 1.13 and 1.35, indicating the non-equivalence of the two methyl groups. The spectrum suggests two sets of $X_3AA'X'_3$ patterns for the MePP′Me′ groups. Further, the proton NMR spectrum of **4** exhibits a singlet at δ 3.89 for the protons of the methoxycarbonyl group while for **5**–**7** a quartet at δ 4.32 [$^3J_{H-H} = 7.12$] is assignable to the $-CH_2-$ protons of ethoxycarbonyl groups ($-CO_2Et$). These patterns suggest the complexes are *N*(2)-bound isomers. It is notable that *N*(1)-bound isomer would exhibit two resonances for its anisochronous methoxy- and ethoxycarbonyl groups. Evidence is available in the literature to indicate that either two isomers *N*(1) and *N*(2) are formed simultaneously [10, 15, 20] or the *N*(2) isomer is formed exclusively [10, 15, 20, 21]. In the present case, the complexes formed are exclusively *N*(2)-bound isomers. The formation of *N*(2)-bound isomer is supported by the spectroscopic data and confirmed by the X-ray analysis of complexes **4** and **9**. $^{31}P\{^1H\}$ NMR spectra of the bisphosphine complexes **4** and **5** showed single resonances at δ 22.83 and δ 22.85 while **6** and **7** showed signals at ca δ 91.16 and 14.64, respectively, very close to reported

values [29, 32]. $^{13}C\{^1H\}$ NMR of the complexes was also studied. Indenyl carbon resonances have been assigned and are in accordance with the proposed η^5-coordination [37, 38]. Köhler proposed a correlation between capacity of the indenyl ligand with $^{13}C\{^1H\}$ chemical shift of indenyl C-3a,7a carbons. An upfield shift of C3a,7a relative to indene indicates η^5-coordination while a downfield shift is indicative of η^3-coordination [39]. Later Baker proposed the parameter $\Delta\delta$(C-3a,7a) as an indicator of indenyl distortion [33]. Calculated values for the complexes are in the range δ −21.28 to −21.95. These are indicative of slight distortion of the η^5-indenyl ring and are consistent with results of the X-ray diffraction study.

3.2. *Reaction of azido complexes with fumaronitrile*

Treatment of the azido complexes with fumaronitrile leads to [3 + 2] cycloaddition of fumaronitrile to the ruthenium azido group and affords yellow triazolato complexes **8**–**10** (scheme 1). The formation of the triazolato complexes is readily confirmed by the disappearance of the azido stretch frequency and appearance of $\nu_{(C=N)}$ in the region 2220–2224 cm^{-1} for **8**–**10**. In principle, the cycloaddition reaction can take place via C=C or C≡N. The reaction of coordinated azide in Ni(II) with CH_2=CHCN gave a triazolinato complex [7]. A pathway *via* direct cyclization of HC≡CCN with azide resulting in the formation of triazolate has also been noted [40]. In addition to the expected resonances in the region of δ 4.7 and 4.8 arising from the H-1,3 and H-2 protons of the indenyl ligand, the ^1H NMR spectrum showed resonances in the region δ 6.93–7.99 assignable to the CH proton and protons of phenyl groups. $^{31}P\{^1H\}$ NMR spectra showed a single resonance at δ 23.21, 92.07 and 15.08 for **8**, **9** and **10** respectively, values which are comparable to those reported [29, 30].

3.3. *Crystal structures*

Molecular structures of **4** and **9** have been determined. ORTEP diagrams of the complexes with atom labelling schemes are shown in figures 1 and 2. In **4** the ruthenium atom is π-bonded to the indenyl group in η^5 fashion with the distance between ruthenium and the centroid of the indenyl ring being 1.897(3) Å. The geometry around the ruthenium atom is distorted octahedral assuming the indenyl ligand occupies three *facial* coordination sites; remaining coordination sites are occupied by the P atoms of PMe_2Ph and an N atom of the coordinated triazolato group. The complex adopts the well-known piano stool geometry with P and N atoms forming the legs. The planar five-membered triazolato ring is coordinated to Ru *via* N(2). N(1)–N(2) and N(2)–N(3) distances of 1.335(3) and 1.350(3) Å, respectively, are about the same, indicating delocalization of electrons in the N(1)–N(2)–N(3) unit. As is seen in other indenyl complexes, the structure shows asymmetric coordination of the metal to the five ring carbons. Thus, Ru–C bond distances between ruthenium and C(4) and C(5) are longer than those to allylic carbons C(1), C(2) and C(3) (table 2). The indenyl ligand exhibits a pronounced "slip-fold" (Δ) distortion [41] relative to planarity; the value of 0.1235 Å is comparable to that found in other indenyl complexes [29, 42, 43]. This is indicative of a slight distortion of the η^5-coordinated indenyl ligand from planarity and is consistent with solution ^{13}C NMR. In contrast, the benzo ring of the indenyl group is planar and

