A Facile, High-yield Synthesis of Bis(2,2'-bipyridine)(carbonyl)chlororuthenium(II) Salts

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Abstract

The reaction of [Ru(bipy)$_2$Cl$_2$] (bipy = 2,2'-bipyridine) with acetone at elevated temperatures and pressures provides a convenient high-yield route to the complex ion [Ru(bipy)$_2$(CO)Cl]$^+$. The reaction of this cation with nucleophiles in the presence of amine *N*-oxides results in the formation of [Ru(bipy)$_2$ClX]$^{n+}$ complexes; a typical preparation of [Ru(bipy)$_2$Cl(py)] [PF$_6$] is described.

Introduction

Salts of the complex ions [Ru(bipy)$_2$(CO)Cl]$^+$ and [Ru(bipy)$_2$(CO)$_2$]$^{2+}$ have been known for some years, and have been shown to be of some synthetic utility [1–11]. We have recently been interested in the preparation of complexes of the type [Ru(bipy)$_2$XY]$^{n+}$ [12] and considered [Ru(bipy)$_2$(CO)Cl]$^+$ salts to be likely starting materials. However, the most convenient preparation of these salts only gives moderate yields (~30%) of the desired products. Thus, [Ru(bipy)$_2$(CO)Cl] [ClO$_4$] may be obtained as a by-product from the preparation of [Ru(bipy)$_2$Cl$_2$] by the reaction of 'ruthenium trichloride' with 2,2'-bipyridine in dmf. In this paper we report a new, high-yielding synthesis of this cation, and describe a useful modification of its reactivity with nucleophiles to yield [Ru(bipy)$_2$ClX]$^{n+}$ complexes, rather than the hitherto reported [Ru(bipy)$_2$(CO)X]$^{n+}$ species.

Experimental

[Ru(bipy)$_2$Cl$_2$] was prepared by the literature method from hydrated ruthenium trichloride (Johnson Matthey) [13]. Electrochemical measurements were made using a PAR Model 170 electrochemistry system; NMR spectra were recorded using Bruker WH 400 or WM 250 spectrometers; high pressure reactions were performed using Berghof 250 cm^3 autoclaves fitted with Teflon liners.

Bis(2,2'-bipyridine)(carbonyl)chlororuthenium(II) Hexafluorophosphate

Method 1

[Ru(bipy)$_2$Cl$_2$] (100 mg, 0.21 mmol) and 2-phenylpyridine (32 mg, 0.21 mmol) were dissolved in acetone (50 cm^3) to give a purple solution. This was heated to 180 °C for 24 h under 50 atm. of dinitrogen with magnetic stirring. After this period, the dark brown solution was filtered, and the filtrate treated with ammonium hexafluorophosphate (0.5 g). The solution was concentrated and cooled, whereupon [Ru(bipy)$_2$(CO)Cl] [PF$_6$] separated as an orange crystalline solid (78 mg, 60%). *Anal.* Found: C, 39.0; H, 2.6; N, 8.7. Calc. for $C_{21}H_{16}N_4ClF_6OPRu$: C, 39.4; H, 2.7; N, 8.8%. IR, 1964 cm^{-1}, C–O str., 335 cm^{-1}, Ru–Cl str.

Method 2

Exactly as above without the inclusion of 2-phenylpyridine. The desired complex was obtained in 60% yield.

Method 3

[Ru(bipy)$_2$Cl$_2$] (100 mg, 0.21 mmol) was dissolved in chloroform (50 cm^3) and heated to 180 °C for 24 h under 50 atm. of carbon monoxide. The deep orange solution was evaporated to dryness, and the residue dissolved in methanol (10 cm^3). The solution was treated with ammonium hexafluorophosphate (0.5 g) to give the title complex in 64% yield.

Bis(2,2'-bipyridine)(pyridine)chlororuthenium(II) Hexafluorophosphate

[Ru(bipy)$_2$(CO)Cl] [PF$_6$] (40 mg, 0.064 mmol) was dissolved in acetonitrile (25 cm^3) and heated to reflux for 15 min. After this period, pyridine (2 cm^3) and trimethylamine *N*-oxide (30 mg, excess) were added, and the solution maintained at reflux for a further 1 h, during which time it darkened to a deep purple colour. The hot solution was treated with

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ammonium hexafluorophosphate (0.2 g) and allowed to cool, when purple crystals of [Ru(bipy)$_2$(py)Cl]-[PF$_6$] separated (20 mg, 46%). *Anal.* Found: C, 41.9; H, 3.2; N, 9.6. Calc. for $C_{25}H_{25}N_5ClF_6O_2PRu$: C, 42.3; H, 3.5; N, 9.8%.

