Reactivity studies of (η⁶-p-cymene)ruthenium complexes with 4,4′-bipyridine and imidazole ligands

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Reactions of [η⁶-p-cymene]RuCl2, (a), [η⁶-p-cymene]Ru(EPh3)Cl2 [E = P (b) or As (c)] with 4,4′-bipyridine yielded bridged complexes of the type [η⁶-p-cymene]RuCl₂-μ-4,4′-bipy(Cl-Ru(η⁶-p-cymene)] (1) and [η⁶-p-cymene]RuCl₂-(EPh₃)-μ-4,4′-bipy(Cl-EPh₃[Ru(η⁶-p-cymene)] [E = P, (2); As, (3)] respectively. Complex (b) with imidazole in the presence of NaBF₄ in methanol gave compound of the type [(η⁶-p-cymene)Ru(EPh₃)(imid)(ClBF₄)] (4) (imid = imidazole). These complexes have been characterized with various spectroscopic techniques.

In the last two decades, the chemistry of [(arene)RuX₂]₂ (arene = benzene and substituted benzenes, X = halides and pseudo halides) have been studied extensively.⁵ These complexes attracted much attention due to their reactivity towards various nucleophiles.⁵⁹ Ruthenium arene complexes also exhibit various homogeneous catalytic activity.⁶ Moreover, the chemistry of these complexes is very similar to their cyclopentadienyl ruthenium analogues.ⁱ⁰ In the literature, very few reports are available of ruthenium arene containing bridging ligands.⁴⁴ 4,4′-Bipyridine is a useful bridging ligand for synthesizing various di- and polynuclear complexes.¹¹-¹⁶

In this note, we report the reactivity of [(η⁶-p-cymene)RuCl₂]₂, (a), [(η⁶-p-cymene)Ru(EPh₃)Cl₂] [E = P (b) or As (c)] with 4,4′-bipyridine and imidazole. All these complexes have been characterized with the help of analytical and various spectroscopic techniques.

Experimental

The solvents were dried by standard methods. Infrared spectra were recorded as KBr pellets using a Perkin-Elmer model 983 spectrophotometer. Proton NMR spectra were recorded on a Bruker ACF 300, spectrometer and referenced to external tetramethylsilane. ³¹P [¹H] NMR chemical shifts are reported relative to H₂PO₄ (85%). Elemental analyses were performed at RSIC, NEHU, Shillong.

[(η⁶-p-cymene)RuCl₂]₂, (a) and [(η⁶-p-cymene)Ru(EPh₃)Cl₂] [E = P (b) or As (c)] were prepared by literature methods. Ruthenium trichloride trihydrate were obtained from Arora Mathey Ltd. and used without further purification.

Preparation of [(η⁶-p-cymene)RuCl₂]₂(μ-4,4′-bipy)](I)

To a suspension of [(η⁶-p-cymene)RuCl₂]₂ (200 mg, 0.327 mmol) in methanol (20 ml) was added little excess of 4,4′-bipyridine (70 mg, 0.45 mmol) and the resulting mixture was refluxed for 3 h during which time an orange compound precipitated out. The solid was filtered and washed twice with ethanol and diethyl ether and dried. Yield: 155 mg (62%). IR (KBr pellets, v, cm⁻¹): 3039, 2972, 1608, 1535, 1474, 1390, 823.

¹H NMR (CDCl₃, δ): 1.33 (d, 6H, CH(CH₃)₂, J(HH) 6.9 Hz), 2.08 (s, 3H, CH₃), 3.0 (sept., 1H, CH(CH₃)₃), 5.3 (d, 2H, ring protons, J(HH) 6.0 Hz), 5.4 (d, 2H, ring protons, J(HH) 6.0 Hz), 7.07 (d, 4H, bipy, J(HH) 6.5 Hz), 9.02 (d, 4H, bipy). Analysis: Found: C, 46.46, H, 4.59, N, 3.91. Cal. C, 46.87, H, 4.69, N, 3.64.

Preparation of [[(η⁶-p-cymene)Ru(EPh₃)Cl₂(μ-4,4′-bipy)](BF₄)₂] (E = P, As):

To a suspension of [(η⁶-p-cymene)Ru(EPh₃)Cl₂] (100 mg) in methanol (20 ml) was added proportional amount of 4,4′-bipyridine and sodium tetrafluoroborate. The resulting mixture was refluxed for 5 h. The solution was cooled to room temperature when an orange precipitate separated out. This was isolated by filtration and the product washed with ethanol and diethyl ether and dried. Yield: 165 mg (67%).

Complex E-P, (2): IR (KBr pellets, v, cm⁻¹): 3060, 2950, 1608, 1481, 1434, 1390, 1098, 749, 702, 527.

