

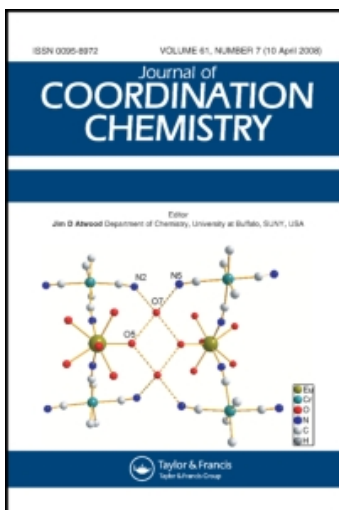
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### Syntheses, spectroscopic and structural studies of indenyl ruthenium complexes incorporating amine and nitrile ligands: molecular structures of $[(^5\text{-C}_9\text{H}_7)\text{Ru}^{(2\text{-dppe})(\text{CH}_3\text{CN})}\text{PF}_6]$ and $[(^5\text{-C}_9\text{H}_7)\text{Ru}^{(2\text{-dppe})(\text{NH}_3)}\text{PF}_6]$

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# Syntheses, spectroscopic and structural studies of indenyl ruthenium complexes incorporating amine and nitrile ligands: molecular structures of $[(\eta^5\text{-C}_9\text{H}_7)\text{Ru}(\eta^2\text{-dppe})(\text{CH}_3\text{CN})]\text{PF}_6$ and $[(\eta^5\text{-C}_9\text{H}_7)\text{Ru}(\eta^2\text{-dppe})(\text{NH}_3)]\text{PF}_6$

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The reaction of  $[(\eta^5\text{-C}_9\text{H}_7)\text{Ru}(\eta^2\text{-dppe})\text{Cl}]$  (**1**) with monodentate nitriles, (L) in the presence of  $\text{NH}_4\text{PF}_6$  afforded the complexes  $[(\eta^5\text{-C}_9\text{H}_7)\text{Ru}(\eta^2\text{-dppe})(\text{L})]\text{PF}_6$ , with  $\text{L} = \text{CH}_3\text{CN}$  (**2a**),  $\text{CH}_3\text{CH}=\text{CHCN}$  (**2b**),  $\text{NCC}_6\text{H}_4\text{CN}$  (**2c**),  $\text{C}_6\text{H}_5\text{CH}_2\text{CN}$  (**2d**), respectively. However, reaction of **1** with  $\text{NH}_4\text{PF}_6$  in methanol yielded an amine complex of the type  $[(\eta^5\text{-C}_9\text{H}_7)\text{Ru}(\eta^2\text{-dppe})(\text{NH}_3)]\text{PF}_6$  (**3a**). The complexes were fully characterized by spectroscopy and analytical data. The molecular structures of the complexes  $[(\eta^5\text{-C}_9\text{H}_7)\text{Ru}(\eta^2\text{-dppe})(\text{CH}_3\text{CN})]\text{PF}_6$  (**2a**) and  $[(\eta^5\text{-C}_9\text{H}_7)\text{Ru}(\eta^2\text{-dppe})(\text{NH}_3)]\text{PF}_6$  (**3a**) have been determined by single crystal X-ray analyses.

*Keywords:* Indenyl; Amine; Ruthenium; Diphenylphosphinoethane; Crystal structure

## 1. Introduction

Indenyl and cyclopentadienyl ruthenium(II) complexes  $[\text{Cp}'\text{Ru}(\text{L}_2)\text{Cl}]$  ( $\text{Cp}' = \text{cyclopentadienyl}$ , indenyl;  $\text{L}_2 = (\text{PPh}_3)_2$ , dppe) have been intensely studied owing to their high reactivity [1], catalytic activity [2] and interesting reactions towards terminal alkynes [3]. An extensive study has been carried out on cyclopentadienyl ruthenium complexes [4–6], in contrast to analogous indenyl complexes. A literature survey reveals that most reactions of indenyl ruthenium(II) phosphine complexes  $[(\eta^5\text{-C}_9\text{H}_7)\text{Ru}(\text{L}_2)\text{Cl}]$  (where,  $\text{L}_2 = \text{PPh}_3$ , dppe) are centered on reactivity studies

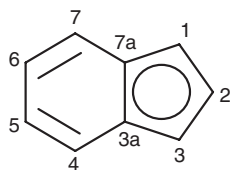
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towards terminal acetylenes [3]. However, reactions  $[(\eta^5\text{-C}_9\text{H}_7)\text{Ru}(\text{L}_2)\text{Cl}]$  with N-base ligands are virtually unknown except for a few reports of complexes containing bidentate N-donors [7]. It is noteworthy that complexes of indenyl differ from analogous cyclopentadienyl complexes in certain aspects such as higher reactivity and the more labile nature of the indenyl ligand. The higher reactivity is attributed to the ring slippage from  $\eta^5$ - to  $\eta^3$ - and back [8].

