

(impy)](PF₆)₂³ were prepared as described previously.

Syntheses. 2-(1-Aminoethyl)pyridine (Meampy). The oxime of 2-acetylpyridine was prepared by the standard literature procedure⁶ (yield 92%; mp 118 °C). The oxime was reduced to the amine in an analogous manner to that used for 3-(1-aminoethyl)pyridine⁷ (yield 81%; bp 107 °C (3 mmHg)).

(2-(1-Aminoethyl)pyridine)bis(2,2'-bipyridine)ruthenium(II) Hexafluorophosphate, [Ru(bpy)₂(Meampy)](PF₆)₂. This complex was prepared by an analogous method to that used for [Ru(bpy)₂(ampy)](PF₆)₂.³ A solution of *cis*-[Ru(bpy)₂Cl₂].2H₂O (5.0 g) and racemic Meampy (8.0 g) in deaerated 1:1 aqueous methanol (250 mL) was refluxed for 1 h. The methanol was evaporated off and NH₄PF₆ added to the filtered solution. The resultant precipitate was washed with ice-cold water, 2-propanol, and ether and dried in vacuo (yield 7.15 g, 90%).

The two diastereoisomeric pairs of [Ru(bpy)₂(Meampy)]²⁺ were partially separated (ca. 80% enrichment) on a large scale by repeated recrystallization from aqueous solution as the iodide salt. The separation was monitored after subsequent conversion to the PF₆⁻ salt by ¹H NMR spectroscopy. The less soluble ΔS(ΔR) diastereoisomer shows a doublet due to the methyl resonance centered at δ 1.51 and the more soluble ΔR(ΔS) at δ 1.68; Me₂SO-*d*₆ solvent, Me₄Si internal reference.

Final purification of the enriched samples was achieved by ion-exchange chromatography using SP-Sephadex C-25 cation exchanger (60 × 8-cm column) with 0.15 M sodium (+)-antimonyl tartrate as eluent. In a typical purification 650 mg of an 80% enriched diastereoisomer was sorbed on to the column in the dark at 4 °C. The band was cycled through the column until separation of the two diastereoisomers occurred, with ΔR(ΔS) eluting faster than ΔS(ΔR). Each band was collected and precipitated as the hexafluorophosphate salt by the addition of NH₄PF₆, and diastereoisomeric purity was verified by ¹H NMR spectroscopy. The visible spectra in water gave ΔS(ΔR): ε₄₇₄^{max} 9500, ε₃₄₀^{max} 11000; ΔR(ΔS): ε₄₇₂^{max} 10200, ε₃₄₃^{max} 10900.

Anal. Calcd for RuC₂₇H₂₆N₆P₂F₁₂: C, 39.3; H, 3.18; N, 10.2. Observed: ΔS(ΔR) C, 39.3; H, 3.13; N, 10.2. ΔR(ΔS) C, 39.6; H, 3.04; N, 10.3.

(2-(Aminomethyl)pyridine)bis(2,2'-bipyridine)ruthenium(II) Bromide, [Ru(bpy)₂(ampy)]Br₂. [Ru(bpy)₂(ampy)](PF₆)₂³ (300 mg) was dissolved in dry 2-butanone (110 mL). Tetra-*n*-butylammonium bromide was added with stirring to produce a flocculant precipitate that yielded a filterable powder upon cooling overnight at 0 °C which was washed with 2-butanone and ether and dried in vacuo (yield 220 mg, 90%).

Bis(2,2'-bipyridine)(2-(*N,N*,1,1-tetradeuterioaminomethyl)pyridine)ruthenium(II) Perchlorate, [Ru(bpy)₂(*d*₄-ampy)](ClO₄)₂. [Ru(bpy)₂(ampy)]Br₂ (200 mg, 3 × 10⁻⁴ mol) was dissolved in deaerated D₂O (9 mL). NaOD/D₂O (600 μL, 30%) was added and the solution sealed in a glass ampule under N₂. The reaction mixture was heated in the dark at 65 °C for 36 h and then acidified upon opening with 35% DCl (~1.0 mL). The product was precipitated by addition of NaClO₄, washed with cold D₂O, and dried in vacuo (yield 200 mg, 92%).

Bis(2,2'-bipyridine)(2-(1,1-dideuterioaminomethyl)pyridine)ruthenium(II) Hexafluorophosphate, [Ru(bpy)₂(*d*₂-ampy)](PF₆)₂. A solution of the cation [Ru(bpy)₂(*d*₄-ampy)]²⁺ was prepared by stirring an aqueous suspension of the perchlorate salt (200 mg) in water (10 mL) with Dowex 1 × 8 anion exchange resin (Cl⁻ form). The solution was filtered, 1 M NaOH (1 mL) was added, and the solution was allowed to react in the dark for 20 min. The mixture was then acidified with HCl, and the complex was precipitated by addition of NH₄PF₆ and washed with ice cold water, 2-propanol, and ether (yield 210 mg, 94%). The visible spectrum in water gave ε₄₇₁^{max} 10300, ε₃₄₁^{max} 10900. Anal. Calcd for RuC₂₆H₂₂D₂N₆P₂F₁₂: C, 38.3; N, 10.4; H/D, 2.97. Observed: C, 38.5; N, 10.2; H, 3.06.

Bis(2,2'-bipyridine)(2-(1-deuterioiminoethyl)pyridine)ruthenium(II) hexafluorophosphate, [Ru(bpy)₂(*d*₁-impy)](PF₆)₂, was prepared in an analogous manner to the nondeuterated imine complex³ except that 1 M D₂SO₄/D₂O was used as the solvent and [Ru(bpy)₂(*d*₂-ampy)](PF₆)₂ as the starting material. The visible spectrum in water gave ε₄₆₅^{max} 12500.

Oxidation by Ce(IV) of [Ru(bpy)₂(*d*₂-ampy)]²⁺. A solution of (N-H₄)₄Ce(SO₄)₄·H₂O in 0.5 M H₂SO₄ (10 mL of 1.92 × 10⁻² M; 1.92 × 10⁻⁴ mol) was added to a solution of [Ru(bpy)₂(*d*₂-ampy)](PF₆)₂ in 0.5 M H₂SO₄ (95 mL of 1.012 × 10⁻³ M; 9.62 × 10⁻⁵ mol) slowly with stirring. NH₄PF₆ was added, the solution cooled and filtered, and the solid washed with ice-cold water and dried in vacuo.

