Bistriphenylstibine Complexes of $\eta^5$-Cyclopentadienylruthenium(II)

K MOHAN RAO, L MISHRA & U C AGARWALA*  
Department of Chemistry, Indian Institute of Technology, Kanpur 208 016  
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Syntheses of complexes $[\eta^5-C_5H_5Ru(SbPh_3)_2X]$, (X = F-, Cl-, Br-, I-, CN-, SCN- and SnCl3) and $[\eta^5-C_5H_5Ru(SbPh_3)_2(MeCN)]^+$ (Y- = BPh4-, HgCl2 and Zn2Cl4-2) have been described. The complexes have been characterized by elemental analyses, IR, UV and visible, PMR, X-ray and mass spectral data.

Although recent literature indicates the syntheses and characterization of a number of cyclopentadienylruthenium (II) complexes with triphenylphosphine and triphenylarsine as coligands leading to the formation of neutral as well as cationic complexes1–5, those with triphenylstibine as coligand have not been much studied. The chemistry of these may possibly be interesting because of pronounced steric interaction and the presence of high electron density on ruthenium from two bulky tertiary stibine ligands linked to the metal ion compared to its triphenylphosphine analogues6,7. It was, therefore, worthwhile to study the reactivity of SbPh3 with $[\eta^5-C_5H_5Ru(AsPh_3)_2Cl]$ (1). In this communication, the results of these reactions are presented. The bonding modes of the various ligands as characterized by the physical studies, have also been discussed herein.

Materials and Methods

All the chemicals used were either chemically pure or of AR grade. The solvents were distilled twice and dried before use. The complex $[\eta^5-C_5H_5Ru(AsPh_3)_2Cl]$ was prepared by the literature method8.

All reactions were carried out under nitrogen atmosphere.

[A] Preparation of monochloromono-$\eta^5$-cyclopentadienylibis(triphenylstibine)ruthenium(II), $[\eta^5-C_5H_5Ru(SbPh_3)_2Cl]$ (1)

A mixture of $[\eta^5-C_5H_5Ru(AsPh_3)_2Cl]$ (100 mg, 0.12 mmol) and SbPh3 (100 mg, = 0.28 mmol) in benzene (20 ml) was heated under reflux for 30 hr, concentrated to about 5 ml and to this, light petroleum was added whereupon brick-red coloured microcrystals of the complex separated out. The crystalline product was recrystallised from CH2Cl2-light petroleum. It was centrifuged, washed with excess of pet. ether and dried in vacuo, yield ~ 90%.

[B] Preparation of mono-$\eta^5$-cyclopentadienyl-monohydridobis(triphenylstibine)ruthenium(II), $[\eta^5-C_5H_5Ru(SbPh_3)_2H]$ (2)

Complex (1) (100 mg, ~ 0.11 mmol) was taken in methanol (20 ml) and sodium metal (5 mg, ~ 0.12 mmol) was added to it. The resulting mixture was heated under reflux for 20 min and the solution slowly concentrated, whereupon 2 separated out as a yellow solid. It was centrifuged, washed with methanol and dried in vacuo, yield 67%.

[C] Preparation of monohalomono-$\eta^5$-cyclopentadienyl-bis(triphenylstibine)ruthenium(II), $[\eta^5-C_5H_5Ru(SbPh_3)_2X]$ (X = Cl-, Br- and I-)

(i) Complex (2) (100 mg, ~ 0.11 mmol) was dissolved in 10-15 ml methanol and a few drops of HX was added to it. It was stirred for 10 min whereby a microcrystalline precipitate appeared whose colour varied from brick-red to brown-red, depending upon the nature of halide ion. It was centrifuged, washed with water, methanol, ether and light petroleum, dried in vacuo, yield 80–90%.

(ii) Monochloro and monobromo substituted derivatives were also synthesised by heating under reflux for 1 hr, complex (1) (100 mg, ~ 0.12 mmol) with a slight excess of KX in ethanol (25 ml), and treating the resulting mixture by the same procedure as described under (i).

(iii) The iodo derivative was prepared by dissolving complex (2) (100 mg, ~ 0.11 mmol) in methanol (10 ml) and treating the resulting solution with Mel (a few drops, ~ 0.2 ml) whereupon a yellowish orange solution was immediately
formed. After stirring the solution for 5 min, brownish orange crystals appeared which were centrifuged, washed with methanol, ether, light petroleum and dried in vacuo.

[D] Preparation of \( \eta^5 \)-cyclopentadienyl-bis(triphenylstibine)trichlororuthenium (II), \( \left[ (\eta^5-C_{5}H_{5})Ru(SbPh_{3})_{2}SnCl_{2} \right] \)

A mixture of complex (1) (100 mg, 0.12 mmol) and SnCl_{2} (50 mg, \( \sim 0.27 \) mmol) was heated under reflux for 30 min in a mixture of benzene (15 ml) and methanol (20 ml), whereupon yellow crystals of the title complex separated out. These were centrifuged and from the centrifugate, more crystals were obtained by concentrating the solution. The complex was recrystallised from CH_{2}Cl_{2}-light petroleum and dried in vacuo, yield 50%.

