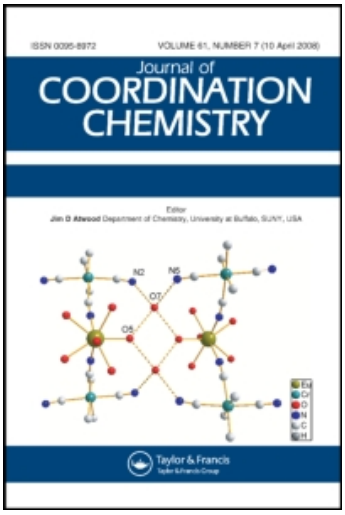


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Syntheses of [(η^6-p-cymene)Ru(EPh_3)$_2$Cl]$^+$ complexes and molecular structure of chloro(η^6-p-cymene)-bis(triphenylphosphine)ruthenium(II) tetrafluoroborate (E = P, As and Sb)

R. Lalrempuia[a]; Patrick. J. Carroll[b]; Mohan Rao Kollipara[a]
[a] Department of Chemistry, North Eastern Hill University, Shillong 793022, India [b] Department of Chemistry, University of Pennsylvania, Philadelphia, PA - 19104, USA

Online publication date: 12 May 2010

To cite this Article Lalrempuia, R. , Carroll, Patrick. J. and Kollipara, Mohan Rao(2003) 'Syntheses of [(η^6-p-cymene)Ru(EPh_3)$_2$Cl]$^+$ complexes and molecular structure of chloro(η^6-p-cymene)-bis(triphenylphosphine)ruthenium(II) tetrafluoroborate (E = P, As and Sb)', Journal of Coordination Chemistry, 56: 17, 1499 — 1504
To link to this Article: DOI: 10.1080/00958970310001628957
URL: http://dx.doi.org/10.1080/00958970310001628957

J. Coord. Chem., Vol. 56, No. 17, 20 November 2003, pp. 1499–1504

SYNTHESES OF $[(\eta^6\text{-}p\text{-CYMENE})Ru(EPh_3)_2Cl]^+$ COMPLEXES AND MOLECULAR STRUCTURE OF CHLORO(η^6-*p*-CYMENE)-BIS(TRIPHENYLPHOSPHINE)RUTHENIUM(II) TETRAFLUOROBORATE (E = P, As AND Sb)

R. LALREMPUIA[a], PATRICK. J. CARROLL[b] and MOHAN RAO KOLLIPARA[a,*]

[a]*Department of Chemistry, North Eastern Hill University, Shillong 793022, India;* [b]*Department of Chemistry, University of Pennsylvania, Philadelphia, PA – 19104, USA*

(Received 17 July 2003; In final form 17 September 2003)

The reaction of $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$ with excess EPh_3 (E = P, As, Sb) in methanol in the presence of ammonium tetrafluoroborate leads to the formation of complexes of the type $[(\eta^6\text{-}p\text{-cymene})Ru(EPh_3)_2Cl]BF_4$, E = P (**1**), As (**2**), Sb (**3**), which arise through cleavage of the chloride bridges. These complexes were characterized by spectral and analytical data. The crystal structure of **1** was solved by single-crystal X-ray crystallography in order to establish the exact structure in the solid state. The complex crystallizes in monoclinic space group $P2_1/n$ (#14) with $a = 12.42500(10)$, $b = 30.1925(3)$, $c = 11.06530(10)$ Å, $\beta = 103.1470(10)^\circ$.

Keywords: *p*-Cymene; Ruthenium; Crystal structure; Triphenylarsine; Triphenylantimony

INTRODUCTION

Arene ruthenium complexes play an important role in organometallic chemistry. Some water-soluble half-sandwich arene ruthenium(II) complexes have shown interesting anti-tumor activity [1]. Syntheses of ruthenium(II) complexes containing phosphine ligands have received considerable attention owing to their catalytic properties. Recently, complexes of the type $[(\eta^6\text{-}p\text{-cymene})RuCl_2(ER_2R')]$ (E = P, As, Sb; R, R′ = H, alkyl, arylalkyl) were synthesized and used as catalysts for ring-opening metathesis polymerization (ROMP) [2]. The activation of propargyl alcohols by $[(arene)Ru(PR_3)Cl_2]$ leading to the formation of cationic allenylidene complexes is also well documented and these were found to be good catalysts for ring-closing metathesis [3]. It has been reported that the reaction of $[(\eta^6\text{-arene})RuCl_2]_2$ with

*Corresponding author. Fax: +91-364-2550076. E-mail: kmrao@nehu.ac.in

ISSN 0095-8972 print: ISSN 1029-0389 online © 2003 Taylor & Francis Ltd
DOI: 10.1080/0095897031000162895 7

excess of dimethylphenylphosphine results in the displacement of the arene moiety, forming $[Ru_2Cl_3(PMe_2Ph)_6]Cl$ [4].