Recently, we described the syntheses of indenyl bis(phosphine)ruthenium complexes containing N, N donor Schiff base [9a] and azine ligands [9b]. As a part of a study of indenyl ruthenium(II) complexes, we report the reaction of **1** with various N-base ligands to give complexes **2a–2d**, and the reaction of **1** with  $\text{NH}_4\text{PF}_6$  in methanol resulting in the formation of the complex **3a**. In the presence of  $\text{NaBF}_4$ , the solvated complex **3b** is obtained. The complexes were characterized by  $^1\text{H}$ ,  $^{31}\text{P}\{^1\text{H}\}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectroscopy and the structures of the complexes **2a** and **3a** were established by single-crystal X-ray studies.

## 2. Experimental

Solvents were dried and distilled prior to use [10]. The nitriles, dicyanobenzene ( $\text{NCC}_6\text{H}_4\text{CN}$ ) (Aldrich), crotonitrile ( $\text{CH}_3\text{CH}=\text{CHCN}$ ), were used as received and acetonitrile was distilled over  $\text{CaH}_2$  while phenylacetonitrile was distilled under reduced pressure.  $[(\eta^5\text{-C}_9\text{H}_7)\text{Ru}(\eta^2\text{-dppe})\text{Cl}]$  was prepared by a literature method [11]. NMR spectra were recorded on a Bruker AMX400 MHz instrument with  $\text{SiMe}_4$  as internal standard. Chemical shifts of  $^{31}\text{P}\{^1\text{H}\}$  resonances were referenced to 85%  $\text{H}_3\text{PO}_4$ . Coupling constants are given in Hz. Infrared spectra were recorded (KBr pellets) on a Perkin-Elmer 983 spectrophotometer. Microanalytical data were obtained from the Sophisticated Analytical Instrumentation Facility (SAIF), NEHU, Shillong, using a Perkin-Elmer 2400 CHN/S analyzer. The following atom labelling scheme is used for the  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectroscopic data.



### 2.1. $[(\eta^5\text{-C}_9\text{H}_7)\text{Ru}(\eta^2\text{-dppe})(\text{CH}_3\text{CN})]\text{PF}_6$ (**2a**)

$[(\eta^5\text{-C}_9\text{H}_7)\text{Ru}(\eta^2\text{-dppe})\text{Cl}]$  (100 mg, 0.15 mmol),  $\text{NH}_4\text{PF}_6$  (73 mg, 0.45 mmol) and  $\text{CH}_3\text{CN}$  ( $30\text{ cm}^3$ ) were mixed in a round bottomed flask. The mixture was refluxed for 4 h, during which time the orange-red suspension turned yellow and a white solid appeared. The solution was filtered and the filtrate evaporated to dryness to give a yellow residue, which was extracted with dichloromethane and filtered to remove  $\text{NH}_4\text{Cl}$  and excess  $\text{NH}_4\text{PF}_6$ . Addition of excess hexane to the filtrate gave a yellow microcrystalline solid. Yield: 97 mg, 79%. Anal. Calcd for  $\text{C}_{37}\text{H}_{34}\text{NP}_3\text{F}_6\text{Ru}$  (%): C, 55.46; H, 4.24; N, 1.74. Found: C, 55.18; H, 4.12; N, 1.87.

NMR  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ): 1.47 (s, 3H), 2.42 (d, 2H,  $J_{\text{HH}}=2.0$ ), 2.47 (d, 2H,  $J_{\text{HH}}=2.3$ ), 4.78 (br, 1H), 4.91 (d, 2H,  $J_{\text{HH}}=2.3$ ), 6.96 (qt, 3H,  $J=3.1$ ), 7.13–7.49 (m, 21H). NMR  $\delta_{\text{C}}$  ( $\text{CDCl}_3$ ): 28.12 (t,  $J_{\text{C-H}}=23$ ), 65.91 (s), 92.77 (s, (indenyl ring C)), 107.99 (s, C-3a, 7a), 124.23–132.25 (m, Ph). NMR  $\delta_{\text{P}}$  ( $\text{CDCl}_3$ ): 82.43.

