SYNTHESES AND CHARACTERIZATION OF $[Ru(\eta^5-C_5H_5)$ (AsPh₃)(L)X] AND $[Ru(\eta^5-C_5H_5)(AsPh_3)(L)(MeCN)]_m^+Y^-$ (L = PPh₃ OR AsPh₃; X = F, Cl, Br, I, CN, H OR SnCl₃; Y = HgCl₃, Zn₂Cl₆ OR BPh₄; m = 1 OR 2)

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Abstract—The syntheses of the complexes $[(\eta^5-C_5H_5)Ru(AsPh_3)(L)X]$ (L = PPh₃ or AsPh₃; X = Cl, F, Br, I, H, CN or SnCl₃) and $[(\eta^5-C_5H_5)Ru(AsPh_3)(L)(MeCN)]^+Y^-$ (Y = HgCl₃, BPh₄ or Zn₂Cl₆) are described. They were characterized by elemental analyses, IR, UV and visible, PMR spectroscopy, X-ray powder diffraction, and mass spectral studies.

The potential chemical reactivities of the complexes $[(\eta^{5}-C_{5}H_{5})RuX(PR_{3})_{2}]$ (X = Cl, Br or I; R = Me or Ph) with various heterocyclic bases, dienes, trienes, NOX (X = Cl, Br, Br₃ or NO₂) etc. have recently received considerable attention in the chemical literature.¹⁻¹⁰ Interest in these molecules stems from the reactions of the substitution-reaction products which they show because of the close proximity of sterically hindered two trialkyl or triaryl phosphine molecules. It has recently been demonstrated that $[(\eta^5 - C_5 H_5) RuCl(PPh_3)_2]$ undergoes a substitution reaction under refluxing conditions for a very long period, giving $[(\eta^5-C_5H_5)RuCl(AsPh_3)_2]$ in good yield. Since, in our previous papers,^{8,9} the substitution of one molecule of PPh₃ by a heterocyclic base like pyridine has been reported, it is anticipated that substitution reactions should proceed through stepwise replacement of one molecule by another. It was, therefore, of interest to extend our investigations of substitution reactions and to attempt to synthesize mixed complexes {[$(\eta^5 C_5H_5$ (A)(B)] (A = PPh₃, AsPh₃ or SbPh₃; $B = PPh_3$, AsPh₃ or SbPh₃), and to interconvert them. In this paper we describe the syntheses of these complexes, which have been characterized by chemical analyses, spectroscopic studies (IR, PMR and mass), the powder X-ray method, and by magnetic-susceptibility measurements.

EXPERIMENTAL

All the reagents were Analar or of chemically pure grade. All the solvents were dried and distilled before use. The reactions were carried out under a dry and pure nitrogen atmosphere. $[(\eta^5-C_5H_5)$ RuCl(PPh₃)₂], $[(\eta^5-C_5H_5)$ RuCl(AsPh₃)₂] and $[(\eta^5-C_3H_5)$ RuCl(AsPh₃)₂H] were prepared by the literature methods.^{7,11}

Preparation of complexes

(A) Preparation of monochloromonocyclopentadienylmonotriphenylphosphine monotriphenylarsine ruthenium(II) {[$(\eta^5-C_5H_5)RuCl(AsPh_3)(PPh_3)$]} (1). A solution of [$(\eta^5-C_5H_5)RuCl(PPh_3)_2$] (0.500 g, 7.0×10^{-4} mol) and AsPh₃ (0.4 g, 1.3×10^{-4} mol) in 60 cm³ benzene was heated to reflux for 25 h. The resulting solution was concentrated to near dryness, the residue extracted by CH₂Cl₂ and the complex precipitated from the extract by using petroleum ether. It was centrifuged and purified by recrystallization from CH₂Cl₂-petroleum ether. It was filtered, washed with petroleum ether, and dried. The orange-yellow complex 1 was analysed (yield ca 78%).

(B) Preparation of monohydridomonocyclopentadienylmonotriphenylarsine monotriphenylphosphine ruthenium(II) {[$(\eta^5-C_5H_5)Ru(AsPh_3)(PPh_3)H$]}. (i) Using NaOMe-MeOH. A mixture of the orangeyellow coloured complex 1 (0.1 g, 1.3×10^{-4} mol) and sodium metal (0.20 g, ca 0.009 g atm) in 15

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cm³ methanol was heated to reflux until all the starting material was dissolved (*ca* 20 min) with the simultaneous formation of a precipitate from the solution near the glass surface, which was separated by centrifugation, washed with small quantities of methanol, and dried *in vacuo*. It was identified as $[(\eta^5-C_5H_5)Ru(AsPh_3)(PPh_3)H]$ by analyses (yield *ca* 50%).

