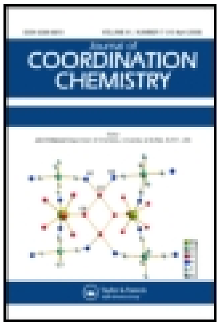

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A. W. Cordes [a] , B. Durham [a] , P. N. Swepston [a] , W. T. Pennington [a] , S. M. Condren [a] , R. Jensen [a] & J. L. Walsh [a]
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STRUCTURAL CHEMISTRY OF NECESSARILY DISTORTED BIS(BIPYRIDINE) COMPLEXES. THE CRYSTAL STRUCTURE OF THE *TRANS*-[BIS(2,2′-BIPYRIDINE)BIS(TRIPHENYLPHOSPHINE)RUTHENIUM(II)] AND *TRANS*-[BIS(4,4′-DIMETHYL-2,2′-BIPYRIDINE)BIS(PYRIDINE)RUTHENIUM(II)] CATIONS

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The cation *trans*-$[Ru(bpy)_2(PPh_3)_2]^{2+}$ and *trans*-$[Ru(Me_2bpy_2)_2(py)_2]^{2+}$ both contain bipyridine ligands which are distorted because of the crowding of the two chelate units. The hexafluorophosphate salt of the first cation crystallizes in space group $P2_1/n$, with $a = 11.630(1)$, $b = 20.245(2)$, $c = 11.299(1)$Å, $\beta = 103.99(1)°$, and $Z = 2$. $R = 0.047$ for 2396 observed reflections. The hexafluorophosphate salt of the second cation crystallizes in space group C2/m, with $a = 18.392(2)$, $b = 11.265(1)$, $c = 13.383(1)$Å, $\beta = 139.42(2)°$, and $Z = 2$. $R = 0.047$ for 1403 observed reflections. The Ru of the first cation lies on an inversion center and the Ru of the second cation lies on a special position of 2/m symmetry. The distortions of a number of bipyridine complexes with the *trans* geometry are analyzed and found to fall into two categories, bowed or twisted. The two complexes of this report were found to have a bowed conformation.

INTRODUCTION

Octahedral complexes containing two 2,2′-bipyridine (bpy) ligands have been found to exist almost exclusively in the *cis* geometry.[2] The scarcity of octahedral metal complexes with *trans* geometry has been attributed to the relative instability of this configuration which results from the steric interaction of the opposing hydrogens on the bipyridine ligands. Surprisingly, several four-coordinate metal complexes containing two bipyridine ligands[2–6] have been prepared.

Durham and coworkers[7a] recently reported the structure of *trans*-$[Ru(bpy)_2(OH_2)(OH)](ClO_4)_2$; that complex and the two complexes of this report are the only octahedral *trans* species which have been structurally characterized. These structures, plus those of the bis-bipyridine square planar complexes, will provide the basis for a discussion of the general types of distortions found in these highly strained molecules.

EXPERIMENTAL

Both crystals were prepared by the methods reported by Durham and Walsh.[7b]

Table I gives the crystal data for *trans*-[bis(2,2′-bipyridine)bis(triphenylphosphine)ruthenium(II)] hexafluorophosphate, $Ru(C_{10}H_8N_2)_2(P(C_6H_5)_3)_2(PF_6)_2$, hereafter *I*, and *trans*-[bis(4,4-dimethyl-2,2′-bipyridine)bis(pyridine)ruthenium(II)] hexafluorophosphate, $Ru(C_{12}H_{12}N_2)_2(C_5H_5N)_2(PF_6)_2$, hereafter *II*. Unit cell refinement and data collection were performed on a GE XRD-5 manually-operated quarter circle diffractometer using Ni-filtered Cu radiation (for unit cell refinement, $CuK_{\alpha 1}$, $\lambda = 1.5405$ Å; for data collection, $CuK_{\alpha av}$, $\lambda = 1.5418$ Å). For the intensity data a θ–2θ scan of 2° was made at a speed of 2° min^{-1}; 10 sec background counts were made at each end of the scan. For both crystals, regularly monitored reflections gave no evidence for crystal or electronic instability.

