between the metal and phosphine ligands. It has long been argued that there is synergic interaction between $\sigma$-donor and $\pi$-acceptor effects, that better donation by the ligand leads to better donation by the metal and enhanced $\pi$ acceptance by the ligand. The two components of bonding, in other words, are coupled in the phosphines to a degree. The CO stretching frequency or force constant has been argued to provide a comparative scale of inherent $\pi$ acidities,[41] but it has been effectively argued that these quantities also reflect $\sigma$ effects,[42] perhaps to a lesser extent. The carbonyl stretch may, in fact, most nearly reflect the effective net charge of the metal center. In the systems studied here, $\nu_{CO}$ or the CO stretching force constant increases nearly monotonically with the apparent electronegativities of the phosphorus substituents from cyclohexyl to fluorine. The corresponding increase in $E_{1/2}$ shows, however, the sharp break following methyl described above, suggesting that in these pseudooctahedral $d^6$ complexes the separation between $\sigma$ and $\pi$ effects may be more pronounced in electrochemical measurements than in measurements of the carbonyl stretch. This is consistent with a recent suggestion by Bursten.[7]

Given the trends observed in this report and by Lappert, Stelzer, and coworkers,[40] it seemed reasonable to expect similar behavior for monodentate phosphines in a plot of $E_{1/2}$ vs $\nu_{CO}$. In fact, with use of data obtained for $Cr(CO)_5$(ligand) by Lloyd et al.,[43] *no* such correlation was observed. The $E_{1/2}$ values of these complexes were also plotted against linear free energy parameters for the phosphines, chromium core electron binding energies, and the electronegativities of the substituents on phosphorus. No correlations were found. At the concentrations used for the cyclic voltammetry scans ($5 \times 10^{-4}$ M), ligand dissociation, much more likely for the monodentates than bidentates, may be a significant factor in this lack of correlation.

## Summary

The results of this study demonstrate that bidentate phoshines can be prepared that achieve a very broad range of effects on the electronic properties of transition metals as reflected in oxidation potentials and CO stretching force constants. Together with other recent work they demonstrate that electrochemical methods provide a sensitive technique for the study of bonding in transition-metal carbonyls. The separation into two distinct groups of the bidentate phosphines lends support to the common, but hotly argued, assumption that phosphines do in many instances engage in significant $\pi$ bonding in complexes of this kind or *at least* that more than simple $\sigma$-donor effects must be considered. Perhaps as important, this separation suggests that in some instances (e.g. $R = CH_3$ or $C_6H_{11}$) $\pi$ bonding may *not* be a significant consideration at all.

**Acknowledgment.** We wish to thank Drs. Brisdon and Griffin for the generous donation of the computer program for the force constants calculation. We also wish to thank Dr. Jack Spence for the use of his electrochemical apparatus (NIH Grant GM08347).

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# Oxidation of Isopropylamine and Related Amines Coordinated to Ruthenium. Formation of Monodentate Imine and Alkylideneamido Complexes of Ruthenium

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*Received June 9, 1983*

The chemical and electrochemical oxidation of $[Ru(tpy)(bpy)(NH_2CHR^1R^2)]^{2+}$ ($NH_2CHR^1R^2$ = isopropylamine, cyclohexylamine, or ($\alpha$-methylbenzyl)amine; tpy = 2,2′:6′,2″-terpyridine; bpy = 2,2′-bipyridine) reveals two consecutive two-electron processes. The first oxidation is irreversible and yields the corresponding imine species. The second oxidation produces a complex identified as containing the N-bound alkylideneamide anion. The second process is reversible chemically or electrochemically. The X-ray crystal structure of $[Ru(tpy)(bpy)(NCMe_2)](ClO_4)_3 \cdot H_2O$ (the four-electron oxidation product of the complex containing isopropylamine) shows a linear Ru–N–C linkage with a Ru–N bond length of 1.831 (10) Å, indicating multiple bonding. The complex of formula $C_{28}H_{27}N_6Cl_3O_{13}Ru$ is orthorhombic, space group $Pna2_1$ (No. 33), with cell dimensions $a$ = 22.034 (13) Å, $b$ = 10.689 (6) Å, $c$ = 14.251 (9) Å, and $Z$ = 4.