Flash Photolysis Studies. The laser photolysis and flash photolysis facilities at the University of Adelaide were used for these studies; a

description of this equipment and of the data acquisition system is given elsewhere.⁸ The experimental conditions for the kinetic study of the oxidative dehydrogenation of [Ru(bpy)₂(*d*₂-ampy)]²⁺ and the two diastereoisomers of [Ru(bpy)₂(Meampy)]²⁺ in perchloric acid media were as described previously for the study of [Ru(bpy)₂(ampy)]²⁺,³ using Fe(III) as quencher. Details of the kinetic analysis of the flash photolysis data have been given previously.³

For the study of the rate of oxidation of Ru(bpy)₂(ampy)²⁺ at pH 3 and pH 4 it was necessary to use Cu(II) as a quencher rather than Fe(III). The complex concentration was maintained at 1 × 10⁻³ M, but the quencher concentration increased to 0.1 M due to the slower quenching rate of the MLCT excited state by Cu(II).⁹ [HClO₄] was varied from 10⁻² to 10⁻⁴ M. No attempt at buffering was made at pH 4 to avoid possible catalytic effects on the reaction by the buffer components. A small (<0.05 pH units) decrease in the pH resulted due to the deprotonation of the complex during the reaction, but this was not significant due to the semiquantitative nature of the analysis of these particular data. The ionic strength was maintained at 1.0 by addition of NaClO₄. Each solution was used for one flash, and the reaction was monitored at 436 nm.

Laser photolysis indicated that the quenching rates, *k*_q, by Fe(III) for the diastereoisomers of [Ru(bpy)₂(Meampy)]²⁺ are 2.8 × 10⁹ M⁻¹ s⁻¹ for ΔS(ΔR) and 8.5 × 10⁸ M⁻¹ s⁻¹ for ΔR(ΔS). Therefore for all the complexes studied the quenching was over within the lifetime of the flash. For the cases studied similar conversions of Ru(II) to Ru(III) as for Ru(bpy)₂(ampy)²⁺ were observed (30–40%).

Structure Determination of Diastereoisomer ΔS(ΔR)-[Ru(bpy)₂(Meampy)]S₂O₆·5H₂O. Collection and Reduction of X-ray Data. An aqueous solution of the complex cation as the Br⁻ salt (prepared in an analogous way to [Ru(bpy)₂(ampy)]Br₂) was converted to the SO₄²⁻ form by addition of a stoichiometric amount of Ag₂SO₄. After the solution was stirred and filtered, the resultant solution was passed down a column of QAE-Sephadex A-25 anion exchanger (S₂O₆²⁻ form). Evaporation of water in a vacuum desiccator over silica gel yielded red crystals of [Ru(bpy)₂(Meampy)]S₂O₆·5H₂O.

A crystal plate of dimensions 0.044 × 0.13 × 0.46 mm³ was mounted on a glass fiber and coated with cyanoacrylate super glue. Lattice parameters at 21 °C were determined by a least-squares fit to the setting angles of 25 independent reflections, measured and refined by scans performed on an Enraf-Nonius CAD-4 four-circle diffractometer employing graphite monochromated Mo Kα radiation (λ 0.7107 Å). Crystal data for C₂₇H₃₆N₆O₁₁S₂Ru (formula weight 785.72): orthorhombic, space group P2₁2₁2₁ with *a* = 12.194 (5), *b* = 13.576 (7), and 19.916 (8) Å so that *V* = 3297.01 Å³; *Z* = 4; ρ_{calcd} = 1.583, ρ_{obsd} = 1.59 g cm⁻³; μ (Mo Kα) = 6.02 cm⁻¹; *F*(000) = 1580 electrons.

Intensity data were collected in the range 1.5 < θ < 24° using an ω - nθ/3 scan, where *n* (= 4) was optimized by profile analysis of a typical reflection. The ω scan angles and horizontal counter apertures employed were (1.20 + 0.35 tan θ)° and (2.40 + 0.5 tan θ) mm, respectively. Three standard reflections, monitored after every 58 min of data collection, indicated that no decomposition had occurred. Data reduction and application of Lorentz and polarization corrections were performed by using the program SUSCAD.¹⁰ Absorption corrections were applied with the program ABSORB.¹⁰ The maximum and minimum transmission factor were estimated to be 0.97 and 0.93, respectively. Of the 2589 reflections collected, 618 with *I* < 2.5σ(*I*) were considered unobserved and not used in the calculations.

Solution and Refinement. The structure was solved and refined by application of the heavy-atom technique. Successive difference syntheses located all non-hydrogen atoms of the structure including five water molecules. In the full-matrix least-squares refinement, the bipyridyl ligands were refined as pairs of rigid pyridine rings and with isotropic temperature factors. Their hydrogen atoms were included as rigid groups in calculated positions (C-H, 1.00 Å). The other non-hydrogen atoms, except the oxygens of the water molecules, were refined anisotropically, and their associated hydrogens (except for those of the waters, which could not be found) were included at calculated positions assuming tetrahedral geometries around C and N (N-H, 0.95 Å). Different group temperature factors were used for the bipyridyl and other hydrogens. A weighting scheme was applied and refined, converging at *w* = 2.27/(σ²(*F*_o) + 0.0008(*F*_o²)). Refinement converged with *R*₁ = 0.0300 and

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(10) Programs used included SUSCAD and ABSORB "data reduction programs for the CAD-4 diffractometer", University of Sydney, 1976; SHELX, "Program for crystal structure determination", G. M. Sheldrick, 1976; and PLUTO-plotting by W. D. S. Motherwell.

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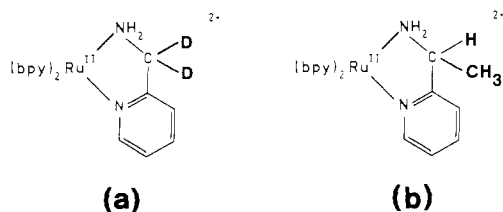


Figure 1. C-deuterated and C-monomethylated analogues of $[\text{Ru}(\text{bpy})_2\text{ampy}]^{2+}$: (a) $\text{Ru}(\text{bpy})_2(\text{d}_2\text{-ampy})^{2+}$ and (b) $\text{Ru}(\text{bpy})_2(\text{Meampy})^{2+}$.

$R_2 = 0.0306$, at which stage the largest peak in the final difference map was less than $0.6 \text{ e} \cdot \text{\AA}^{-3}$. The absolute configuration of the crystal was confirmed by repeating the last three cycles of refinement with all coordinates inverted through the origin; the higher corresponding R values of 0.0310 and 0.0319 suggest the initial configuration was correct. All scattering factors and anomalous terms were taken from International Tables for Crystallography.¹¹ The final positional parameters of the non-hydrogen atoms are listed in Table I. The thermal parameters are available as supplementary material, as well as the calculated positional parameters for the hydrogen atoms, and the observed and calculated structure factors. Table II contains selected bond lengths and angles, omitting values for the rigid pyridine rings in the ligands bpy and Meampy.