TABLE I
Crystal data

	$[Ru(bpy)_2(PPh_3)_2]^{2+}$	$[Ru(Me_2bpy)_2(py)_2]^{2+}$
Formula	$RuC_{56}H_{46}N_4P_4F_{12}$	$RuC_{34}H_{34}N_6P_2F_{12}$
Formula weight	1228.01	917.75
Space group; molecules/cell	$P2_1/n$; 2	C2/m; 2
a (Å)	11.630(1)	18.392(2)
b (Å)	20.245(2)	11.265(1)
c (Å)	11.299(1)	13.383(1)
β (deg)	103.99(1)	139.42(2)
V (Å^3)	2581.4	1803.8
Reflections used for unit cell; 2θ range	15; 70–90	15; 70–100
Calculated density (g cm^{-3})	1.58	1.69
Reflections scanned; observed	2757; 2369	1418; 1403
2θ range of reflections scanned	0–100°	0–120°
$\mu(CuK_\alpha)$ (cm^{-1})	44.9	54.1
Range of absorption correction	0.73–0.81	0.54–0.72
Crystal faces; face-to-center distance (mm)	(010), $(0\bar{1}0)$; 0.071 (001), $(00\bar{1})$; 0.122 (100), $(\bar{1}00)$; 0.050	(001), $(00\bar{1})$; 0.070 $(20\bar{1})$, $(\bar{2}01)$; 0.140 $(9\bar{5}\bar{4})$, $(\bar{4}7\bar{1})$; 0.16 $(77\bar{6})$, $(\bar{4}\bar{6}0)$; 0.16
Final R; R_w	0.047; 0.068	0.047, 0.066
Largest shift in final cycle (σ)	0.56	0.08
Max. peak, final diff. map (eÅ^{-3})	0.9	0.7
Stan. dev. of obs. of unit wt.	0.44	0.71

Analytical absorption corrections were made for both crystals. Atomic scattering factors and real and imaginary corrections for anomalous dispersion were taken from Ref. 8.

The Ru atoms of both structures lie on special positions: in I the Ru is on an inversion center, and in II it is at a site symmetry of 2/m. In both structures the Fourier map phased by the Ru atom revealed all of the non-hydrogen atom positions. Full-matrix least-squares refinements used anisotropic thermal parameters for non-hydrogen atoms and constrained isotropic factors (B = 5.0 Å^2) for hydrogen atoms. All hydrogen atoms were located on difference maps. The positional parameters of the bipyridine hydrogen atoms were refined in both structures (except for two poorly behaved atoms of the methyl group in II); the phenyl hydrogen atoms of the triphenylphosphine ligand were held to calculated positions (C—H = 0.95 Å). Refinement of structure II in the acentric space group Cm led to unreasonable bond distances and bond angles. The weighting of the least squares refinement used $w = 1/(2F\ \mathrm{min} + F_0 + 2\ F_0^2/F\ \mathrm{max})$.

The $[PF_6]^-$ anion in II is disordered. In the major component the P atom and two F atoms lie on a crystallographic mirror, and the minor component (13%) of the disorder is related to the main component by a 90° rotation about the axis which includes the P atom and is normal to the mirror.

Analysis of the final refinement for both crystals showed no dependence of $\Delta F/\sigma(F)$ on either F or sin θ. Final positional parameters are listed in Table II; atom numbering for these structures is indicated in Figure 1a.

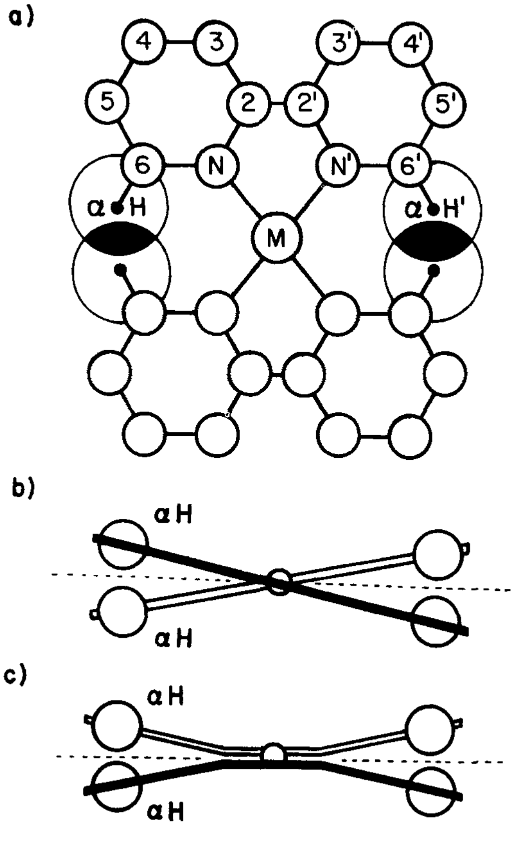

FIGURE 1 a) Atom numbering used for the bipyridine units. The circles around the α hydrogen atoms are van der Waals radii and show the steric crowding. (b) General schematic for the twisted conformation. The solid and hollow bars represent bpy planes. c) General schematic for the bowed conformation.