**2.2.  $[(\eta^5\text{-C}_9\text{H}_7)\text{Ru}(\eta^2\text{-dppe})(\text{L})]\text{PF}_6$  [ $\text{L}=\text{CH}_3\text{CH}=\text{CHCN}$  (**2b**),  $\text{NCC}_6\text{H}_4\text{CN}$  (**2c**),  $\text{C}_6\text{H}_5\text{CH}_2\text{CN}$  (**2d**)]**

The complexes were prepared by following a general method in which  $[(\eta^5\text{-C}_9\text{H}_7)\text{Ru}(\eta^2\text{-dppe})\text{Cl}]$  (100 mg, 0.15 mmol), L (0.30 mmol) and  $\text{NH}_4\text{PF}_6$  (73 mg, 0.45 mmol) were refluxed in 30  $\text{cm}^3$  of methanol for 3 h. Solvent was removed under reduced pressure and the yellow residue was dissolved in dichloromethane and filtered. The solution, on subsequent concentration to ca 5  $\text{cm}^3$  and addition of excess hexane, gave a yellow solid. Complex **2b**: Yield: 62 mg, 78%. Anal. Calcd for  $\text{C}_{39}\text{H}_{36}\text{NP}_3\text{F}_6\text{Ru}$  (%): C, 56.69; H, 4.36; N, 1.69. Found: C, 56.38; H, 4.12; N, 1.27.  $^1\text{H}$  NMR ( $\delta$ ,  $\text{CDCl}_3$ ): 2.17 (s, 3H), 2.45–2.52 (m, 4H), 4.88 (d, 2H,  $J_{\text{HH}}=3.2$ ), 4.95 (br, 1H), 6.97–9.14 (m, 26H).  $\delta_{\text{P}}$  ( $\text{CDCl}_3$ ): 81.60 (d,  $J_{\text{HP}}=33.52$ ). IR (KBr,  $\text{cm}^{-1}$ ): 2236. Complex **2c**: Yield: 60 mg, 82%. Anal. Calcd for  $\text{C}_{43}\text{H}_{35}\text{N}_2\text{P}_3\text{F}_6\text{Ru}$  (%): C, 58.20; H, 3.94; N, 3.15. Found: C, 57.83; H, 3.56; N, 2.89. NMR  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ): 2.16–2.30 (m, 2H), 2.52–2.56 (m, 2H), 4.48 (d, 2H,  $J_{\text{HH}}=3.2$ ), 4.97 (br, 1H, unresolved), 6.68–7.92 (m, 28H).  $\delta_{\text{P}}$  ( $\text{CDCl}_3$ ): 81.85 (s) and 82.85 (s). IR (KBr,  $\text{cm}^{-1}$ ): 2229. Complex **2d**: Yield: 58 mg, 75%. Anal. Calcd for  $\text{C}_{43}\text{H}_{38}\text{NP}_3\text{F}_6\text{Ru}$  (%): C, 58.93; H, 4.34; N, 1.59. Found: 59.28; H, 4.52; N, 1.96. IR (KBr,  $\text{cm}^{-1}$ ): 2234. NMR  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ): 2.38–2.77 (m, 4H), 3.21 (m, 2H), 4.81 (d, 2H,  $J_{\text{HH}}=3.46$ ), 4.94 (br, 1H), 6.28–7.48 (m, 29H).  $\delta_{\text{P}}$  ( $\text{CDCl}_3$ ): 82.05 (s).

**2.3.  $[(\eta^5\text{-C}_9\text{H}_7)\text{Ru}(\eta^2\text{-dppe})(\text{NH}_3)]\text{PF}_6$  (**3a**)**

$[(\eta^5\text{-C}_9\text{H}_7)\text{Ru}(\eta^2\text{-dppe})\text{Cl}]$  (100 mg, 0.15 mmol), and  $\text{NH}_4\text{PF}_6$  (0.048 g, 0.30 mmol) were refluxed in 40  $\text{cm}^3$  of methanol for 3 h. The orange solution turned yellow as the reaction proceeded. The solution was cooled to room temperature and the mixture evaporated to dryness. The residue was extracted with dichloromethane and filtered, and the filtrate on subsequent concentration to ca 5  $\text{cm}^3$  and addition of excess hexane gave a yellow solid. The product was washed with hexane and finally with diethylether. Yield: 97 mg, 82%. Anal. Calcd for  $\text{C}_{35}\text{H}_{34}\text{NP}_3\text{F}_6\text{Ru}$  (%): C, 54.11; H, 4.38; N, 1.80. Found: C, 53.82; H, 4.13; N, 2.08. NMR  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ): 2.36–2.46 (m, 4H), 4.63 (br, 1H, unresolved), 4.96 (d, 2H,  $J_{\text{HH}}=2.08$ ), 7.04–7.50 (m, 31H). NMR  $\delta_{\text{P}}$  ( $\text{CDCl}_3$ ): 84.94.