(ii) Using NaOEt-EtOH. The hydrido derivative was also prepared by the same procedure as given in B(i), except that ethanol (15 cm^3) was used in place of methanol. The yellow complex was collected and identified by chemical analyses and by comparing it with that prepared in B(i). Both samples were found to be identical.

(C) Preparation of mono(fluoro, bromo or iodo)monocyclopentadienylmonotriphenylarsine monotri- $\{[(\eta^{5}-C_{5}H_{5})Ru$ phenylphosphine ruthenium(II) $(AsPh_3)(PPh_3)X$ (X = F, Br or I). (i) Using HX (X = F, Br or I). A yellow suspension of $[(\eta^{5}-C_{5}H_{5})Ru(AsPh_{3})(PPh_{3})H]$ (0.1 g, 1.4×10^{-3} mol) in methanol (15 cm³) was treated with concentrated HX (five or six drops). Immediately, the yellow suspension dissolved to form a light yellowish-orange coloured solution which was stirred for about 10 min, whereby a brownishorange precipitate deposited. It was collected by centrifuging the solution, washed with methanol and ether, and dried in vacuo. On analysis it was identified as $[(\eta^5 - C_5 H_5)Ru(AsPh_3)(PPh_3)X]$ (yield ca 90%).

(ii) Using KX (X = Br or I). Complexes of $[(\eta^{5}-C_{5}H_{5})RuX(AsPh_{3})(PPh_{3})]$ (X = Br or I) were also prepared by heating under reflux a solution of $[RuCl(AsPh_{3})_{4}(PPh_{3})(\eta^{5}-C_{5}H_{5})]$ (0.1 g, 1.3×10^{-4} mol) in ethanol (20 cm³) with KX (0.200 g, ca 0.17 mol) for 1 h, whereupon brownish-orange crystals were deposited. These were separated by centrifuging the solution, washed with water, methanol and diethyl ether, and dried. On analysis the complex was identified as $[(\eta^{5}-C_{5}H_{5})Ru$ (AsPh₃)(PPh₃)X] (X = Br or I) (yield ca 80%).

(iii) Using MeI. The iodo analogue of the complex was prepared by the procedure described in C(i) by treating $[(\eta^{5}-C_{5}H_{5})Ru(AsPh_{3})(PPh_{3})H]$ (0.1 g, 1.4×10^{-4} mol) with methyl iodide (five or six drops) in methanol (10 cm³). The resulting complex was identified as $[(\eta^{5}-C_{5}H_{5})Ru(AsPh_{3})(PPh_{3})I]$.

(iv) The bromo analogue $[(\eta^5-C_5H_5)Ru$ (AsPh₃)(PPh₃)Br] was also prepared by heating to reflux a solution of $[(\eta^5-C_5H_5)Ru(PPh_3)_2Br]$ (0.1 g, 1.2×10^{-4} mol) in ethanol (30 cm³) with AsPh₃ (0.1 g, 3.3×10^{-4} mol) for 15 h, whereupon brown crystals were deposited. These were separated by centrifuging the suspension, washed with ethanol, diethyl ether and petroleum ether. The complex was dried and identified as the bromo derivative (yield ca 70%).

(D) Preparation of monocyclopentadienylmonotriphenylarsine monotriphenylphosphinetrichlorotin ruthenium(II) $\{[(\eta^5-C_5H_5)Ru(AsPh_3)(PPh_3)SnCl_3]\}$. A mixture of $[(\eta^5-C_5H_5)Ru(AsPh_3)(PPh_3)Cl]$ (0.1 g, 1.3×10^{-4} mol) and tin(II) chloride (0.05 g, 2.5×10^{-4} mol) was heated to reflux in 15 cm³ of benzene to which 20 cm³ of methanol was added. After about half an hour yellow crystals had appeared, which were separated by centrifugation. The centrifugate was further concentrated by heating on a water bath whereby more compound appeared in the concentrate. It was centrifuged, recrystallized from CH₂Cl₂-petroleum ether, washed with petroleum ether, and dried in vacuo. The complex was identified as $[(\eta^{5} C_5H_5$)Ru(AsPh₃)(PPh₃)SnCl₃] (yield ca 60%).