TABLE II

Fractional coordinates[a] and anisotropic temperature factors[b,c] for $[Ru(bpy)_2(PPh_3)_2](PF_6)_2$ and $[Ru(Me_2bpy)_2(py)_2](PF_6)_2$

Atom	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
A. $[Ru(bpy)_2(PPh_3)_2](PF_6)_2$									
Ru	0.5	0.5	0.5	0.0047(1)	0.00151(5)	0.0055(1)	0.0000(1)	0.0012(1)	0.0000(1)
N	0.5172(3)	0.3981(2)	0.5155(3)	0.0057(4)	0.0022(1)	0.0057(4)	0.0001(2)	0.0019(3)	0.0000(2)
C(2)	0.4176(5)	0.3625(3)	0.4638(5)	0.0094(6)	0.0020(2)	0.0067(5)	−0.0001(3)	0.0028(4)	−0.0003(2)
C(3)	0.4181(6)	0.2942(3)	0.4579(6)	0.0114(7)	0.0023(2)	0.0106(7)	−0.0007(3)	0.0038(5)	−0.0002(3)
C(4)	0.5204(7)	0.2599(4)	0.5107(6)	0.0144(8)	0.0017(2)	0.0124(8)	0.0005(3)	0.0044(7)	−0.0002(3)
C(5)	0.6194(6)	0.2951(3)	0.5712(6)	0.0109(7)	0.0022(2)	0.0113(7)	0.0012(3)	0.0032(6)	0.0003(3)
C(6)	0.6150(5)	0.3627(3)	0.5702(5)	0.0087(5)	0.0023(2)	0.0083(5)	0.0006(3)	0.0023(5)	−0.0003(2)
N′	0.3251(3)	0.4672(2)	0.4643(3)	0.0055(4)	0.0021(1)	0.0077(4)	−0.0002(2)	0.0018(3)	0.0000(2)
C(2′)	0.3091(5)	0.4020(3)	0.4339(4)	0.0088(6)	0.0025(2)	0.0064(5)	−0.0008(3)	0.0027(4)	0.0003(2)
C(3′)	0.1955(5)	0.3754(3)	0.3928(5)	0.0063(5)	0.0029(2)	0.0105(6)	−0.0012(3)	0.0001(4)	0.0005(3)
C(4′)	0.0977(5)	0.4148(4)	0.3886(6)	0.0055(5)	0.0045(3)	0.0120(7)	−0.0015(3)	0.0004(5)	0.0014(3)
C(5′)	0.1148(6)	0.4793(4)	0.4234(6)	0.0075(7)	0.0035(2)	0.0104(6)	0.0003(3)	0.0031(5)	0.0018(3)
C(6′)	0.2286(6)	0.5036(3)	0.4635(6)	0.0062(6)	0.0029(2)	0.0079(6)	0.0001(2)	0.0027(5)	0.0007(2)
H(C3)	0.347(7)	0.270(4)	0.424(7)						
H(C4)	0.518(6)	0.210(5)	0.505(6)						
H(C5)	0.686(7)	0.268(4)	0.611(7)						
H(C6)	0.687(6)	0.396(4)	0.613(6)						
H(C3′)	0.200(6)	0.331(4)	0.369(7)						
H(C4′)	0.013(7)	0.397(4)	0.375(6)						
H(C5′)	0.054(8)	0.512(3)	0.431(7)						
H(C6′)	0.242(6)	0.550(4)	0.493(7)						
P(1)	0.4981(1)	0.49687(5)	0.2842(1)	0.0060(1)	0.0019(1)	0.0064(1)	−0.0002(1)	0.0014(1)	−0.0001(1)
C(7)	0.5150(4)	0.5784(2)	0.2187(4)	0.0076(5)	0.0021(1)	0.0057(5)	0.0000(2)	0.0021(4)	0.0001(2)
C(8)	0.4307(5)	0.6060(3)	0.1228(5)	0.0081(5)	0.0022(2)	0.0087(6)	−0.0001(2)	0.0006(4)	0.0006(2)
C(9)	0.4472(5)	0.6691(3)	0.0829(5)	0.0106(6)	0.0028(2)	0.0089(6)	0.0000(3)	0.0011(5)	0.0007(3)
C(10)	0.5455(6)	0.7055(3)	0.1351(5)	0.0127(7)	0.0023(2)	0.0093(6)	−0.0009(3)	0.0024(5)	0.0009(3)
C(11)	0.6318(5)	0.6775(3)	0.2295(5)	0.0095(5)	0.0024(2)	0.0085(6)	−0.0012(2)	0.0027(5)	0.0007(2)
C(12)	0.6160(5)	0.6151(3)	0.2699(5)	0.0072(5)	0.0027(2)	0.0066(5)	−0.0005(2)	0.0020(4)	0.0000(2)
C(13)	0.3610(4)	0.4645(2)	0.1833(4)	0.0067(5)	0.0019(1)	0.0070(5)	−0.0007(2)	0.0013(4)	0.0003(2)
C(14)	0.2559(6)	0.4969(2)	0.1844(5)	0.0074(6)	0.0025(2)	0.0069(6)	0.0000(2)	0.0011(5)	0.0000(2)
C(15)	0.1498(5)	0.4745(3)	0.1093(5)	0.0073(6)	0.0032(2)	0.0092(6)	0.0002(3)	0.0009(5)	0.0004(3)
C(16)	0.1480(5)	0.4210(3)	0.0361(5)	0.0078(6)	0.0032(2)	0.0108(6)	−0.0015(3)	−0.0009(5)	−0.0008(3)
C(17)	0.2515(6)	0.3880(3)	0.0353(6)	0.0119(7)	0.0027(2)	0.0103(6)	−0.0007(3)	0.0016(5)	−0.0009(3)
C(18)	0.3590(5)	0.4101(3)	0.1095(5)	0.0073(5)	0.0027(2)	0.0092(6)	−0.0006(2)	0.0012(4)	−0.0010(3)
C(19)	0.6171(4)	0.4474(2)	0.2480(4)	0.0059(4)	0.0022(2)	0.0062(5)	−0.0002(2)	0.0011(4)	−0.0002(2)
C(20)	0.6252(5)	0.3812(3)	0.2785(5)	0.0085(6)	0.0024(2)	0.0076(5)	0.0005(2)	0.0021(4)	−0.0004(2)
C(21)	0.7144(5)	0.3423(3)	0.2561(5)	0.0098(6)	0.0025(2)	0.0098(6)	0.0005(3)	0.0023(5)	−0.0005(3)
C(22)	0.7979(5)	0.3690(3)	0.2032(5)	0.0081(5)	0.0033(2)	0.0108(6)	0.0009(3)	0.0021(5)	−0.0013(3)
C(23)	0.7917(5)	0.4341(3)	0.1716(6)	0.0077(5)	0.0034(2)	0.0136(7)	0.0004(3)	0.0052(5)	−0.0004(3)
C(24)	0.7012(5)	0.4738(3)	0.1939(5)	0.0067(5)	0.0031(2)	0.0102(6)	0.0003(3)	0.0027(5)	0.0006(3)
P(2)	0.4913(1)	0.16934(8)	0.1793(1)	0.0092(2)	0.0031(1)	0.0099(2)	−0.0009(1)	0.0008(1)	0.0003(1)
F(1)	0.5797(3)	0.1931(2)	0.3009(3)	0.0121(4)	0.0052(1)	0.0103(4)	−0.0005(2)	−0.0002(3)	−0.0006(2)