In this article we report the syntheses of $[(\eta^6\text{-}p\text{-cymene})Ru(EPh_3)_2Cl]BF_4$, E = P (**1**), As (**2**), Sb (**3**) complexes and their characterization by spectral data and in the case of complex **1** by single-crystal X-ray diffraction.

EXPERIMENTAL

All solvents were dried and distilled by standard methods. PPh_3, $AsPh_3$ and $SbPh_3$ were purchased from Merck and used as supplied. $[(\eta^6\text{-}p\text{-Cymene})RuCl_2]_2$ was prepared by a literature method [5]. Infrared spectra were recorded as KBr pellets using a Perkin-Elmer model 983 spectrophotometer. ^1H NMR and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker ACF 300 spectrometer and referenced to external tetramethylsilane and H_3PO_4 (85%) respectively from the service center (Regional Sophisticated Instrumentation Centre, RSIC), NEHU, Shillong, India.

Preparation and Characterization of $[(\eta^6\text{-}p\text{-Cymene})Ru(EPh_3)_2Cl]BF_4$

A mixture of $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$ (100 mg, 0.163 mmol), NH_4BF_4 (85 mg, 0.815 mmol) and for **1** PPh_3 (256 mg, 0.978 mmol); for **2** $AsPh_3$ (174 mg, 0.570 mmol); for **3** $SbPh_3$ (201 mg, 0.570 mmol) was refluxed in dry methanol (25 cm^3) for 4 h under nitrogen atmosphere. The solvent was removed on a rotary evaporator and the residue was redissolved in chloroform (15 cm^3) and then filtered through a short silica-gel column to remove the white precipitate. For complex **1**, slow evaporation of this solution overnight resulted in the formation of red crystals. For complexes **2** and **3**, the solution was concentrated to about 2 cm^3 and addition of excess diethyl ether resulted in the precipitation of an orange–red solid.

Anal. Calcd. for $RuC_{46}BH_{44}P_2F_4Cl$ (**1**) (%): C, 62.6; H, 5.0. Found: C, 62.4; H, 5.0. ^1H NMR ($CDCl_3$, δ): 7.43–7.22 (m, 30H, Ph), 5.67 (broad s, 2H, cymene ring), 5.07 (d, 2H, cymene ring), 2.70 (sept, 1H, *H*C(Me)$_2$), 1.23 (d, 6H, HC(*Me*)$_2$), 1.12 (s, 3H, *Me*). $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 21.18. IR (KBr, cm^{-1}): 1082 ($\nu_{B\text{-}F}$).

Anal. Calcd. for $RuC_{46}BH_{44}As_2F_4Cl$ (**2**) (%): C, 59.7; H, 4.8. Found: C, 59.4; H, 4.5. ^1H NMR ($CDCl_3$, δ): 7.78–7.33 (m, 30H, Ph), 5.77 (d, 2H, cymene ring), 5.57 (d, 2H, cymene ring), 2.75 (sept, 1H, *H*C(Me)$_2$), 1.92 (s, 3H, *Me*).1.07 (d, 6H, HC (*Me*)$_2$). IR (KBr, cm^{-1}): 1080 ($\nu_{B\text{-}F}$).

Anal. Calcd. for $RuC_{46}BH_{44}Sb_2F_4Cl$ (**3**) (%): C, 56.8; H, 4.6. Found: C, 56.5; H, 4.4. ^1H NMR ($CDCl_3$, δ): 7.93–7.37 (m, 30H, Ph), 5.83 (d, 2H, cymene ring), 5.66 (d, 2H, cymene ring), 2.82 (sept, 1H, *H*C(Me)$_2$), 1.96 (s, 3H, *Me*).1.02 (d, 6H, HC(*Me*)$_2$). IR (KBr, cm^{-1}): 1080 ($\nu_{B\text{-}F}$).

