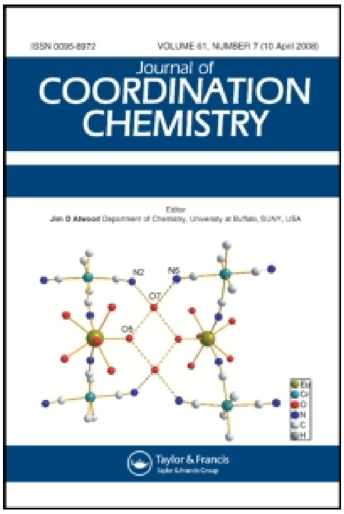

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Nicholas C. Thomas[a]; Jean Fischer[b]
[a] Chemistry Department, Auburn University at Montgomery, Montgomery, Alabama, USA [b] Laboratoire de Cristallochemie et de Chimie Structurale, Institut Le Bel, Université Louis Pasteur, Strasbourg Cedex, France

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RUTHENIUM CARBONYL COMPLEXES OF *N*-HETEROCYCLIC MOLECULES. PART 2.[1] PREPARATION, PROTONATION AND DECARBONYLATION REACTIONS OF COMPLEXES WITH A BIDENTATE TERPYRIDYL LIGAND. STRUCTURE OF $[Ru(CO)_2(phen)(tpyH)](BF_4)_3$.

NICHOLAS C. THOMAS*

Chemistry Department, Auburn University at Montgomery, Montgomery, Alabama 36193-0401, U.S.A.

and JEAN FISCHER

Laboratoire de Cristallochemie et de Chimie Structurale, Institut Le Bel, Université Louis Pasteur, 4 rue Blaise Pascal, 67070 Strasbourg, Cedex, France

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The complexes $Ru(CO)_2(CF_3SO_3)_2$(bidentate) {bidentate = 2,2'-bipyridyl (bpy) or 1,10-phenanthroline (phen)} react with 2,2':6',2''-terpyridyl (tpy) forming octahedral $[Ru(CO)_2(bidentate)(tpy)]^{2+}$ compounds (II) which contain a bidentate tpy. Complex II (bidentate = phen) can be protonated to give $[Ru(CO)_2(phen)(tpyH)](BF_4)_3$, the structure of which has been established by X-ray crystallography. Treatment of II with trimethylamine *N*-oxide in methanol at room temperature gives the monocarbonyl compounds $[Ru(CO)(bidentate)(tpy)]^{2+}$ (IV) which contain a tridentate tpy. Complex IV is also obtained by photolysis of II.

Keywords: Ruthenium, carbonyl, terpyridyl, complexes, decarbonylation, bidentate

INTRODUCTION

Oxygen donor ligands such as nitrate, perchlorate and trifluoromethanesulfonate bind weakly to transition metal ions and consequently are readily displaced from complexes. Of particular interest is the trifluoromethanesulfonate group ($CF_3SO_3^-$) which has been employed as a facile leaving group in a variety of inorganic reactions.[2] In earlier studies,[3,4] we have outlined the preparation and reactions of $Ru(CO)_2(CF_3SO_3)_2$(bidentate) complexes (I) (bidenate = 1,10-phenanthroline (phen) or 2,2'-bipyridyl (bpy)), and shown that the $CF_3SO_3^-$ groups are readily displaced by bidentate ligands indicating that I is a convenient reagent for the synthesis of other ruthenium complexes containing nitrogen donor ligands. The reaction of I with 2,2':6',2''-terpyridyl (tpy) has now been studied and yields the octahedral $[Ru(CO)_2(bidentate)(tpy)]^{2+}$ cationic complexes (II) which contain a novel bidentate terpyridyl ligand. This form of coordination has been proposed for a

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* Author for correspondence.

number of terpyridyl complexes, largely on the basis of spectroscopic data,[5] and recently we established conclusively, by X-ray crystallography, the presence of bidentate terpyridyl in $Ru(CO)_2X_2(tpy)$ complexes (X = Cl, Br).[6] In acidic solution, complex **II** (bidentate = phen) undergoes protonation of the free pyridyl ring, and the product of this reaction has been examined by crystallography. Decarbonylation reactions of **II** are also described.