TABLE V
Configurational parameters for *trans*-M(bpy)$_2$ fragments

Compound	Configuration	Intra-ligand (N1–C6)–(N1′–C6′) dihedral angle (°)	Pyramidalization angles (°)		Twist angle (σ) about C_2—$C_{2'}$ bond τ	Interligand H...H distance (Å)	Ref.
			χ_{C2}	$\chi_{C2'}$			
[Pt(bpy)$_2$](TCNQ)$_2$	bowed[b]	22.7	8(2)	9(2)	2(3)	2.0[a]	4
[Pt(bpy)$_2$](TCNQ)$_3$	bowed[b]	21	14(4)	8(4)	3(4)	2.1[a]	5
[Ru(bpy)$_2$(PPh$_3$)$_2$](PF$_6$)$_2$	bowed[b]	22.1(2)	9.3(9)	8.2(9)	2(1)	1.9(1)	this paper
[Ru(Me$_2$bpy)$_2$(py)$_2$](PF$_6$)$_2$	bowed[c]	18.0(2)	6.2(9)	6.2(9)	0	2.5(2)	this paper
[Ru(bpy)$_2$(OH$_2$)(OH)](ClO$_4$)$_2$	twist[d]	9.7	2.8(6)	0.7(6)	−9.7(8)	2.18(8); 1.9(1)	6
[Cu(bpy)$_2$](ClO$_4$)$_2$	twist	13	4(4)	0(4)	13(4)	2.4; 2.2[a]	3
		4	0(4)	1(4)	6(6)		
[Pd(bpy)$_2$](NO$_3$)$_2$	twist	1.8	4(1)	2(2)	5(2)	2.0 (mean)	2
		7.6	3(1)	−3(1)	10(2)		

[a] Hydrogen atoms positions that were not originally reported were calculated at distances 0.95 Å from the C_6 atoms in the direction of the C_3–C_6 vectors.