X-ray Structure Determination

Single crystals were grown by diffusion of diethyl ether into a chloroform solution of complex **1**. X-ray intensity data were collected on a Rigaku R-AXIS IIc area detector employing graphite-monochromated Mo Kα radiation ($\lambda = 0.71069$ Å). Indexing was performed from a series of 1° oscillation images with exposures of 100 s per frame. A hemisphere of data was collected using 5° oscillation angles with exposures of 100 s

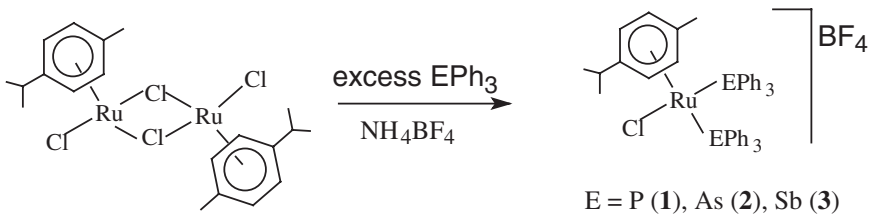
per frame and a crystal-to-detector distance of 82 mm. Oscillation images were processed using bioteX [6], producing a listing of unaveraged F^2 and $\sigma(F^2)$ values which were then passed to the teXsan [7] program package for further processing and structure solution on a Silicon Graphics O2 computer. The intensity data were corrected for Lorentz and polarization effects and for absorption using REQAB [8] (minimum and maximum transmission 0.814, 1.000).

The structure was solved by direct methods (SIR92) [9]. Refinement was by the full-matrix least-squares method based on F^2 using SHELXL-93 [10]. All reflections were used during refinement (F^2 values that were experimentally negative were replaced by $F^2 = 0$). The weighting scheme used was $w = 1/[\sigma^2(F_o^2) + 0.0594P^2 + 2.2812P]$ where $P = (F_o^2 + 2F_c^2)/3$. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a "riding" model. The maximum Δ/σ in the final cycle of least squares was -0.054 and the two most prominent peaks in the final difference Fourier were $+0.558$ and $-0.602\,e/Å^3$.

Table I lists cell information, data collection parameters, and refinement data. Table II lists bond distances and bond angles. Figure 1 is an ORTEP [11] representation of the molecule using 30% probability thermal ellipsoids.

RESULTS AND DISCUSSION

[(*p*-Cymene)$RuCl_2$]$_2$ reacts with excess EPh_3 in methanol under reflux to form disubstituted products which are soluble in most polar solvents.



E = P (**1**), As (**2**), Sb (**3**)

The same reaction may be carried out in methanol at room temperature, but even a prolonged reaction time does not yield the anticipated product, but only known neutral monosubstituted products of composition [(*p*-cymene)$RuCl_2(EPh_3)$] [4]. Moreover, in the preparation of complexes **2** and **3**, the amount of the ligand, i.e., $AsPh_3/SbPh_3$, must be reduced (see Experimental Section), otherwise displacement of *p*-cymene occurs under the stated reaction conditions. Preliminary investigation of the reactivity of complex **1** with substituted propargyl alcohols in methanol has not given vinylidene or allenylidene complexes as monitored by IR spectroscopy, whereas an alkynyl complex [(*p*-cymene)Ru(phen)(CCR)]BAr'_4 has been reported [12], and other attempts to introduce neutral monodentate ligands, with or without halide scavengers have so far been unsuccessful.

^{1}H NMR spectral data of the complexes are reported in the Experimental Section. Complex **1**, unlike complexes **2** and **3**, exhibited an unexpected up-field shift of the methyl protons of the cymene ring at 1.12 ppm, compared with 1.92 and 1.96 ppm respectively for complexes **2** and **3**. The complexes [(*p*-cymene)$RuCl_2(PPh_3)$] [4] and [(*p*-cymene)$RuH(PPh_3)_2$]PF_6 [13] showed the resonance for the same protons

TABLE I Crystal data and structure refinement

Formula	$RuC_{46}BH_{44}P_2F_4Cl$
Formula weight	882.08
Crystal class	Monoclinic
Space group	$P2_1/n$ (#14)
Z	4
a (Å)	12.42500(10)
b (Å)	30.1925(3)
c (Å^3)	11.06530(10)
β (°)	103.1470(10)
V (Å^3)	4042.26(6)
μ (cm^{-1})	5.85
Crystal size (mm)	$0.46 \times 0.38 \times 0.32$
D_{calc} (g/cm^3)	1.449
$F(000)$	1808
Radiation	Mo Kα ($\lambda = 0.71069$ Å)
2θ range	5.2 – 54.96 °
Index ranges	$16 \le h \le 16$; $-39 \le k \le 39$; $-14 \le l \le 14$
No. reflections measured	39833
No. unique reflections	9179 ($R_{int} = 0.0279$)
No. observed reflections	8566 ($F > 4\sigma$)
No. reflections used in refinement	9179
No. parameters	500
R indices ($F > 4\sigma$)	$R_1 = 0.0422$
	$wR_2 = 0.1066$
R[a] indices (all data)	$R_1 = 0.0464$
	$wR_2 = 0.1102$
GOF[b]	1.104
Final difference peaks (e/Å^3)	+0.558, −0.602