EXPERIMENTAL

The $Ru(CO)_2(CF_3SO_3)_2$(bidentate) complexes were prepared by the reported method[3] and recrystallized prior to use from acetone/ether. Photolysis experiments were conducted in standard 1 cm quartz cuvettes using a 200 W medium pressure mercury lamp. Molar conductances were measured for *ca* 10^{-3} M solutions in acetone using a YSI 31A conductance bridge. Other analytical and spectroscopic methods have been reported previously.[7] Analytical data and yields for all complexes are given in Table III.

*Preparation of [Ru(CO)₂(bidentate)(terpyridyl-*N,N′*)](PF₆)₂ (II)*

A mixture of **I** (bidentate = phen or bpy) (0.20 mmol) and terpyridyl (0.25 mmol) in absolute ethanol (10 cm^3) was heated under reflux in an atmosphere of nitrogen for 1 h. The solution was evaporated to dryness and the residue was dissolved in hot water (10 cm^3). The solution was then filtered into excess aqueous KPF_6 and the resulting precipitate was collected and recrystallized twice from acetone/ethanol giving a white powder.

*Preparation of [Ru(CO)₂(phenanthroline)(terpyridinium-*N,N′*)]-(BF₄)₃ hydrate (III)*

The complex $[Ru(CO)_2(phen)(tpy\text{-}N,N')](PF_6)_2$ (0.13 g, 0.15 mmol) was dissolved in a warm aqueous solution of 48% HBF_4 (1.0 cm^3). After the addition of water (3.0 cm^3) the solution was filtered and allowed to stand until crystallization was complete. The product was filtered, washed with water and dried *in vacuo* for 24 h at 60°C. The microanalytically pure sample analyzed for the anhydrous complex. Crystals suitable for X-ray analysis were obtained by redissolving the product in hot aqueous HBF_4 and allowing the solution to stand for several days. Crystals were kept suspended in the solution until the crystal structure was determined since in air they readily lose water and break up.

Preparation of [Ru(CO)(bidentate)(terpyridyl)](PF₆)₂ (IV)

Method 1

A mixture of **II** (0.10 mmol, bidentate = phen or bpy) and anhydrous Me_3NO (0.13 mmol) was stirred in methanol (20 cm^3) at room temperature under nitrogen for 1 h. The resultant yellow solution was evaporated to dryness and the residue was recrystallized twice from acetone/ethanol giving a yellow powder.

Method 2

A suspension of $[Ru(CO)(MeCN)_3(bidentate)](PF_6)_2$ (0.10 mmol, bidentate = phen or bpy)[7] and terpyridyl (0.12 mmol) in 2-ethoxyethanol ($15\,cm^3$) was heated under reflux, under nitrogen, for 1 h. On cooling and addition of ether (*ca* $5\,cm^3$) the impure yellow-brown product precipitated from solution. Purification as above gave IV which were identified spectroscopically.

Structure determination

A summary of crystal data for the complex $[Ru(CO)_2(phen)(tpyH)(BF_4)_3.3H_2O$ is given in Table I. Data were collected on an ENRAF-NONIUS CAD4F diffractometer using the $\theta/2\theta$ scan method and yielded 6622 $\pm$ *hkl* independent reflections giving 4558 reflections with $I > 3\sigma(I)$. Patterson and Fourier techniques were used to solve the structure. Positional and anisotropic thermal parameters for all non-hydrogen atoms were refined by full-matrix least-squares minimizing $\Sigma w(|F_o|-|F_c|)^2$, $w(F^2) = (\sigma^2\text{count} + (0.08F^2)^2)^{-1}$. Hydrogen atoms were introduced in structure factor calculations by their computed coordinates (C–H = 0.95 Å) and isotropic temperature factors such that $B(\mathrm{H}) = 1.3\,B\mathrm{eqv(C)}$, but not refined. Positional parameters for all non-hydrogen atoms are in Table II. For all computations the ENRAF-NONIUS SDP/VAX package was used. Tables of hydrogen positions, bond lengths and angles, thermal parameters and observed and calculated structure factors are available from the authors upon request.

TABLE I
Crystal structure data for complex III.