[E] Preparation of monon(\( \eta^5 \)-cyclopentadienyl)-mono(cyanato or thiocyanato)bis(triphenylstibine)-ruthenium(II), \( \left[ (\eta^5-C_{5}H_{5})Ru(SbPh_{3})_{2}X \right] \) (\( X = \text{CN} \) or NCS)

A solution of complex (1) (100 mg, 0.12 mmol) and three-fold excess of KCN or KSCN in methanol or ethanol (20 ml) was heated to reflux for 5 hr in the case of cyanato complex and for 2 hr in the case of thiocyanato complex. Concentration of the resulting solution led to the separation of yellowish-green crystals (cyanato) or yellow crystals (thiocyanato) complexes. These were centrifuged, washed with water, ethanol and light petroleum and dried in vacuo (for cyanato, yield 50%, and for thiocyanato complex, yield \( \sim 60% \)).

[F] Preparation of the salts of \( \left[ (\eta^5-C_{5}H_{5})Ru(SbPh_{3})_{2} \right] \) (MeCN)\( ^{+} \) Y\( ^{-} \) (Y = BPh\( _{4} \), HgCl\( _{3} \) and Zn\( _{2} \)Cl\( _{6} \) - )

[F\(_{1}\)] Tetraphenylborate salt

Addition of NaBPh\(_{4}\) (60 mg, 0.17 mmol) to a solution of complex (1) (100 mg, 0.12 mmol) in acetonitrile (20 ml), followed by heating for a brief period under reflux gave a yellow solution. The resulting solution was filtered and the filtrate concentrated to half the volume. Addition of ether to the concentrate gave a yellow microcrystalline precipitate which was centrifuged, washed with ethanol, ether and petroleum ether, and recrystallised from acetonitrile-ether to give the tetraphenylborate salt, yield \( \sim 50% \).

[F\(_{2}\)] Trichloromercury salt

The reaction was carried out by the procedure similar to that described in [F\(_{1}\)] except that mercury (II) chloride (20 mg, 0.74 mmol) was used in the place of triphenylborate to obtain \( \left[ (\eta^5-C_{5}H_{5})Ru(SbPh_{3})_{2}(\text{MeCN})\right] \)HgCl\(_{3}\) in 53% yield.

[F\(_{3}\)] Hexachlorodizincate salt

The reaction was carried out by the procedure similar to that described in [F\(_{1}\)] except that zinc (II) chloride (20 mg, 0.16 mmol) was used in the place of triphenylborate to obtain \( \left[ (\eta^5-C_{5}H_{5})Ru(SbPh_{3})_{2}(\text{MeCN})\right] \)Zn\(_{2}\)Cl\(_{6}\) in 55% yield.

Physical measurements

IR, UV-vis, magnetic moments and melting points were determined by the procedure described elsewhere\(^{1}\). Mass spectra were recorded on a JEOL 01SG-2 mass spectrometer with an ionising energy of 70 eV. X-ray powder diffraction pattern of complex (1) was recorded with ISO-Debyeflex 2002 diffractometer.

Results and Discussion

Characterization data of the complexes including characteristic IR bands are given in Table 1. The analytical data of the complex (1) suggests its formula \( \left[ (\eta^5-C_{5}H_{5})Ru(SbPh_{3})_{2}Cl \right] \). Complex (1) is formed as a result of substitution reaction of \( \left[ (\eta^5-C_{5}H_{5})Ru(AsPh_{3})_{2}Cl \right] \) by triphenylstibines. Complex (1) is air-stable, highly soluble in chloroform, \( CH_2Cl_2 \), benzene, partially soluble in ethanol, methanol, diethyl ether, and insoluble in pet ether, and n-hexane. The formulation for 1 is further confirmed by its molecular weight by mass spectrometry which exhibits the molecular ion peak at \( m/\ell 908 \). Other prominent peaks appear at \( m/\ell 829, 828, 727 \) and 279 due to fragment ions shown in Chart 1. These fragments have been postulated on the basis of the appearance of similar fragments in analogous systems\(^{9,10}\). Besides these, others with masses corresponding to SbPh\(_{3}\), SbPh\(_{2}\), Ph, CsH\(_{5}\) etc. have also been observed in the mass spectrum of 1.

The X-ray powder pattern of 1 is found to be identical with that of \( \left[ (\eta^5-C_{5}H_{5})Ru(PPh_{3})_{2}Cl \right] \) as far as the peak positions are concerned; however, the peak intensity in the two cases are found to be different, indicating that both the complexes...