(E) Preparation of monocyanomonocyclopentadienylmonotriphenylarsine monotriphenylphosphine ruthenium(II) {[$(\eta^{5}-C_{5}H_{5})Ru(AsPh_{3})(PPh_{3})CN]$ }. A mixture of [$(\eta^{5}-C_{5}H_{5})Ru(AsPh_{3})(PPh_{3})CI$] (0.1 g, 1.3×10^{-4} mol) and excess KCN (0.2 g, 3.3×10^{-3} mol) was heated under reflux for 4–5 h in methanol (20 cm³), whereupon greenishyellow crystals separated, which were centrifuged. The centrifugate was further concentrated, yielding more of the complex as precipitate. The complex was centrifuged, washed with water, methanol and ether, and dried *in vacuo*. It was identified as [$(\eta^{5}-C_{5}H_{5})Ru(AsPh_{3})(PPh_{3})CN$] (yield *ca* 50%).

(F) Preparation of monocyclopentadienylmonotriphenylarsine monotriphenylhosphineacetonitrile ruthenium(II) cationic salts { $[(\eta^5-C_5H_5)Ru(AsPh_3)]$ $(PPh_3)(MeCN)]^+X^- (X = BPh_4, HgCl_3 \text{ or } Zn_2Cl_6)\}.$ (i) Tetraphenylborate salt. Addition of sodium tetraphenylborate (0.05 g, 1.1×10^{-4} mol) to solution of $[(\eta^5-C_5H_5)Ru(AsPh_3)(PPh_3)Cl]$ a $(0.07 \text{ g}, 1.0 \times 10^{-4} \text{ mol})$ in 20 cm³ acetonitrile, followed by heating for about 20 min under reflux, yielded a yellow solution, which was filtered. The filtrate was concentrated to nearly one-third of the volume ($\sim 5 \text{ cm}^3$). Ether was then added to the concentrate, whereby the complex precipitated. It was then centrifuged and recrystallized from acetonitrile-ether. It was washed with ether and dried in vacuo. The complex was identified as $[(\eta^5-C_5H_5)Ru(AsPh_3)(PPh_3)(MeCN)]BPh_4.$

(ii) Trichloromercurate salt. The reaction was carried out by a procedure similar to that described in F(i) except that mercury(II) chloride was used instead of sodium tetraphenylborate to obtain $[(\eta^{5}-C_{5}H_{5})Ru(AsPh_{3})(PPh_{3})(MeCN)]HgCl_{3}$.

(iii) *Hexachlorodizincate salt*. The reaction was carried out by a procedure similar to that described

in F(i) except that zinc(II) chloride was used instead of tetraphenylborate to obtain $[(\eta^5-C_5H_5)Ru$ (AsPh₃)(PPh₃)(MeCN)]₂Zn₂Cl₆.

The corresponding $[(\eta^5-C_5H_5)Ru(AsPh_3)_2X]$ (X = Cl, Br, I, CN or SnCl₃) complexes have also been prepared using the same procedures as described in the above sections.

Interconversions (Scheme 1)

Conversion of $[(\eta^5-C_5H_5)Ru(SbPh_3)_2Cl]$ to $[(\eta^5-C_5H_5)Ru(AsPh_3)_2Cl]$. A mixture of $[(\eta^5-C_5H_5)Ru(SbPh_3)_2Cl]$ (prepared by a method described elsewhere)¹³ (0.1 g, 1.1×10^{-4} mol) and triphenylarsine (0.1 g, 3.3×10^{-4} mol) was refluxed in 20 cm³ benzene for 12 h. The resulting orange solution was evaporated to dryness, and the residue extracted with 10 cm³ of dichloromethane. Excess petroleum ether was added to the extract to give the corresponding arsine complex. It was identified by comparing its spectral and analytical data with those of the authentic sample, and by determining the mixed melting point.

Conversion of $[(\eta^{5}-C_{5}H_{5})Ru(SbPh_{3})_{2}Cl]$ to $[(\eta^{5}-C_{5}H_{5})Ru(PPh_{3})_{2}Cl]$. A mixture of $[(\eta^{5}-C_{5}H_{5})Ru(SbPh_{3})_{2}(Cl]$ (0.1 g, 1.1×10^{-4} mol) and triphenylphosphine (0.1 g, 3.8×10^{-4} mol) was refluxed in 30 cm³ of ethanol for 10 h. The resulting solution was evaporated to nearly 5 cm³, whereby an orange crystalline precipitate appeared. It was centrifuged, washed with ethanol, recrystallized from CH₂Cl₂-petroleum ether, and dried *in vacuo*. The complex was identified as $[(\eta^{5}-C_{5}H_{5})Ru(PPh_{3})_{2}Cl]$.