Formula	$C_{29}H_{26}B_3N_5O_5F_{12}Ru$
Mol.wt.	886.10
Space group	$P2_1/c$
a, Å	20.762(6)
b, Å	13.504(4)
c, Å	12.434(4)
β, deg.	101.08(2)
Cell vol., A^3	3421
Z	4
D_c, g/cm^3	1.718
Cryst. dimens., mm	0.36 × 0.32 × 0.12
Temp., °C	25
Radiation	MoKα, λ = 0.71073 Å
GOF	1.26
$R(F)$	0.063
$R_w(F)$	0.102

RESULTS AND DISCUSSION

The reaction of $Ru(CO)_2(CF_3SO_3)_2$(bidentate) (I) with 2,2′:6′,2″-terpyridyl (tpy) yields the cationic complexes $[Ru(CO)_2(bidentate)(tpy)]^{2+}$ (bidentate = phen or bpy) (II), which are isolated as the white hexafluorophosphate salts (*1*).

TABLE II

Positional parameters for complex III for non-hydrogen atoms.

Atom	*x*/*a*	*y*/*b*	*z*/*c*	$B(\text{Å}^2)$
Ru	0.25085(2)	0.51194(4)	0.61832(4)	1.952(9)
N1	0.1734(3)	0.5387(4)	0.7000(4)	2.3(1)
C2	0.1103(3)	0.5353(5)	0.6567(6)	2.9(1)
C3	0.0629(4)	0.5538(6)	0.7150(6)	3.4(2)
C4	0.0790(4)	0.5803(6)	0.8237(7)	3.9(2)
C5	0.1472(3)	0.5861(5)	0.8722(6)	2.9(1)
C6	0.1924(3)	0.5626(5)	0.8071(5)	2.2(1)
C7	0.2635(3)	0.5657(5)	0.8484(6)	2.3(1)
C8	0.2898(4)	0.5724(5)	0.9608(6)	3.1(1)
C9	0.3567(4)	0.5750(6)	0.9945(6)	3.7(2)
C10	0.3963(3)	0.5766(6)	0.9158(6)	3.3(2)
C11	0.3673(3)	0.5710(5)	0.8077(6)	2.7(1)
N12	0.3016(3)	0.5616(4)	0.7725(4)	2.3(1)
C13	0.4101(3)	0.5868(6)	0.7221(6)	3.2(1)
N14	0.4602(3)	0.5198(5)	0.7268(6)	3.9(1)
C15	0.5050(4)	0.5312(7)	0.6607(8)	4.4(2)
C16	0.4996(4)	0.6059(8)	0.5887(8)	5.1(2)
C17	0.4487(4)	0.6739(6)	0.5812(7)	3.7(2)
C18	0.4037(3)	0.6622(6)	0.6515(6)	3.2(2)
N19	0.1903(3)	0.4443(4)	0.4879(4)	2.3(1)
C20	0.1582(3)	0.4867(5)	0.3960(6)	2.6(1)
C21	0.1184(3)	0.4293(6)	0.3135(6)	3.1(2)
C22	0.1118(4)	0.3316(6)	0.3251(6)	3.4(2)
C23	0.1461(3)	0.2837(5)	0.4202(6)	2.9(1)
C24	0.1845(3)	0.3447(5)	0.5002(5)	2.3(1)
C25	0.1430(4)	0.1802(6)	0.4387(7)	3.8(2)
C26	0.1770(4)	0.1386(5)	0.5340(7)	3.9(2)
C27	0.2156(3)	0.1995(5)	0.6173(6)	2.8(1)
C28	0.2504(4)	0.1623(5)	0.7152(6)	3.3(2)
C29	0.2854(4)	0.2224(6)	0.7895(6)	3.7(2)
C30	0.2861(3)	0.3250(5)	0.7685(6)	2.8(1)
N31	0.2532(3)	0.3634(4)	0.6748(4)	2.4(1)
C32	0.2185(3)	0.3008(5)	0.6009(6)	2.5(1)
O1	0.3619(3)	0.4614(4)	0.5017(4)	3.6(1)
C3	0.3217(3)	0.4839(5)	0.5476(6)	2.4(1)
O2	0.2301(3)	0.7164(3)	0.5163(4)	3.6(1)
C34	0.2390(3)	0.6420(5)	0.5557(6)	2.6(1)
B1	0.3233(5)	0.8527(8)	0.8057(8)	4.3(2)
F1	0.3674(4)	0.8953(7)	0.7663(7)	14.0(2)
F2	0.2886(4)	0.7885(5)	0.7346(6)	8.6(2)
F3	0.2808(3)	−0.4256(5)	0.3334(6)	7.7(2)
F4	0.3463(5)	0.8023(8)	0.8971(7)	11.8(3)
B2	0.0065(5)	0.6832(7)	0.4266(9)	4.7(2)
F5	0.0207(3)	0.3819(4)	0.5121(5)	6.1(1)
F6	0.0117(3)	0.2211(4)	0.5483(6)	7.8(2)
F7	0.0186(5)	0.3294(6)	0.6812(6)	10.4(2)
F8	0.0730(3)	0.6749(6)	0.4427(7)	10.0(2)
B3	0.4179(6)	0.2019(8)	0.5930(9)	4.9(2)
F9	0.4518(5)	0.148(1)	0.557(1)	9.6(3)
F10	0.4130(6)	0.189(1)	0.6996(9)	7.0(3)

