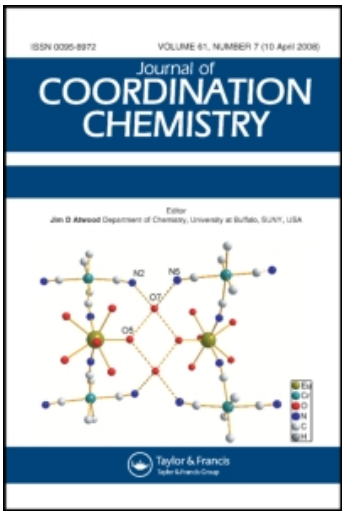

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Studies of ^{5}-cyclichydrocarbon ruthenium(II) complexes containing para-amino-N-(pyrid-2-ylmethylene)phenylamine ligand: molecular structure of $[(^{5}\text{-}C_5H_5)Ru(PPh_3)(C_5H_4NCH{=}N\text{-}C_6H_4\text{-}p\text{-}NH_2)]BF_4$

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Studies of η^5-cyclichydrocarbon ruthenium(II) complexes containing *para*-amino-*N*-(pyrid-2-ylmethylene)phenylamine ligand: molecular structure of $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(C_5H_4NCH{=}N\text{-}C_6H_4\text{-}p\text{-}NH_2)]BF_4$

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Reaction of $[(\eta^5\text{-Cp})Ru(PPh_3)_2Cl]$ (**1**) with excess *para*-amino-*N*-(pyrid-2-ylmethylene)-phenylamine ligand (app) in methanol in the presence of NH_4BF_4 leads to the formation of $[\eta^5\text{-CpRu}(PPh_3)(aap)]BF_4$ (**6**BF_4). Similarly, $[(\eta^5\text{-ind})Ru(PPh_3)_2(CH_3CN)]BF_4$ (**4**BF_4) and $[(\eta^5\text{-Cp*})Ru(PPh_3)_2(CH_3CN)]BF_4$ (**5**BF_4) react with app to yield the cationic complexes $[(\eta^5\text{-ind})Ru(PPh_3)(app)]BF_4$ (**7**BF_4) and $[(\eta^5\text{-Cp*})Ru(PPh_3)(app)]BF_4$ (**8**BF_4), respectively. The complexes were characterized by analysis and spectroscopic data. The structure of a representative complex (**6**BF_4) was established by single-crystal X-ray methods.

Keywords: Cyclopentadienyl; Indenyl; Pentamethylcyclopentadienyl; Pyridine-2-carboxaldehyde; Ruthenium(II); Crystal structure

1. Introduction

The chemistry of cyclopentadienyl in its ruthenium bisphosphine complexes, $[Cp'Ru(PPh_3)_2Cl]$ [Cp′ = cyclopentadienyl (Cp), indenyl, pentamethylcyclopentadienyl (Cp*)] has generated much interest during the past few decades owing to high reactivity [1] and catalytic activity [2, 3]. Their chemistry is characterized by the ready displacement of triphenylphosphine and/or chloride to yield neutral or cationic complexes [4–8]. The complexes $[(\eta^5\text{-indenyl})Ru(PPh_3)_2Cl]$ and $[(\eta^5\text{-Cp*})Ru(PPh_3)_2Cl]$ differ from $[(\eta^5\text{-Cp})Ru(PPh_3)_2Cl]$ in certain aspects such as high reactivity and lability of the

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organic moiety. High reactivity of indenyl complexes is attributed to η^5- to η^3-ring slippage and the inductive effect of the methyl group [9]. Our current interest in these species involves substitution of two sites in $[Cp'Ru(PPh_3)_2Cl]$ by various nitrogenous bases as a route to explore their chemistry. We have already reported the reaction of indenyl and pentamethylcyclopentadienyl complexes with various nitrogenous ligands [10, 11]. As a part of this study, we report the syntheses and structures of cyclopentadienyl, indenyl and pentamethylcyclopentadienyl complexes of *para*-amino-*N*-(pyrid-2-ylmethylene)-phenylamine ligand (app).