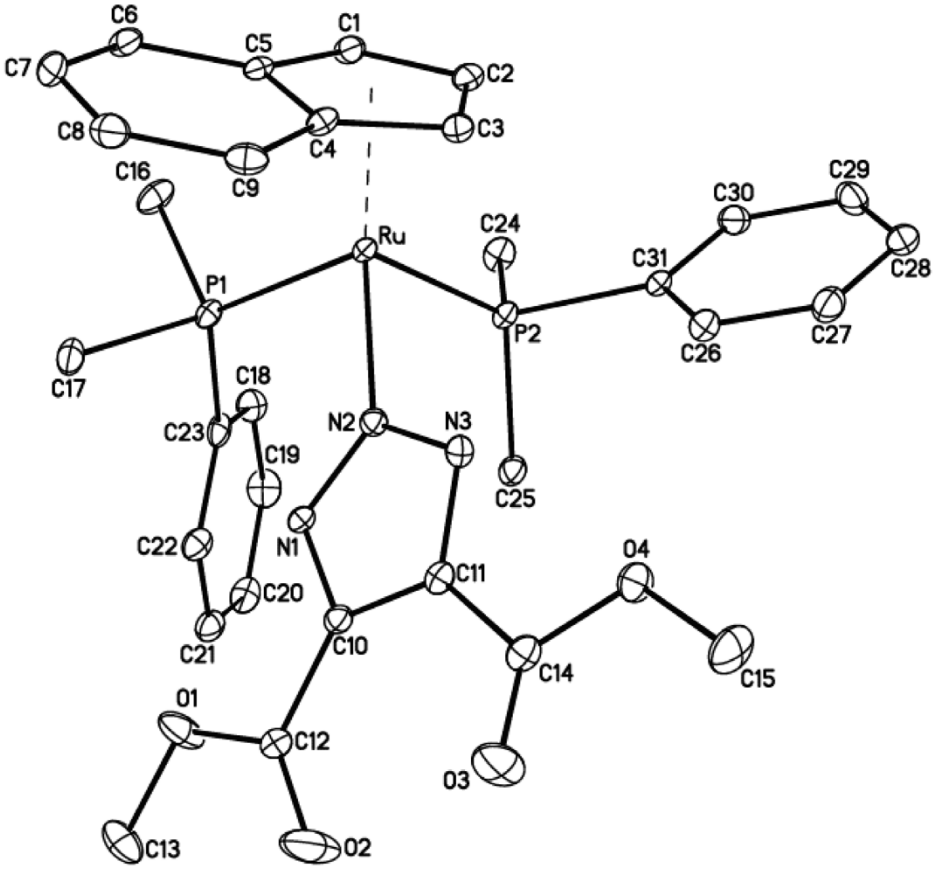


Figure 1. Molecular structure of $[(\eta^5\text{-}C_9H_7)Ru(PMe_2Ph)_2\{N_3C_2(CO_2Me)_2\}]$ (**4**). Thermal ellipsoids are depicted at the 30% probability level. Hydrogen atoms are omitted for clarity.

shows significant delocalization of double bonds at the C(8)–C(9) (1.373(4)) Å and C(6)–C(7) (1.372(4)) Å.

In **9**, ruthenium is bonded to the indenyl ligand in η^5 fashion with a ruthenium to ring centroid distance of 1.903(3) Å. The five membered triazolato ring is coordinated to the ruthenium atom *via* the N(2) atom. As was observed in **4** and other indenyl complexes, the structure shows asymmetric coordination of the indenyl ligand (table 2). The slip fold parameter (Δ) in this structure is 0.1120 Å, which is comparable to that observed in complex **4**. The C≡N bond length in the complex is 1.147(4) Å, comparable to what is observed in related complexes [30]. The Ru–N(2) bond distance in both complexes is comparable (2.095(3) Å for complex **4**, 2.093(2) Å for complex **9**).

Supplementary material

Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre (CCDC), CCDC 289501 for **4**, CCDC 289502 for **9**. Copies of this information

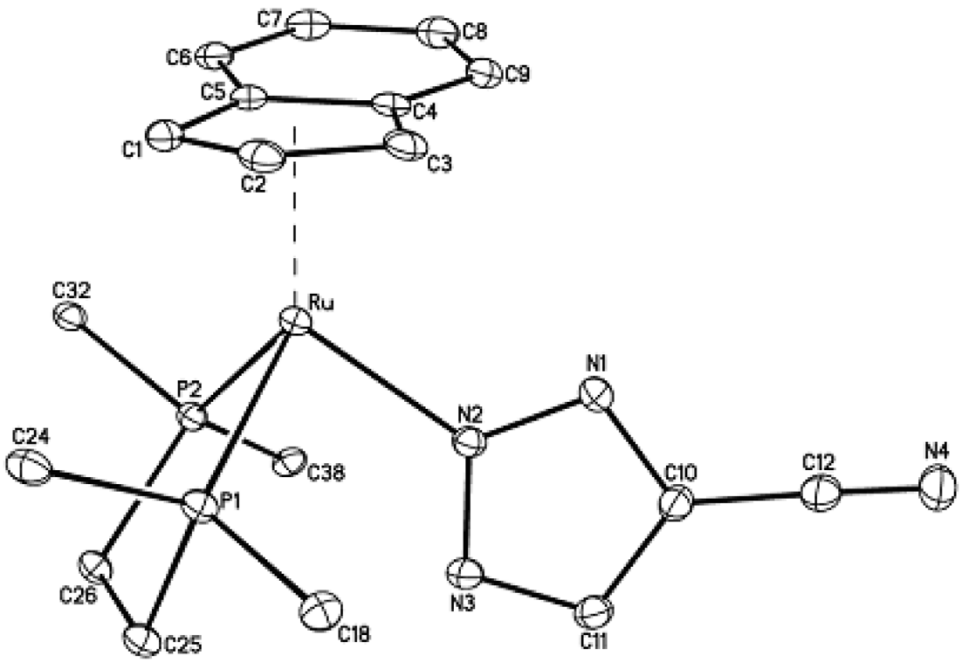


Figure 2. Molecular structure of $[(\eta^5\text{-}C_9H_7)Ru(dppe)(N_3C_2HCN)]$ (**9**). Thermal ellipsoids are depicted at the 30% probability level. The terminal phenyl groups are shown as pivotal atoms only. Hydrogen atoms are omitted for clarity.

may be obtained free of charge from the director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; Email: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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