TABLE II (*continued*)

Atom	x/a	y/b	z/c	$B(\text{Å}^2)$
F11	0.4632(9)	0.272(1)	0.614(1)	13.9(5)
F12	0.3576(5)	0.214(1)	0.5330(9)	7.3(3)
OW1	0.1744(3)	0.9114(5)	0.6370(5)	5.1(1)
OW2	0.4635(5)	0.1441(5)	0.3414(6)	7.5(2)
OW3	0.0433(4)	0.8792(7)	0.6481(7)	9.3(2)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: (4/3) [a^2.β(1,1) + b^2.β(2,2) + c^2.β(3,3) + ab(cos gamma).β(1,2) + ac(cos beta).β(1,3) + bc(cos alpha).β(2,3).

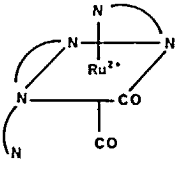
TABLE III
Analytical data for the complexes.

Compound	C[a]	H	N	% Yield	Λ[b]
$[\mathrm{Ru(CO)_2(bpy)(tpy)](PF_6)_2}$	38.4 (38.8)	2.4 (2.3)	8.2 (8.4)	83	187
$[\mathrm{Ru(CO)_2(phen)(tpy)](PF_6)_2}$	40.5 (40.5)	2.5 (2.2)	8.2 (8.1)	78	179
$[\mathrm{Ru(CO)_2(phen)(tpyH)](BF_4)_3}$	41.6 (41.9)	2.6 (2.6)	8.2 (8.2)	65	288
$[\mathrm{Ru(CO)(bpy)(tpy)](PF_6)_2}$	38.6 (38.6)	2.6 (2.4)	8.3 (8.7)	75	205
$[\mathrm{Ru(CO)(phen)(tpy)](PF_6)_2}$	40.8 (40.4)	2.9 (2.3)	8.0 (8.4)	70	213

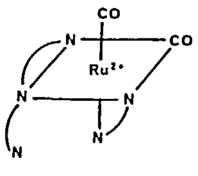
[a] Calculated values are given in parentheses. [b] In S cm^2 mol^{-1}.

$$\mathrm{Ru(CO)_2(CF_3SO_3)_2(bidentate)} + \mathrm{tpy} \xrightarrow{\mathrm{KPF_6}} [\mathrm{Ru(CO)_2(bidentate)(tpy\text{-}}N,N')](\mathrm{PF_6})_2 \qquad (1)$$

This formulation for **II** is consistent with the analytical, conductivity and spectroscopic data (Tables III and IV) for these complexes. Two strong ν(CO) absorptions clearly indicate *cis* carbonyl groups, and the presence of a bidentate terpyridyl is strongly indicated by the similarity of these absorption frequencies to those of the related octahedral $[\mathrm{Ru(CO)_2(bidentate)_2}]^{2+}$ complexes (bidentate = phen or bpy).[3] The ^{1}H n.m.r spectra in the aromatic region for **II** show complex patterns as expected for the unsymmetrical terpyridyl ligand but integrate for 19 protons as required. Structure **IIa** is more likely for these complexes rather than the alternative **IIb** due to steric crowding of the free pyridyl ring in the latter.



IIa



IIb

TABLE IV
Spectroscopic data for the complexes.