2. Experimental

All synthetic operations were performed in a nitrogen atmosphere. Solvents were dried over appropriate agents and distilled prior to use [12]. Ligands were made by the condensation of pyridine-2-carboxaldehyde with *p*-phenylenediamine in a 1 : 1 mol ratio in ethanol. The starting materials, $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl]$ (**1**) [13], $[(\eta^5\text{-}C_9H_7)Ru(PPh_3)_2Cl]$ (**2**) [14] and $[(\eta^5\text{-}C_5Me_5)Ru(PPh_3)_2Cl]$ (**3**) [15], $[(\eta^5\text{-}C_9H_7)Ru(PPh_3)_2(CH_3CN)]BF_4$ (**4**BF_4) [10] and $[(\eta^5\text{-}C_5Me_5)Ru(PPh_3)_2(CH_3CN)]BF_4$ (**5**BF_4) [11] were prepared following literature methods. NMR spectra were recorded on Bruker ACF-300 MHz instruments with $SiMe_4$ as internal standard. Chemical shifts for ^{31}P resonances were referred to 85% H_3PO_4. Electronic spectra were recorded on a Hitachi-U-2300 spectrophotometer in (*ca* 10^{-4} M dichloromethane solutions). Microanalytical data were obtained from the Regional Sophisticated Instrumentation Centre (RSIC) NEHU, Shillong, using a Perkin-Elmer 2400 CHN/S instrument.

2.1. *[(η⁵-Cp)Ru(PPh₃)(app)]BF₄ (6BF₄)*

$[(\eta^5\text{-}Cp)Ru(PPh_3)_2Cl]$ (100 mg, 0.14 mmol), app (60 mg, 0.28 mmol), NH_4BF_4 (29 mg, 0.28 mmol) and methanol (40 cm^3) were mixed in a 100 cm^3 round-bottomed flask and the mixture refluxed under nitrogen for 4 h. The colour of the solution changed progressively from yellow–orange to dark red as the reaction progressed. The solution was cooled to room temperature and solvent was removed on a rotary evaporator. The residue was extracted with dichloromethane then filtered through a short silica gel column. The filtrate, on concentration to *ca* 5 cm^3 and addition of excess hexane afforded a dark red solid. The solid was collected by centrifugation and washed with hexane (2×20 cm^3) then diethylether and dried under vacuum. Yield: 90 mg (86%). Anal. Calcd for $C_{35}H_{31}N_3BF_4PRu$ (%): C, 54.5; H, 4.0; N, 5.4. Found: C, 54.2; H, 3.9; N, 5.1. ^1H NMR (δ, $CDCl_3$): 9.21 (d, 1H, $J_{HH} = 5.52$), 8.26 (d, 1H, $J_{HH} = 2.98$), 7.63 (m, 4H), 7.34–6.92 (m, 17H), 6.52 (d, 2H, $J_{HH} = 8.72$), 4.69 (s, 5H), 4.10 (s, 2H). ^{31}P $\{^1H\}$ NMR (δ, $CDCl_3$): 48.22. UV-Vis (λ_{max}, nm): 423, 419, 400, 393, 349, 335.

2.2. *[(η⁵-indenyl)Ru(PPh₃)(app)]BF₄ (7BF₄)*

$[(\eta^5\text{-indenyl})Ru(PPh_3)_2(CH_3CN)]BF_4$ (**4**BF_4) (100 mg, 0.107 mmol), app (42 mg, 0.215 mmol) and methanol (40 cm^3) were refluxed under dry nitrogen for 3 h. The yellow–orange suspension turned dark brown as the reaction proceeded. The solution