Chirality Studies of Oxidation of the Diastereoisomers of $[\text{Ru}(\text{bpy})_2(\text{Meampy})]^{2+}$. Bis(2,2'-bipyridine)(2-(1-iminoethyl)pyridine)ruthenium(II) Bromide, $[\text{Ru}(\text{bpy})_2(\text{MeImpy})]\text{Br}_2$. $[\text{Ru}(\text{bpy})_2(\text{MeImpy})](\text{PF}_6)_2$ was prepared electrochemically in 97% yield in an analogous manner to that used for $[\text{Ru}(\text{bpy})_2(\text{Impy})](\text{PF}_6)_2^3$ and was converted to the bromide salt by precipitation from an acetone solution using tetra-*n*-butylammonium bromide ($\epsilon_{465}^{\text{max}} 12\,500$ in water).

Resolution of $[\text{Ru}(\text{bpy})_2(\text{MeImpy})]^{2+}$. $[\text{Ru}(\text{bpy})_2(\text{MeImpy})]\text{Br}_2$ (3.47 g, 5.0 mmol) and $\text{Ag}_2(\text{Sb}_2(+)\text{tart}_2)$ (3.80 g, 5 mmol) in water (25 mL) were stirred with glass balls for 30 min. The solution was filtered and diluted with water to 75 mL. Acetone was added to incipient crystallization (ca. 150 mL) and the solution left to stand for 1 week at 0 °C. The resulting crystals were filtered, washed with acetone/water (5:1) and acetone, and dried in vacuo (yield 1.37 g, 24% of total diastereoisomer). Two recrystallizations from water/acetone gave a product whose molecular rotation was not increased by further recrystallization (yield 0.82 g, 30% of one chiral form of the cation; $[\text{M}]_{389}^{25} +9700$). Anal. Calcd for $[\text{Ru}(\text{bpy})_2(\text{MeImpy})](\text{Sb}_2(+)\text{tart}_2) \cdot 4\text{H}_2\text{O}$: C, 36.1; N, 7.42; H, 3.38. Observed: C, 36.1; N, 7.22; H, 3.10.

(+)- $[\text{Ru}(\text{bpy})_2(\text{MeImpy})](\text{PF}_6)_2$ was precipitated quantitatively by adding NH_4PF_6 to an aqueous solution of the diastereoisomer and showed $[\text{M}]_{389}^{25} +8500$ (water).

The enantiomeric (-)- $[\text{Ru}(\text{bpy})_2(\text{MeImpy})]^{2+}$ was not isolated.

Resolution of Meampy. Meampy (4.9 g, 40 mmol) and (+)-tartaric acid (6.0 g, 40 mmol) were dissolved in water (7 mL) with slight heating. Ethanol (25 mL) was added and the solution cooled slowly to ice temperature. After standing (2 h) the crystals were filtered, washed with ethanol and ether, and air dried (yield 3.5 g, 32% of total diastereoisomer). Two recrystallizations from water/ethanol yielded the optically pure diastereoisomer ((S)(-)-MeampyH)((+)-Htart)·H₂O (2.2 g) (40% of one chiral form of the amine; $[\alpha]_{389}^{25} +4.7^\circ$ (water); mp 162 °C (lit.¹² $[\alpha]_{389}^{25} +5.1^\circ$, mp 161–163 °C)). Anal. Calcd for $\text{C}_{11}\text{H}_{18}\text{N}_2\text{O}_7$: C, 45.5; H, 6.25; N, 9.65. Observed: C, 45.5; H, 6.20; N, 9.75.

Δ - and Λ - $[\text{Ru}(\text{bpy})_2(\text{S})(-)\text{Meampy}]^{2+}$. The ligand (S)(-)-Meampy was released from the tartrate diastereoisomer by basifying an aqueous solution, extracting with ether, and evaporating off the solvent. The complex cation was prepared and the internal diastereoisomers separated as detailed for the racemic ligand. For (+)- $[\text{Ru}(\text{bpy})_2(\text{S})(-)\text{Meampy}]^{2+}$, $[\text{M}]_{389}^{25} +6700$, and for (-)- $[\text{Ru}(\text{bpy})_2(\text{S})(-)\text{Meampy}]^{2+}$, $[\text{M}]_{389}^{25} -6700$ (water).

Chemical Oxidation of (+)- and (-)- $[\text{Ru}(\text{bpy})_2(\text{S})(-)\text{Meampy}]^{2+}$. The two diastereoisomers were separately oxidized by a two-molar ratio of Ce(IV) in 1 M H₂SO₄ solution in an analogous manner to the oxidation of $[\text{Ru}(\text{bpy})_2(\text{d}_2\text{-Impy})]^{2+}$ described above. The resultant $[\text{Ru}(\text{bpy})_2(\text{MeImpy})]^{2+}$ products were precipitated as the PF₆⁻ salts, which were filtered, washed with ice-cold water, 2-propanol, and ether, and dried in vacuo. Measurement of rotations (in water) showed $[\text{M}]_{389}^{25}$ 8600 for the oxidation product of (+)- $[\text{Ru}(\text{bpy})_2(\text{S})(-)\text{Meampy}]^{2+}$ and

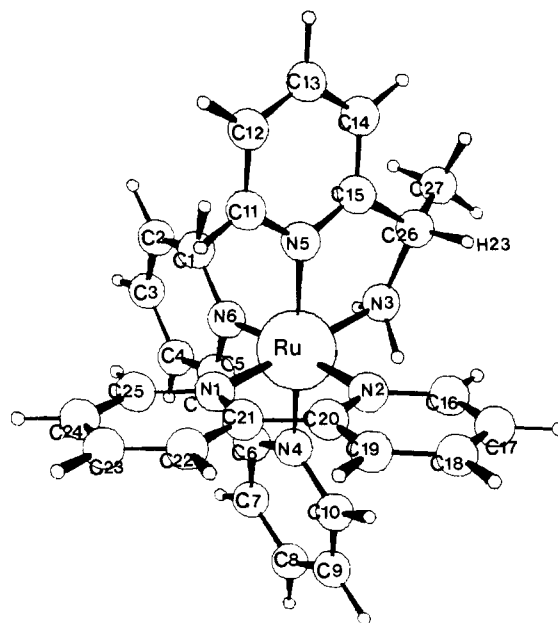


Figure 2. A PLUTO plot of $\Delta\text{S}(\Delta\text{R})\text{-}[\text{Ru}(\text{bpy})_2(\text{Meampy})]\text{S}_2\text{O}_6 \cdot 5\text{H}_2\text{O}$ showing atom labeling.

$[\text{M}]_{389}^{25} -8600$ for the oxidation product of the levorotatory diastereoisomer.

Results and Discussion

Comments on the Synthesis and Characterization of Complexes.

