

## The Substitutional Photochemistry of Tris(bipyridyl)-ruthenium(II)chloride

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In a recent publication [1], Meyer has discussed the substitutional photochemistry of  $[\text{Ru}(\text{bipy})_3]\text{Cl}_2$  (bipy = 2,2'-bipyridyl) in a variety of different solvents and compared it with that of the more labile  $[\text{Ru}(\text{bipy})_2(\text{py})_2]\text{Cl}_2$  (py = pyridine). He concludes that  $[\text{Ru}(\text{bipy})_3]^{2+}$  is essentially inert in such solvents as water, acetone and acetonitrile, in the absence of added chloride ion [2] and that the chloride source in the previously reported [3] formation of  $\text{RuCl}_2(\text{bipy})_2$  on irradiation of  $[\text{Ru}(\text{bipy})_3]\text{Cl}_2$  in chlorinated hydrocarbons is the counter anion rather than the solvent.

We confirm this last result since no  $\text{RuCl}_2(\text{bipy})_2$  is formed on irradiation of  $[\text{Ru}(\text{bipy})_3][\text{PF}_6]_2$  in dichloromethane, but find that, *in the absence of oxygen*,  $[\text{Ru}(\text{bipy})_3]\text{Cl}_2$  is photolabile in several solvents of medium polarity. In  $\text{CH}_2\text{Cl}_2$  and acetone the photoproduct is  $\text{RuCl}_2(\text{bipy})_2$ , whilst in acetonitrile,  $[\text{RuCl}(\text{MeCN})(\text{bipy})_2]\text{Cl}$  [4] is the only product. In nitromethane, the substitution reaction is not simple but one of the final products appears to be  $[\text{RuCl}(\text{MeNO}_2)(\text{bipy})_2]\text{Cl}$ .

The rate of reaction is very sensitive to solvent polarity, being fastest in the least polar solvent ( $\text{CH}_2\text{Cl}_2$ ) in which  $[\text{Ru}(\text{bipy})_3]\text{Cl}_2$  is soluble. However, the photosubstitution reaction is sufficiently fast in all of these solvents to make the colour change of dilute solutions (from yellow to purple ( $\text{CH}_2\text{Cl}_2$  or acetone) or red (MeCN or  $\text{MeNO}_2$ )) visible within a short time after beginning irradiation with a high energy light source\*\*. For acetone, and  $\text{CH}_2\text{Cl}_2$  we find that the reaction also proceeds in the presence of air, although the rate is significantly greater under anaerobic conditions. Similar results obtained in dimethylformamide (DMF) have been briefly reported [5] and although the product was not identified,  $[\text{Ru}(\text{bipy})_3][\text{SCN}]_2$  apparently gives both  $[\text{Ru}(\text{SCN})(\text{DMF})(\text{bipy})_2]\text{SCN}$  and  $\text{Ru}(\text{SCN})_2(\text{bipy})_2$ .

The observation that photochemical substitution occurs in acetonitrile is of particular importance since

photochemical studies of  $[\text{Ru}(\text{bipy})_3]\text{Cl}_2$  have been carried out [6] in acetonitrile. However, the suppression of the photo-substitution reaction by dissolved oxygen (20% conversion after 15 h *cf.* 1h in the absence of air), presumably because of the quenching of the photochemically excited state of  $[\text{Ru}(\text{bipy})_3]\text{Cl}_2$ , allows the use of acetonitrile as a solvent for photochemical studies of  $[\text{Ru}(\text{bipy})_3]\text{Cl}_2$  under aerobic conditions.

$[\text{RuCl}(\text{MeCN})(\text{bipy})_2]\text{Cl}$  can also be formed from  $\text{RuCl}_2(\text{bipy})_2$  in acetonitrile and this reaction occurs much more rapidly under reflux. We do not find that further substitution occurs to give  $[\text{Ru}(\text{MeCN})_2(\text{bipy})_2]^{2+}$  on prolonged reflux. Interestingly, evaporation of acetonitrile solutions of  $[\text{RuCl}(\text{MeCN})(\text{bipy})_2]\text{Cl}$ , prepared from  $\text{RuCl}_2(\text{bipy})_2$  or  $[\text{Ru}(\text{bipy})_3]\text{Cl}_2$ , to dryness and dissolving the residue in  $\text{CH}_2\text{Cl}_2$  slowly gives  $\text{RuCl}_2(\text{bipy})_2$ , again by a photoinitiated pathway. Since diffuse sunlight is sufficient to promote this reaction it is possible to prepare  $\text{RuCl}_2(\text{bipy})_2$  by irradiation of  $[\text{Ru}(\text{bipy})_3]\text{Cl}_2$  in acetonitrile followed by evaporation to dryness and extraction of  $[\text{RuCl}(\text{MeCN})(\text{bipy})_2]\text{Cl}$  into  $\text{CH}_2\text{Cl}_2$ , but yields are low.