[b] The metal atom is located at a crystallographic center of symmetry.

[c] The metal atom is located at a site symmetry of 2/m.

[d] The metal atom is located on a crystallographic two-fold rotation axis.

TABLE III
Selected distances (Å) and angles (°)[a]

Ruthenium coordination

	I	II
Ru–N	2.075(5)	2.095(1)
Ru–N′	2.084(4)	
Ru–X[b]	2.434(2)	2.100(1)
X–Ru–N	92.1(1)	92.4(2)
X–Ru–N′	91.5(1)	
N–Ru–N′	76.7(2)	71.1(2)
Ru–N–C(2)	115.6(3)	114.3(4)
Ru–N′–C(2′)	115.1(3)	
Ru–N–C(6)	128.0(4)	129.4(4)
Ru–N′–C(6′)	127.0(4)	
Ru–P(1)–C(7)	113.8(2)	
Ru–P(1)–C(13)	115.2(2)	
Ru–P(1)–C(19)	114.4(2)	
Ru–N(py)–C(py 1)		121.2(4)

Bipyridyl ligand

	I	II
N–C(2)	1.370(7)	1.357(8)
N′–C(2′)	1.366(7)	
C(2)–C(2′)	1.462(8)	1.460(9)
C(2)–C(3)	1.386(8)	1.385(9)
C(2′)–C(3′)	1.398(8)	
C(3)–C(4)	1.382(9)	1.380(8)
C(3′)–C(4′)	1.380(9)	
C(4)–C(5)	1.386(9)	1.384(11)
C(4)–C(Me)		1.497(12)
C(4′)–C(5′)	1.364(11)	
C(5)–C(6)	1.369(9)	1.364(10)
C(5′)–C(6′)	1.382(9)	
N–C(6)	1.360(7)	1.343(6)
N′–C(6′)	1.341(7)	
N–N′	2.580(6)	2.612(5)
C(3)–H	0.96(7)	0.94(9)
C(3′)–H	0.95(8)	
C(4)–H	1.01(9)	
C(4′)–H	1.02(8)	
C(5)–H	0.97(7)	1.0(1)
C(5′)–H	0.98(9)	
C(6)–H	1.09(7)	0.94(15)
C(6′)–H	0.99(7)	
H(C6)–H(C6*)[c]	1.9(1)	2.5(2)
H(C3)–H(C3′)	2.1(1)	2.0(1)
N–C(6)–C(5)	123.9(5)	124.0(6)
N–C(6′)–C(5′)	122.8(6)	
C(4)–C(5)–C(6)	119.0(6)	120.2(5)
C(4′)–C(5′)–C(6′)	119.7(6)	
C(5)–C(4)–C(Me)		122.4(7)
C(3)–C(4)–C(Me)		121.1(6)
C(3)–C(4)–C(5)	118.8(6)	116.5(7)
C(3′)–C(4′)–C(5′)	118.8(6)	
C(2)–C(3)–C(4)	119.6(6)	120.8(5)
C(2′)–C(3′)–C(4′)	119.5(6)	
N–C(2)–C(3)	122.2(5)	122.0(6)
N′–C(2′)–C(3′)	121.1(5)	
C(2)–N–C(6)	116.3(4)	116.2(6)
C(2′)–N′–C(6′)	117.8(4)	
N–C(2)–C(2′)	113.9(5)	115.1(5)

TABLE III (*continued*)
Selected distances (Å) and angles (°)[a]

Bipyridyl ligand

N'–C(2')–C(2)	114.3(5)	
C(2')–C(2)–C(3)	123.2(5)	122.6(6)
C(2)–C(2')–C(3')	124.1(5)	
N–C(6)–H	110(4)	113(6)
N'–C(6')–H	117(4)	
C(5)–C(6)–H	126(4)	120(6)
C(5')–C(6')–H	121(4)	
C(6)–C(5)–H	127(5)	119(6)
C(6')–C(5')–H	122(2)	
C(4)–C(5)–H	114(5)	121(6)
C(4')–C(5')–H	128(5)	
C(5)–C(4)–H	124(4)	
C(5')–C(4')–H	117(4)	
C(3)–C(4)–H	118(4)	
C(3')–C(4')–H	124(4)	
C(4)–C(3)–H	119(5)	119(6)
C(4')–C(3')–H	130(5)	
C(2)–C(3)–H	121(5)	118(6)
C(2')–C(3')–H	110(5)	