**2.4.  $[(\eta^5\text{-C}_9\text{H}_7)\text{Ru}(\eta^2\text{-dppe})(\text{MeOH})]\text{PF}_6$  (**3b**)**

This complex was prepared in a similar manner as **3a**, using  $\text{NaBF}_4$  instead of  $\text{NH}_4\text{PF}_6$ . Anal. Calcd for  $\text{C}_{36}\text{H}_{35}\text{OP}_3\text{F}_6\text{Ru}$  (%): C, 54.60, H, 4.42. Found: C, 54.18; H, 4.25. IR (KBr,  $\text{cm}^{-1}$ ): 3065. NMR  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ): 2.43–2.52 (m, 4H), 4.85 (t, 1H,  $J_{\text{HH}}=2.03$ ), 4.93 (d, 2H,  $J_{\text{HH}}=2.47$ ), 6.91–7.82 (m, 31H). NMR  $\delta_{\text{P}}$  ( $\text{CDCl}_3$ ): 82.35.

## 2.5. Structure analysis and refinement

X-ray quality crystals of **2a** and **3a** were grown by slow diffusion of hexane into dichloromethane solutions. X-ray intensity data were measured at 133(2) K on a Bruker Smart 1000 CCD diffractometer, using graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Intensity data were corrected for absorption [12]. The structures were solved by direct methods using SHELXS-97 [13] and refined by full-matrix least-squares based on  $F^2$  using SHELXL-97 [14]. The weighting scheme used was  $w = 1/[\sigma^2(F_o^2) + aP^2 + bp]$  where  $P = (F_o^2 + 2F_c^2)/3$ . Non-hydrogen atoms were refined anisotropically and hydrogen atoms were included using a riding model, except for the acetonitrile methyl in **2a**, which was treated as a rigid group, and the ammonia hydrogens in **3a**, which were refined freely. For **3a**, distance restraints for the ammonia group and the water molecule were used, and the refinement of the structure was divided into two blocks. Refinement converged at  $R = 0.0263$  for complex **2a** and 0.0412 for complex **3a** (for observed data), and  $wR_2 = 0.0729$  and 0.0993 for complexes **2a** and **3a**, respectively (for all data). A summary of crystal data and refinement parameters is given in table 1 and selected bond lengths and angles including torsion angles are listed in tables 2 to 5.

Table 1. Summary of crystal data and refinement details for **2a** and **3a**.

Empirical formula	$C_{74}H_{68}F_{12}N_2P_6Ru_2$ , <b>2a</b>	$C_{35.5}H_{36}Cl F_6NO_{0.5}P_3Ru$ , <b>3a</b>
Formula weight	1601.26	828.08
Temperature (K)	133(2)	133(2)
Wavelength ( $\text{\AA}$ )	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
Unit cell dimensions ( $\text{\AA}$ , $^\circ$ )	$a = 19.0899(10)$ $b = 9.0951(4)$ $c = 21.5870(12)$ $\beta = 112.914(3)$	$a = 12.0131(8)$ $b = 14.3224(10)$ $c = 40.883(3)$ $\alpha = 86.042(3)$ $\beta = 87.527(3)$ $\gamma = 85.357(3)^\circ$
Volume ( $\text{\AA}^3$ )	3452.3(3)	6989.3(8)
Z	2	8
Density (calculated) ( $\text{Mg m}^{-3}$ )	1.540	1.574
Absorption coefficient ( $\text{mm}^{-1}$ )	0.654	0.724
$F(000)$	1624	3360
Crystal size (mm)	$0.38 \times 0.26 \times 0.21$	$0.40 \times 0.34 \times 0.25$
Theta range for data collection ( $^\circ$ )	1.16 to 30.03	1.43 to 30.03
Index ranges	$-26 \leq h \leq 26$ $-12 \leq k \leq 12$ $-30 \leq l \leq 30$	$-16 \leq h \leq 16$ $-20 \leq k \leq 20$ $-57 \leq l \leq 57$
Reflections collected	69488	148762
Independent reflections	10066 [ $R(\text{int}) = 0.0362$ ]	40660 [ $R(\text{int}) = 0.0322$ ]
Completeness to $\theta$ ( $^\circ$ )	30.00	30.00
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.8749 and 0.7931	0.8398 and 0.7484
Refinement method	Full-matrix least-squares on $F^2$	
Data/restraints/parameters	10066/0/34	40660/139/1791
Goodness-of-fit on $F^2$	1.053	1.070
Final $R$ indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0263$ , $wR_2 = 0.0694$	$R_1 = 0.0412$ , $wR_2 = 0.0930$
$R$ indices (all data)	$R_1 = 0.0337$ , $wR_2 = 0.0729$	$R_1 = 0.0560$ , $wR_2 = 0.0993$
Largest diff. peak and hole ( $e \text{\AA}^{-3}$ )	0.825 and $-0.422$	1.314 and $-0.918$

