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Synthesis and characterization of some arene hydrido-complexes $[Ru(\eta^6\text{-arene})(EPh_3)_2H]^+$ (η^6-arene = benzene, p-cymene or hexamethylbenzene; E = P, As or Sb). Crystal structure of $[Ru(\eta^6\text{-}C_6H_6)(PPh_3)_2H]BF_4$

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Abstract

$[\{Ru(\eta^6\text{-arene})Cl_2\}_2]$ (η^6-arene = benzene, p-cymene or hexamethylbenzene) reacts with EPh_3 (E = P, As or Sb) in methanol to give monomeric cationic arene hydrido complexes $[Ru(\eta^6\text{-arene})(EPh_3)_2H]^+$ in presence of $AgBF_4$ or $AgPF_6$. However, reactions in presence of triphenylphosphine also yield a symmetrically bridged tris (μ-methoxy) complex $[(PPh_3)_3Ru(\mu\text{-OMe})_3Ru(PPh_3)_3]^+$. The crystal structure of $[Ru(\eta^6\text{-}C_6H_6)(PPh_3)_2H]BF_4$ has been determined. Crystal data, monolinic system, space group $P2_{1/n}$, $a = 14.792$ (2) Å; $b = 14.351$ (1) Å; $c = 17.661$ (2) Å; $\beta = 102.25$ (1)° and $Z = 4$. Crystal structure determination reveals the distortion of the $Ru(PPh_3)_2H^+$ unit in the cation $[Ru(\eta^6\text{-}C_6H_6)(PPh_3)_2H]^+$.

Keywords: Arene hydrido complexes; Ruthenium; Phosphine; Arsine; Stibine

1. Introduction

A series of dinuclear mono-, bis- and tris- (μ-hydrido) complexes derived from $[\{M(C_5Me_5)Cl_2\}_2]$ (M = Rh, Ir) having additional bridging ligands viz. halide, acetate or trifluoroacetate groups are very active homogenous catalysts for olefin hydrogenation [1]. In this regard, isoelectronic arene ruthenium complexes $[\{Ru(\eta^6\text{-arene})Cl_2\}_2]$ (arene = benzene and it's derivatives) have also drawn special attention ([2]a,d). It has been known for some time, that in olefin hydrogenation reactions, involving arene ruthenium complexes, arene hydrido complexes, serve as the key intermediates ([3]a,b). Therefore, the synthesis, characterization and evaluation of catalytic potential towards olefin hydrogenation, of the arene hydrido complexes, has been the subject of several previous publications ([4]a–i). Preparation of arene hydrido ruthenium complexes from reactions of $[\{Ru(\eta^6\text{-arene})Cl_2\}]_2$ with 1M Na_2CO_3 in propanol or from reaction of H_2 (4 atm) in dichloromethane containing triethylamine or by using reducing agents like $LiAlH_4$ or $NaBH_4$ in tetrahydrofuran is well documented ([4]a,b). Preparation of monomeric arene hydrido complexes with the formulations $[MHX(\eta^6\text{-arene})L]$ (M = Ru, Os: $X = Cl^-$, CF_3COO^-) in methanol in presence of Zn dust is also reported ([4]c, [5]). Because of our interest in the ruthenium (II) arene complexes and as a prelude to our detailed investigations towards the synthesis of hydrido complexes and evaluation of their catalytic activities,

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we have examined the reactivity of $[\{Ru(\eta^6\text{-arene})Cl_2\}_2]$ (η^6-arene = benzene, p-cymene or hexamethylbenzene) in methanol in the presence of $AgBF_4$ or $AgPF_6$ with EPh_3 (E = P, As or Sb). We observed that the reaction resulted in the formation of cationic monomeric arene hydrido complexes $[Ru(\eta^6\text{-arene})(EPh_3)_2H]^+$. However in such a reaction involving triphenylphosphine, we could also isolate a tris (μ-methoxy) complex with the formulation $[(PPh_3)_3Ru(\mu\text{-OMe})_3Ru(PPh_3)_3]^+$. In this communication, we describe simple, convenient single step reproducible syntheses of some monomeric, cationic, arene hydrido ruthenium complexes under very mild reaction conditions. We also describe herein, the single crystal X-ray structure of one of such hydrido complexes $[Ru(\eta^6\text{-}C_6H_6)(PPh_3)_2H]BF_4$.