Table 1—Characterisation Data of Various Complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>m.p. (°C)</th>
<th>Colour</th>
<th>Found (Calc.), %</th>
<th>IR bands (cm⁻¹)</th>
<th>C₂H₅NMR (δ ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[η⁵-CsH₅Ru(SbPh₃)₂Cl]</td>
<td>153-5</td>
<td>BR</td>
<td>54.4, 4.2</td>
<td>830</td>
<td>4.16</td>
</tr>
<tr>
<td>[η⁵-CsH₅Ru(SbPh₃)₂H]</td>
<td>135&lt;br&gt;(873)</td>
<td>Y</td>
<td>56.5, 4.5</td>
<td>840, 1950</td>
<td>4.15</td>
</tr>
<tr>
<td>[η⁵-CsH₅Ru(SbPh₃)₂F]</td>
<td>145-7</td>
<td>BR</td>
<td>54.7, 4.2</td>
<td>830, 500, 480&lt;</td>
<td>4.16</td>
</tr>
<tr>
<td>[η⁵-CsH₅Ru(SbPh₃)₂Br]</td>
<td>148&lt;br&gt;(952)</td>
<td>B</td>
<td>52.1, 4.1</td>
<td>840</td>
<td>4.16</td>
</tr>
<tr>
<td>[η⁵-CsH₅Ru(SbPh₃)₂I]</td>
<td>150&lt;br&gt;(999)</td>
<td>BO</td>
<td>49.5, 4.0</td>
<td>840</td>
<td>4.18</td>
</tr>
<tr>
<td>[η⁵-CsH₅Ru(SbPh₃)₂SnCl₃]</td>
<td>210&lt;br&gt;(1097)</td>
<td>OY</td>
<td>44.2, 3.5</td>
<td>840</td>
<td>4.10</td>
</tr>
<tr>
<td>[η⁵-CsH₅Ru(SbPh₃)₂CN]</td>
<td>245&lt;br&gt;(898)</td>
<td>YG</td>
<td>55.9, 4.2</td>
<td>840, 2100</td>
<td>4.50</td>
</tr>
<tr>
<td>[η⁵-CsH₅Ru(SbPh₃)₂NCS]</td>
<td>135&lt;br&gt;(930)</td>
<td>Y</td>
<td>54.4, 4.1</td>
<td>850, 2120</td>
<td>4.30</td>
</tr>
<tr>
<td>[η⁵-CsH₅Ru(SbPh₃)₂(MeCN)]Br₄</td>
<td>148-50&lt;br&gt;(1232)</td>
<td>OY</td>
<td>64.8, 5.1</td>
<td>850</td>
<td>—</td>
</tr>
<tr>
<td>[η⁵-CsH₅Ru(SbPh₃)₂(MeCN)]HgCl₃</td>
<td>152-5&lt;br&gt;(1220)</td>
<td>OY</td>
<td>42.5, 3.5</td>
<td>850, 4 in CH₂Cl₂</td>
<td>—</td>
</tr>
<tr>
<td>[η⁵-CsH₅Ru(SbPh₃)₂(MeCN)]₂ZnCl₆</td>
<td>190-5&lt;br&gt;(2170)</td>
<td>OY</td>
<td>47.5, 3.7</td>
<td>850</td>
<td>—</td>
</tr>
</tbody>
</table>

*Halogen and sulphur were analysed by standard methods (ref. 8) in the aqueous filtrate obtained after fusing the sample with KNO₃ + NaOH.

[a] BR = brick-red; Y = yellow; B = brown; BO = brownish orange; OY = orange-yellow; YG = yellowish green.

[b] Solvent CDCl₃; aromatic protons of the other coligands appeared in the region δ 7-8 as broad multiplets, and in the case of acetonitrile complex additional signals in the region δ 1.8-2.0 were observed due to the methyl protons.


are isomorphous. The structure of [η⁵-CsH₅Ru(PPh₃)₂Cl] has already been worked out previously. On the basis of this, we assign the stibine complex, a structure analogous to that of phosphine analogue.

The complex (1) was further subjected to substitution reactions in order to confirm the above formulation. It has been experimentally observed that all the reactions bring about cleavage of Ru-Cl bond leading to the formation of substitution products with other halogens and pseudo-halogen like F⁻, H⁻, Br⁻, I⁻, SnCl₃, CN⁻ and NCS⁻.

Reactions between the chloro complex and zinc and mercury (II) chloride in acetonitrile produce rapid colour change from orange to yellow of the solution from which stable yellow complexes are isolated. Initially we believed these to be 1:1 adducts in which the ruthenium complex acted as a Lewis base. Further investigation revealed that the products were the salts of the cation [η⁵-CsH₅Ru(SbPh₃)₂(MeCN)]⁺.