Conversion of $[(\eta^{5}-C_{5}H_{5})Ru(AsPh_{3})(PPh_{3})Cl]$ to $[(\eta^{5}-C_{5}H_{5})Ru(PPh_{3})_{2}Cl]$. A mixture of $[(\eta^{5}-C_{5}H_{5})Ru(AsPh_{3})(PPh_{3})Cl]$ (0.1 g, 1.3×10^{-4} mol) and triphenylphosphine (0.1 g, 4.0×10^{-4} mol was refluxed in 20 cm³ ethanol for 12 h. The resulting solution was filtered and the filtrate was concentrated to 5 cm³, whereby an orange crystalline precipitate appeared. It was filtered, washed with ethanol and diethyl ether, and dried *in vacuo*. The complex was identified as $[(\eta^{5}-C_{5}H_{5})Ru(PPh_{3})_{2}Cl]$.

Conversion of $[(\eta^5-C_5H_5)Ru(AsPh_3)(PPh_3)Cl]$

to $[(\eta^{5}-C_{5}H_{5})Ru(AsPh_{3})_{2}Cl]$. A mixture of $[(\eta^{5}-C_{5}H_{5})Ru(AsPh_{3})(PPh_{3})Cl]$ (0.5 g, $ca 6.5 \times 10^{-4}$ mol and triphenylarsine (0.2 g, 6.4×10^{-4} mol) was refluxed in benzene (20 cm³) for 24 h. The solution was then centrifuged and the centrifugate evaporated to near dryness. The residue was extracted with CH₂Cl₂, and excess petroleum ether was added to the extract to yield a crystalline product which was identified as $[(\eta^{5}-C_{5}H_{5})Ru(AsPh_{3})_{2}Cl]$.

Physical measurements

Carbon, hydrogen and nitrogen analyses were carried out by the Microanalytical Laboratory of the I.I.T., Kanpur, India. The percentage of halide in the sample was determined by the standard method¹² in the filtrate obtained after fusing the sample with the fusion mixture, extracting it with distilled water and filtering it. IR, UV and visible, ¹H NMR, ³¹P NMR and mass spectra, magnetic measurements and powder X-ray data were determined by the methods described elsewhere.¹³ The results are given in Table 1. All the complexes were found to be diamagnetic. The molecular weight of complex 1 was determined by using a Knauer vapour pressure osmometer.

RESULTS AND DISCUSSION

The analytical data of the yellowish-orange, airstable complex 1 and other substitution products suggested that their formula was $[(\eta^5-C_5H_5)$ Ru(AsPh₃)(PPh₃)X]. Complex 3 was obtained as a result of the substitution reaction of $[(\eta^5-C_5H_5)$ Ru(PPh₃)₂Cl] with triphenylarsine. It was found to be highly soluble in CHCl₃ and CH₂Cl₂, partially soluble in ethanol, methanol and diethyl ether, and insoluble in petroleum ether and *n*hexane. This formulation was further confirmed by the results of the following experiments:

(i) Its experimentally determined molecular weight (752) by osmometer as against the theoretical value of 770.

(ii) By the presence of peaks in its mass spectrum



Scheme 1. Interconversion of various complexes.