2. Results and discussion

Pale yellow to golden yellow crystalline complexes resulting from the reaction of $[\{Ru(\eta^6\text{-arene})Cl_2\}]_2$ (arene = benzene, p-cymene or hexa methylbenzene) with EPh_3 in presence of $AgBF_4$ or $AgPF_6$ with the formulation $[Ru(\eta^6\text{-arene})(EPh_3)_2H]^+$ are air stable solids soluble in acetone, acetonitrile, nitromethane, dimethylformamide and dimethyl sulfoxide, partially soluble in methanol, dichloromethane, chloroform, insoluble in benzene, petroleum ether and diethylether. However, the tris (μ-methoxy) complex is insoluble in most of the common organic solvents. These complexes gave conducting solution in nitromethane with characteristic values of 1:1 electrolyte.

The infrared spectra of the complex (**1a–1c**, **2a–2c** and **3a–3c**) displayed sharp strong bands in the region 1995–2025 cm^{-1} along with the characteristic bands due to η^6-arene, EPh_3 and counter anions BF_4 or PF_6. The band in the region (1995–2025 cm^{-1}) has been assigned to ν(Ru–H). It is interesting to note that, the position of ν(Ru–H) band is dependent on the nature of η^6-arene, present in the complex viz. this band shifts towards higher wave number side as one moves from the benzene complex to hexamethylbenzene complex. Thus, it appears that the position of ν(Ru–H) is sensitive to methyl substitution on the arene ring. Infrared spectra of the complex (**4**) exhibited strong band in the region 1200–950 and 600–300 cm^{-1}, assignable to methoxy vibrations [10]. However, the characteristic bands due to triphenylphosphine and counter anion PF_6 also appear in the same region, hence unambiguous assignments cannot be made. But, presence of methoxy group in the complex is evident by ^1H NMR signal of the methoxy group in the NMR spectra of the complex.

The ^1H NMR spectra of the complex **(1a, 2a, 3a)** displayed triplets in the region δ −9.0 to −10.0 ppm, whereas complex **(1b, 1c, 2b, 2c, 3b, 3c)** displayed sharp singlets in the region δ −8.92 to −11.5 ppm, assignable to metal-bound hydride (Ru–H). The triplet present in the high field side with $J_{H\text{-}P} = 32–37.2$ Hz in the ^1H NMR spectra of **(1a, 2a, 3a)** suggest that the hydride ligand is coupled with two equivalent phosphine ligands [11]. It is interesting to note that the chemical shifts of the Ru–H resonance in these complexes is dependent upon the nature of η^6-arene. This observation is in keeping with the conclusions drawn from IR spectral studies. The ^1H NMR spectra of complex (**4**) exhibited a sharp singlet at δ 3.12 ppm and a broad multiplet in the region δ 7.03–7.70 ppm. The singlet at δ 3.12 ppm is assigned to methoxy protons and the broad multiplet at δ 7.03–7.70 ppm as to the aromatic protons of triphenylphosphine ligand. The presence of a sharp singlet corresponding to methoxy group suggests that all these protons are chemically equivalent and it is only possible if the methoxy groups form a symmetrical bridge between the two Ru(II) centers.

FAB mass spectra of the complex (**1a**) displayed a peak corresponding to molecular ion $[Ru(\eta^6\text{-arene})H(PPh_3)_2]^+$ at m/z 705. Fragmentation pattern indicated that the molecular ion looses the hydride ligand in the next step to form $[Ru(\eta^6\text{-}C_6H_6)(PPh_3)_2]^{2+}$ ion, the corresponding peak is present at m/z 704 in the spectra. This ion in the next step loses the $\eta^6\text{-}C_6H_6$ to give $[Ru(PPh_3)_2]^{2+}$, which is evident from the presence of basal peak at m/z 625. This step ligand suggests that the $[Ru(PPh_3)_2]^{2+}$ moiety is more stable as compared to $[Ru(\eta^6\text{-}C_6H_6)(PPh_3)]^{2+}$. The overall fragmentation pattern for this molecule may be given as:

$$\underset{m/z,\ 705\ (\text{calcd. } 706)}{[Ru(\eta^6\text{-}C_6H_6)(PPh_3)_2H]^+} \xrightarrow[\text{Step I}]{-H^+} \underset{m/z,\ 704\ (\text{calcd. } 705)}{[Ru(\eta^6\text{-}C_6H_6)(PPh_3)_2]^+} \xrightarrow[\text{Step II}]{-C_6H_6} \underset{m/z,\ 625\ (\text{calcd. } 626)}{[Ru(PPh_3)_2]^{2+}}$$

$$[Ru(PPh_3)_2]^{2+} \xrightarrow[\text{Step III}]{-PPh_3} \underset{m/z,\ 363\ (\text{calcd. } 364)}{[Ru(PPh_3)]^{2+}} \xrightarrow{-PPh_3} M^{2+}$$