Table 2. Selected bond lengths (Å), angles (°) and 'slip fold' parameter  $\Delta$  for **2a**.

<i>Bond lengths</i>			
Ru–C*	1.8926(6)	Ru–C(53)	2.2111(15)
Ru–C(51)	2.2178(15)	Ru–C(54)	2.3063(14)
Ru–C(52)	2.2075(15)	Ru–C(59)	2.3351(14)
Ru–P(1)	2.3091(4)	Ru–P(2)	2.2564(4)
N(1)–C(3)	1.136(2)	Ru–N(1)	2.0488(14)
	$\Delta^a$	0.1063	
<i>Bond angles</i>			
N(1)–Ru–P(1)	86.15(4)	N(1)–Ru–P(2)	89.73(4)
P(2)–Ru–P(1)	83.147(14)		

C\* = Centroid of C(51), C(52), C(53), C(54), C(59).

<sup>a</sup>  $\Delta = (d_{\text{avg}}(\text{Ru}-\text{C}(54), \text{C}(59)) - d_{\text{avg}}(\text{Ru}-\text{C}(51), \text{C}(53)))$ .Table 3. Selected torsion angles (°) for **2a**.

N(1)–Ru–P(1)–C(11)	–52.09(7)	N(1)–Ru–P(1)–C(21)	–179.05(7)
N(1)–Ru–P(1)–C(1)	65.03(7)	N(1)–Ru–P(2)–C(41)	33.65(7)
N(1)–Ru–P(2)–C(31)	156.66(7)	N(1)–Ru–P(2)–C(2)	–85.64(7)

Table 4. Hydrogen bonds (Å) and angles (°) for **2a**.

D–H...A	d(D–H)	d(H...A)	d(D...A)	$\angle(\text{DHA})$
C(16)–H(16)...F(5)#1	0.95	2.41	3.140(2)	133.5
C(25)–H(25)...F(4)#2	0.95	2.57	3.154(2)	119.9
C(26)–H(26)...F(4)#2	0.95	2.57	3.154(2)	120.3
C(51)–H(51)...F(4)#2	0.95	2.45	3.376(2)	165.4
C(33)–H(33)...F(2)#3	0.95	2.57	3.450(2)	154.7
C(34)–H(34)...F(6)#3	0.95	2.44	3.215(2)	138.5

Symmetry transformations used to generate equivalent atoms are #1:  $x, y+1, z$ ; #2:  $x, -y+1/2, z+1/2$ ; #3:  $-x, y+1/2, -z+1/2$ .Table 5. Selected bond lengths (Å), angles (°) and  $\Delta$  for **3a**.

<i>Bond lengths</i>			
Ru–C**	1.8834(11)	Ru(1)–C(4)	2.311(2)
Ru(1)–C(1)	2.193(2)	Ru(1)–C(9)	2.321(2)
Ru(1)–C(2)	2.189(2)	C(10)–C(20)	1.529(4)
Ru(1)–C(3)	2.222(2)	Ru(1)–N(1)	2.179(2)
Ru(1)–P(1)	2.2552(7)	Ru(1)–P(2)	2.2909(7)
	$\Delta^a$	0.1085	
<i>Bond angles</i>			
N(1)–Ru(1)–P(1)	88.93(7)	N(1)–Ru(1)–P(2)	93.82(7)
P(1)–Ru(1)–P(2)	84.19(2)		

C\*\* = Centroid of C(1), C(2), C(3), C(4), C(9).