Triphenylphosphine and pyridine ligands

PPh$_3$		*Py*	
P–C range	1.832(5)–1.842(5)	N(py)–C(py 1)	1.343(8)
P–C average	1.837	C(py 1)–C(py 2)	1.378(1)
C–P–C range	103.3(2)–104.8(2)	C(py 2)–C(py 3)	1.369(9)
C–P–C average	104.0	C(py 1)–N(py)–C(py 1)'	117.6(6)
P–C–C range	117.2(4)–123.5(4)	N(py)–C(py 1)–C(py 2)	122.6(7)
P–C–C average	120.6	C(py 1)–C(py 2)–C(py 3)	118.9(5)
C–C range	1.359(9)–1.400(8)	C(py 2)–C(py 3)–C(py 2)'	119.5(7)
C–C average	1.381		
C–C–C range	118.2(5)–121.6(6)		
C–C–C average	120.0		

Hexafluorophosphate anions

	I	II[d]
P–F range	1.569(5)–1.598(4)	1.536(17)–1.569(12)
P–F average	1.583	1.555
F–P–F range (*cis*)	88.8(2)–91.2(3)	86.2(7)–94.5(5)
F–P–F average (*cis*)	90.01	90.14
F–P–F range (*trans*)	178.7(3)–179.2(2)	175.9(5)
F–P–F average (*trans*)	178.93	

[a] Unlabelled H atoms are those attached to the atom preceding the H on the table entry.
[b] X is P(1) for structure I and N(py) for structure II.
[c] H(C6*) is 1 − x, 1 − y, 1 − z of H(C6').
[d] Includes both components of the disordered anion.

Table III gives selected distances and angles, and Table IV gives best plane data. Observed and calculated structure factors and thermal parameters have been deposited.†

RESULTS AND DISCUSSION

The octahedral coordination of the Ru(II) atoms is relatively undistorted with the exception of the N—Ru—N angle of 76.7(2)° (in I) and 76.6° (in II) caused by the 2.58 Å bite of the chelate (Figures 2 and 3). In both structures the crystallographic symmetry at the Ru atom makes all of the *trans* angles 180°; the two in-

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†The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Leasheld Road, Cambridge CB2 1EW, U.K. Any request should be accompanied by the full literature citation.

TABLE IV
Best planes[a] and dihedral angles

Plane 1			Plane 2		Plane 3			Plane 4		
Atom	Dis(Å)[b]		Atom	Dis(Å)	Atom	Dis(Å)		Atom	Dis(Å)	
	I	*II*		*I*		*I*	*II*		*I*	*II*
N	−0.016(4)	−0.019(3)	N′	−0.018(4)	Ru	0.0	0.0	N	−0.002(4)	0.0
C(2)	0.030(6)	0.026(4)	C(2′)	0.022(5)	N	0.0	0.0	C(2)	0.005(6)	0.0
C(3)	−0.008(7)	−0.011(4)	C(3′)	−0.007(6)	N′	0.0	0.0	N′	0.002(4)	0.0
C(4)	−0.028(8)	−0.016(4)	C(4′)	−0.010(7)	C(2)*	−0.376(5)	−0.363(3)	C(2′)	−0.005(5)	0.0
C(5)	0.025(7)	0.017(4)	C(5′)	−0.001(7)	C(2′)*	−0.386(5)	−0.363(3)	Ru*	−0.4977(1)	−0.4838(1)
C(6)	0.012(6)	0.011(4)	C(6′)	0.030(7)	H(C6)*	0.67(8)	0.78(6)	H(C6)*	0.34(8)	0.55(7)
H(C6)*	0.04(8)	0.30(6)	H(C6′)*	0.08(8)	H(C6′)*	0.64(8)	0.78(6)	H(C6′)*	0.35(8)	0.55(7)
Ru*	−0.1253(1)	−0.2331(1)	Ru*	−0.2322(1)						
Me*		−0.003(6)								

Dihedral angles

Planes	Angle (°)		Planes	Angle (°)	
	I	*II*		*I*	*II*
1–2	22.1	—	2–3	18.2	—
1–3	18.6	17.5	2–4	9.9	—
1–4	12.9	9.3	3–4	17.8	17.2

[a] Each atom included in the calculation for a plane was weighted by $1/\sigma^2$, where σ is the positional uncertainty component perpendicular to the plane. Asterisks indicate atoms not included in the calculation of the best plane.