The above pattern supports well our formulation for the complex. The molecular ion peaks in the corresponding p-cymene and hexamethylbenzene complexes

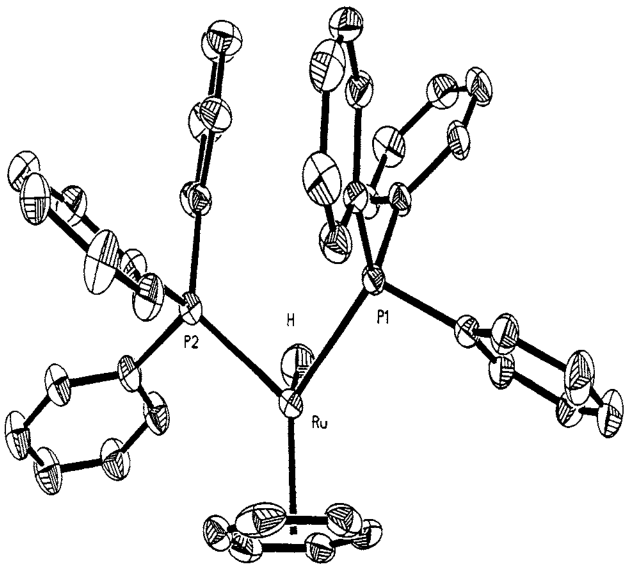

Fig. 1. ORTEP drawing of cation $[Ru(\eta^6\text{-}C_6H_6)(PPh_3)_2H]^+$.

(**2a** and **3a**) appeared at m/z 761 and 789, respectively. However, it was observed that fragmentation pattern for these complexes are different in step II, as compared to that for complex (**1a**). Interestingly, the fragmentation pattern for (**2a**) and (**3a**) in step II involves loss of a PPh_3 ligand rather than η^6-arene, as indicated by presence of peaks at m/z 498 and 525, respectively. This, clearly suggests that for p-cymene and hexamethylbenzene complexes, $[Ru(\eta^6\text{-arene})(PPh_3)]^{2+}$ moiety is more stable as compared to $[Ru(PPh_3)_2]^{2+}$, it may be due to the effect of methyl substitution on the arene rings [12].

The cation in the molecule adopted a distorted 'piano stool' structure in which the $[RuH(PPh_3)_2]^{2+}$ unit exhibited a slippage away from idealized η^6-position (Fig. 1). The arene ring is planar with average Ru–C distances of 2.273(12) Å [range 2.243(17)–2.353(15) Å]. The metal center Ru lies 1.8112 Å from the arene ring plane, which is longer than the average ruthenium arene ring distances in other Ru(II)–arene complexes [13]. The C–C distances within the benzene ring are comparable [average 1.403(30) Å, range 1.298(34)–1.482(37) Å].

The Ru–P(1) and Ru–P(2) distances are 2.329(2) and 2.327(2) Å, respectively and these are comparable with Ru–P distances in closely related system like $[Ru(\eta^6\text{-arene})H(PPh_3)_2]^+$ (η^6-arene = toluene), $[RuH(PPh_3)_2(nPh\text{-}PPh_2)]^+$ and $[Ru(PPh_3)_2(Pys)_2]$ ([7]d,e) The P(1)–Ru–P(2) angle in the complex is 97.2(1)° which is comparable to the one reported in $[Ru(PPh_3)_2H(nPh\text{-}PPh_2]^+$ where the P(1)–Ru–H and P(2)–Ru–H angles are 85.1(31) and 76.6(27)°, respectively. These indicate that the hydride hydrogen is not symmetrically placed with respect to two metal bonded phosphorus atoms. The Ru–H distance in the cation is 1.62(9) Å, which is comparable to the Ru–H distances in an analogous complex $[Ru(\eta^6\text{-arene})(PPh_3)_2H]^+$ (η^6-arene = toluene) ([4]f). However it is a longer than the Ru–H bond lengths in $[RuH(\eta^5\text{-}C_5H_5)(PMe_3)_2]$ and $[RuH(C_6H_6)(dippe)]^+$ ([4]i).