was cooled to room temperature and the solvent removed on a rotary evaporator. The brown residue was dissolved in dichloromethane and filtered through a short silica gel column. The filtrate on subsequent concentration to *ca* 5 ml and addition of excess hexane gave a dark brown solid, which was washed with hexane ($2 \times 10\,cm^3$) and dried under vacuum. Yield: 67 mg (82%). Anal. Calcd for $C_{39}H_{33}N_3BF_4PRu$ (%): C, 61.41; H, 4.33; N, 5.51. Found: C, 60.98; H, 4.22; N, 5.41. ^{1}H NMR (δ, $CDCl_3$): 9.37 (d, 1H, $J_{HH} = 5.42$), 9.13 (d, 1H, $J_{HH} = 5.84$), 8.54 (m, 2H), 7.55–6.73 (m, 22H), 6.51 (d, 2H, $J_{HH} = 8.62$), 4.87 (t, 1H, $J_{HH} = 3.29$), 4.58 (d, 2H, $J_{HH} = 2.86$), 4.01 (s, 2H). ^{31}P $\{^1H\}$ NMR: (δ, $CDCl_3$): 54.28. UV-Vis (λ_{max}, nm): 436, 433, 400, 389, 354, 337.

2.3. *[(η^5-Cp*)Ru(PPh$_3$)(app)]BF$_4$ (8BF$_4$)*

The complex was prepared by following a similar method as described for **7**BF_4, using the **5**BF_4 instead of **4**BF_4. Yield: 67 mg (80%). Anal. Calcd for $C_{40}H_{41}N_3BF_4PRu$ (%): C, 61.3; H, 5.24; N, 5.37. Found: C, 60.89; H, 5.14; N, 5.21. ^{1}H NMR (δ, $CDCl_3$): 9.24 (d, 1H, $J_{HH} = 5.21$), 8.92 (d, 1H, $J_{HH} = 2.94$), 8.41 (m, 2H), 7.86–7.14 (m, 18H), 6.91 (d, 2H, $J_{HH} = 2.93$), 4.13 (s, 2H), 1.35 (s, 15H). ^{31}P $\{^1H\}$ NMR (δ, $CDCl_3$): 46.28. UV-Vis (λ_{max}, nm): 421, 418, 395, 387, 354, 337.

2.4. *Structure analysis*

X-ray quality crystals of complex **6**BF_4 were grown by slow diffusion of hexane into an acetone solution of **6**BF_4. X-ray intensity data were measured at 120(2) K on a Bruker AXS Apex CCD area detector employing a graphite monochromater using Mo Kα radiation ($\lambda = 0.71073$ Å). Intensity data were corrected for Lorentz and polarization effects and absorption correction was made using the SAINT program [16]. An empirical absorption correction was made by modelling a transmission surface by spherical harmonics employing equivalent reflections with $I > 2\sigma(I)$ with SADABS [17]. The structure was solved by direct methods [18] and refined by full-matrix least-squares based on F^2 using SHELXL-97 software [19]. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a "riding" model. Figure 1 is the molecular graphic [20] representation of the complex with 50% probability thermal ellipsoids displayed. Refinement converged at $R = 0.0421$ for observed data (F) and $wR_2 = 0.1007$ for unique data (F^2). A summary of crystallographic data is given in table 1.

3. Results and discussion

[(η^5-Cp)Ru(PPh_3)(app)]BF_4 can be prepared by reaction of [(η^5-Cp)Ru(PPh_3)$_2$Cl] with app in methanol in the presence of NH_4BF_4.

However, the analogous complexes [(η^5-indenyl)Ru(PPh_3)(app)]BF_4 and [(η^5-Cp*)Ru(PPh_3)(app)]BF_4 were prepared starting from the acetonitrile complexes (**4**BF_4 and **5**BF_4), respectively, in methanol or dichloromethane-benzene (scheme 1). It is noteworthy that the acetonitrile complexes are better precursors for the syntheses of indenyl or Cp* complexes containing nitrogenous ligands, as compared with the chloro analogues.