Magnetic moments and electronic spectra

All the complexes were found to be diamagnetic, indicating spin pairing. In all of them the symmetry of the donor atoms around the metal centre may be considered to be distorted octahedral. This is based upon the assumption that the cyclopentadienyl group occupies three coordinate sites or distorted tetrahedral if the perpendicular axis of the Cs-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 tetrahedral environment.

The UV/visible spectrum of complex (1) exhibited bands at 380 nm and shoulder at 480 nm due to (M−L) charge transfer band. A comparison of the absorption spectrum of 1 with those of [ Ru(η⁵-CsH₅)(PPh₃)₂Cl ] and [ Ru(η⁵-CsH₅)(AsPh₃)₂Cl ], revealed red shifts in the absorption bands. The red shift in the triphenylstibine complex may be due to weak crystal field of the stibine compared to those of arsine and phosphine.

Infrared spectra

IR spectra of all the complexes exhibited two bands of medium intensity in the regions 830-840 and 420 cm⁻¹. These were assigned to out-of-
plane bending mode of C₅H₅ and the skeletal modes of the ring vibration, respectively. In addition, the characteristic bands of triphenylstibine\textsuperscript{11,12} were present in the spectra. In the spectrum of the hydride complex, the band at 1950 cm\textsuperscript{-1} was assigned to $\nu(\text{Ru-H})$\textsuperscript{5} and those at 2100 and 2120 cm\textsuperscript{-1}, respectively in the case of cyanato and thiocyanato complexes to $\nu(\text{CN})$ modes\textsuperscript{13}.

The salts of the complex cation $[(\eta^5$-C₅H₅)Ru(SbPh₃)₂(MeCN)]⁺ can be formed directly by dissolution of \textbf{1} in acetonitrile in the presence of triphenylborate ion, HgCl₂ or ZnCl₂ to yield yellow crystalline products. IR spectra of these salts exhibited only a very weak band around 2150 cm\textsuperscript{-1} due to $\nu(\text{CN})$ of the coordinated acetonitrile\textsuperscript{7}. Besides, the spectra also displayed extra bands in the region 400-200 cm\textsuperscript{-1} characteristic of $[\text{ZnCl}_6]^{2-}$ or HgCl\textsubscript{5} anions. The spectrum of HgCl\textsubscript{5} salt exhibited a band at 285 cm\textsuperscript{-1} which has been assigned to $\nu_{as}(\text{HgCl}_3)$ mode. This band was not present in the spectrum of $[\text{ZnCl}_6]^{2-}$ salt. Instead, four bands at 330, 300, 242 and 230 cm\textsuperscript{-1} were present in the spectrum of zinc salt. The positions and relative intensities of these bands are similar to those present in the IR spectra of complexes $\text{B}^+(\text{ZnCl}_3)^-$ (B = bipy, BPh\textsubscript{5}) where it has been shown\textsuperscript{14,15} that $\text{ZnCl}_3$ is present in the dimeric bridge form, $[\text{ZnCl}_6]^{2-}$, rather than as a mononuclear $[\text{ZnCl}_5]$ anion. It has, therefore, been suggested that in the $\text{ZnCl}_5$ salt of the ruthenium complex cation, $[(\eta^5$-C₅H₅)Ru(SbPh₃)₂(MeCN)]⁺, ZnCl\textsubscript{5} is present as $[\text{ZnCl}_6]^{2-}$ species.

**PMR spectra**

PMR spectra of all the complexes exhibited a sharp triplet in the region $\delta$ 4.2-4.3. Although it is difficult to assign any definite reason for the presence of this triplet in this region, it has, however, been observed that in a few complexes the triphenylphosphine derivative also exhibited\textsuperscript{3,7} triplet around $\delta$ 4.55 due to the coupling of phenyl protons with those of cyclopentadienyl moiety. The presence of three peaks (approx. 1:2:2; in some cases 1:3:1) in the expected range of $[\eta^5$-C₅H₅] (δ 4.0-5.0)\textsuperscript{8}, may suggest that the five protons of cyclopentadienyl ring are not equivalent. This non-equivalence may be caused by the slight tilt of cyclopentadienyl ring towards one of the triphenylstibine molecules, so that the phenyl protons of SbPh₃ interact with the cyclopentadienyl protons or hinder the rotation of Ru-Cp bond, because of bulky SbPh₃ ligands. When one of the SbPh₃ ligands was replaced by pyridine, the PMR spectrum of the resulting compound exhibited a single sharp peak due to cyclopentadienyl protons\textsuperscript{16}. However, it is only a tentative explanation. In the case of acetonitrile cationic complexes, additional signal due to the methyl protons was observed in the region $\delta$ 1.8 to $\delta$ 2.0. The aromatic protons of the triphenylstibine showed characteristic bands in the range of $\delta$ 7.0-8.0 ppm.

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**References**

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