The crystal structure determination confirms the distortion of $[RuH(PPh_3)_2]^+$ unit in the cation and supports well the molecular orbital calculations at the extended huckel level to explore the structural distortion in such systems by Siedle et al. ([4]f).

Table 1
Summary of data for the crystal structure analysis of $[Ru(\eta^6\text{-}C_6H_6)(PPh_3)_2H]BF_4$

Formula	$C_{42}H_{37}BF_4P_2Ru$
Formula weight	791.5
Color, habbit.	Yellow, prism
Crystal system	Monoclinic
Space group	$P2_{1/n}$
Unit cell dimensions	$a = 14.792(2)$ Å
	$b = 14.351(1)$ Å
	$c = 17.66$ (2) Å
	$\beta = 102.25(1)°$
Volume	3663.8(7) Å^3
Z	4
Density calculated	1.435 mg m^{-3}
Absorption coefficient	0.565 mm^{-1}
$F(000)$	1616
Reflections collected	8744
Independent reflections	8424 (R(int) = 0.506%)
Observed reflections	4818 ($F > 4.0\sigma$ (F))
R; $R\omega$	0.0589; 0.0663
GOF	1.09

3. Experimental

All the synthetic operations were performed under oxygen free nitrogen atmosphere. The solvents were dried and distilled before use. α-Phellandrene, triphenylphosphine, triphenylarsine, triphenylstibine (all Fluka) hydrated ruthenium (III) chloride, cyclohexa-1,3-diene, silver tetrafluoroborate and silver hexafluorophosphate (all Aldrich) were used as received.

The complexes $[Ru(\eta^6\text{-}C_6H_6)Cl_2\}_2]$ [6], $[\{Ru(\eta^6\text{-}C_{10}H_{14})Cl_2\}_2]$ [7] and $[Ru(\eta^6\text{-}C_6Me_6)Cl_2\}_2]$ [7] were prepared following the literature procedures.

Elemental analyses in the complexes were performed by the microanalytical laboratory of RSIC, Central Drug Research Institute, Lucknow. Infrared spectra were recorded on a Perkin Elmer 577 Spectrophotometer. NMR spectra were taken on a Bruker WM-400 and Bruker DRX-300MHZ spectrometers with tetramethylsilane as the internal standard. FAB mass spectra were obtained on a JEOL SX-120 A mass spectrometer with NBA as the matrix.

Table 2
Positional parameters and U(eq) for $[Ru(\eta^6\text{-}C_6H_6)(PPh_3)_2H]BF_4$. (atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$) for $[(Ph_3P)_2\ Ru\ H\ C_6H_6]^+[BF_4]^-$)