Compound	ν(CO)[a]/cm^{-1}	Electronic spectral data[b]	N.m.r. data[c]
$[Ru(CO)_2(bpy)(tpy)](PF_6)_2$	2073 2010	390sh (3.40), 290sh (4.36), 269 (4.42)	9.25 (1H,d), 9.04 (1H,d), 8.95 (1H,d), 8.86 (1H,d), 8.82 (1H,d), 8.78–8.70 (2H,m), 8.53 (1H,dd), 8.37–8.27 (3H,m), 8.24–8.15 (2H,m), 8.02 (1H,dd), 7.78 (1H,dd), 7.67–7.61 (2H,m), 7.46 (1H,d), 7.34 (1H,d)
$[Ru(CO)_2(phen)(tpy)](PF_6)_2$	2090 2022	390sh (3.20), 292sh (4.37), 266 (4.58), 215sh (4.67)	9.66 (1H,d), 9.16 (1H,d), 9.08 (1H,d), 8.96 (1H,d), 8.92 (1H,d), 8.85 (1H,d), 8.77 (1H,dd), 8.42–8.19 (7H,m), 7.96 (1H,dd), 7.79–7.75 (2H,m), 7.45–7.40 (2H,m)
$[Ru(CO)_2(phen)(tpyH)](BF_4)_3$	2096 2045	390sh (3.50), 296sh (4.38), 266 (4.66), 216sh (4.75)	9.65 (1H,d), 9.15 (1H,d), 9.06 (1H,d), 8.95 (1H,d), 8.91 (1H,d), 8.84 (1H,d), 8.76 (1H,dd), 8.41–8.18 (7H,m), 7.95 (1H,dd), 7.78–7.73 (2H,m), 7.45–7.39 (2H,m)
$[Ru(CO)(bpy)(tpy)](PF_6)_2$	1985	353 (3.68), 323 (4.20), 312 (4.41), 280 (4.48), 259 (4.51)	9.60 (1H,d), 9.01–8.98 (3H,m), 8.87–8.83 (3H,m), 8.73 (1H,dd), 8.49 (1H,dd), 8.27 (2H,dd), 8.23 (1H,d), 8.06 (1H,dd), 7.81 (2H,d), 7.57 (2H,dd), 7.44 (1H,dd), 7.35 (1H,dd)
$[Ru(CO)(phen)(tpy)](PF_6)_2$	1988	369sh (3.68), 325 (4.23), 312 (4.31), 279sh (4.56), 267 (4.63), 222 (4.61)	9.99 (1H,d), 9.13 (1H,d), 9.03 (2H,d), 8.86–8.83 (3H,m), 8.77 (1H,dd), 8.50 (1H,d), 8.41 (1H,dd), 8.35 (1H,d), 8.23 (2H,dd), 7.80–7.76 (2H,m), 7.69 (2H,d), 7.74 (2H,dd)

[a] I.r. spectra recorded in Nujol, all bands strong. [b] Recorded in methanol at 25°C; λ/nm with log ε in parentheses, ε in M^{-1} cm^{-1}. [c] Recorded in d_6-DMSO with a Bruker AM 400 instrument.

Further evidence for the above formulation of **II** is provided from the reaction of $[Ru(CO)_2(phen)(tpy)](PF_6)_2$ with aqueous HBF_4 which results in protonation of the free pyridine ring yielding the cationic complex $[Ru(CO)_2(phen)(tpyH)]^{3+}$ (**III**) (*2*)

$$[Ru(CO)_2(phen)(tpy)](PF_6)_2 + 3HBF_4 \longrightarrow [Ru(CO)_2(phen)(tpyH)](BF_4)_3 + 2HPF_6 \qquad (2)$$

Similar electronic and n.m.r. spectral data for both **III** and **II** (L = phen) indicate similar structures for both complexes, and this has been confirmed by a crystal structure of **III** (below). The higher ν(CO) values for **III** (Table IV) provide indirect evidence for the presence of a protonated free pyridyl ring since this is indicative of reduced electron density on the metal which would be expected for the protonated pyridyl group. Conductivity data for **III** indicate it to be 1:3 electrolyte in solution, further supporting a protonated pyridyl group. A strong ν(P–F) infrared absorption at *ca* 830 cm^{-1} is observed for **II** and is replaced by a broad band at *ca* 1050 cm^{-1} in the spectrum of **III** due to the ν(B–F) absorption.

