

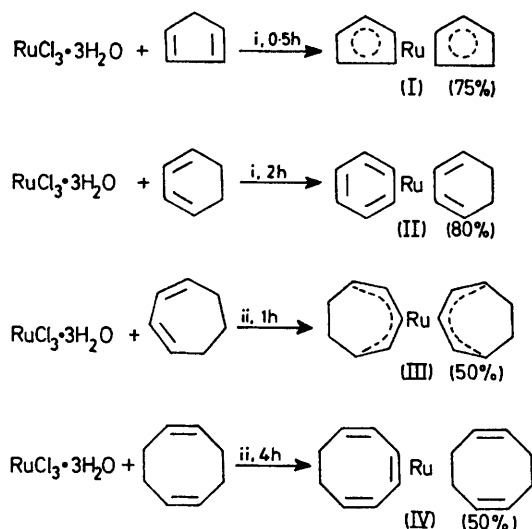
Improved Synthesis of Cyclo-olefin Complexes of Ruthenium *via* Metallic Zinc Reduction

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Summary A simple and efficient method of preparation of cyclo-olefin complexes of ruthenium is described.

THERE is considerable interest in cyclo-olefin derivatives of transition metals.¹ Complexes containing only olefins as



SCHEME. i, Zn, EtOH, 20 °C; ii, Zn, EtOH, 80 °C.

ligands can be important in homogeneous catalysis.² They are normally difficult to prepare and the yields are often

low: the classical methods involve Grignard reagents and u.v. irradiations or Ziegler catalysts.³ We report a simple and widely applicable method for the preparation of cyclo-olefin complexes of ruthenium *via* metallic zinc reduction.

η -Cyclo-olefin-ruthenium(0) and -ruthenium(II) complexes can be prepared in high yields by reaction of cyclo-olefins and $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ in the presence of zinc dust and ethanol (Scheme). In a typical experiment a mixture of cyclo-octa-1,5-diene (10 ml), $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ (0.533 g), ethanol (4 ml), and zinc dust were stirred at reflux temperature under nitrogen for 4 h. Filtration, followed by evaporation and recrystallisation from n-pentane at -78°C gave (IV) as yellow crystals (*ca.* 50%, based on RuCl_3). Similarly, reaction of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ with cyclopentadiene, cyclohexa-1,3-diene, and cyclohepta-1,3-diene gave (I) (75%), (II) (80%), and (III) (50%) respectively.

The compounds (I)–(IV) were characterised by elemental analysis, and by comparison of their n.m.r., i.r., and mass spectra with those of authentic samples.⁴

A possible mechanism for the formation of ruthenium(0) compounds, (II) and (IV), involves an intermolecular hydrogen migration with disproportionation of diene into triene and monoene.⁵ G.l.c. of the mother liquor shows the presence of cyclomono-olefin.

η -Cycloolefinic species, (I) and (III), obtained from cyclopentadiene and cyclohepta-1,3-diene respectively, are probably intermediates in the formation of the ruthenium(0) complexes.

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¹ R. Edwards, J. A. S. Howell, B. F. G. Johnson, and J. Lewis, *J.C.S. Dalton*, 1974, 2105, and references therein; S. A. R. Knox and F. G. A. Stone, *Accounts Chem. Res.*, 1974, 7, 321.

² G. Wilke, *Angew. Chem. Internat. Edn.*, 1963, 2, 105.

³ E. O. Fischer and H. Werner, 'Metal π -complexes', Vol. 1, Elsevier, Amsterdam, 1966, pp. 23–24.

⁴ M. D. Rausch, E. O. Fischer, and H. Grubert, *Chem. and Ind.*, 1958, 756; D. Jones, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 1962, 4458; J. Muller, C. G. Kreiter, B. Mertschenk, and S. Schmitt, *Chem. Ber.*, 1975, 108, 273; E. O. Fischer and J. Muller, *ibid.*, 1963, 96, 3217.

⁵ I. S. Kolomnikov, V. P. Kukolev, and M. E. Vol'pin, *Russ. Chem. Rev.*, 1974, 43, 399, and references therein; R. A. Zelonka, and M. C. Baird, *J. Organometallic Chem.*, 1972, 35, C43; M. A. Bennett and A. K. Smith, *J.C.S. Dalton*, 1974, 233.