[b] Distance out of calculated plane in Å.

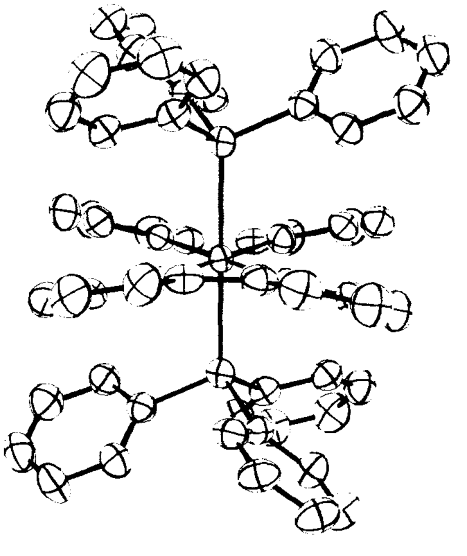

FIGURE 2 The $[Ru(bpy)_2(PPh_3)_2]^{2+}$ cation.

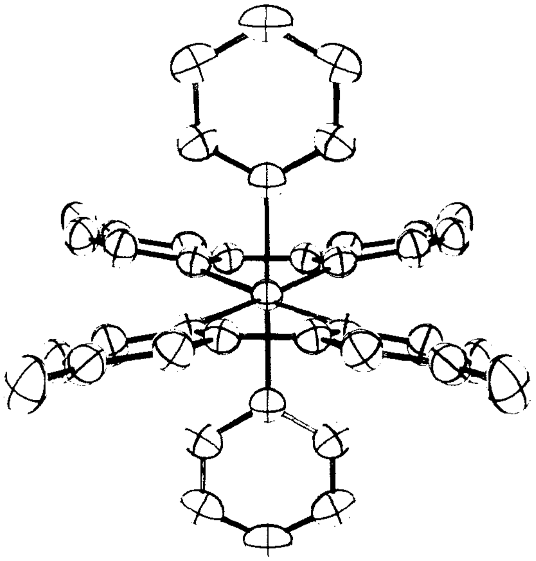

FIGURE 3 The $[Ru(Me_2bpy)_2(py)_2]^{2+}$ cation.

dependent P-Ru-N angles in I are 91.5(1) and 92.1(1)°. The Ru-N distances of 2.075(5) to 2.084(4)Å are only slightly shorter than the 2.104 Å distance found in $[Ru(NH_3)_6]^{3+}$,[9] and suggest little or no multiple bond character to these linkages. The bond distances and bond angles within the pyridyl units of the bipyridyl moiety agree with accepted values and the values found for free bipyridine.[10] The $[PF_6]^-$ anion, the pyridine ring, and the triphenylphosphine ligand also have typical bond distances and angles. The phenyl rings of the triphenylphosphine ligand are all planar within 0.011(7)Å.

In I, the Ru–P distance of 2.434(2)Å is in agreement with previously reported values for six-coordinate Ru compounds with *trans* triphenylphosphine ligands, e.g., 2.439(2)Å in $[RuCl(CO)_2(HN_2Ph)(PPh_3)_2]^{1+}$,[11] 2.456(1)Å in $RuCl_3(NO)(PPh_3)_2$,[12] and 2.436(2) and 2.437(2)Å in $RuCl_3(N_2C_6H_4CH_3)(PPh_3)_2$.[12] The Ru—N (pyridine) distance of 2.100(1)Å in II is the same as that found for $[Ru(py)_6]^{2+}$.[13]

The packing of the ions in I gives a layered arrangement at x = 0 and 0.5, with rows of anions and cations in a CAACAA sequence along the $y\bar{z}$ diagonal. The packing of II is the same, with the ions aligned on the xz diagonal. There are no possibilities for conventional H-bonding in either structure, and the intermolecular contacts are all longer than the corresponding sums of the van der Waals radii.

Molecules with *trans* $M(bpy)_2$ units necessarily have structural distortions due to the steric crowding of the α-hydrogens on opposite ligands. Figure 1 illustrates this steric problem for idealized ligands and shows the two distinct modes of distortion found in *trans* $M(bpy)_2$ structures. The twisted conformation[15] is characterized by the two α-hydrogens of the same ligand lying on opposite sides of the idealized MN_4 plane. The bowed conformation involves structures in which both α-hydrogens from one ligand are displaced to the same side of the idealized MN_4 plane, and on the opposite side from the α-hydrogens of the opposing bpy ligand. The bowed conformation is found in the two structures of this report.