Results and Discussion

We recently reported the preparation of [Ru(bipy)$_2$L] [PF$_6$] (HL = 2-phenylpyridine), a carbon-bonded analogue of [Ru(bipy)$_3$]$^{2+}$ salts [12]. In our attempts to prepare this compound, we investigated the reaction of [Ru(bipy)$_2$Cl$_2$] with 2-phenylpyridine in a range of solvents. The only products obtained from such reactions were the 'normal' coordination complexes, [Ru(bipy)$_2$(HL)$_2$]$^{2+}$. In an attempt to force one of the ligands into the cyclometallated bidentate mode, we performed the reactions at elevated temperature and pressure in an autoclave. Instead of the anticipated cyclometallated compounds, we obtained an orange compound, identical with authentic [Ru(bipy)$_2$(CO)Cl] [PF$_6$], in better than 60% yield. The same compound was obtained in similar yield upon heating [Ru(bipy)$_2$Cl$_2$] to 180 °C in acetone.

The product was identified by spectroscopic methods, and shown to be identical to an authentic sample of the complex. The infrared spectrum of the compound exhibited a characteristic carbonyl stretching mode at 1964 cm^{-1} and a ruthenium–chlorine stretching mode at 335 cm^{-1}. The ^{1}H NMR spectrum of an acetone-d$_6$ solution of the complex is presented in Fig. 1. This fully confirms the symmetry of the molecule, in which each pyridyl ring is chemically and magnetically unique. The most distinct feature of the spectrum is the presence of two one proton doublets of doublets at δ 9.7 and δ 9.55. The cyclic voltammogram of an acetonitrile solution of [Ru(bipy)$_2$(CO)Cl] [PF$_6$] (tetra-n-butylammonium tetrafluoroborate supporting electrolyte) exhibited a reversible oxidation wave at +1.20 V and two quasi-reversible reductions at −1.65 V and −1.90 V (all converted to NHE scale 50 mV s^{-1} scan rate). Upon cooling, the two reductions became more reversible, and at −20 °C two fully reversible waves, with $E_{1/2}$ −1.64 and −1.83 V, were observed. This is completely in accord with the reported electrochemical properties of the salt [6].

It is clear that the elements of carbon monoxide have been abstracted from the acetone. This was confirmed by repeating the reaction, both in the presence and absence of 2-phenylpyridine, in chloroform under similar conditions of temperature and pressure. In each case, the only isolated compound was unreacted starting material, recovered in greater than 95% yield. The organic product of the reaction was tentatively identified as tert-butyl methyl ether. We have not investigated the mechanism of the reaction, but suggest a process akin to that indicated in Scheme 1. There is some support for this conjectural mechanism. The reverse reaction, the reductive elimination of ketones from carbonylalkylruthenium-(II) centres has recently been described Mawby [14].

Kelly and co-workers have described the reaction of [Ru(bipy)$_2$(CO)Cl] with a wide range of nucleophiles to give [Ru(bipy)$_2$(CO)Cl]$^{n+}$ complexes [6]. In all cases the incoming nucleophile displaced the