¹H NMR (CDCl₃, δ): 1.1 (d, 6H, CH(CH₃)₂, J(HH) 2.9 and 2.8 Hz), 1.6 (s, 3H, CH₃), 2.4 (sept., 1H, CH(CH₃)₃), 5.3-5.5 (d, 2H, ring protons, J(HH) 6.0 and 7.1 Hz), 5.9-6.1 (d, 2H, ring protons, J(HH) 6.0 and 7.6 Hz), 7.2-7.4 (m, PPh₃), 8.7 (d, 4H, bipy, J(HH) 6.8 Hz).
[(η⁶-p-cymene)RuCl₂], (a) and [(η⁶-p-cymene)Ru(EPPh₃)Cl₂] \( (E = P \text{ (b) or As (c)} \)} with 4,4'-bipyridine yielded dimeric complexes 1, 2, and 3 respectively.

\[
\begin{align*}
[(\eta^6-p\text{-cymene})\text{RuCl}_2]_2 + 4,4'\text{-bipy} \rightarrow & \quad [\text{Ru}^{\eta^6-p\text{-cymene}}\text{Cl}(\mu-4,4'\text{-bipy})\text{ClRu}^{\eta^6-p\text{-cymene}}]_2^+ \\
\end{align*}
\]

All these complexes are air stable, sparingly soluble in polar solvents and insoluble in nonpolar solvents. The conductivity measurement of the complex 1 in acetonitrile show molar conductance value of the order 7-10 mho cm² mol⁻¹ which conform to the covalent nature of chloro groups bonded to ruthenium. Conductivity measurements of the complexes 2 and 3 in acetonitrile shows molar conductance value ~ 180 mho cm² mol⁻¹, thereby conforming 1:2 electrolytic nature of the complexes. All these complexes show characteristic IR bands for 4,4'-bipyridine in the region 1610s, 1535 cm⁻¹ indicating the presence of bipyridine ligand. In complexes 2 and 3 an additional band due to \( v_{BF} \) stretching frequency ~ 1098 cm⁻¹ is also observed. The \(^1\)H NMR spectrum of complex 1 exhibited two doublets at \( \delta 7.06 \) d, and 9.02 d for 4, 4'-bipyridine. The p-cymene group exhibited a sharp doublet at \( \delta 1.33 \) d for methyl groups of isopropyl, and a singlet for methyl group at \( \delta 2.16 \), septet for proton of isopropyl at \( \delta 3.0 \) and two doublets for ring protons at \( \delta 5.03 \) and 5.22 respectively. Complexes 2 and 3 exhibited one singlet at \( \delta 1.6 \) for the methyl protons, two doublets around \( \delta 1.1 \) for methyl protons of isopropyl group, a septet at \( \delta 2.4 \) for proton of isopropyl group and two pairs of doublets in the region \( \delta 5.3-5.5 \) and \( \delta 5.9-6.1 \) were attributed to the ring protons of the p-cymene group respectively. The split in the ring proton and isopropyl group may be due to loss of planarity of p-cymene group. The same pattern was observed in the case of substitution of...
Schiff base ligands. Signals for phenyl groups of phosphine ligands in their proton NMR spectra as well as characteristics bands in their IR spectra were also observed in the complexes of 2 and 3. $^{31}$P NMR spectrum of the complex 2 exhibited single sharp peak at $\delta$ 37.8 which is attributed to the presence of triphenylphosphine group. Electronic spectrum of complex 1 has shown two absorption bands at 325 and 410 nm which are assigned to MLCT transition arising due to transfer of charge density from the filled $t_2g$ orbitals of metal to low lying $\pi^*$ orbitals of 4,4′-bipyridine ligand. The proton NMR spectrum of the complex 4 has shown two absorption bands at 325 and 410 cm$^{-1}$ which are assigned to MLCT transition arising due to transfer of charge density from the filled $t_2g$ orbitals of metal to low lying $\pi^*$ orbitals of 4,4′-bipyridine ligand. On the basis of the above data, the following structures were proposed.

Reactions of complex c with imidazole yielded monomeric complex shown below:

$$\begin{align*}
[(\eta^6-p\text{-cymene})\text{Ru}(\text{PPh}_3)\text{Cl}_2] + \text{imidazole} & \rightarrow \\
[(\eta^6-p\text{-cymene})\text{RuCl}(\text{PPh}_3)(\text{imid})]\text{BF}_4 & \rightarrow 4
\end{align*}$$

The conductivity measurement of the complex 4 in acetonitrile conforms to 1:1 electrolytic nature.

The IR spectrum of the complex 4 shows a strong band at 1050 cm$^{-1}$ due to $v_{\text{as}-\text{Ph}}$. Other characteristic bands due to triphenylphosphine are also observed. The proton NMR spectrum of the complex 4 has shown two doublets in the region $\delta$ 1.06-1.12 for the methyl protons of isopropyl group and one singlet at $\delta$ 1.8 due to methyl protons. A septet at $\delta$ 2.4 for the proton of isopropyl group and two doublet of doublets were also observed in the region $\delta$ 5.01-5.4 and $\delta$ 5.7-5.8 due to aromatic protons of 4-cymene group. Signals due to phenyl groups of phosphine are also observed as multiplets in the region $\delta$ 7.3-7.4. Imidazole protons were observed at $\delta$ 6.7, 7.1 and 8.05 respectively for three protons as singlets and a broad singlet at $\delta$ 12.8 for NH. $^{31}$P NMR spectrum of the complex 4 shows a sharp singlet at $\delta$ 36.45 due to the presence of triphenylphosphine group. The electronic spectrum of the complex 7 exhibited a strong intensity band at 340 nm having $\epsilon$ value 10,000 which may be due to metal to ligand charge transfer band.

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**References**