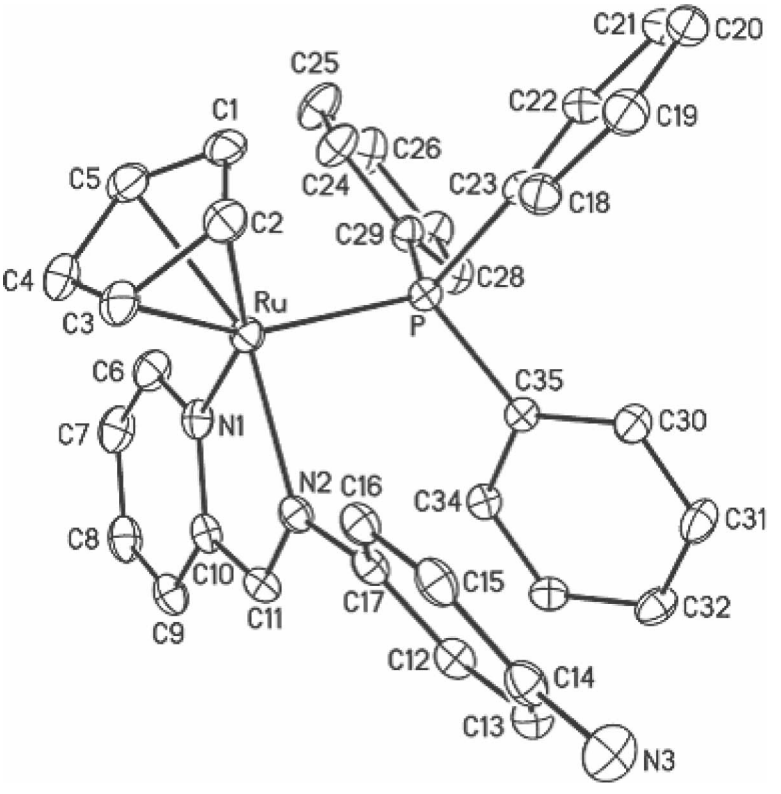


Figure 1. Molecular structure of $[(\eta^5\text{-}C_5H_5)Ru(PPh_3)(C_5H_4NCH{=}N\text{-}C_6H_4\text{-}p\text{-}NH_2)]BF_4$. Hydrogen atoms and the BF_4^- ion have been omitted for clarity.

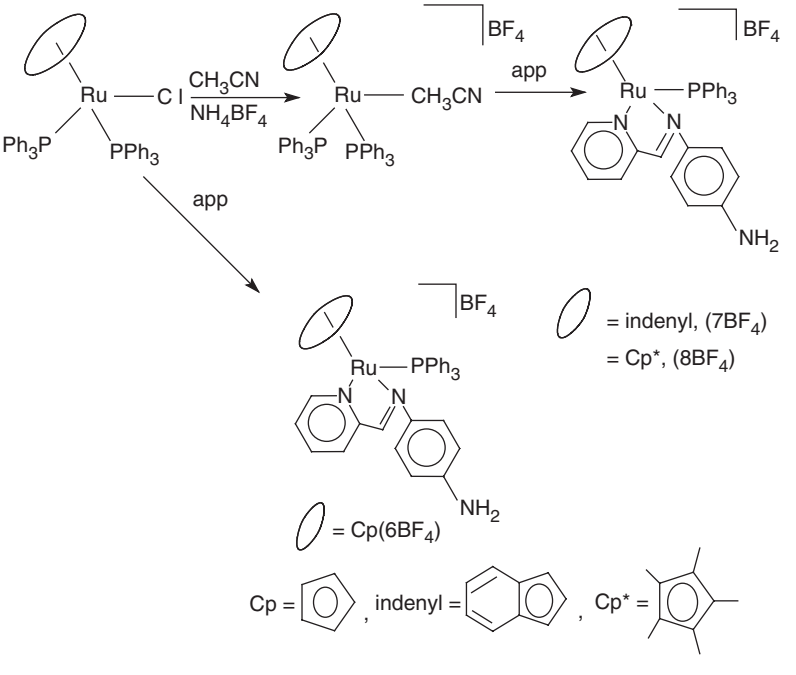
The complexes are highly soluble in chlorinated solvents. Proton NMR spectra of the complexes display a single peak at δ4.0 assignable to the protons of $-NH_2$ group of the coordinated ligand. Complex **6**BF_4 exhibits a single resonance at δ4.63 for the protons of Cp while **7**BF_4 displays a doublet at δ4.48 ($J_{HH} = 3.2$) and a triplet at δ ($J_{HH} = 2.7$ Hz) characteristic of protons of the indenyl ligand. In the case of **8**BF_4, a single resonance is observed at δ1.43 for the methyl proton of the Cp* ligand. Electronic spectra of the complexes display three distinct peaks in the ranges 436–418, 400–387 and 354–335 nm. Low energy bands at 418–436 nm are assigned to MLCT transition {Ru ($d\pi \rightarrow (L\pi)$} while the bands below 400 nm are composed of MLCT, ligand field or intra-ligand transitions ($\pi \rightarrow \pi^*$). Analytical and spectroscopic data are consistent with the formulations.