	Complex	b a M		:	Analysis [fou	nd (calc.)] (%)		IR bands $(m - 1)$	C,H,
	(molecular weight)	(°Č)	Colour	C	Н	Z	X/S	(C,H,)	$[\delta (ppm)]^{c}$
1	[(η^{5} -C ₅ H ₅)Ru(AsPh ₃)(PPh ₃)CI]	140d	YO	63.1	4.8		5.0	843	4.10
7	(//)) [(η^5 -C ₅ H ₅)Ru(AsPh ₃)(PPh ₃)F]	138d	УO	(03.8) 65.5	(1.0) 4.2		(4.0)	843	4.10
	(753)			(65.3)	(4.6)	1	1	8	
th	[(η ² -C ₅ H ₅)Ru(AsPh ₃)(PPh ₃)Br] (814)	145d	æ	62.3 (60.4)	3.4 (4.3)		10.0	843	4.15
4	$[(\eta^5-C_5H_5)R_0(ASPh_3)(PPh_3)I]$	150d	OR	57.2	().4 ().6 ()		(7.0) 13.4	843	4.12
ŝ	(801) [(η ⁵ -C ₅ H ₅)Ru(AsPh ₃)(PPh ₃)H]	135d	Y	(1./c) 66.4	(3.7) 5.2	1	(14.6) —	845, 1950	4.10
	(735)			(60.9)	(4.9)	I	1	v(Ru—H)	
9	[(η ⁵ -C ₅ H ₅)Ru(AsPh ₃)(PPh ₃)SnCl ₃] (959)	198	УO	51.4 (51.2)	3.6 (3.6)		12.0	840	4.45
٢	[(η^5 -C,H ₃)R ₀ (AsPh ₃)(PPh ₃)CN] (760)	240	ΥG	(5.5) (46.2)	4.1 4.5	2.3		845, 2050	4.45
80	[(η^{5} -C ₅ H ₃)Ru(AsPh ₃)(PPh ₃)(MeCN)]BPh ₄	140d	ΥG	(13.2) 13.2	6.6 2.6	(1.5 (1.5		850	
0	(1104) [(n ⁵ -C,H,)Ru(AsPh,)(PPh,)(MeCN)]HgC],	145d	ХG	(7.2) 47.5	(7.C) 4.1	(f.1) 1.5	10.6	850	
		1)	(47.7)	(3.5)	(1.3)	(9.8)	200	
10	[(η^{5} -C ₅ H ₅)Ru(AsPh ₃)(PPh ₃)(MeCN)] ₂ Zn ₂ Cl ₆ (1894)	180	YG	55.4	4.5	1.7	11.9 11.3	850	
11	[(η^5 -C ₅ H ₅)Ru(AsPh ₅) ₂ F]	140d	BR	67.9 67.9	(). 2.0		(c.11)	840	4.10
12	(/9/) [(n⁵- C.H.)Ru(AsPh.).Br]	146d	æ	(61.7) 58.0	(4.4) 3.6	1	10.6	840	4 20
	(858)		1	(57.2)	(4.0)		(6.3)		07.4
13	[(η^5 -C ₅ H ₅)Ru(AsPh ₃) ₂ I] (905)	152	OR	55.2 (54.4)	3.5 (3.8)		13.5 (14.0)	840	4.20
14	[(η ⁵ -C,H ₅)Ru(AsPh ₃) ₂ SnCl ₃] (1003)	203-205	λО	49.8 (191)	3.6		11.2	840	4.50
15	[(η^{5} -C ₅ H ₅)Ru(AsPh ₃) ₂ CN] (804)	250	YG	63.2 63.7	4.5	2.1.2		843, 2050 "(CN)	4.50
16	$[(\eta^5-C_5H_5)Ru(AsPh_3)_2(MeCN)]BPh_4$	138	ΥG	71.0	5. 4.	1.5 1.5		850	
17	(1140) [(^w 2,C H \D _i ,(A ₆ Db \ (M ₆ CNN)ID ₂ CC)	140	022	(6.0/)	(0.c)	(7:1)	:	050	
11	1(17 - Callynu(Aar 113)2(1916)-19) (1125)	140	DI	40.2 (45.8)	6.9 (9.6)	1.0 (1.2)	(9.5)	068	
18	[(ŋ [*] -C ₅ H ₅)Ru(AsPh ₅) ₂ (MeCN)] ₂ Zn ₂ Cl ₆ (1982)	180	YG	<u>52.5</u> (52.1)	4.2 (3.5)	(1.4) (1.4)	(10.7)	850	
p,	= decomposition.								

Table 1. Characterization data

^b YO = yellowish-orange, B = brown, OR = orange-red, Y = yellow, YG = yellowish-green, BR = brick-red. ^c Solvent CDCI₃. Aromatic protons of the other coligands appeared in the region of δ 7–8 as broad multiplets, and in the case of acetonitrile additional signals in the δ -1.8– 2.0 region were observed due to the methyl protons.

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with m/z values of 306, 262 and 201, corresponding to AsPh₃, PPh₃ and [RuCpCl], respectively. (Since the purpose of this study was just to detect the presence of AsPh₃ and PPh₃ fragments, no attempt has been made to explain other relatively less intense peaks.)