In the course of this study, the $(\text{bpy})_2\text{Ru}(\text{II})$ complexes of the ampy analogues $\text{d}_2\text{-ampy}$ (Figure 1a) and Meampy (Figure 1b) were developed.⁴

Dissolution of the complex $[\text{Ru}(\text{bpy})_2(\text{ampy})]^{2+}$ in D₂O at pD ca. 13 resulted in complete exchange of the amine protons in 20 min at 25 °C, detected by the loss of the broad NH₂ resonances (centered at 5.41 and 4.92 ppm relative to Me₄Si) in the ¹H NMR spectrum (PF₆⁻ salt; Me₂SO-*d*₆ solvent), and the concomitant sharpening of the AB quartet arising from the methylene protons (4.61, 4.41, 4.19, 3.99 ppm). Exchange of the methylene protons occurs on a much slower time scale (36 h at 65 °C; pD ca. 14). The choice of appropriate conditions therefore allows selective or complete exchange of amine and methylene protons in the ampy complex.

Synthesis of the species $[\text{Ru}(\text{bpy})_2\text{Meampy}]^{2+}$ (Figure 1b) realized the two diastereoisomeric forms in approximately equal amounts, which were separated by a combination of fractional crystallization and ion-exchange chromatography. ¹H NMR spectroscopy showed distinct methyl doublet resonances for the two diastereoisomers ($\Delta\text{S}(\Delta\text{R})$, centered at 1.51 ppm; $\Delta\text{R}(\Delta\text{S})$, 1.68 ppm; PF₆⁻ salts, Me₂SO-*d*₆ solvent, Me₄Si reference). These ¹H NMR spectra also reveal the different chemical environments of each of the two amine protons in each of the diastereoisomers: $\Delta\text{S}(\Delta\text{R})$ shows two broad resonances centered at 5.90 ppm and 4.56 ppm and $\Delta\text{R}(\Delta\text{S})$ at 5.34 ppm and 4.82 ppm.

Description of the Structure of $\Delta\text{S}(\Delta\text{R})\text{-}[\text{Ru}(\text{bpy})_2(\text{Meampy})]\text{S}_2\text{O}_6 \cdot 5\text{H}_2\text{O}$. A perspective view of the structure of the cation is shown in Figure 2. The structure assigns the relative chiralities about the metal center and the methine carbon as $\Delta\text{S}(\Delta\text{R})$. The cation has normal hydrogen bonds from the amino group N(3) to a dithionate oxygen (O(1), 3.21 Å) and to a water molecule (O(10), 3.18 Å). All the dithionate oxygen atoms have a single hydrogen bond to water molecules in the range 2.76–3.07 Å. A hydrogen bond from water O(9) to both waters O(7), 2.71 Å, and O(8), 2.76 Å, completes the hydrogen bonding pattern.

The two bipyridine ligands exhibit structural features reported previously for $[\text{Ru}(\text{bpy})_3]^{2+}$:¹³ the chelate bite angle averages 78.7°, and the short Ru–N(bpy) bond length of 2.053 Å (average)

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Table I. Final Positional Parameters for Non-Hydrogen Atoms in $\Delta S(\Delta R)$ -[Ru(bpy)₂(Meampy)]S₂O₆·5H₂O

atom	x	y	z
Ru(1)	0.37069 (6)	-0.04675 (5)	0.67946 (3)
S(1)	0.0831 (2)	0.4588 (2)	0.5485 (1)
S(2)	0.0122 (2)	-0.0231 (2)	0.8618 (1)
N(3)	0.3594 (6)	0.0297 (5)	0.5868 (3)
O(1)	-0.0561 (6)	0.0439 (6)	0.9924 (3)
O(2)	-0.0466 (6)	-0.1336 (5)	0.9814 (4)
O(3)	-0.1957 (5)	-0.0454 (6)	0.9291 (3)
O(4)	-0.0208 (6)	0.0699 (5)	0.8351 (4)
O(5)	0.1253 (6)	-0.0258 (5)	0.8856 (4)
O(6)	-0.0193 (6)	-0.1042 (6)	0.8204 (4)
O(7)	0.3627 (9)	0.4659 (6)	0.4713 (4)
O(8)	0.4462 (8)	0.2956 (7)	0.2771 (4)
O(9)	0.4711 (11)	0.3131 (7)	0.4145 (5)
O(10)	0.2182 (10)	0.1126 (10)	0.9693 (5)
O(11)	0.2511 (10)	0.3648 (10)	0.9305 (6)
N(1)	0.3861 (4)	-0.1060 (3)	0.7734 (2)
C(21)	0.4829 (4)	-0.0823 (3)	0.8071 (2)
C(22)	0.4996 (4)	-0.1153 (3)	0.8727 (2)
C(23)	0.4195 (4)	-0.1718 (3)	0.9046 (2)
C(24)	0.3228 (4)	-0.1955 (3)	0.8709 (2)
C(25)	0.3061 (4)	-0.1626 (3)	0.8053 (2)
N(2)	0.5290 (3)	-0.0064 (3)	0.7036 (2)
C(16)	0.6025 (3)	0.0411 (3)	0.6608 (2)
C(17)	0.7064 (3)	0.0676 (3)	0.6840 (2)
C(18)	0.7367 (3)	0.0466 (3)	0.7500 (2)
C(19)	0.6632 (3)	-0.0008 (3)	0.7928 (2)
C(20)	0.5593 (3)	-0.0274 (3)	0.7696 (2)
N(4)	0.4082 (5)	-0.1786 (4)	0.6356 (3)
C(6)	0.3195 (5)	-0.2333 (4)	0.6119 (3)
C(7)	0.3374 (5)	-0.3215 (4)	0.5778 (3)
C(8)	0.4442 (5)	-0.3551 (4)	0.5673 (3)
C(9)	0.5330 (5)	-0.3004 (4)	0.5910 (3)
C(10)	0.5150 (5)	-0.2121 (4)	0.6251 (3)
N(5)	0.3153 (4)	0.0885 (3)	0.7122 (2)
C(11)	0.2804 (4)	0.1066 (3)	0.7777 (2)
C(12)	0.2325 (4)	0.1968 (3)	0.7940 (2)
C(13)	0.2195 (4)	0.2689 (3)	0.7448 (2)
C(14)	0.2544 (4)	0.2508 (3)	0.6792 (2)
C(15)	0.3023 (4)	0.1606 (3)	0.6629 (2)
N(6)	0.2171 (4)	-0.1009 (4)	0.6580 (3)
C(1)	0.1189 (4)	-0.0515 (4)	0.6706 (3)
C(2)	0.0198 (4)	-0.0914 (4)	0.6485 (3)
C(3)	0.0190 (4)	-0.1808 (4)	0.6139 (3)
C(4)	0.1172 (4)	-0.2302 (4)	0.6014 (3)
C(5)	0.2162 (4)	-0.1902 (4)	0.6234 (3)
C(26)	0.3477 (8)	0.1365 (6)	0.5956 (4)
C(27)	0.2873 (11)	0.1822 (9)	0.5380 (6)