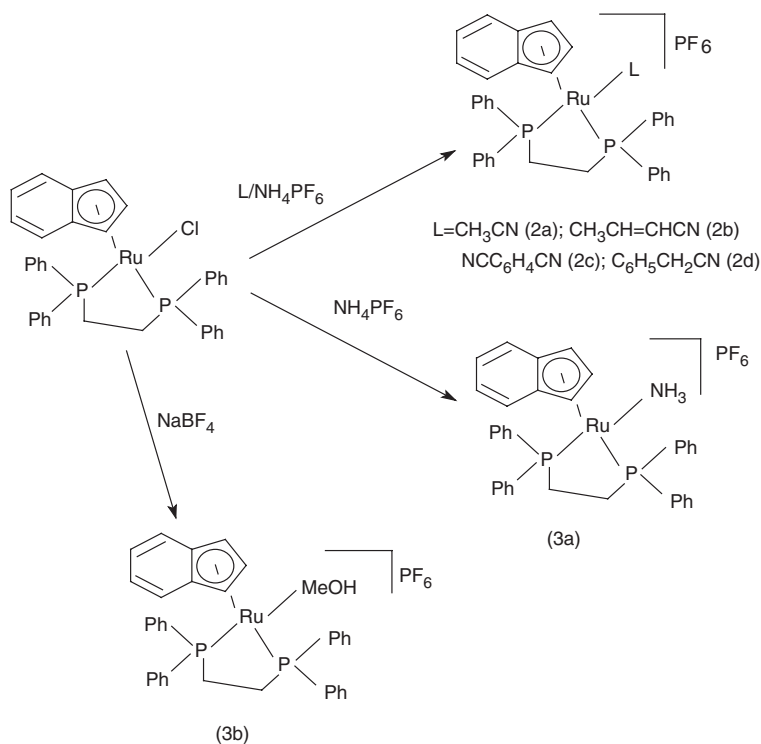
<sup>a</sup>  $\Delta = d_{\text{avg}}(\text{Ru}-\text{C}(4), \text{C}(9)) - d_{\text{avg}}(\text{Ru}-\text{C}(1), \text{C}(3))$ .

### 3. Results and discussion

#### 3.1. Reaction of **1** with nitriles

Reaction of indenyl complex  $[(\eta^5\text{-C}_6\text{H}_7)\text{Ru}(\eta^2\text{-dppe})\text{Cl}]$  (**1**) with acetonitrile in the presence of  $\text{NH}_4\text{PF}_6$  gave **2a** in good yield (scheme 1). Similarly, reaction of complex **1**

with nitriles in methanol in the presence of excess  $\text{NH}_4\text{PF}_6$  yields the mononuclear complexes  $[(\eta^5\text{-C}_9\text{H}_7)\text{Ru}(\eta^2\text{-dppe})\text{L}]\text{PF}_6$  (scheme 1). The complexes are soluble in chlorinated solvents. IR spectra of the complexes showed characteristic  $\nu_{\text{CN}}$  absorption bands of coordinated nitrile in the region  $2229\text{--}223\text{ cm}^{-1}$ . Proton NMR spectra exhibit resonances for  $\text{H}^{1,3}$  and  $\text{H}^2$  protons of indenyl at around  $\delta$  4.48 and 4.97, respectively (occasionally unresolved). In the proton NMR spectrum of **2a**, the protons of acetonitrile appear as a singlet at  $\delta$  1.43.  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra of the complexes showed a single resonance at  $\delta$  81.85–82.43, except for **2c**, where the spectrum showed two singlets at  $\delta$  81.85 and 82.85 ppm, indicative of chemical inequivalence of the two phosphorous atoms.  $^{13}\text{C}\{^1\text{H}\}$  NMR of **2a** suggests a pronounced ‘slip fold’ distortion of the coordinated indenyl ligand persists in solution. Köhler proposed a correlation between  $^{13}\text{C}\{^1\text{H}\}$  chemical shifts of indenyl ring junction carbons, C(3a), C(7a) and hapticity of the indene [15]. The indenyl carbon resonance for C(3a), C(7a) in the complex is  $\delta$  107.99. The upfield shift relative to indene is indicative of  $\eta^5$ -coordination. Further, the calculated parameter  $\Delta\delta^a$  (C-3a, 7a) is  $-22.09$  and suggests a slight distortion of the indenyl ring [16], consistent with the X-ray diffraction study.



Scheme 1. Reaction scheme.