Atom	x	y	z	U(eq)[a] ($Å^2 \times 10^3$)
Ru	3541(1)	2033(1)	2378(1)	34(1)
P(1)	4665(1)	2510(1)	1716(1)	32(1)
P(2)	4316(1)	2482(1)	3611(1)	35(1)
C(1A)	2819(12)	893(11)	2886(7)	55(5) sof = 0.78(4)
C(2A)	3316(10)	413(10)	2430(18)	85(9) sof = 0.78(4)
C(3A)	3115(12)	765(13)	1623(13)	71(7) sof = 0.78(4)
C(4A)	2458(19)	1507(18)	1370(16)	65(7) sof = 0.78(4)
C(5A)	2007(8)	1885(10)	1846(10)	51(4) sof = 0.78(4)
C(6A)	2178(10)	1592(13)	2632(10)	54(5) sof = 0.78(4)
C(1B)	3170(36)	796(38)	1392(31)	39(12) sof = 0.22(4), Uiso
C(2B)	2505(60)	1281(53)	1368(57)	44(17) sof = 0.22(4), Uiso
C(3B)	2065(28)	1635(32)	2083(31)	33(10) sof = 0.22(4), Uiso
C(4B)	2445(37)	1220(39)	2775(28)	39(11) sof = 0.22(4), Uiso
C(5B)	3269(61)	584(54)	2870(39)	75(21) sof = 0.22(4), Uiso
C(6B)	3252(34)	494(37)	2114(31)	35(11) sof = 0.22(4), Uiso
C(7)	5803(4)	1968(6)	2007(3)	40(2)
C(8)	5844(5)	989(6)	2105(5)	52(3)
C(9)	6668(6)	534(7)	2292(5)	62(3)
C(10)	7491(6)	1015(8)	2410(5)	65(3)
C(11)	7485(5)	1975(8)	2342(5)	62(3)
C(12)	6647(5)	2463(6)	2142(4)	44(2)
C(13)	4310(4)	2185(5)	678(4)	40(2)
C(14)	4707(5)	1455(5)	339(4)	47(2)
C(15)	4387(7)	1276(7)	−446(5)	68(4)
C(16)	3704(7)	1790(7)	−881(5)	70(4)
C(17)	3309(6)	2514(7)	−552(5)	63(3)
C(18)	3613(5)	2706(6)	227(4)	49(3)
C(19)	4912(5)	3746(5)	1582(4)	39(2)
C(20)	5451(6)	3982(6)	1060(4)	52(3)
C(21)	5634(6)	4909(7)	922(5)	64(3)
C(22)	5273(6)	5607(6)	1307(5)	59(3)
C(23)	4727(6)	5375(6)	1817(5)	59(3)
C(25)	5185(4)	1682(5)	4156(4)	37(2)
C(26)	5702(5)	1905(5)	4890(4)	49(3)
C(24)	4536(5)	4444(5)	1957(4)	45(2)
C(27)	6341(6)	1295(6)	5275(5)	57(3)
C(28)	6493(6)	449(6)	4963(5)	56(3)
C(29)	6003(7)	229(6)	4241(5)	66(3)
C(30)	5342(6)	826(6)	3850(5)	53(3)
C(31)	3466(5)	2617(5)	4231(4)	40(2)
C(32)	2676(5)	3158(6)	3956(5)	55(3)
C(33)	2017(6)	3282(7)	4407(5)	61(3)
C(34)	2125(6)	2856(7)	5118(5)	64(3)
C(35)	2892(6)	2313(6)	5386(5)	62(3)
C(36)	3562(5)	2191(5)	4946(4)	48(3)
C(37)	4952(5)	3588(5)	3763(4)	37(2)
C(38)	4538(6)	4419(6)	3911(5)	56(3)
C(39)	5043(7)	5248(6)	3981(6)	70(4)
C(40)	5951(7)	5259(7)	3933(6)	71(4)
C(41)	6362(6)	4437(7)	3785(6)	70(4)
C(42)	5875(5)	3609(6)	3690(5)	51(3)
B	5015(8)	8276(9)	2656(8)	70(4)
F(1A)	5939(6)	8502(7)	2884(6)	91(4) sof = 0.75
F(2A)	4743(8)	8972(8)	2022(6)	124(5) sof = 0.75
F(3A)	4964(9)	7457(7)	2328(10)	153(8) sof = 0.75
F(4A)	4556(8)	8551(7)	3193(6)	108(5) sof = 0 75
F(1B)	4549(21)	7796(25)	2126(19)	89(9) sof = 0.25, Uiso
F(2B)	5565(30)	8793(30)	2642(25)	125(15) sof = 0.25, Uiso
F(3B)	5187(22)	7492(26)	3270(21)	125(10) sof = 0.25, Uiso
F(4B)	4154(25)	8480(27)	2706(22)	117(12) sof = 0.25, Uiso

[a] Equivalent isotropic U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

4. Preparation of the complexes

The following general method was used for the preparation of all the complexes: $[\{Ru(\eta^6\text{-arene})Cl_2\}_2]$ (0.5 mmol) in methanol (15 ml) was treated with $AgBF_4/AgPF_6$ (2.0 mmol) and stirred at room temperature. After 30 min. the white ppt. of AgCl was filtered off and the orange/yellow solution was treated with EPh_3 (1.5 mmol) dissolved in methanol (25 ml). Immediately upon addition, color of the solution turned from orange/yellow to yellow. It was stirred at room temperature for 3 h, filtered to remove any solid and left for slow crystallization in a refrigerator. Yellow crystal separated out and color of the solution turned bluish. The product was filtered, washed several times with methanol, diethyl ether and dried in a vacuum (yield 40–60%).

It was also observed that in reactions involving triphenylphosphine, just after addition of PPh_3, a white compound separated out. After filtration of this white compound, we get hydrido complexes from the solution and white compound analyses for tris (μ-methoxy) complex $[(PPh_3)_3Ru(\mu\text{-OMe})_3Ru(PPh_3)_3]^+$.