reflects the π back-bonding between the delocalized $\pi^*(\text{bpy})$ and $t_{2g}(\text{Ru})$ orbitals. For the Meampy ligand, the Ru-N(amine) bond length is longer (2.121 Å) than Ru-N(py) (2.062 Å), which demonstrates this effect. The bite angle for the Meampy chelate (N(5)-Ru-N(3)) of 79.5° is comparable with that of ampy in the complex [Fe(ampy)₃]²⁺ (75.4° for high spin, 81.6° for low spin).^{14,15} The bond angles within the chelate ring about the amine nitrogen N(3) (112.7°) and the methine carbon C(26) (111.4°) correspond to the equivalent angles for ampy in the complex [Zn(ampy)₃]²⁺¹⁵ (average 111.8° and 110.9°, respectively). The pyridine ring in the Meampy is planar, but the chelate ring itself is puckered. Consequently, the non-ring substituents on the methine carbon (C(26)) are distinctly either axial or equatorial, in agreement with the clearly separated methyl resonances observed in the ¹H NMR spectra of the two diastereoisomers. For the $\Delta S(\Delta R)$ diastereoisomer, the methyl substituent (C(27)) is equatorial.

Kinetic Studies. Our previous study³ of the mechanism of the oxidative dehydrogenation of coordinated 2-(aminomethyl)pyridine in [Ru(bpy)₂(ampy)]²⁺ (eq 1) indicated the intermediacy of a

Table II. Selected Bond Lengths (Å) and Bond Angles (deg) for $\Delta S(\Delta R)$ -[Ru(bpy)₂(Meampy)]S₂O₆·5H₂O

Distances			
N(3)-Ru(1)	2.121 (6)	N(1)-Ru(1)	2.046 (4)
N(2)-Ru(1)	2.064 (3)	N(4)-Ru(1)	2.044 (5)
N(5)-Ru(1)	2.062 (4)	N(6)-Ru(1)	2.057 (5)
O(4)-S(2)	1.427 (7)	O(5)-S(2)	1.459 (8)
O(6)-S(2)	1.429 (8)	C(26)-N(3)	1.468 (10)
C(20)-C(21)	1.409 (6)	C(5)-C(6)	1.407 (8)
C(26)-C(15)	1.486 (10)	C(27)-C(26)	1.497 (14)
Angles			
N(1)-Ru(1)-N(3)	173.7 (2)	N(2)-Ru(1)-N(3)	97.7 (2)
N(2)-Ru(1)-N(1)	78.8 (2)	N(4)-Ru(1)-N(3)	94.1 (2)
N(4)-Ru(1)-N(1)	91.5 (2)	N(4)-Ru(1)-N(2)	97.0 (2)
N(5)-Ru(1)-N(3)	79.5 (2)	N(5)-Ru(1)-N(1)	95.2 (2)
N(5)-Ru(1)-N(2)	89.8 (2)	N(5)-Ru(1)-N(4)	171.2 (2)
N(6)-Ru(1)-N(3)	86.3 (3)	N(6)-Ru(1)-N(1)	97.7 (2)
N(6)-Ru(1)-N(2)	174.4 (2)	N(6)-Ru(1)-N(4)	78.6 (2)
N(6)-Ru(1)-N(5)	94.9 (2)	O(5)-S(2)-O(4)	114.2 (4)
O(6)-S(2)-O(4)	113.1 (5)	O(6)-S(2)-O(5)	115.0 (5)
C(26)-N(3)-Ru(1)	112.7 (5)	C(21)-N(1)-Ru(1)	115.3 (1)
C(25)-N(1)-Ru(1)	124.6 (1)	C(20)-C(21)-N(1)	115.2 (2)
C(20)-C(21)-C(22)	124.8 (2)	C(16)-N(2)-Ru(1)	125.6 (1)
C(20)-N(2)-Ru(1)	114.4 (1)	N(2)-C(20)-C(21)	115.7 (2)
C(19)-C(20)-C(21)	124.1 (2)	C(6)-N(4)-Ru(1)	115.9 (2)
C(10)-N(4)-Ru(1)	124.0 (2)	C(5)-C(6)-N(4)	114.7 (3)
C(5)-C(6)-C(7)	125.2 (3)	C(11)-N(5)-Ru(1)	123.5 (1)
C(15)-N(5)-Ru(1)	116.1 (1)	C(26)-C(15)-N(5)	115.9 (4)
C(26)-C(15)-C(14)	124.0 (4)	C(1)-N(6)-Ru(1)	124.9 (2)
C(5)-N(6)-Ru(1)	114.8 (2)	N(6)-C(5)-C(6)	115.8 (3)
C(4)-C(5)-C(6)	124.2 (3)	C(15)-C(26)-N(3)	111.2 (6)
C(27)-C(26)-N(3)	111.4 (8)	C(27)-C(26)-C(15)	114.6 (8)

Ru(IV) species containing the deprotonated amine (eq 5). With the use of flash photolysis techniques developed in that work, we have now examined the oxidation of the complexes [(Ru(bpy)₂(d₂-ampy)]²⁺ (Figure 1a) and the diastereoisomers of [Ru(bpy)₂(Meampy)]²⁺ (Figure 1b) over the pH range 0–2 to allow a detailed study of the nature of the final step in the reaction scheme (*k*₆; eq 5). We have also extended the pH range for the study of the oxidation of [Ru(bpy)₂(ampy)]²⁺ from pH 2–4 in a semiquantitative way to test the predicted pH dependence of the mechanistic scheme³ shown in eq 2–5.

Table III gives the observed rate constants for the oxidation of Ru(bpy)₂(ampy)²⁺, Ru(bpy)₂(d₂-ampy)²⁺, and two diastereoisomers of Ru(bpy)₂(Meampy)²⁺ studied over the pH range 0–2 in perchloric acid media and calculated by use of a computer analysis described elsewhere.³

Deuterium Isotope Effect and Deuterium Exchange Studies. Since the final reaction in the scheme (*k*₆; eq 5) is ultimately rate determining in the pH range studied, the relative importance of the electron transfer(s) and deprotonation steps involved in that reaction might be revealed by deuterium isotope effect studies.

From Table III, for the oxidations of [Ru(bpy)₂(ampy)]²⁺ and [Ru(bpy)₂(d₂-ampy)]²⁺, the values of *k*₂–*k*₅ are within experimental error for the two systems. However, the values of *k*₆ (eq 5) are 93 ± 3 and 52 ± 3 s⁻¹ for the nondeuterated and deuterated cases, respectively, giving *k*_H/*k*_D = 1.78 (±0.15). The existence of a primary isotope effect¹⁶ for the reaction shows that the deprotonation at the methylene carbon is rate determining, and its low magnitude implies that the transition state is either linear but asymmetric¹⁹ or nonlinear.²⁰

(16) The double deuteration of the methylene carbon in [Ru(bpy)₂(d₂-ampy)]²⁺ could lead to a secondary isotope effect, but by comparison with studies of deuterium exchange in PhCH₃¹⁷ and PhCH₂NO₂,¹⁸ this would not be expected to be >1.15.