[a] $R_1 = \sum \|F_o\| - F_c\| / \sum F_o$, $wR_2 = \left\{\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2\right\}^{1/2}$; [b] GOF $= \left\{\sum w(F_o^2 - F_c^2)^2/(n-p)\right\}^{1/2}$. where n = the number of reflections and p = the number of parameters refined.

TABLE II Selected bond distances (Å) and bond angles (°)

Ru–C39	2.235(2)	Ru–C41	2.241(2)	Ru–C(42)	2.271(2)
Ru–C38	2.279(2)	Ru–C40	2.299(2)	Ru–C(37)	2.344(2)
Ru–P1	2.3649(6)	Ru–Cl	2.3911(7)	Ru–P(2)	2.4042(6)
C(37)–C(38)	1.393(4)	C(37)–C(42)	1.414(4)	C(38)–C(39)	1.414(4)
C(39)–C(40)	1.407(4)	C(40)–C(41)	1.415(4)	C(41)–C(42)	1.400(4)
P(1)–Ru–Cl	87.61(2)	P1–Ru–P2	97.97(2)	P2–Ru–Cl	90.13(2)

at 1.19 ppm and 2.33 ppm respectively. The molecular structure does not reveal any useful information regarding this unusual chemical shift. The $^{31}P\{^1H\}$ NMR spectrum of **1** exhibits a singlet at 21.18 ppm indicating the equivalence of the two phosphorus atoms.

Complex **1** adopts a three-legged piano-stool structure with Cl and two phosphorus atoms as the legs and the π-bonded *p*-cymene moeity occupying three facial coordination sites. The average C–C bond length in the *p*-cymene ring is 1.407 Å with alternate short and long bond lengths. C(37)–C(38), C(39)–C(40) and C(41)–C(42) bonds are shorter than C(38)–C(39), C(40)–C(41) and C(37)–C(42) bonds, which could be due to the loss of planarity of the cymene ring. This is also clearly shown by the relatively long bond length of Ru–C(37) 2.344 Å against the average Ru–C bond length of 2.278 Å. The alternate short–long bond lengths indicate that the cyclohexatriene resonance structure contributes to the overall resonance hybrid [14].