(iii) Complex 1 was subjected to substitution reactions which led to the scission of the Ru—Cl bond and yielded $[(\eta^5-C_5H_5)Ru(AsPh_3)(PPh_3)X]$ as substituted products (X = Br, I, F, CN or SnCl₃) (Table 1).

(iv) Reactions between complex 1 and zinc or mercury(II) chlorides in acetonitrile produced a rapid colour change from orange to yellow of the solution from which stable yellow complexes were isolated. They were initially thought to be 1:1 adducts of the Ru complex acting as a Lewis base. Further investigations revealed that the products were salts of the cation $[(\eta^5-C_5H_5)Ru(AsPh_3)$ (PPh₃) (MeCN)]⁺. The cationic nature has been tested by ion exchange studies.

It has been observed that, by refluxing a solution of $[(\eta^{5}-C_{5}H_{5})Ru(AsPh_{3})(PPh_{3})Cl]$ with either PPh₃ or AsPh₃, it was possible to convert them to the known compounds $[(\eta^{5}-C_{5}H_{5})Ru(MPh_{3})_{2}Cl]$ (M = P or As). These reactions have been further extended and the PPh₃ or AsPh₃ can easily be substituted by triphenylstibine (SbPh₃) simply by refluxing the solution of $[(\eta^{5}-C_{5}H_{5})Ru(MPh_{3})_{2}Cl]$ (M = P or As) with SbPh₃. It has, however, been observed that the time of refluxing for the substitution reaction of the complex having PPh₃ as a coligand with AsPh₃, was much longer compared to the complex having a AsPh₃ as coligand. This could possibly be due to the similarity of some of the chemical properties of the alternate elements in a group.¹⁴ This is, however, a tentative explanation.

The properties of the substitution products of $[(\eta^5-C_5H_5)Ru(AsPh_3)(PPh_3)Cl]$ and $[(\eta^5-C_5H_5)Ru(AsPh_3)(PPh_3)(MeCN)]^+$ are given in Table 1. Their formulae have been assigned on the basis of the chemical analyses and other properties discussed below.

IR spectra

The IR spectra of all the complexes exhibited two bands of medium intensity in the 840–850- and 420cm⁻¹ regions, corresponding to the C—H out-ofplane and skeletal bending modes of the C_3H_5 ring, respectively, besides the characteristic bands¹⁵ of triphenylphosphine and triphenylarsine (1490, 1440, 1100, 750, 700 and 535 cm⁻¹). Since the band positions due to the phenyl groups of AsPh₃ and PPh₃ in their IR spectra do not appreciably vary it was difficult to distinguish the presence of both triphenylarsine and triphenylphosphine in the same complexes by the IR spectra. However, it has been observed that all the phenyl bands in the IR spectra of the complexes $[(\eta^5-C_5H_5)Ru(AsPh_3)(PPh_3)X]$ were relatively broader compared to those found in $[(\eta^{5}-C_{5}H_{5})Ru(MPh_{3})_{2}X]$ (M = P or As). This broadness could possibly be taken tentatively as evidence for the presence of both AsPh₃ and PPh₃ in the complexes, as indicated by other experiments. The IR spectra of all the complexes displayed a characteristic pattern of three bands decreasing in intensity from 535 to 495 cm⁻¹, which suggests the presence of a triphenylphosphine- or triphenylarsine-coordinated ligand.¹⁶ Spectra of the cyanato and hydrido complexes exhibited mediumintensity, slightly broad bands at 2050 and 1950 cm⁻¹, assigned to v(CN) and v(Ru-H), respectively, 7,8,17 confirming the presence of a CN⁻ or H^- ion bonded to ruthenium in the complexes.

It is interesting to observe that the v(CN) band in all complexes having a coordinated isonitrile around 2100 cm^{-1} is very weak. A low value of the transition moment is usually observed in these type of complexes.^{18,19} In the 400–200-cm⁻¹ region bands assignable to $[Zn_2Cl_6]^{2-}$ and $[HgCl_3]^{-}$ anions, besides those due to v(Ru-Cl), have been observed. In the spectrum of the mercury derivative a band at 285 cm^{-1} , assigned to the asymmetric mode in [HgCl₃]⁻, and for the zinc complex the characteristic bands of $[Zn_2Cl_6]^{2-}$ at 335, 305, 252 and 242 cm^{-1} , were present. The positions and relative intensities of the $[Zn_2Cl_6]^{2-}$ bands were found to be similar to those observed in the IR spectra of the solutions of the complexes B^+MCl_3 ($B = bipyBPh_2$, M = Zn or Hg), where it has been suggested²⁰ that the zinc is present as the bridged $[Zn_2Cl_6]^{2-}$ rather than the mononuclear $[ZnCl_3]^-$ anion.²¹