4.1. Selected data for the complexes

$[RuH(\eta^6\text{-}C_6H_6)(PPh_3)_2]BF_4$ (**1a**): color: yellow; m.p. 218°C; Anal. calcd. for $BC_{42}F_4H_{37}P_2Ru$: C, 63.70%; H, 4.67%; Found: C, 63.71%; H, 4.67%; IR (KBr, cm^{-1}): 2004 ν(Ru–H); NMR: ^1H (δ) 7.17–7.38 (br m, PPh_3), 5.62 (sh s, C_6H_6), −9.0 (t, Ru–H); FABMS (NBA, m/z): 705 ($[M]^+$) 704 ($[M–H]^+$), 625 ($[M–H–C_6H_6]^+$), 363 ($[M–H–C_6H_6–PPh_3]^+$), 101 ($[M–H–C_6H_6–PPh_3–PPh_3]^+$).

$[RuH(\eta^6\text{-}C_6H_6)(AsPh_3)_2]PF_6$ (**1b**): color: yellow; m.p. 225°C; Anal. calcd. for $As_2C_{42}F_6H_{37}PRu$: C, 53.78%; H, 3.92%; Found: C, 53.82%; H, 4.02%; IR (KBr, cm^{-1}): 2005 ν(Ru–H); NMR: ^1H (δ) 7.2–7.8 (brm, $AsPh_3$), 5.65 (s,C_6H_6), −9.2 (s, Ru–H).

Table 3
Selected bond distances (Å) and angles (°) in $[Ru(\eta^6\text{-}C_6H_6)(PPh_3)_2H]BF_4$

Ru–H	1.62(9)	P(1)–Ru–P(2)	97.2(1)
Ru–P(1)	2.329(2)	H–Ru–P(2)	85.1(31)
Ru–P(2)	2.327(2)	H–Ru–P(1)	76.6(27)

$[RuH(\eta^6\text{-}C_6H_6)(SbPh_3)_2]PF_6$ (**1c**): color: yellow; m.p. 208°C; Anal. calcd. for $C_{42}F_7H_{37}PRuSb_2$: C, 48.90%, H, 4.97%; Found: C, 48.62%, H, 3.62%; IR (KBr, cm^{-1}): 2008 ν(Ru–H); NMR: ^1H (δ) 7.1–7.7 (brm, $SbPh_3$), 5.63 (s,C_6H_6), −9.36 (s, Ru–H).

$[RuH(\eta^6\text{-}C_{10}H_{14})(PPh_3)_2]PF_6$ (**2a**): color: pale yellow; m.p. 190°C; Anal. calcd. for $C_{46}F_6H_{45}P_3Ru$: C, 60.90%, H, 4.97%; Found: C, 61.24%, H, 6.81%; IR (KBr, cm^{-1}): 2020 ν(RuH); NMR: ^1H (δ) 7.30–7.68 (brm, PPh_3), 5.39, 5.98 (AB pattern, C_6H_4), 2.88 (sp, $CHMe_2$), 2.33 (s, CH_3), 1.35 (d, $CHMe_2$), −9.6 (t, Ru–H); FABMS (NBA, m/z): 761 ($[M]^+$), 760 ($[M-H]^+$), 498 ($[M-H-PPh_3]^+$), 363 ($[M-H-PPh_3-C_{10}H_{14}]^+$), 101 ($[M-H-C_{10}H_{14}-2PPh_3]^+$).

$[RuH(\eta^6\text{-}C_{10}H_{14})(AsPh_3)_2]PF_6$ (**2b**): color: yellow; m.p. 178°C; Anal. calcd. for $As_2C_{46}F_6H_{45}PRu$: C, 55.50%, H, 4.53%; Found: C, 55.56%, H, 4.82%; IR (KBr, cm^{-1}): 2015 ν(Ru–H); NMR: ^1H (δ) 7.30–7.68 (brm, $AsPh_3$), 5.39, 5.98 (AB pattern, C_6H_4), 2.88 (sp, $CHMe_2$), 2.33 (s, CH_3), 1.35 (d, $CHMe_2$), −8.92 (s, Ru–H).