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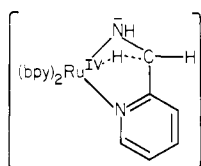
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Table III. Rate Constants for the Scheme given in Eq 3-5 Using Rate Data from Flash Photolysis in Perchlorate Media ($\lambda = 436 \text{ nm}$; $\mu = 1.0$, NaClO_4 ; $T = 24 \pm 1 \text{ }^\circ\text{C}$; all solutions deaerated)^a

complex [Ru(bpy) ₂ (X-Y)] ²⁺ X-Y =	10 ⁻⁶ k ₂ , s ⁻¹	10 ⁻⁹ k ₃ , M ⁻¹ s ⁻¹	10 ⁻⁹ k ₄ , M ⁻¹ s ⁻¹	10 ⁻⁶ k ₅ , M ⁻¹ s ⁻¹	k ₆ , s ⁻¹
ampy ^{b,c}	5.1 ± 0.2	1.3 ± 0.2	1.1 ± 0.2	5.3 ± 0.2	93 ± 3
d ₂ -ampy ^c	5.2 ± 0.2	1.1 ± 0.1	1.1 ± 0.1	4.8 ± 0.3	52 ± 3
Meampy ^c	5.7 ± 0.1	1.4 ± 0.05	1.2 ± 0.1	2.4 ± 0.2	103 ± 2
diastereoisomer $\Delta S(\Delta R)$ Meampy ^c	13 ± 1	1.0 ± 0.1	1.3 ± 0.1	31 ± 2	76 ± 2
diastereoisomer $\Delta R(\Delta S)$					

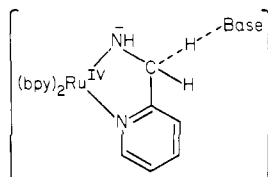
^a All values are averages obtained over pH range 0-2 for 10 different runs; errors quoted are experimental deviations. ^b Values from ref 3. ^c There were two solutions to the numerical analysis, one of which has been eliminated as less reasonable in a chemical sense.

A nonlinear transition state would correspond to intramolecular hydride transfer from the methylene carbon atom to the ruthenium metal center, shown below.



Upon the intramolecular transfer of two electrons, Ru^{IV}-H⁻ becomes Ru^{II}-H⁺, so that elimination of the proton would form the Ru^{II}-imine product. A mechanism of this type has been postulated previously in studies of the oxidation of monodentate amines coordinated to ruthenium, although no kinetic evidence was presented.²¹ It has been suggested²² that in Ru^{II}-H⁺ species, the H⁺ would lie on one of the faces of the coordination octahedron, and studies with molecular models reveal that such a location for the hydride bridge is appropriate in the proposed transient.

A linear asymmetric transition state for the final step (k₆; eq 5) would arise from base-assisted removal of a proton from the methylene carbon atom.



The proton abstraction and the intramolecular transfer of two electrons to the metal center result in the Ru^{II}-imine product.

The chemical oxidation of [Ru(bpy)₂(d₂-ampy)]²⁺ by Ce(IV) was studied in 0.5 M H₂SO₄. Figure 3 shows the proton-decoupled ¹³C NMR spectra of the complexes Ru(bpy)₂(impy)²⁺, Ru(bpy)₂(d₁-impy)²⁺, and the product of the Ce(IV) oxidation of Ru(bpy)₂(d₂-ampy)²⁺ in aqueous (H₂O) solution. A singlet in the fully protonated spectrum of the imine complex (arrowed; Figure 3A) would be expected to become a triplet in the complex deuterated at the methine carbon, due to ²H-¹³C coupling in the latter, but is of such low intensity it cannot be observed (Figure 3B). The product of the Ce(IV) oxidation of the deuterated complex shows the same spectrum (Figure 3C) as the authentic deuterated sample (Figure 3B), so that clearly no hydrogen exchange with the solvent occurs during the oxidation at the methylene carbon. Consequently, if the mechanism involves base-assisted proton removal, each act of deprotonation leads to ligand oxidation. Therefore, either deprotonation and intramolecular electron-transfer are concerted or they are consecutive with the electron transfer being very rapid (i.e., faster than the re-protonation of the carbanion). A concerted process (with OH⁻ as the base) has been postulated for the dehydrogenation of

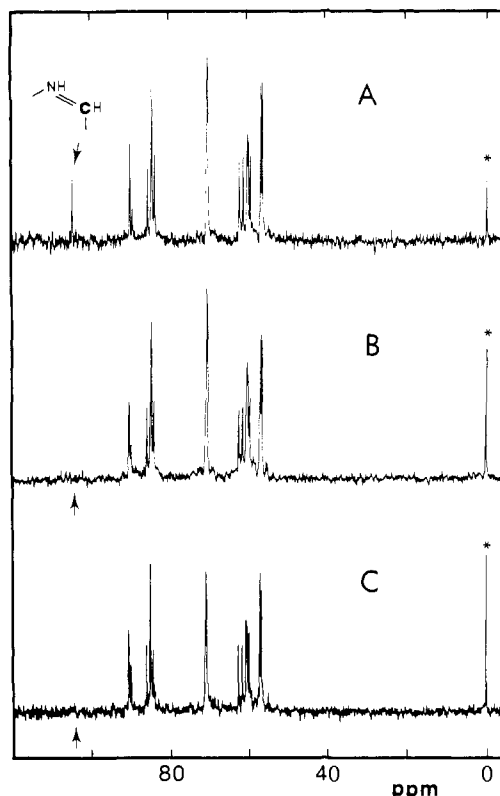


Figure 3. 60-MHz ¹³C NMR spectra of (A) [Ru(bpy)₂(impy)]²⁺; (B) [Ru(bpy)₂(d₁-impy)]²⁺; and (C) the product of the Ce(IV)-promoted oxidation of [Ru(bpy)₂(d₂-ampy)]²⁺ in 0.5 M H₂SO₄. Spectra run in D₂O with *p*-dioxane as internal reference (*). The position of resonance of the imine carbon of [Ru(bpy)₂(impy)]²⁺ is indicated by an arrow in each of the spectra.

ethylenediamine coordinated to Os.²³

For a base-assisted proton-abstraction process, the variation of k_H/k_D with ΔpK_a (where ΔpK_a is the difference between the pK_a values of the acid and the base) is expected to exhibit a maximum at $\Delta pK_a = 0$, and k_H/k_D will become < 2 when $\Delta pK_a > 12$.²⁴ In the present instance where H₂O is the base, pK_a for H₃O⁺/H₂O is -1.74,²⁵ so that k_H/k_D could be < 2 if the pK_a of the acid (i.e. the acidity of the methylene protons in the ampy chelate ring of the Ru(IV) transient) is > 10 . The methylene protons do undergo deuterium exchange in the Ru(II) species [Ru(bpy)₂ampy]²⁺ under vigorous conditions (pH \sim 14; 65 $^\circ\text{C}$ for 36 h), and the pK_a would be expected to be considerably lower in a Ru(IV) complex because of the higher charge, so that a pK_a value of 10 is not unreasonable.