¹H NMR spectra

¹H NMR spectra of all the complexes showed a sharp resonance in the δ -4.0–4.5 region. The sharp singlet in this region is characteristic of π -bonded cyclopentadiene. The aromatic group on the triphenylphosphine and triphenylarsine ligands showed broad complex resonances in the usual range of δ 7.0–8.0 for the C₆H₆ protons. The integrated intensity ratio of the signals of C₅H₅ and MPh₃ (M = P or As) (1:6) corresponded to the ratio of the number of hydrogen atoms of the cyclopentadienyl anion and the sum of those present in triphenylphosphine and triphenylarsine. It was reported earlier that a sharp resonance in the NMR spectra of $[(\eta^5-C_5H_5)Ru(PPh_3)_2Cl]$ and $[(\eta^5-C_5H_5)Ru(PPh_3)_2Cl]$ C_5H_5 Ru(AsPh₃)₂Cl] appears at δ 4.0 and 4.2 (Fig. 1), respectively.¹ The presence of a peak at δ 4.1 in



Fig. 1. ¹H NMR spectra of Ru complexes.

the complex $[(\eta^{5}-C_{5}H_{5})Ru(AsPh_{3})(PPh_{3})Cl]$, therefore, suggests the environment of the cyclopentadienyl protons to be different from that in the former two complexes. Furthermore, the presumption that the complex $[(n^5-C_5H_5)Ru$ $(AsPh_3)(PPh_3)Cl]$ is a 1.1 mixture of $[(\eta^5 C_5H_5$ Ru(PPh₃)₂Cl] and [(η^5 -C₅H₅)Ru(AsPh₃)₂Cl] is also not tenable because of the fact that the NMR spectra of the mixture is expected to exhibit two independent peaks due to cyclopentadienyl protons at δ 4.0 and 4.2, one for each component of the mixture. The presence of only one sharp peak at δ 4.1 suggests only one type of electronic environment around the cyclopentadienyl protons. Further, the spectra of all the complexes showed a broad multiplet in the region of δ 7.8 different from the one present in the spectra of triphenylphosphine and triphenylarsine complexes. The spectra of latter two together did not match the one of complex 1 in the region of δ 7.0, indicating again that it is not a mixture of the phosphine and arsine complexes. In the case of the acetonitrile complexes, an additional signal in the δ -1.8–2.0 region was observed for the methyl protons. ³¹P NMR exhibited a sharp resonance at δ 39.01, indicating the presence of at least one triphenylphosphine molecule in our complex. The literature indicates one

single sharp ³¹P signal in $[(\eta^{5}-C_{5}H_{5})Ru(PPh_{3})_{2}Cl]$ at δ 38.6, indicating the presence of two symmetrical triphenylphosphine molecules.²² The shifting of the signal in our complex towards a lower value by about δ 0.5 suggests that triphenylphosphine in our complex has different surroundings than in $[(\eta^{5}-C_{5}H_{5})Ru(PPh_{3})_{2}Cl]$. These data, along with those of other physical measurements, further confirm the formula to contain one molecule each of triphenylphosphine and triphenylarsine.

Magnetic moments and electronic spectra

All the complexes were found to be diamagnetic, indicating spin pairing. The symmetry of the donor atoms around the metal centre in all these complexes may be considered to be distorted octahedral, based upon the assumption that the cyclopentadienyl group occupies three coordinate sites, or distorted tetrahedral if the perpendicular axis of the C₅-ring is considered to occupy one position. The diamagnetism of the complexes is, however, strongly suggestive of the former alternative, because of the definite possibility of there being spin-free complexes in a tetrahedral environment.

The position of the absorption bands shown in the UV and visible region of the electronic spectra of complex 1 were at 375 nm and a shoulder at 455 nm due to a $M \rightarrow L$ charge-transfer band. When we compared complex 1 with the $[(\eta^5-C_5H_5)Ru$ (PPh₃)₂Cl] complex the absorption band showed red shifts.

