

Synthesis and characterization of ruthenium (II) complexes with monotertiary phosphines and arsines

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The reaction of ruthenium (III) perchlorate with some monotertiary phosphines and arsines has been investigated. Ionic complexes of the type $[\text{RuL}_5(\text{ClO}_4)](\text{ClO}_4)$ where $\text{L} = \text{PPh}_3$, AsPh_3 , PMe_2Ph , AsMe_2Ph or AsEt_2Ph have been isolated. Some of these complexes react with nitric oxide to give complexes of the type $[\text{RuL}_5(\text{NO})](\text{ClO}_4)_2$ where $\text{L} = \text{PPh}_3$ or AsPh_3 . The complexes have been characterized on the basis of their elemental analysis, IR, NMR, conductivity and magnetic moment data.

A number of stable ionic ruthenium complexes containing a wide variety of phosphorus^{1,2} or arsine² ligands have been reported during the past few years. These compounds are of interest in view of their catalytic role in a variety of homogeneous reactions³⁻⁶.

In the present note preparation of ionic complexes of ruthenium (II) by the interaction of ruthenium (III) perchlorate with some unidentate phosphine and arsine ligands is reported.

Experimental

Ruthenium trichloride was a Johnson Matthey product while silver perchlorate was a BDH reagent. The ligand PPh_3 was obtained from the Ventron Corporation, U.S.A. AsPh_3 and PMe_2Ph were obtained from the Maybridge Chem. Co., U.K. AsMe_2Ph and AsEt_2Ph were prepared by reacting AsMe_2I and AsEt_2I respectively with PhMgBr in dry ether. AsMe_2I and AsEt_2I were prepared by standard methods⁷.

Nitric oxide was prepared by the reaction of nitric acid with copper turnings and was purified according to the literature method⁸.

Microanalyses for carbon, hydrogen and chlorine were carried out by the Australian Mineral Development Laboratories (amdel), Australia (Table 1). The magnetic susceptibilities of the solid samples were measured at room temperature (302K) on a Faraday balance using $\text{Hg}[\text{Co}(\text{SCN})_4]$ as the external calibr-

ant. ¹H NMR spectra were recorded on a FX 100 MHz spectrometer in CDCl_3 . Melting points were determined on a Toshniwal hot stage melting point apparatus. Conductivity measurements were done on a Digisun direct reading conductivity bridge (DL-90) using a cell which had been calibrated previously. Infrared spectra were recorded on a Beckman IR-12 spectrophotometer in KBr phase.

Ruthenium (III) perchlorate²

Ruthenium trichloride (0.261 g, 1 mmol) was stirred with a stoichiometric amount of silver perchlorate (0.622 g, 3 mmol) in absolute ethanol for 2-3 h and the precipitated silver chloride removed by centrifugation. The remaining light red-brown ruthenium (III) perchlorate solution was immediately utilised for subsequent preparations.

Preparation of ruthenium (II) complexes

Complexes of the type $[\text{RuL}_5(\text{ClO}_4)](\text{ClO}_4)$; $[\text{L} = \text{PPh}_3$ (1), AsPh_3 (2), PMe_2Ph (3), AsMe_2Ph (4), AsEt_2Ph (5)]

An ethanolic solution of ruthenium (III) perchlorate (0.40 g, 1.0 mmol) was added to a refluxing ethanolic solution of the ligand (6 mmol) ($\text{L} = \text{PPh}_3$, AsPh_3 , PMe_2Ph , AsMe_2Ph and AsEt_2Ph) under nitrogen atmosphere and the contents were refluxed for 6 h. The colour of the solution remained brown in the case of $\text{L} = \text{PPh}_3$ and AsPh_3 . In the case of $\text{L} = \text{PMe}_2\text{Ph}$, AsMe_2Ph and AsEt_2Ph , the initial red-brown colour changed to yellow. The solutions were evaporated to a small volume *in vacuo* and the products precipitated by the addition of dry ether. The products were filtered, washed with ether and dried *in vacuo*. The complexes were recrystallized from dichloromethane and *n*-hexane.

(ii) Complexes of the type $[\text{RuL}_5(\text{NO})](\text{ClO}_4)_2$; $[\text{L} = \text{PPh}_3$ (6), AsPh_3 (7)]

Complexes 6 and 7 were obtained by bubbling nitric oxide through dichloromethane solutions of the parent ionic complexes 1 and 2 (0.1 mmol) for 4-5 h. The solutions were evaporated *in vacuo* at room temperature and the compounds precipitated by the addition of petroleum ether (40-60°) and dried *in vacuo*.

Results and discussion

Complexes 1-5 (Table 1) contain one perchlorate group and five phosphine or arsine ligands in the coordination sphere of the metal ion. The metal ion was