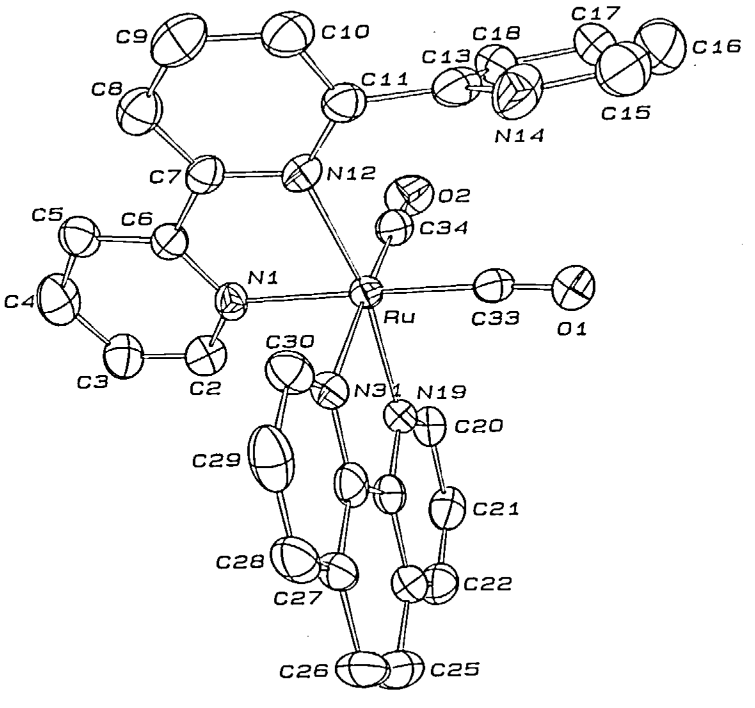


FIGURE 1 Structure of $[Ru(CO)_2(phen)(tpyH)](BF_4)_3.3H_2O$.

The structure of the title compound, $[Ru(CO)_2(phen)(tpyH)](BF_4)_3$ (**III**), is shown in Figure 1 and bond distances and selected bond angles are presented in Tables V and VI, respectively. The structure determination establishes the assigned stoichiometry and molecular configuration of **III**, and hence **II**, and therefore confirms the presence of a bidentate terpyridyl. The complex crystallizes with three molecules of water. However, a sample prepared for microanalysis by drying at 60°C analyzed for the anhydrous complex (Table III). The complex also contains three tetrafluoroborate ions and hence the cation is tripositive. This fact in conjunction with the above spectroscopic and conductance data indicate that the uncoordinated pyridyl ring is protonated. However, the presence of the proton at N(14) could not be detected crystallographically. The distance between the ruthenium and phenanthroline nitrogen atoms varies by about 0.06 Å. This difference is presumably steric in nature due to the presence of the bulky terpyridyl ligand adjacent to the Ru–N(31) bond. The uncoordinated pyridyl ring is disposed pseudoparallel to the carbonyl C(33)–O(1), offering scope for intramolecular interligand interaction.

TABLE V
Bond distances (Å) for III.

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
Ru	N1	2.092(4)	C13	N14	1.370(6)	C30	N31	1.337(6)
Ru	N12	2.112(4)	C13	C18	1.335(8)	N31	C32	1.349(6)
Ru	N19	2.064(4)	N14	C15	1.363(8)	O1	C33	1.139(6)
Ru	N31	2.123(4)	C15	C16	1.34(2)	O2	C34	1.117(6)
Ru	C33	1.890(5)	C16	C17	1.39(1)	B1	F1	1.258(9)
Ru	C34	1.918(6)	C17	C18	1.406(7)	B1	F2	1.344(9)
N1	C2	1.319(6)	N19	C20	1.337(6)	B1	F3	1.409(9)
N1	C6	1.352(6)	N19	C24	1.361(6)	B1	F4	1.332(8)
C2	C3	1.354(7)	C20	C21	1.418(7)	B2	F5	1.356(8)
C3	C4	1.375(8)	C21	C22	1.337(8)	B2	F6	1.398(9)
C4	C5	1.430(8)	C22	C23	1.414(8)	B2	F7	1.353(9)
C5	C6	1.389(7)	C23	C24	1.414(7)	B2	F8	1.36(1)
C6	C7	1.467(7)	C23	C25	1.421(7)	B3	F9	1.16(2)
C7	C8	1.402(8)	C24	C32	1.442(7)	B3	F10	1.37(1)
C7	N12	1.346(7)	C25	C26	1.377(9)	B3	F11	1.33(1)
C8	C9	1.373(8)	C26	C27	1.440(7)	B3	F12	1.34(2)
C9	C10	1.395(8)	C27	C28	1.385(8)	F9	F11	1.83(2)
C10	C11	1.364(7)	C27	C32	1.386(7)	F10	F11	1.99(2)
C11	N12	1.357(7)	C28	C29	1.336(9)			
C11	C13	1.527(7)	C29	C30	1.411(8)			

TABLE VI
Selected bond angles (deg.) for III.

