Isolation, Structure, Chemistry, and Photochemistry of *cis*-Bis(2,2'-bipyridyl)carbonylchlororuthenium(II) Perchlorate

By JAMES M. CLEAR, JOHN M. KELLY,* CATHERINE M. O'CONNELL, JOHANNES G. VOS, CHRISTINE J. CARDIN,*
and SONIA R. COSTA
(*Department of Chemistry, Trinity College, University of Dublin, Dublin* 2)
and ANTHONY J. EDWARDS
(*Chemistry Department, University of Birmingham, Birmingham* B15 2TT)

Summary The molecular structure and chemical and photochemical reactions of $[Ru(bpy)_2(CO)Cl]^+ClO_4^-$, which has been isolated from the reaction of ruthenium trichloride and 2,2'-bipyridyl(bpy) in dimethylformamide, are described.

THERE is at present great interest in the chemistry of 2,2'-bipyridyl (bpy) complexes of ruthenium, in part because their electrochemical and photochemical properties make them attractive candidates as catalysts and solar energy converters. We now report a new and unexpected synthesis and full structural and spectroscopic characterisation of $[Ru(bpy)_2(CO)Cl]^+ClO_4^-$ (**1**). This compound has chemical and photochemical reactivity which we show makes it a versatile reagent for preparing bis(bipyridyl)-ruthenium(II) complexes; current synthetic methods for most $Ru(bpy)_2$ complexes employ $Ru(bpy)_2Cl_2.2H_2O$ as starting material.

We have prepared $Ru(bpy)_2Cl_2.2H_2O$, for our studies of polyvinylpyridine-bound ruthenium complexes,[1] by the convenient method reported by the North Carolina group.[2,3] In this procedure commercial ruthenium trichloride is allowed to react with two moles of 2,2'-bipyridyl in refluxing dimethylformamide, most of the solvent is then removed by distillation, and the crude $Ru(bpy)_2Cl_2$ is precipitated by addition of acetone. The yields obtained by us and by the original authors[2,3] lie in the range 60—70%. We now report that if sodium perchlorate is added to the mother liquor remaining after the removal of $Ru(bpy)_2Cl_2$, then the complex *cis*-$[Ru(bpy)_2(CO)Cl]ClO_4$ may be isolated in 30—40% yield based on the ruthenium trichloride starting material. Although this complex had previously been isolated in low yield from the reaction of $[RuCl_3(CO)(norbornadiene)]^-$ with 2,2′-bipyridyl,[4] no report of its spectroscopic and chemical properties has been published to the best of our knowledge.

The complex $[Ru(bpy)_2(CO)Cl]ClO_4$ (**1**), isolated as mentioned above, was purified by column chromatography on neutral alumina using 1 : 1 benzene–acetonitrile as eluant and recrystallised from benzene–acetonitrile as air-stable yellow crystals. The structure of the complex, surmised from elemental and spectroscopic analysis,† was confirmed by *X*-ray crystallography.‡ (Figure). It consists of discrete $[Ru(bpy)_2(CO)Cl]^+$ cations and ClO_4^- anions. The geometry of the cation is normal, with the expected *cis* geometry of the bipyridyl rings. The Ru–N distance *trans* to the CO group is, at 2·18(2) Å, slightly longer than those *trans* to N [mean value 2·10(2) Å] {*cf.* $Ru(bpy)_3^{2+}$, 2·056(6) Å;[5] $[(bpy)_2(NO_2)Ru^{III}–O–Ru^{III}(NO_2)(bpy)_2]^{2+}$, 2·08(2) Å[6]} and to Cl 2·07(1) Å, in accordance with the expected *trans* influence order CO>N_{bipy}>Cl. The C–O distance of 1·12(3) Å and Ru–C–O angle of 175(3)° are close to previously recorded values.[7]

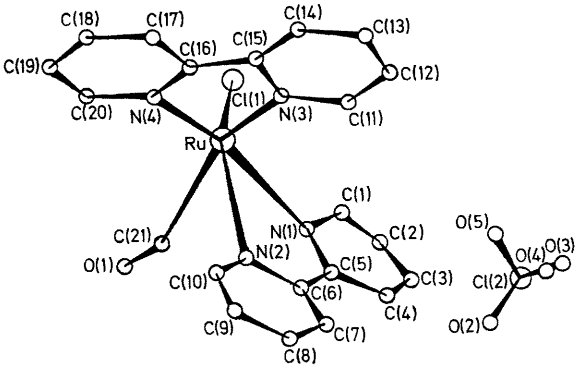

FIGURE. The structure of (**1**). Bond distances to the Ru atom are: N(1) 2·097(12), N(2) 2·066(10), N(3) 2·177(16), N(4) 2·104(15), Cl(1) 2·396(7), and C(21) 1·861(29) Å. C(21)–O(1) 1·122(32) Å, ∠Ru–C(21)–O(1) 174·8(2·6)°.