### 3.2. Reaction of 1 with $\text{NH}_4\text{PF}_6$ or $\text{NaBF}_4$

Reaction of **1** with  $\text{NH}_4\text{PF}_6$  in methanol yields a yellow complex **3a** in good yield (scheme 1). It is believed that the complex forms as a result of amination of **1**

by the  $\text{NH}_4\text{PF}_6$  present in the reaction mixture. The IR spectrum of **3a** displays an absorption band at  $3065\text{ cm}^{-1}$ , corresponding to  $\nu(\text{N-H})$  of  $\text{NH}_3$ . The presence of  $\text{NH}_3$  is also confirmed by analytical data and X-ray analysis. Spectroscopic and analytical data are consistent with the formulation  $[(\eta^5\text{-C}_9\text{H}_7)\text{Ru}(\eta^2\text{-dppe})(\text{NH}_3)]\text{PF}_6$ . Further evidence for the coordination of  $\text{NH}_3$  from  $\text{NH}_4\text{PF}_6$  comes from the following experiment. Reaction of **1** with  $\text{NaBF}_4$  in methanol does not give **3a**. The analogous complex **3b** presumably forms. A few reports on similar coordination of  $\text{NH}_3$  ligand to ruthenium stems from ammonium salts are known [17]. A very closely related reaction was also reported by Faller *et al.* [18], in which reaction of  $[\text{CpRu}(\text{PPh}_3)_2\text{Cl}]$  with  $\text{PhCHO}$  in the presence of  $\text{NH}_4\text{PF}_6$  gave the benzaldimine complex,  $[\text{CpRu}(\text{PPh}_3)_2(\text{NH}=\text{CHPh})]\text{PF}_6$ . Complexes **3a** and **3b** are soluble in chlorinated solvents. In proton NMR spectra, ammonia and methanol ligands could not be found in  $\text{CDCl}_3$  solution. However, coordination of  $\text{NH}_3$  and  $\text{MeOH}$  was unambiguously revealed by analytical and spectroscopic data. The structure of **3a** was established by single-crystal X-ray analysis.

### 3.3. Crystal structures

**3.3.1. Complex 2a.** The structure consists of a mononuclear cation and a  $\text{PF}_6$  ion. A perspective view of the compound with the atom labelling scheme is shown in figure 1. Selected bond lengths and angles are presented in table 2. The unit cell contains two independent molecules. The geometry around the ruthenium atom in the complex can be described as distorted octahedral if the indenyl ligand is assumed to occupy three *facial* coordination sites. The indenyl ligand is bonded to the ruthenium

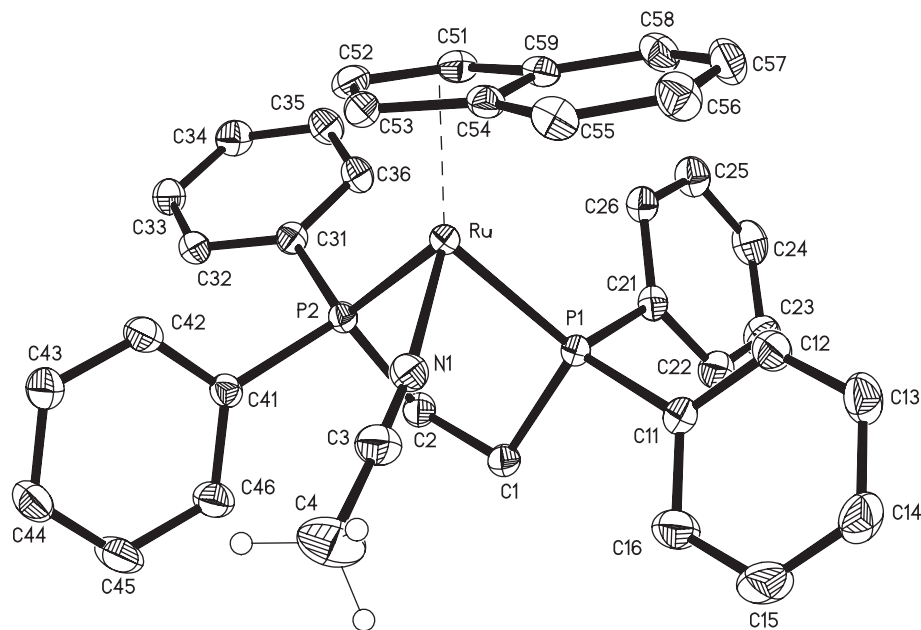


Figure 1. Molecular structure of **2a** showing 50% probability ellipsoids and the atom numbering scheme. Hydrogen atoms (except methyl protons) and the  $\text{PF}_6$  ion are omitted for clarity.