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Both the deuterium exchange and deuterium isotope effect studies are therefore consistent with either of the proton-abstraction schemes, as well as with the hydride transfer proposal.

Oxidation of the Diastereoisomers of [Ru(bpy)₂(Meampy)]²⁺. The nature of the final step (*k*₆; eq 5) of the oxidation was also probed by studying the relative rates of oxidation of the two diastereoisomeric pairs of Ru(bpy)₂(Meampy)²⁺. In one of the two diastereoisomeric pairs, the methine proton removed during the oxidation is axial (and in the other it is equatorial), so that any observed deviations in the value of *k*₆ would reflect the difference between the two geometries. In contrast to the study of the deuterated and nondeuterated ampy complex, the rate constants for the two diastereoisomers may show deviations in both the proton transfer (*k*₂, *k*₃)²⁶ and electron-transfer steps (*k*₄, *k*₅)²⁷ as well as the final rate-determining step of the reaction (*k*₆), where the rate constant for the oxidation of diastereoisomer Δ*S*(Δ*R*) is considerably greater than that for Δ*R*(Δ*S*) (103 ± 3 s⁻¹ cf. 76 ± 2 s⁻¹). Such an observation shows that there is a significant difference in the reactivity of the axial and equatorial methine protons.

Cyclic voltammetric studies of the two diastereoisomers of [Ru(bpy)₂(Meampy)]²⁺ in acetonitrile/0.1 M tetraethylammonium perchlorate and in 5.4 M H₂SO₄ (at -16 °C) media are in accord with the kinetic observations given above. In both instances, the oxidation of diastereoisomer Δ*S*(Δ*R*) is observed to be considerably faster than that of Δ*R*(Δ*S*).

Both general mechanistic proposals are consistent with the observation that the Δ*S*(Δ*R*) diastereoisomer is the more readily oxidized. In this form, the axial orientation of the methine hydrogen H(23) means that it has relatively unhindered access to the nearest face of the coordination octahedron, allowing ready formation of a hydride-bridged transient. Similarly, since the methyl substituent is equatorial in this diastereoisomer, it is closer (than an axial methyl) to its ultimate position in the plane of the Meampy chelate ring.

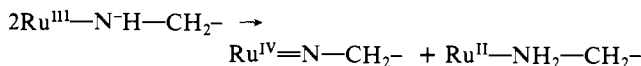
The ligand Meampy is chiral, and the (-)-enantiomer has previously been assigned the *S* configuration.¹² Synthesis of the complex [Ru(bpy)₂((*S*)-(-)-Meampy)]²⁺ using the resolved ligand realized the two internal diastereoisomers Λ(+)-[Ru(bpy)₂((*S*)-(-)-Meampy)]²⁺ and Δ(-)-[Ru(bpy)₂((*S*)-(-)-Meampy)]²⁺. The oxidized ligand Meampy is achiral, so that the [Ru(bpy)₂(Meampy)]²⁺ product of the oxidation reaction may only exhibit chirality about the metal center.

The chemical oxidations by Ce(IV) in 1 M H₂SO₄ of Λ(+)-[Ru(bpy)₂((*S*)-(-)-Meampy)]²⁺ and Δ(-)-[Ru(bpy)₂((*S*)-(-)-Meampy)]²⁺ produce (+)-[Ru(bpy)₂(Meampy)]²⁺ and (-)-[Ru(bpy)₂(Meampy)]²⁺ with equal and opposite rotatory power, identical with that obtained for independently resolved (+)-[Ru(bpy)₂(Meampy)]²⁺ (which can now be assigned the absolute configuration Λ). Thus there is no loss of configurational integrity about the metal center during the oxidation process.

The hydride transfer mechanism involves a seven-coordinate hydride transient, and configurational rearrangement about the metal might be expected to occur during oxidation. For the base-assisted proton abstraction proposal, the configuration about the metal center would be expected to be retained. On the basis of the present chirality experiments, the latter proposal would be preferred, although it is possible that because of the small size of the hydride ion and the brevity of its association with the metal that no rearrangement would result from a hydride transfer process.

Oxidation Studies at Higher pH. An essential feature of the proposed reaction mechanism is that the rate of the reaction should reach a maximum when the pH equals the p*K*_a of the Ru^{III}-(bpy)₂(ampy)³⁺ complex (eq 3; p*K*_a = 2.4³), since the rate of formation of the Ru(IV) intermediate (eq 4) would then be optimal. In order to compare the rate of oxidation at various pH

conditions, a reaction "half-life" was computed which was defined as the time required for the imine concentration to equal one-fourth of the initial concentration of Ru^{III}(bpy)₂(ampy)³⁺ generated by the flash. The pH-"half-life" profile was indeed bell shaped, but the maximum occurred at a pH between 3 and 4 (rather than between pH 2 and 3). Thus the predicted relationship between pH and rate is observed, but only in a qualitative sense. The deviation from the bell-shaped pH-rate profile with a maximum at pH = p*K*_a for eq 3 would seem to show that an alternative mechanism is available when pH > p*K*_a. This alternative path may be the formation of Ru(IV) via the disproportionation reaction



by analogy with the ruthenium aquo/hydroxo/oxo system studied by Thompson and Meyer.²⁸ Such a scheme would become more favorable as the pH increased and may only become significant at pH > 3. Practical difficulties preclude detailed kinetic studies of the present system at pH > 3; however, current studies on the oxidation of the analogous alcohol complex [Ru(bpy)₂(hmpy)]²⁺ and of [Ru(NH₃)₄(ampy)]²⁺ may elucidate this issue.

Conclusions

Our earlier studies³ of the mechanism of the oxidative dehydrogenation of [Ru(bpy)₂ampy]²⁺ revealed the intermediacy of a Ru(IV) species allowing a low-energy pathway for the two-electron ligand oxidation process.

The present work indicates that the final rate-determining step of this reaction (*k*₆; the decay of the Ru(IV) complex of the deprotonated amine to the Ru^{II}-imine product) can occur by *either* (i) the loss of hydrogen from the aliphatic carbon and the intramolecular transfer of two electrons from ligand to metal concomitantly via a hydride transfer from C to Ru *or* (ii) base (solvent water)-assisted proton abstraction of a hydrogen from the carbon atom with a concerted or rapid subsequent transfer of two electrons from ligand to metal. The question of simultaneous two-electron movement or consecutive (though rapid) one-electron transfers remains ambiguous for both proposals.