The powder X-ray photograph of complex 1 is found to be identical to that of $[(\eta^5-C_5H_5)Ru$ (PPh₃)₂Cl] and $[(\eta^5-C_5H_5)Ru(AsPh_3)_2Cl]$ as far as peak positions are concerned. However, the peak intensities were different from those of the phosphine and arsine analogues as expected because of the difference in the scattering power of P and As. It suggests that these three complexes are isomorphous and the same structure may be assigned to the complex $[(\eta^5-C_5H_5)Ru(AsPh_3)$ (PPh₃)Cl] as to $[(\eta^5-C_5H_5)Ru(PPh_3)_2Cl]$.

CONCLUSIONS

From the above discussion it is postulated that, during the substitution reaction of $[(\eta^5-C_5H_5)$ Ru(PPh₃)₂Cl] by AsPh₃ to yield $[(\eta^5-C_5H_5)$ Ru (AsPh₃)₂Cl] the phosphine molecules are not both simultaneously substituted by two molecules of triphenylarsine, but the reaction proceeds by a stepwise mechanism with the formation of a stable intermediate complex having one molecule of phosphine and one molecule of arsine as coligands. Various derivatives of the $[(\eta^5-C_5H_5)Ru(AsPh_3)]$ $(PPh_3)X]$ (X = Br, I, CN or SnCl₃) have been prepared and characterized. Their structures are assumed to be the same as those of their respective phosphine analogues. Although it has also been observed that phosphine, arsine and stibine analogues of the complexes [$(\eta^5-C_5H_5)Ru(MPh_3)_2Cl$] (M = P, As or Sb) can be interconverted simply by refluxing the complex with the appropriate compound (MPh₃), the substitution of phosphine or stibine involves a much shorter time of refluxing compared to that of arsine.

REFERENCES

- T. Blackmore, M. I. Bruce and F. G. A. Stone, J. Chem. Soc. A 1971, 2376.
- M. I. Bruce, R. C. F. Gardner and F. G. A. Stone, J. Chem. Soc., Dalton Trans. 1976, 81.
- M. I. Bruce and R. Wallis, Aust. J. Chem. 1979, 32, 1471.
- G. S. Ashby, M. I. Bruce, I. B. Tomkins and R. Wallis, Aust. J. Chem. 1979, 32, 1003.
- M. I. Bruce and F. S. Wong, J. Chem. Soc., Dalton Trans. 1981, 1398.
- 6. M. I. Bruce, F. S. Wong, B. W. Skelton and A. H. White, J. Chem. Soc., Dalton Trans. 1982, 687.

- M. I. Bruce, M. G. Humphrey, A. G. Swincer and R. C. Walls, *Aust. J. Chem.* 1984, 37, 1747.
- R. F. N. Ashok, M. Gupta, K. S. Arulsamy and U. C. Agarwala, *Inorg. Chim. Acta* 1985, 98, 161.
- R. F. N. Ashok, M. Gupta, K. S. Arulsamy and U. C. Agarwala, *Inorg. Chim. Acta* 1985, 98, 169.
- H. Nagasimha, K. Yamaguchi, K. Mukai and K. Itoh, J. Organomet. Chem. 1985, 191, C20.
- M. I. Bruce and N. J. Windsor, Aust. J. Chem. 1977, 30, 1601.
- A. I. Vogel, A Textbook of Quantitative Inorganic Analysis, 4th Edn, p. 491. Longmans Green, London (1978).
- 13. K. Mohan Rao, Lallan Misra and U. C. Agarwala, J. Organomet. Chem. (communicated).
- 14. J. E. Huheey, *Inorganic Chemistry*, 3rd Edn, p. 841 (1983).
- 15. L. Maier, Proc. Inorg. Chem. 1963, 5, 27.
- 16. R. Uson et al., J. Organomet. Chem. 1983, 256, 331.
- 17. S. D. Ross, *Infrared and Raman Spectra*, p. 136. McGraw-Hill, London (1971).
- P. M. Treichel, R. L. Shubkin, K. W. Barnett and D. Reichard, *Inorg. Chem.* 1966, 5, 1171.
- S. G. Davies and F. Schott, J. Organomet. Chem. 1980, 188, C41.
- 20. G. E. Coats and Ridley, J. Chem. Soc. 1964, 166.
- 21. H. Bloom et al., Aust. J. Chem. 1970, 23, 843.
- 22. T. Wilczewski, M. Bochenska and J. F. Biernat, J. Organomet. Chem. 1981, 215, 87.