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Synthesis and Spectroscopic Characterisation of $[Ru(bpy)_2(CO)_2](PF_6)_2$

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Ruthenium carbonyls [1] and ruthenium complexes of 2,2′-bipyridyl [2] (bpy) have been studied intensively and have been used as catalysts for a wide range of reactions. Mixed CO-bipy complexes attracted less attention, probably because they were not readily synthesised. Recently we have reported the synthesis and molecular structure of $[Ru(bpy)_2(CO)Cl]ClO_4$ [3]. This compound has been proposed as a catalyst for the water-gas shift reaction [4] and this would indicate that this type of complex also has interesting catalytic properties.

In the present work we wish to report the synthesis and spectroscopic characterisation of $[Ru(bpy)_2(CO)_2](PF_6)_2$. This complex is the first example of a ruthenium compound with a $RuN_4(CO)_2$ moiety. Earlier attempts to prepare this complex failed because of loss of CO [5, 6]. The compound has now been synthesised as follows:

$$RuCl_3\cdot 3H_2O \xrightarrow[\Delta,\,6h]{CO,\ EtOH} \text{Red carbonyl solution}$$

$$\xrightarrow[\Delta,\,2h]{bpy,\ H_2O} Ru(bpy)(CO)_2Cl_2$$

yellow needles

$$\xrightarrow[\Delta,\,2h,\ NH_4PF_6]{EtOH,\ H_2O,\ bpy} [Ru(bpy)_2(CO)_2](PF_6)_2$$

Satisfactory elemental analyses were obtained for both the $[Ru(bpy)_2(CO)_2](PF_6)_2$ and the yellow mono bpy complex†.

The red carbonyl solution, first described by Chatt [7], has been used before by Wilkinson *et al.* [6] for the preparation of ruthenium carbonyl complexes. Using ethanol as a solvent, we obtained a red–purple compound which we identified as $Ru(bpy)(CO)_2Cl_2$, as previously reported by Wilkinson. Using 50:50 ethanol/water as a solvent in the second step, a yellow species is produced. Both the yellow and the red–purple compound can be recrystallised from ethanol, but the yellow species is more soluble in this solvent. The red–purple complex can be converted into the yellow isomer by addition of water to a refluxing ethanol solution.

Some spectroscopic data have been listed in Table I. The presence of two strong ν_{CO} vibrations indicates a *cis* coordination of the carbonyl groups [6]. A strong band in the IR spectrum of the $Ru(bpy)(CO)_2Cl_2$ compounds at 330 cm^{-1} has been assigned to a terminal ν_{M-Cl} vibration; similar bands are found in other ruthenium chloride complexes [6b]. ^1H NMR spectra of $[Ru(bpy)_2(CO)_2](PF_6)_2$ support a *cis* coordination of the carbonyls. All compounds have their principal electronic absorptions below 400 nm, except the red–purple isomer (see Table I). This was also observed for the compounds $[Ru(bpy)_2COCl]ClO_4$ and $[Ru(bpy)_2NOCl](PF_6)_2$ [8] and has been explained by postulating a strong back-donation from the metal to the carbonyl and nitrosyl ligands. The spectroscopic data suggest that both mono(bpy) compounds are mononuclear. We therefore suggest the

TABLE I. Spectroscopic Data for Ru(bpy)(CO)-Complexes.

Compound	$\nu_{CO}{}^a$ (cm^{-1})	$\nu_{M-Cl}{}^a$ (cm^{-1})	λ_{max} in CH_3CN nm (log ε)
$[Ru(bpy)_2(CO)_2](PF_6)_2$	2035, 2084 s	–	316sh(4.44)310sh(4.46)305(4.51)250(4.55)
$[Ru(bpy)_2(CO)Cl]ClO_4$	1965 s	335 m	416(3.34)353(3.66)315(4.23)282(4.41)262(4.36)^b
$Ru(bpy)(CO)_2Cl_2$ yellow	1997, 2055 s	330 s	354(3.08)313(4.08)300(3.99)284(3.97)
$Ru(bipy)(CO)_2Cl_2$ red–purple	1980, 2040 s	330 s, 302 m	500sh, 448, 360sh, 311, 300

^{a}Recorded as KBr disc. ^{b}In methanol.

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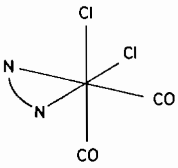
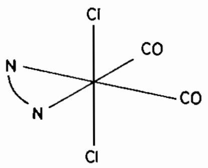
† $[Ru(bpy)_2(CO)_2](PF_6)_2$ Found: C, 34.67; H, 2.16; N, 7.30. Calculated: C, 34.80; H, 2.12; N, 7.38%.
$Ru(bpy)(CO)_2Cl_2$ Found: C, 37.40; H, 1.97; N, 7.58; Cl, 18.86. Calculated: C, 37.48; H, 2.08; N, 7.28; Cl, 18.46%.

structures (1) and (2) for respectively the red–purple and the yellow isomer. Presently we are further investigating the nature of these species.



(1)



(2)

Irradiation of $[Ru(bpy)_2(CO)_2](PF_6)_2$ with UV-light results in loss of CO,

$$[Ru(bpy)_2(CO)_2]^{2+} \xrightarrow[2L]{h\nu} [Ru(bpy)_2L_2]^{2+}$$

L = methanol, H_2O, CH_3CN

The photochemical reactions could be followed conveniently by UV/Vis spectroscopy. Because of the photolability of the carbonyls the compound can be used as a precursor for the rather oxygen sensitive $[Ru(bpy)_2(H_2O)_2]^{2+}$ species.

Note added in proof:

A recent publication [9a] has made us aware of a previous report of the synthesis of $[Ru(bpy)_2(CO)_2]^{2+}$ by reaction of $[Ru(bpy)(CO)_2(NCMe)_2]^{2+}$ and bpy in 2-ethoxyethanol [9b].

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References

1 (a) M. Wrighton, *Chem. Rev., 74,* 401 (1979) and references therein. (b) R. M. Laine, R. G. Rinker and P. C. Ford, *J. Am. Chem. Soc., 99,* 252 (1977).
2 (a) B. A. Moyer, M. S. Thompson and T. J. Meyer, *J. Am. Chem. Soc., 102,* 2310 (1980). (b) G. J. Samuels and T. J. Meyer, *J. Am. Chem. Soc., 103,* 307 (1981). (c) O. Haas and J. G. Vos, *J. Electroanal. Chem., 113,* 139 (1980).
3 J. M. Clear, J. M. Kelly, C. M. O'Connell, J. G. Vos, C. J. Cardin, S. R. Costa and A. J. Edwards, *J. Chem. Soc., Chem. Comm.,* 750 (1980).
4 D. J. Cole-Hamilton, *J. Chem. Soc., Chem. Comm.,* 1213 (1980).
5 L. Ruiz-Ramirez and T. A. Stephenson, *J. Chem. Soc. Dalton,* 1640 (1974).
6 (a) J. V. Kingston, J. W. S. Jamieson and G. Wilkinson, *J. Inorg. Nucl. Chem., 29,* 133 (1967). (b) J. D. Gilbert, D. Rose and G. Wilkinson, *J. Chem. Soc. (A),* 2765 (1970).
7 J. Chatt, B. L. Shaw and A. E. Field, *J. Chem. Soc.,* 3466 (1964).
8 R. W. Callahan and T. J. Meyer, *Inorg. Chem., 16,* 574 (1976).
9 D. St. C. Black, G. B. Deacon and N. C. Thomas (a) *Inorg. Chim. Acta, 54,* L143 (1981); (b) *Trans. Met. Chem., 5,* 317 (1980).