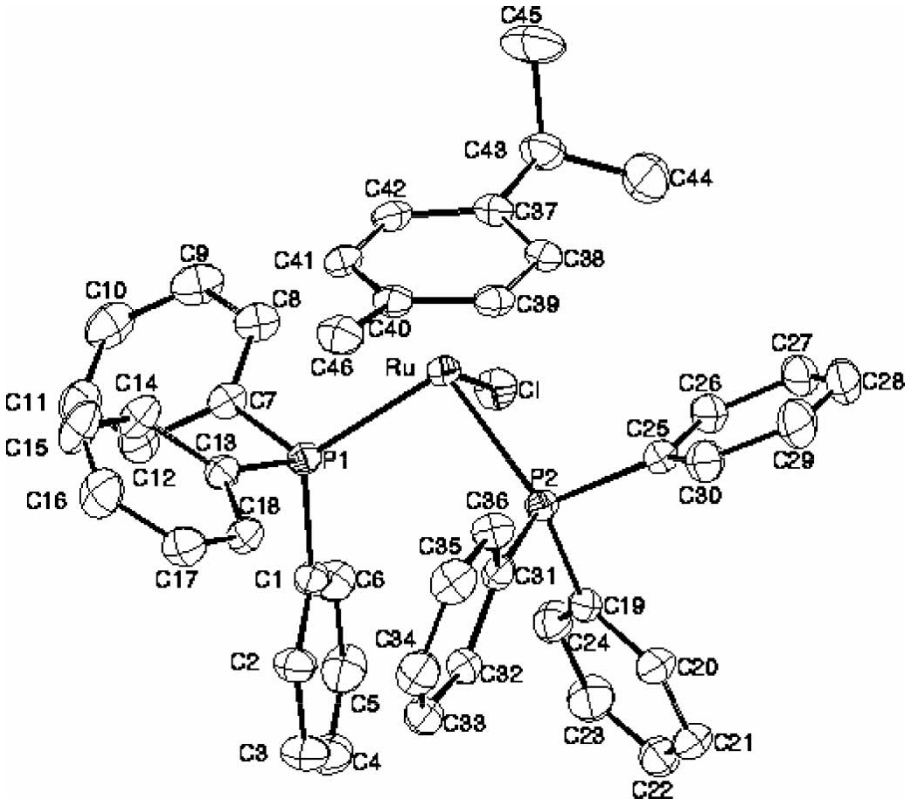


FIGURE 1 ORTEP drawing of **1** with 30% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity.

The Ru–Cl bond length (2.3911 Å) is within the range reported for half-sandwich *p*-cymene ruthenium complexes [15] containing a ruthenium–chlorine bond. Ru–P1 and Ru–P2 bond lengths are similar, 2.3649(6) and 2.4042(6) Å respectively, and are slightly longer than in the related compound $[(\eta^6\text{-benzene})Ru(PPh_3)_2H]^+$ [13]. The bond angles P1–Ru–Cl (87.61°), P2–Ru–Cl (90.13°), P1–Ru–P2 (97.97°) confirm the piano-stool structure of the complex.

Acknowledgements

KMR thanks the DST (DST SERC: SP/S1/F-22/98), New Delhi for financial support.

Supplementary Material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre (CCDC), CCDC No. 212964 for complex **1**. Copies of the 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] (a) C.S. Allardyce, P.J. Dyson, D.J. Ellis and S.L. Heath, *Chem. Commun*. 1936 (2001); (b) H. Chen, J.A. Parkinson, S. Parsons, R.A. Coxall, R.O. Gould and P.J. Sadler, *J. Am. Chem. Soc*. **124**, 3064 (2002); (c) R.E. Aird, J. Cummings, A.A Ritchie, M. Muir, R.E. Morris, H. Chen, P.J. Sadler and D.I. Jodrell, *Brit. J. of Cancer* **86**, 1652 (2002); (d) R.E. Morris, R.E. Aird, P. del S. Murdoch, H. Chen, J. Cummings, N.D. Hughes, S. Parsons, A. Parkin, G. Boyd, D.I. Jodrell and P.J. Sadler, *J. Med. Chem*. **44**, 3616 (2001).
[2] D. Jan, L. Delaude, F. Simal, A. Demonceau and A.F. Noels, *J. Organomet. Chem*. **606**, 64 (2000).
[3] A. Furstner, M. Picquet, C. Bruneau and P.H. Dixneuf, *Chem. Commun*. 1315 (1998).
[4] M.A. Bennett and A.K. Smith, *J. Chem. Soc*., *Dalton Trans*. 233, (1974).
[5] M.A. Bennett, T.N. Huang, T.W. Matheson and A.K. Smith, *Inorg. Synth*. **21**, 74 (1982).
[6] bioteX: A suite of Programs for the Collection, Reduction and Interpretation of Imaging Plate Data (Molecular Structure Corporation, 1995).
[7] teXsan: Crystal Structure Analysis Package (Molecular Structure Corporation, The Woodlands, Texas, 1985, 1992).
[8] R.A. Jacobsen, REQAB4. Private Communication (1994).
[9] A. Altomare, M.C. Burla, M. Camalli, M. Cascarano, C. Giacovazzo, A. Guagliardi and G. Polidoro, *J. Appl. Crystallog*. **27**, 435 (1994).
[10] G.M. Sheldrick, SHELXL-93: Program for the Refinement of Crystal Structures (University of Göttingen, Göttingen, 1993).
[11] C.K. Johnson, ORTEP-II: A Program for Thermal Ellipsoid Plotting, Oak Ridge National Laboratory, Oak Ridge, TN (1976).
[12] C. Menedez, D. Morales, J. Perez and V. Riera, *Organometallics* **20**, 2775 (2001).
[13] O.M. Sisodia, A.N. Sahay, D.S. Pandey, U.C. Agarwala, N.K. Jha, P. Sharma, A. Toscano and A. Cabrera, *J. Organomet. Chem*. **560**, 35 (1998).
[14] P. Lahuerta, J. Latorre, M. Sanau, F.A. Cotton and W. Schwotzer, *Polyhedron* **7**, 1311 (1988).
[15] R. Lalrempuia, P.J. Carroll and M.R. Kollipara, *Polyhedron* **22**, 605 (2003).