Both of the above proposals are consistent with the detailed kinetic studies of the oxidation, with deuterium exchange and deuterium isotope effect studies, and with stereochemical considerations. However, the observation of retention of the configurational integrity about the metal during the oxidation process favors the base-assisted proton-abstraction proposal, although the hydride transfer mechanism is by no means excluded.

Unfortunately, studies of general base catalysis of the oxidation process are excluded for this system for practical reasons since the detailed kinetics could only be studied by flash photolysis techniques at pH < 3. Mechanistic studies are in progress²⁸ of the corresponding oxidation of the osmium analogue, [Os(bpy)₂ampy]²⁺. For such a system, the optimal pH range is more compatible with general base catalysis studies, and an osmium hydride species (if formed) may be more readily observed since it would have enhanced stability compared with its ruthenium counterpart.

The semiquantitative study of the pH-rate profile for the oxidation of [Ru(bpy)₂ampy]²⁺ indicates an optimal pH for the rate, as predicted by the mechanistic scheme.

Acknowledgment. We are grateful to the Department of Physical and Inorganic Chemistry, University of Adelaide, for the use of flash photolysis facilities, and particularly to Dr. G. S. Laurence and Mr. H. Novello for their assistance. This work was supported by the Australian Research Grants Scheme.

Registry No. Δ*S*(Δ*R*)-[Ru(bpy)₂(Meampy)]₂O₆·5H₂O, 87306-04-5; [Ru(bpy)₂(Meampy)](PF₆)₂, 87306-05-6; [Ru(bpy)₂(d₂-ampy)](PF₆)₂, 87306-07-8; [Ru(bpy)₂(d₁-impy)](PF₆)₂, 87306-09-0; Ce, 7440-45-1;

(26) p*K*_a values are 2.4 ± 0.1 (Δ*S*(Δ*R*)) and 2.15 ± 0.05 (Δ*R*(Δ*S*)).

(27) Equilibrium constants determined for the electron transfer are 477 (Δ*S*(Δ*R*)) and 42 (Δ*R*(Δ*S*)), so that the Ru^{IV}/III couple for the complex of the deprotonated amine is 0.16 and 0.09 V cathodic of the Ru^{III}/II couple for the complex of the nondeprotonated amine for the respective diastereoisomers.

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[Ru(bpy)₂(Meimpy)]Br₂, 87306-10-3; (+)-[Ru(bpy)₂(Meimpy)](Sb₂(+)-tart₂), 87334-87-0; (+)-[Ru(bpy)₂(Meimpy)](PF₆)₂, 87334-88-1; Δ-(+)-[Ru(bpy)₂((S)(-)-Meampy)]²⁺, 87334-89-2; Δ-(-)-[Ru(bpy)₂((S)(-)-Meampy)]²⁺, 87334-90-5; Ru(bpy)₂(ampy)²⁺, 56889-71-5; deuterium, 7782-39-0.

Supplementary Material Available: Tables of thermal param-

eters for the non-hydrogen atoms (Supplementary Table 1), calculated positional parameters for the hydrogen atoms (Supplementary Table 2), and observed and calculated structure factors (Supplementary Table 3) for the structure determination (16 pages). Ordering information is given on any current masthead page.

Chemical Reaction Paths. 9. Conformational Interconversions of Wilkinson's Catalyst and of Related Square-Planar XM(PR₃)₃ Compounds As Determined from Systematic Analysis of Solid-State Structural Data^{1,2}

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Contribution from the Laboratorium für chemische und mineralogische Kristallographie der Universität, CH-3012 Bern, Switzerland. Received March 1, 1983

Abstract: Structural data on 15 independent molecules of the type XM(PR₃)₃ (X = H⁻, F⁻, CO₃²⁻, Cl⁻; M = Rh(I), Pt(II); R = CH₃, CH₂CH₃, CH(CH₃)₂, C₆H₅) have been retrieved from the Cambridge Structural Database. The conformation of each molecule has been characterized by torsion angles about the M-P bonds, one for each of the three PR₃ groups. The symmetry of the molecules has been analyzed in terms of a group of order 108. The analysis is based on a nonrigid molecular model of three C_{3v}-symmetric rotors PR₃ on a C_{2v}-symmetric frame XMP₃. The 15 sets of 108 symmetry-equivalent conformations are not distributed randomly in the space defined by the three torsion angle coordinates but delineate two distinct pathways of conformational interconversion. The changes in conformation along one of them may be described in terms of a simple mechanical analogy, namely gearing motion of three interlocked cogwheels. Along the other, the analogy is to gearing motion on one side of the central PR₃ group and to gear slippage on the other. The observed changes of the C-P-M bond angles are related to changes in torsion angles about the M-P bonds and so are the changes in the nonplanarity of the XMP₃ frame. The analysis exemplifies possible mechanisms for transmission of structural information from one side of a metal complex to the other as is postulated for asymmetric hydrogenation catalysts. Implications of the analysis on the relationship between structure in the solid state and in solution are also discussed.

1. Introduction

Crystal structure determinations for square-planar molecules of the type XM(PR₃)₃ (Figure 1) include examples with M = Rh(I), Pt(II), X = H⁻, CO₃²⁻, F⁻, Cl⁻, and R = CH₃, CH₂CH₃, CH(CH₃)₂, C₆H₅.³⁻¹³ Such molecules show a bewildering variety of conformations, a wide variation in R-P-M and P-M-P bond angles, and XMP₃ skeletons, which are sometimes planar and sometimes not (Table I). Of course, one could argue that

structural detail in these complexes depends on the chemical nature of R, X, and M and that understanding these structures requires an understanding of the individual interactions in these molecules. We have chosen a different viewpoint, however: All XM(PR₃)₃ molecules are considered to contain the same basic molecular fragment, namely XM(PC₃)₃, which is essentially square planar with X-M-P, P-M-P, and C-P-M bond angles of 80 ± 10°, 100 ± 10°, and 117 ± 13°, respectively. We are not interested in the detailed effects of a particular M, X, or R on an individual molecular structure. We rather want to analyze whether or not there is an overall pattern in the observed conformations and other structural parameters. In this approach the chemical nature of M, X, and R is not important by itself, it merely takes the part of a structural perturbation that serves to probe the flexibility of the molecular fragment of interest.^{14,15} This viewpoint has enabled us to perform a detailed conformational analysis of XM(PR₃)₃ molecules and to delineate the effects of conformational changes on bond angles and the planarity of the XMP₃ skeleton. Indispensable tools for an efficient analysis turn out to be (1) The Cambridge Structural Database (CSD),¹⁶ (2) the concept of symmetry of nonrigid molecules,^{17,18} and (3) statistical methods.¹⁹

(1) Dedicated to Prof. Dr. Jack D. Dunitz on the occasion of his 60th birthday, in remembrance of past collaborative efforts in this series (ref 2b).

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