Atom 1	Atom 2	Atom 3	Angle
N1	Ru	N12	78.5(2)
N1	Ru	N19	92.8(2)
N1	Ru	N31	88.5(1)
N1	Ru	C33	178.0(2)
N1	Ru	C34	89.3(2)
N12	Ru	N19	167.4(1)
N12	Ru	N31	91.4(1)
N12	Ru	C33	100.9(2)
N12	Ru	C34	94.6(2)
N19	Ru	N31	79.2(1)
N19	Ru	C33	87.5(2)
N19	Ru	C34	94.3(2)
N31	Ru	C33	89.7(2)
N31	Ru	C34	173.1(2)
C33	Ru	C34	92.6(2)

When treated with excess trimethylamine-*N*-oxide (Me_3NO) at room temperature, **II** undergoes decarbonylation to form the monocarbonyl cationic complexes $[Ru(CO)(bidentate)(tpy)]^{2+}$ (**IV**) in which the tpy now assumes its usual terdentate role (*3*)

$$[Ru(CO)_2(bidentate)(tpy\text{-}N,N')](PF_6)_2 + Me_3NO \longrightarrow [Ru(CO)(bidentate)(tpy)](PF_6)_2 + Me_3N + CO_2 \qquad (3)$$

Formation of the monocarbonyl derivatives is evident from the single ν(CO) band at *ca* 1985 cm^{-1}. In addition, the n.m.r spectra of **IV** are less complex than those of **II** indicating a more symmetrical environment for terpyridyl as expected when it functions as a terdentate ligand. Failure of the monocarbonyl complexes to form directly during reaction (*1*) is not unexpected, since the related $[Ru(CO)_2(bidentate)_2]^{2+}$ compounds do not readily decarbonylate in the absence of Me_3NO.[9] As we have previously reported,[8] **IV** may also be obtained by thermal displacement of coordinated MeCN in the $[Ru(CO)(MeCN)_3(bidentate)]^{2+}$ complexes by treating the latter with tpy in refluxing 2-ethoxyethanol.

Electronic spectra for all complexes (Table IV) are dominated by strong bands below 300 nm, which may be assigned to heterocyclic ligand $\pi \rightarrow \pi^*$ transitions. While no well-resolved bands are observed in the visible region, it is probable that the weak absorptions between 350 and 400 nm are due to $d_\pi \rightarrow \pi^*$ transitions as has been observed for related *bis*-bidentate ruthenium compounds.[10] On exposure to U.V.-visible radiation, a colourless acetone solution of **II** (bidentate = bpy) turns yellow and this colour change is accompanied by significant changes in the ν(CO) region of the solution IR spectrum. The two bands at 2040 and 2078 cm^{-1} decrease in intensity as irradiation proceeds and a new band at 1995 cm^{-1} appears. After 15 min the latter band completely replaces the former two. Irradiation also results in changes in the electronic spectrum of **II**, which after 15 min is similar to that of **IV** (bidentate = bpy). These results indicate that the dicarbonyl complex $[Ru(CO)_2(bpy)(tpy)]^{2+}$ also undergoes photochemical decarbonylation to give the same monocarbonyl complex as formed in (*3*). Prolonged irradiation of **II** (> 30 min) yields a red species with an absorption maximum at 480 nm. Furthermore, a solution of $[Ru(CO)(bpy)(tpy)]^{2+}$ undergoes similar spectral changes when irradiated, indicating a further reaction with light. Although this species has not yet been identified, it is possibly due to the formation of the solvated complex $[Ru(solvent)(bpy)(tpy)]^{2+}$ formed by further photochemical decarbonylation of **IV**. Electronic spectra of the related compounds $[RuX(bpy)(tpy)]^{2+}$ ($X = H_2O$, halide, NO_2^-) all have similar maxima in the 450–500 nm region.[11]

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