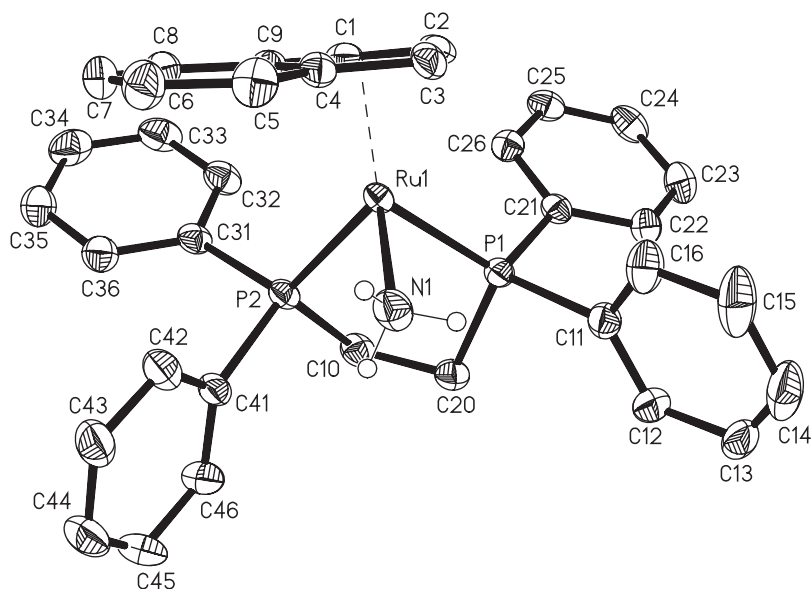


Figure 2. Molecular structure of **3a** showing 50% probability ellipsoids and the atom numbering scheme. Hydrogen atoms are omitted for clarity.

atom in  $\eta^5$  mode and displays the asymmetric coordination generally observed with this ligand [19]. Thus, Ru–C(51) (2.2178(15) Å), Ru–C(52) (2.2075(15) Å) and Ru–C(53) (2.2111(15) Å) bond lengths are shorter than for those between ruthenium and ring junction carbon atoms, Ru–C(54) (2.3063(14) Å) and Ru–C(59) (2.3351(14) Å). The asymmetric metal–carbon bond distance is due to slipping of ruthenium from  $\eta^5$ - to  $\eta^3$ -coordination [20]. The indenyl ligand exhibits a pronounced ‘slip-fold’ ( $\Delta$ ) distortion [21] relative to a plane, the value being 0.1063 Å, and which is comparable to that found in other indenyl complexes [9b]. The Ru–N(1) bond distance 2.0488(14) Å is very close to the Ru–NCCH<sub>3</sub> bond distance of closely related complexes [9a]. The structure shows the presence of hydrogen bonding between hydrogen atoms of the phenyl ring and a fluorine atom of the PF<sub>6</sub> ion. Hydrogen bond lengths and angles are presented in table 3.

**3.3.2. Complex 3a.** A perspective view of the complex with the atom labelling scheme is shown in figure 2 and selected bond lengths and angles are listed in table 5. The unit cell has four complex molecules in the asymmetric unit and two molecules each of CH<sub>2</sub>Cl<sub>2</sub> and H<sub>2</sub>O. The ruthenium atom is coordinated to the dppe ligand, one NH<sub>3</sub> molecule and to the indenyl ligand in the  $\eta^5$  mode, leading to the usual piano stool geometry. The distorted octahedron has three *facial* sites occupied by the indenyl ligand. As observed in **2a** and other indenyl complexes, the structure shows asymmetric coordination of ruthenium to carbons of the five-membered carbon rings (table 2). Ru–P distances are comparable with those of **2a** and other reported Ru–P bond distances [22]. The indenyl ligand is slightly distorted relative to planarity. The ‘slip-fold’ ( $\Delta$ ) distortion value is 0.1085 Å, which is comparable to that of **2a** and other indenyl complexes [3a, 9b].

## Supplementary material

Crystallographic data for the structural analyses have been deposited at the Cambridge Crystallographic Data Centre (CCDC), CCDC Nos 272618 for **2a** and 272619 for **3a**. Copies of this information may be obtained free of charge from the director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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