3.1. *Crystal structure*

The complex **6**BF_4 crystallizes with one acetone molecule per formula unit. The geometry about the metal can be regarded as distorted octahedral with three sites occupied by Cp and the rest by the two nitrogen atoms of the coordinated ligand and a triphenylphosphine ligand. The average Ru–C (Cp) bond length is 2.197 Å, which is comparable to those in other related Cp complexes [21]. There is

Table 1. Summary of crystal structure data for **6** $BF_4 \cdot CH_3COCH_3$.

Empirical formula	$C_{38}H_{37}BF_4N_3OPRu$
M	770.56
Temperature	120(2) K
Wavelength	0.71073 A
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	$a = 16.034(3)$ Å
	$b = 19.147(4)$ Å
	$c = 11.372(2)$ Å
	$\beta = 96.609(3)^\circ$
V	3468.1(11) $Å^3$
Z	4
Calculated density	1.476 $Mg\,m^{-3}$
Absorption coefficient	0.555 mm^{-1}
$F(000)$	1576
Crystal size	$0.22 \times 0.18 \times 0.06\,mm^3$
Theta range for data collection	2.09 to 28.25°
Limiting indices	$-21 \le h \le 21$,
	$-25 \le k \le 25$,
	$-15 \le l \le 15$
Reflections collected/unique	38960/8168 [R(int) = 0.0457]
Completeness to theta	28.25–95.2%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9674 and 0.8876
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	8168/34/444
Goodness-of-fit on F^2	1.055
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0421$, $wR2 = 0.1007$
R indices (all data)	$R1 = 0.0650$, $wR2 = 0.1098$
Largest diff. peak and hole	1.355 and −0.480 e $Å^{-3}$



Scheme 1.

Table 2. Selected bond lengths (Å) and angles (°) for the complex **6**BF_4.

Bond lengths			
Ru–P	2.3079(8)	C(11)–N(2)	1.295(3)
Ru–N(1)	2.080(2)	Ru–N(2)	2.092(2)
N(2)–C(17)	1.435(3)	C(14)–N(3)	1.382(4)
Ru–C(1)	2.173(3)	Ru–C(4)	2.207(4)
Ru–C(2)	2.216(3)	Ru–C(5)	2.167(3)
Ru–C(3)	2.226(3)		
Bond angles			
N(1)–Ru–N(2)	76.57(9)	C(10)–C(11)–N(2)	117.4(2)
P–Ru–N(1)	91.73(6)	P–Ru–N(2)	91.46(6)
Ru–N(1)–C(10)	115.96(18)	Ru–N(2)–C(11)	115.68(18)

no significant difference in the C–C bond lengths in Cp°, the bond lengths falling in the range 1.412(4)–1.436(4) Å. Ru–N(1) 2.080(2) and Ru–N(2) 2.092(2) Å are within the range found for other reported compounds. The Ru–PPh_3 bond distance is 2.3079(8) Å, which also is within the usual range of Ru–P bond distances (2.20–2.43 Å) [22]. The bite angle N(1)–Ru(1)–N(2), 76.57(9)° is very close to that observed in related complexes [10].