$$cis\text{-}[Ru(bpy)_2(CO)Cl]^+ + L \xrightarrow{\text{heat}} cis\text{-}[Ru(bpy)_2\text{-}(CO)L]^{2+} + Cl^-$$

(L = MeCN, pyridine, 4-methylpyridine, 4-vinylpyridine, poly-4-vinylpyridine)

$$cis\text{-}[Ru(bpy)_2(CO)Cl]^+ + L' \xrightarrow{h\nu} cis\text{-}[Ru(bpy)_2ClL']^+ + CO$$

[L′ = solvent (MeOH, pyridine, or MeCN); PEt_3 or PPh_3 in $MeNO_2$ solution]

SCHEME

Reactions of complex (**1**) are shown in the Scheme. Substitution of the chloride may be induced thermally, giving access to a new series of ruthenium carbonyl complexes. U.v. irradiation of (**1**) and the other carbonyl complexes at room temperature causes expulsion of CO. These photoreactions, which were monitored spectrophotometrically, show clean isosbestic points indicating that secondary photoreactions are insignificant. The usefulness of the photochemical substitution reaction of (**1**) for the preparation of other $[Ru(bpy)_2ClX]^+$ complexes is illustrated by the formation of $[Ru(bpy)_2(PR_3)Cl]^+$ upon irradiation of nitromethane solutions of (**1**) containing triphenylphosphine or triethylphosphine.[3] Attempts to use this mild route to prepare the monodentate 2,2′-bipyridyl complex $[Ru(bpy)_2(\eta^1\text{-}bpy)Cl]^+$ {proposed as the product of photolysis of $[Ru(bpy)_3]^{2+}$ in hydrochloric acid solution at 100 °C}[8] have been unsuccessful.§

Polymer-bound complexes have been prepared by reaction of (**1**) with atactic poly-4-vinylpyridine (4-vpy) or by copolymerisation of $[Ru(bpy)_2(CO)(4\text{-}vpy)]^{2+}$ with other monomers (*e.g.* methylmethacrylate).

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† I.r. (Nujol) ν_{CO} 1963 cm^{-1}. ^1H N.m.r. multiplets in range δ 9·7—7·3, 16 inequiv. protons.

‡ *Crystal data:* $C_{21}H_{16}Cl_2N_4O_5Ru$, M = 576·308, monoclinic, space group C_2, a = 31·77, b = 11·13, c = 7·24 Å, β = 96·0°, Z = 4, D_m = 1·524 g cm^{-3}, D_c = 1·504 g cm^{-3}, μ(Mo-K_α) = 7·72 cm^{-1}. Data were collected on a Stoe 2-circle diffractometer on a crystal mounted in a capillary in the presence of benzene–acetonitrile vapour. The structure was solved by heavy-atom methods using 2442 unique observations and refined by full-matrix least squares to R = 11·7% using anisotropic temperature factors for Ru, Cl(1), and Cl(2) only. At the current stage of refinement the bipyridyl rings are treated as rigid groups, and the perchlorate group is poorly resolved with high thermal motion of the oxygen atoms. The programmes SHELX and XANADU were used for all calculations. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

§ The photo-induced reactions of (**1**) in solutions containing 2,2′-bipyridyl were investigated spectrophotometrically. In non-co-ordinating solvents such as nitromethane and nitropropane the product observed was $[Ru(bpy)_3]^{2+}$; in co-ordinating solvents such as acetonitrile or pyridine the product was the corresponding $[Ru(bpy)_2Cl\ (solvent)]^+$; and in water or methanol $[Ru(bipy)_2Cl\ (solvent)]^+$ was initially formed but then reacted slowly to give $[Ru(bpy)_3]^{2+}$. Were $[Ru(bpy)_2(\eta^1\text{-}bpy)Cl]^+$ sufficiently stable to be formed under the conditions reported in ref. 8, it should have been possible to isolate it under the mild conditions employed above. These present observations support other findings (ref. 9) that the photolysis of $[Ru(bpy)_3]^{2+}$ in hydrochloric acid yields $[Ru(bpy)_2(H_2O)Cl]^+$ and not $[Ru(bpy)_2(\eta^1\text{-}bpy)Cl]^+$.