$[RuH(\eta^6\text{-}C_{10}H_{14})(SbPh_3)_2]PF_6$ (**2c**): color: yellow; m.p. 180°C; Anal. calcd. for $C_{46}F_6H_{45}PRuSb_2$: C, 50.08%. H, 4.14%; Found: C, 51.02%, H, 4.16%; IR (KBr, cm^{-1}): 2010 ν(Ru–H); NMR: ^1H (δ) 7.2–7.8 (brm, $SbPh_3$), 6.12, 6.30 (AB pattern, C_6H_4), 2.80 (m, $CHMe_2$), 2.26 (s, CH_3), 1.32 (d, $CHMe_2$).

$[RuH(\eta^6\text{-}C_6Me_6)(PPh_3)_2]PF_6$ (**3a**): color: yellow; m.p. 210°C; Anal. calcd. for $C_{48}F_6H_{49}P_3Ru$: C, 61.73%, H 5.25%; Found: C, 61.62%, H, 5.24%; IR (KBr, cm^{-1}): 2020 ν(Ru–H); NMR: ^1H (δ) 7.24–7.82 (brm, PPh_3), 2.16 (s, C_6Me_6), −9.8 (t, Ru–H); FABMS (NBA, m/z): 789 ($[M]^+$), 788 ($[M–H]^+$), 525 ($[M-H-PPh_3]^+$), 363 ($[M-H-PPh_3-C_6Me_6]^+$), 101 ($[M-H-2PPh_3-C_6Me_6]^+$).

$[RuH(\eta^6\text{-}C_6Me_6)(AsPh_3)_2]PF_6$ (**3b**): color: yellow; m.p. 208°C; Anal. calcd. for $As_2C_{48}F_6H_{49}PRu$: C, 53.70%, H, 5.09%; Found: C, 53.72%, H, 5.16%; IR (KBr, cm^{-1}): 2015 ν(Ru–H); NMR: ^1H (δ) 7.31–7.82 (brm, $AsPh_3$), 2.15 (s, C_6Me_6), −9.56 (s, Ru–H).

$[RuH(\eta^6\text{-}C_6Me_6)(SbPh_3)_2]PF_6$ (**3c**): color: yellow; m.p. 210(d)°C; Anal. calcd. for $C_{48}F_6H_{49}PRuSb_2$: C, 53.70%, H, 4.64%; Found: C, 49.20%, H, 4.82%; IR (KBr, cm^{-1}): 2012 ν(Ru–H); NMR: ^1H (δ) 7.25–7.48 (brm, $SbPh_3$), 2.15 (s, C_6Me_6), −9.62 (s, Ru–H).

$[(PPh_3)_3Ru(\mu\text{-}OMe)_3Ru(PPh_3)_3]PF_6$ (**4**): color: white; m.p. 245°C; Anal. calcd. for $C_{111}H_{99}F_6O_3P_7Ru$: C, 66.30%, H, 4.90%; Found C, 66.27%, H, 4.54%; NMR: ^1H (δ) 7.03–7.70 (brm, PPh_3), 3.12 (s, OCH_3).

s, singlet; brm, broad multiplet; d, doublet; t, triplet.

4.2. Crystallographic analysis

Diffraction data were collected with Siemens P4/PC diffractometer from yellow prismatic crystal of dimensions $0.52 \times 0.28 \times 0.26$ mm in ω, scan mode (2θ range from 3.0 to 55°). The crystal parameters along with data collection details are recorded in Table 1. Intensities were measured by the ω scan method using Mo–Kα radiation ($\lambda = 0.71073$ Å). A variable scan speed between 4.00–60.00° min^{-1} in ω was used. Throughout the data collection intensities of three standard reflections were measured every 97 reflections as a check of stability of the crystal and no decay was observed. A total of 8424 reflections ($2\theta < 55°$) were measured and out of these 4118 reflections with $F > 4.0\sigma$ were used in solution and refinement of the structures.

The structure was solved by direct methods with SIR-92 [8] and refined by block matrix least square procedure using SHELXTL [9]. All the non hydrogen atoms were refined with anisotropic thermal parameters by full matrix least square method and hydrogen atoms were calculated at the ideal positions and were not refined. The function minimized was $\Sigma\omega(F_0 - F_c)^2$ where $\omega^{-1} = \sigma^2(F) + 0.0008F^2$ resulting in $R = 0.0589$, $\omega R = 0.0663$ and $S = 1.09$. Crystallographic data are recorded in Table 1. Fractional atomic coordinates, U(eq) and selected bond lengths and angles are given in Tables 2 and 3, respectively.

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