Supplementary material

Crystallographic data for the structural analysis have been deposited at the Cambridge Crystallographic Data Centre (CCDC), CCDC 270844. 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).

References

[1] M.A. Bennett, K. Khan, E. Wenger. *Comprehensive Organometallic Chemistry (II)*, Elsevier, Oxford (1995).
[2] B.M. Trost, R.J. Kulawiec. *J. Am. Chem. Soc.*, **115**, 2027 (1993).
[3] B.M. Trost, A. Indolese. *J. Am. Chem. Soc.*, **115**, 4361 (1993).
[4] S.G. Davies, J.P. Mc Nally, A.J. Smallridge. *Adv. Organomet. Chem.*, **30**, 1 (1990).
[5] G.S. Ashby, M.I. Bruce, I.B. Tomkins, R. Wallis. *Aust. J. Chem.*, **32**, 1003 (1979).
[6] S.G. Davies, S.J. Simpson, H. Felkin, T. Fellebeen-Khan. *Organometallics*, **2**, 539 (1983).
[7] M.I. Bruce, F.S. Wong, B.W. Skelton, A.H. White. *J. Chem. Soc., Dalton Trans.*, 1398 (1981).
[8] R. Uso, L.A. Oro, M.A. Ciriano, M.M Naval, M.C. Apreda, C.F. Foces, F.H. Cano, S.G. Blanco. *J. Organomet. Chem.*, **256**, 331 (1983).
[9] S.A. Westcott, A.K. Kakkar, G. Stringer, N.J. Taylor, T.P. Marder. *J. Organomet. Chem.*, **394**, 777 (1990).
[10] K.S. Singh, Y.A. Mozharivskyj, P.J. Carroll, M.R. Kollipara. *J. Organomet. Chem.*, **689**, 1249 (2004).
[11] K.S. Singh, P.J. Carroll, M.R. Kollipara. *Polyhedron*, **24**, 391 (2005).
[12] A.I. Vogel. *Text Book of Practical Organic Chemistry*, ELBS, New York (1984).
[13] M.I. Bruce, N.J. Windsor. *Aust. J. Chem.*, **30**, 1601 (1997).
[14] L.A. Oro, M.A. Ciriano, M. Campo, C. Foces, F.H. Cano. *J. Organomet. Chem.*, **289**, 117 (1985).
[15] M.I. Bruce, B.C. Hall, N.N. Zaitseva, B.W. Skelton, A.H. White. *J. Chem. Soc., Dalton Trans.*, 1793 (1998).
[16] D. Beck. *J. Chem. Phys.*, **98**, 5648 (1993).

[17] G.M. Sheldrick. *Bruker/Stemens Area Detector Absorption Correction Program*, Bruker AXS, Madison, WI, USA (2002).
[18] G.M. Sheldrick. *SHELXS-97: Program for Crystal Structure Solution*, University of Göttingen, Germany (1990).
[19] G.M. Sheldrick. *SHELXL-97: Program for the Refinement of Crystal Structures*, University of Göttingen, Germany (1997).
[20] G.M. Sheldrick. *SHELXTL: Program for Computing Molecular Graphics*, University of Göttingen, Germany (2001).
[21] R. Lalrempuia, P. Govindaswamy, Y.A. Mozharivskyj, M.R. Kollipara. *Polyhedron*, **23**, 1069 (2004).
[22] W.J. Geary. *Coord. Chem. Rev.*, **7**, 81 (1971); L.G. Guggenberger. *Inorg. Chem.*, **12**, 1317 (1973).