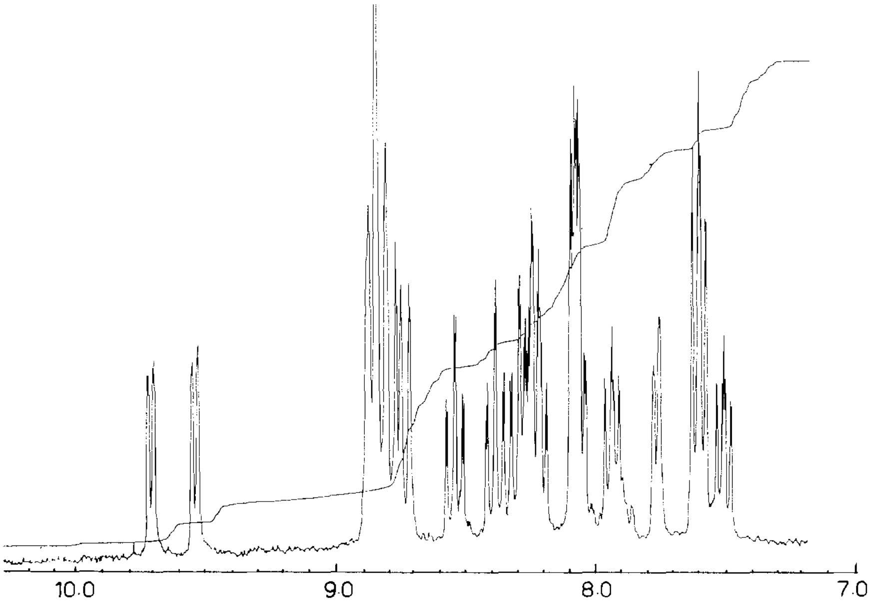
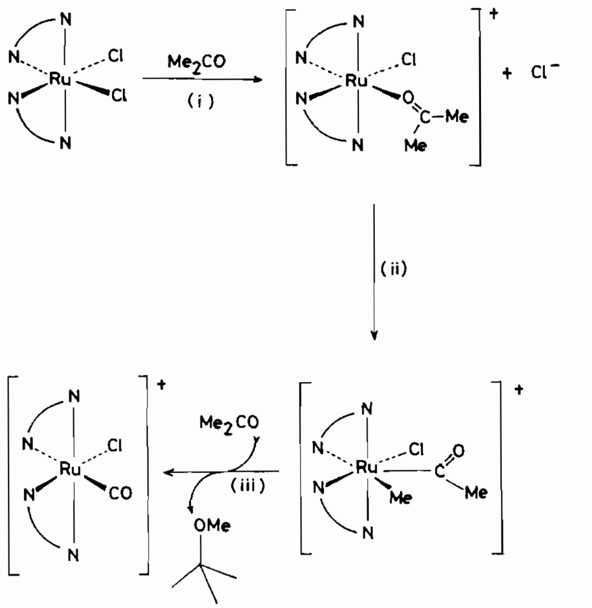


Fig. 1. 250 MHz ^{1}H NMR spectrum of an acetone-d$_6$ solution of [Ru(bipy)$_2$(CO)Cl] [PF$_6$].



Scheme 1. Proposed mechanism for the formation of [Ru(bipy)$_2$(CO)Cl]$^+$ from [Ru(bipy)$_2$Cl$_2$] and acetone.

chloride rather than the carbonyl ligand. We were interested in the displacement of the carbonyl group to give [Ru(bipy)$_2$XCl]$^{n+}$ salts, and investigated amine oxide labilisation of the carbonyl. Black and co-workers have shown that trimethylamine *N*-oxide may be used to labilise carbonyls in ruthenium(II) complexes, and we have extended this method to reactions of [Ru(bipy)$_2$(CO)Cl] [PF$_6$] [15].

Treatment of an acetonitrile solution of [Ru(bipy)$_2$(CO)Cl] [PF$_6$] with an excess of pyridine and trimethylamine *N*-oxide resulted in a smooth reaction to give a deep purple solution, from which the complex [Ru(bipy)$_2$(py)Cl] [PF$_6$] could be precipitated by the addition of ammonium hexafluorophosphate. This complex is difficult to obtain by other routes, and has not been fully characterised hitherto. The ^{1}H NMR spectrum of the complex confirms the geometry, and 21 distinct resonances may be detected. The cyclic voltammogram of an acetonitrile solution of the complex exhibited a reversible oxidation at +0.45 V and two irreversible reductions (tetra-n-butylammonium tetrafluoroborate supporting electrolyte, adjusted to NHE scale). Upon cooling to –25 °C, the reductions became reversible, with $E_{1/2}$ values of –1.84 V and –2.10 V. This suggests that pyridine is a considerably worse pi-acceptor than a carbonyl ligand, and hence destabilises the ruthenium(II) state with respect to ruthenium(III).

The use of amine oxide to labilise the carbonyl group in [Ru(bipy)$_2$(CO)Cl]$^+$ salts appears to be a valuable new route to [Ru(bipy)$_2$ClX]$^{n+}$ complexes. This will be of particular interest in view of the high-yield preparation of the starting material that we describe.

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