$\text{RuCl}_2(\text{bipy})_2$  may also be prepared directly in *ca.* 40% yield from  $[\text{Ru}(\text{bipy})_3]\text{Cl}_2$  by irradiating a Soxhlet extractor (without thimble) containing  $[\text{Ru}(\text{bipy})_3]\text{Cl}_2$  whilst extracting with  $\text{CH}_2\text{Cl}_2$ .

Although production of large amounts of  $\text{RuCl}_2(\text{bipy})_2$  (identified as the *cis* isomer by its IR spectrum [9]) by these methods is impractical, they represent easier preparative routes than those currently available [9, 10], particularly if  $[\text{Ru}(\text{bipy})_3]\text{Cl}_2$  is prepared by refluxing  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  with excess bipyridyl in DMF rather than by any of the methods discussed by Seddon [11]. This preparation, which is similar to that used [12] for certain surfactant analogues of  $[\text{Ru}(\text{bipy})_3]\text{Cl}_2$ , affords pure (micro analysis, IR spectrum UV spectrum)  $[\text{Ru}(\text{bipy})_3]\text{Cl}_2 \cdot 5\text{H}_2\text{O}$  after recrystallisation from wet methanol-acetone.

Finally, it has been reported [12] that  $\text{RuCl}_2(\text{bipy})_2$  may also be prepared from  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  and two moles of bipy in refluxing DMF. We find that, although  $\text{RuCl}_2(\text{bipy})_2$  is undoubtedly formed, it is contaminated by a species with a weak peak in the IR spectrum at  $1970\text{ cm}^{-1}$ . This impurity is not completely removed using the work up procedure employed [12] by Sprintschnik *et al.*, but is absent from samples prepared photochemically as described in this paper since no absorption at  $1970\text{ cm}^{-1}$  is present in the IR spectra.

It is possible that this absorption at  $1970\text{ cm}^{-1}$  arises from  $\nu\text{ Ru-H}$  of an hydrido impurity. If so, it is possible that this hydrido species also contaminates monolayers of surfactant analogues of  $[\text{Ru}(\text{bipy})_3]$

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\*\*An upper limit for the quantum yield in MeCN is  $10^{-2}$ .

$\text{Cl}_2$  prepared from  $\text{RuCl}_2(\text{bipy})_2$  and may be responsible for the irreproducible [12–15] production of hydrogen on irradiation of such monolayers in water.

We have recently shown [16] that other monohydrido metal complexes such as  $[\text{HPd}(\text{PEt}_3)_3]^+$  can act as catalysts for the production of hydrogen from water and mild reducing agents.

## Experimental

Microanalyses are by Butterworth Laboratories. UV-visible spectra were recorded on a Perkin-Elmer SP 800 spectrophotometer and IR spectra on a Perkin Elmer PE 255 spectrophotometer.

Acetonitrile was purified by refluxing under nitrogen over  $\text{CaH}_2$  and distilling.

### Preparation of $[\text{Ru}(\text{bipy})_3]\text{Cl}_2$

$\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  (2.0 g) and bipyridyl (5.0 g) were refluxed in dimethylformamide (100 ml) for 48 hours. DMF was then distilled from the solution at one atmosphere until 20 ml remained. Acetone (500 ml) and water (1 ml) were added and the resulting suspension cooled to  $-30^\circ\text{C}$ . The resulting red crystals were collected and recrystallised from wet methanol–acetone at  $-30^\circ\text{C}$ . Yield 3.5 g (63%); after recrystallisation, 2.0 g (36%).

*Anal.* Found: C, 50.0; H, 4.85; N, 11.15; Cl, 9.6. Calcd. for  $[\text{Ru}(\text{bipy})_3]\text{Cl}_2 \cdot 5\text{H}_2\text{O}$ : C, 49.3; H, 4.7; N, 11.5; Cl, 9.7%; vis.  $\lambda_{\text{max}} = 452 \text{ nm}$ ,  $\epsilon = 1.44 \times 10^4$  (lit. [17]  $455 \text{ nm}$ ,  $1.4 \times 10^4$ ). Before recrystallisation, strong IR absorptions near  $1600 \text{ cm}^{-1}$  are observed, presumably from DMF of recrystallisation, these are completely removed on recrystallisation.