The distortions from planarity within the individual bpy ligands are directly linked to the twisted and bowed conformations, In general, twisted structures are not required to have distorted bpy ligands in order to reduce the α-hydrogen interaction, while a bowed configuration requires some amount of pyramidalization at one or both of the C2 atoms. The different components of these distortions can be analyzed by employing two out-of-plane bending coordinates, χ_{C2} and $\chi_{C2'}$, and an intraligand twisting coordinate τ, in a manner similar to Dunitz's calculation[16] for amide groups. These three coordinates can be described by four torsion angles: $\chi_{C2} = \omega_1 - \omega_3 + \pi = -\omega_2 + \omega_4 + \pi$ (modulo 2π), $\chi_{C2'} = \omega_2 - \omega_3 + \pi = \omega_1 + \omega_4 + \pi$ (modulo 2π), and $\tau = (\omega_1 + \omega_2)/2$, where $\omega_1 = \omega_{(N-C2-C2'-N')}$, $\omega_2 = \omega_{(C3-C2-C2'-C3')}$, $\omega_3 = \omega_{(C3-C2-C2'-N')}$, and $\omega_4 = \omega_{(N-C2-C2'-C3')}$. Thus χ_{C2} and $\chi_{C2'}$ are measures of the pyramidalization of the C2 and C2′ atoms and τ is a measure of the twist about the C2–C2′ bond between the two pyridyl groups. If no pyramidalization occurs the angle τ is approximately equal to the dihedral angle

TABLE V
Configurational parameters for *trans*-M(bpy)$_2$ fragments

Compound	Configuration	Intra-ligand (N1–C6)–(N1′–C6′) dihedral angle (°)	Pyramidalization angles (°)		Twist angle (σ) about C_2—$C_{2'}$ bond τ	Interligand H...H distance (Å)	Ref.
			χ_{C2}	$\chi_{C2'}$			
[Pt(bpy)$_2$](TCNQ)$_2$	bowed[b]	22.7	8(2)	9(2)	2(3)	2.0[a]	4
[Pt(bpy)$_2$](TCNQ)$_3$	bowed[b]	21	14(4)	8(4)	3(4)	2.1[a]	5
[Ru(bpy)$_2$(PPh$_3$)$_2$](PF$_6$)$_2$	bowed[b]	22.1(2)	9.3(9)	8.2(9)	2(1)	1.9(1)	this paper
[Ru(Me$_2$bpy)$_2$(py)$_2$](PF$_6$)$_2$	bowed[c]	18.0(2)	6.2(9)	6.2(9)	0	2.5(2)	this paper
[Ru(bpy)$_2$(OH$_2$)(OH)](ClO$_4$)$_2$	twist[d]	9.7	2.8(6)	0.7(6)	−9.7(8)	2.18(8); 1.9(1)	6
[Cu(bpy)$_2$](ClO$_4$)$_2$	twist	13	4(4)	0(4)	13(4)	2.4; 2.2[a]	3
		4	0(4)	1(4)	6(6)		
[Pd(bpy)$_2$](NO$_3$)$_2$	twist	1.8	4(1)	2(2)	5(2)	2.0 (mean)	2
		7.6	3(1)	−3(1)	10(2)		

[a] Hydrogen atoms positions that were not originally reported were calculated at distances 0.95 Å from the C_6 atoms in the direction of the C_3–C_6 vectors.
[b] The metal atom is located at a crystallographic center of symmetry.
[c] The metal atom is located at a site symmetry of 2/m.
[d] The metal atom is located on a crystallographic two-fold rotation axis.

between the two pyridyl groups; if either C2 or C2′ have tetrahedral pyramidalization then $\chi = 60°$ for that atom. These deformation parameters for *trans* M(bpy)$_2$ type structures are tabulated, along with the reported overall dihedral angles, in Table V.

The structures with bowed conformations tend to have small twist angles and large intraligand dihedral angles which arise from significant pyramidalization of the C2 and C2′ atoms. The small values of τ are to be expected: In structures of this type the metal atom lies either on a crystallographic center of symmetry so any intraligand twist forces the α-hydrogens closer together, or it lies on a 2/m site which forces the twist to be 0. For the *trans* M(bpy)$_2$ structures which exhibit an overall twisted conformation there is a good correlation between the intraligand dihedral angle and the twist parameter τ, because intraligand twisting reduces the amount of overall twist distortion required for α-hydrogen separation. It is of interest to note that the results of both of these distortions give α-H...α-H contacts equal to, or greater than, twice the van der Waals radii of hydrogens; coplanar *trans* bpy units would would make this contact approximately 1.45 Å.

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