Table 1—Physicochemical data for ruthenium (II) complexes

Sl. No.	Complex	Colour (%, yield)	Melting/Dec. point	Found (Calc.), %		
				C	H	Cl
1	[Ru(PPh ₃) ₅ (ClO ₄)](ClO ₄)	Dark brown (80)	182	65.73 (67.08)	4.56 (4.65)	4.81 (4.40)
2	[Ru(AsPh ₃) ₅ (ClO ₄)](ClO ₄)	Grey (65)	154	57.87 (59.00)	4.15 (4.09)	4.23 (3.88)
3	[Ru(PMe ₂ Ph) ₅ (ClO ₄)](ClO ₄)	Greenish Yellow (61)	175	46.90 (48.50)	5.37 (5.55)	8.04 (7.17)
4	[Ru(AsMe ₂ Ph) ₅ (ClO ₄)](ClO ₄)	Orange (83)	158	38.64 (39.66)	4.50 (4.54)	6.12 (5.87)
5	[Ru(AsEt ₂ Ph) ₅ (ClO ₄)](ClO ₄)	Yellow (59)	143	43.11 (44.44)	5.63 (5.55)	5.18 (5.25)
6	[Ru(PPh ₃) ₅ (NO)](ClO ₄) ₂	Brown (50)	210	65.21 (65.77)	4.49 (4.57)	—
7	[Ru(AsPh ₃) ₅ (NO)](ClO ₄) ₂	Grey (50)	182	57.22 (58.06)	4.07 (4.03)	—

also reduced to the divalent state during the reaction with the use of one equivalent excess of phosphine or arsine. Such simple ionic complexes are not known in the literature and they present the first examples with a C_4 symmetry. Magnetic susceptibility measurements showed that the complexes were diamagnetic and possessed spin paired (t_{2g})⁶ configuration. The molar conductivity values of all the complexes in dimethylacetamide corresponded to 1:1 electrolytic behaviour (64-185 ohm⁻¹cm²mol⁻¹).

The infrared spectra of the complexes suggest the presence of a monodentate coordinated perchlorate. Very strong bands observed at 1070 and 1165 cm⁻¹ in complex 1, at 1080 and 1140 cm⁻¹ in complex 2, at 1080 and 1150 cm⁻¹ in complex 3, at 1070 and 1150 cm⁻¹ in complex 4 and at 1040 and 1100 cm⁻¹ in complex 5 due to the split peaks of ν_3 mode⁹ confirm this assignment.

The presence of coordinated phosphine or arsine was indicated^{10,11} by a strong band at 520 or 475 cm⁻¹. In the far infrared spectra of all the complexes, the region 250-350 cm⁻¹ was devoid of bands that could be assigned to the Ru-Cl stretching mode¹².

The NMR spectra of complexes 1-5 supported the assigned configuration. The phenyl protons were observed at δ 7.47 ppm and δ 7.55 ppm in the case of phosphine and arsine complexes respectively.

The NMR spectrum of complex 4 was very well resolved and supported the suggested configuration. The methyl protons of dimethylphenylarsine ligand were observed as two singlets of 4:1 intensity at δ 1.50

ppm and δ 1.20 ppm respectively. The phenyl protons for all the ligands merged to give a broad multiplet centered at δ 7.25 ppm.

The NMR spectrum of complex 5 showed a triplet centered at δ 1.00 ppm corresponding to methyl protons (CH₃) and a quartet centered at δ 2.00 ppm corresponding to methylene (CH₂) protons of diethylphenylarsine ligand. The phenyl protons were observed as a large multiplet centered at δ 7.37 ppm. The integration values of phenyl protons, methyl protons and methylene protons were in the ratio of 5:6:4.

The nitric oxide derivatives (6 and 7) were obtained by passing nitric oxide through the dichloromethane solutions of complexes 1 and 2. The substitution of perchlorate by NO suggest the lability of the weakly coordinated perchlorate groups. The resulting products were tentatively characterised on the basis of elemental analysis, conductivity and infrared data. The conductivity measurements showed that they were 1:2 electrolytes with the coordinated perchlorate displaced by nitric oxide. These complexes showed a strong band 1890 cm⁻¹ due to coordinated NO¹³. A broad and intense absorption band was also observed around 1850 cm⁻¹ due to ionic perchlorate. The far infrared spectra of the complexes showed bands at 520 and 460 cm⁻¹ that could be assigned to Ru-P and Ru-As stretching modes.

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References

- 1 Chatt J & Hayter R G, *J chem Soc*, (1961) 896.
- 2 Taqui Khan M M, Bajaj H C, Siddiqui R H, Khan B T, Satyanarayan Reddy M & Veera Reddy K, *J chem Soc Dalton Trans*, (1985) 2603.
- 3 Bancroft G M, Mays M J, Prater B F & Stefanini F F, *J chem Soc A*, (1970) 2146.
- 4 Sandars J R, *J chem Soc Dalton Trans*, (1973) 743.
- 5 Taqui Khan M M & Martel A E, *Homogeneous catalysis by metal complexes*, Vol 1 (Academic Press, New York) 1974, 11.
- 6 Cavit B E, Grandy K R & Roper W, *J chem Soc Chem Commun*, (1972) 60.
- 7 Burrows G J & Turner E E, *J chem Soc*, (1921) 426.
- 8 (a) James B R, Ochiai E & Rampel G L, *Inorg nucl chem Lett*, 7 (1971) 781.
(b) Evans I P, Spencers A & Wilkinson G, *J chem Soc Dalton Trans*, (1973) 204.
- 9 Hathaway B J & Underhill A E, *J chem Soc*, (1961) 3091.
- 10 Shobatako K, Postmus C, Ferraro J R & Nakamoto R, *Appl Spectrosc*, 23 (1969) 12.
- 11 Dwing J R, McAllister W A & Mercen E E, *J inorg nucl Chem*, 29 (1967) 1441.
- 12 Deacon G B & Green J H, *Chem Commun*, (1963) 629.
- 13 Robinson S D & Uttley M F, *J chem Soc Dalton Trans*, (1972) 1.