### Photochemistry of $[\text{Ru}(\text{bipy})_3]\text{Cl}_2$

A dilute solution of  $[\text{Ru}(\text{bipy})_3]\text{Cl}_2$  in degassed acetonitrile (4 ml) under nitrogen was placed near the focus of a lens through which light from a 500 W tungsten filament bulb was passing. Within 5 hours the colour of the solution had changed from yellow to red and UV-visible spectra identified [4] the product as  $[\text{RuCl}(\text{MeCN})(\text{bipy})_2]\text{Cl}$  ( $\lambda_{\text{max}}$  342, 476 nm), although complete conversion took *ca.* 15 h.

Similar anaerobic reactions were performed in acetone, and dichloromethane to give  $\text{RuCl}_2(\text{bipy})_2$ , but complete conversion was observed in  $<1 \text{ h}$ .

The same procedure using nitromethane gave a red solution which apparently contained two species ( $\lambda_{\text{max}}$  440 and 485 nm) after 48 h. Intermediate compounds with  $\lambda_{\text{max}}$  at 425 and 505 nm were detected after 7 h. We have not investigated this reaction further, but assume that the compound with  $\lambda_{\text{max}}$  at 485 nm is  $[\text{RuCl}(\text{MeNO}_2)(\text{bipy})_2]\text{Cl}$  by comparison with other similar derivatives [4].

In air, significant photosubstitution was only observed in acetone and dichloromethane, although in MeCN, *ca.* 20% reaction was observed after 15 h photolysis.

### Preparation of $\text{RuCl}_2(\text{bipy})_2$

#### In acetonitrile

$[\text{Ru}(\text{bipy})_3]\text{Cl}_2$  (0.1 g) was dissolved in dry degassed acetonitrile (100 ml) in a flat-sided water cooled reactor (path length  $\cong 2 \text{ cm}$ ). This was placed near the lens of the optical system described above, in such a way that the entire solution was irradiated for 36 hours. The resulting red solution was evaporated to dryness and extracted with  $\text{CH}_2\text{Cl}_2$  to give a red solution which became purple on standing in diffuse sunlight for 3 hours. The solution was washed with 1 M HCl (100 ml), and water ( $2 \times 100 \text{ ml}$ ) to remove unreacted  $[\text{Ru}(\text{bipy})_3]\text{Cl}_2$  and bipyridyl, dried quickly over sodium sulphate and evaporated to dryness. The resulting black-purple crystals were collected and washed with petroleum. Yield, 0.01 g (16%).

#### In dichloromethane

$[\text{Ru}(\text{bipy})_3]\text{Cl}_2$  (0.1 g) was placed in a thimbleless soxhlet extractor on top of a plug of cotton wool. This was extracted with degassed dichloromethane while the soxhlet was irradiated using the optical system described above in such a way that all of the collector was illuminated. (To increase the light intensity, aluminium foil was placed on the side of the collector remote from the lamp.) When no further colour appeared in the extractor (*ca.* 4 hours), the red-purple dichloromethane solution was washed with 100 ml 1 M HCl and  $2 \times 100 \text{ ml}$  water to remove unreacted  $[\text{Ru}(\text{bipy})_3]\text{Cl}_2$  and bipyridyl, dried quickly with anhydrous sodium sulphate and evaporated to dryness, to give  $\text{RuCl}_2(\text{bipy})_2$  (0.025 g, 38%) as purple crystals which were collected and washed with petroleum ( $40\text{--}60^\circ\text{C}$  boiling range). Purification of the  $\text{CH}_2\text{Cl}_2$  by passing down an alumina column before use does not appear to affect the yield significantly.

### Reaction Between $\text{RuCl}_2(\text{bipy})_2$ and Acetonitrile

$\text{RuCl}_2(\text{bipy})_2$  (0.05 g) was refluxed in acetonitrile (50 ml) for 1.5 h in air. A UV-visible spectrum of the resulting red solution showed it to contain only  $[\text{RuCl}(\text{MeCN})(\text{bipy})_2]\text{Cl}$  ( $\lambda_{\text{max}}$ : 342, 476 nm). No change in the UV-visible spectrum was observed on refluxing for a further 4 h.

At room temperature complete conversion to  $[\text{RuCl}(\text{MeCN})(\text{bipy})_2]\text{Cl}$  took several days.

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