## Introduction

There has been considerable recent interest in the oxidative dehydrogenation of coordinated amines to the corresponding imines or nitriles.[3-7] Many of these studies have involved ruthenium as the metal center, and while the formation of complexes containing the $\alpha,\alpha'$-diimine moiety has been relatively common,[3,5] complexes containing coordinated simple monodentate imines had not been isolated although their intermediacy had been either observed or inferred in a few cases.[3,4]

We recently communicated[8] aspects of the oxidation of isopropylamine in the complex $[Ru(tpy)(bpy)(NH_2CHMe_2)]^{2+}$,[9] in which two major processes were observed. Initially, a two-electron oxidation yielded the corre-

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(9) Abbreviations for ligands: bpy = 2,2′-bipyridine; tpy = 2,2′:6′,2″-terpyridine; bpic = 4,4′-dimethyl-2,2′-bipyridine.

sponding imine complex (eq 1). This product in turn underwent a further reversible two-electron oxidation to yield a product characterized as $[Ru(tpy)(bpy)(NCMe_2)]^{3+}$ (eq 2).

$$Ru(tpy)(bpy)(NH_2CHMe_2)^{2+} \xrightarrow{-2e^-} Ru(tpy)(bpy)(NH{=}CMe_2)^{2+} + 2H^+ \quad (1)$$

$$Ru(tpy)(bpy)(NH{=}CMe_2)^{2+} \underset{2e^-}{\overset{-2e^-}{\rightleftharpoons}} Ru(tpy)(bpy)(NCMe_2)^{3+} + H^+ \quad (2)$$

The nature of these two oxidation products is significant, since the two-electron oxidation product represents the first isolated monodentate imine complex of ruthenium, and the suspected structure of the four-electron oxidation product is novel in ruthenium chemistry as it was formulated to contain an N-bound isopropylideneamide anion.

We now report details of the synthesis and characterization of these species, together with aspects of their chemical and electrochemical behavior.

## Experimental Section

**Physical Measurements.** Electronic spectra were recorded with a Cary 219 spectrophotometer, and $^1H$ NMR spectra were obtained in $CD_3CN$ or 0.1 M DCl solutions on a JEOL FX-100 NMR spectrometer. The DCl solutions were prepared by stirring a suspension of the $PF_6^-$ salt of the cation in 0.1 M DCl with Dowex 1-X8 anion-exchange resin (200–400 mesh; $Cl^-$ form) and filtering into the NMR tube. The reference signal was obtained with the aid of a capillary containing $Me_4Si$ in $CCl_4$.

Magnetic susceptibilities were measured by the Faraday method. Conductance measurements in $CH_3CN$ were performed with a Wayne Kerr Universal B221 conductance bridge. All meausrements were corrected for solvent background, and data were analyzed by the Feltham method.[10] Comparisons of equivalent conductances and slopes of Feltham plots were made with the 3:1 complex $[Ru(tpy)(bpy)(NO)](PF_6)_3$.

All electrochemical measurements were made vs. the saturated sodium chloride calomel electrode (SSCE) and are uncorrected for junction potentials. Potential control was obtained by using a Utah Electronics 0152 potentiostat, in conjunction with a Utah Electronics 0151 sweep generator for cyclic voltammetry. Cyclic voltammograms were recorded with a Rikadenki RW-101 X-Y recorder. Coulometry was performed with a potentiostat built in the department.

Elemental analyses (C, H, N, P, F) were carried out by the Australian Microanalytical Service, AMDEL, Melbourne, Australia. Ruthenium analyses were performed (0.1 M HCl solutions) on a Varian AA6 atomic absorption spectrometer using an oxidizing acetylene/air flame at $\lambda = 349.9$ nm. $K_2[RuCl_5(OH)_2]$ (Matthey-Garrett) reduced to Ru(II) ($Na_2SO_3$/HCl) was used as a standard.

**Materials.** 4-Picoline (Fluka, Prakt.) was distilled at atmospheric pressure (bp 144–146 °C) immediately before use. For electrochemical studies, acetonitrile (May and Baker, LR) was fractionated and stored over BDH 4A molecular sieves. For conductance measurements, acetonitrile (Merck, Uvasol) was used without purification. Palladium (10% on charcoal; Fluka, puriss.), ruthenium trichloride (Matthey-Garrett), 2,2′-bipyridine, and 2,2′:6′,2″-terpyridine (Sigma), and ceric ammonium sulfate (Fluka, puriss.) were used without purification. Activated alumina (507C) was obtained from Fluka.

**Syntheses.**[9] **4,4′-Dimethyl-2,2′-bipyridine (bpic)** was prepared by a modification of the method reported by Whitten et al.[11] Palladium (10%) on activated charcoal (4 g) was added to freshly distilled 4-picoline (100 mL). The mixture was refluxed under an $N_2$ atmosphere for 3 days. After boiling benzene was added (35 mL), refluxing was continued for 0.5 h. The catalyst was removed from the hot solution by vacuum filtration and the filtrate concentrated to ca. 40 mL. The crude product crystallized from the solution on cooling and was immediately recrystallized from ethyl acetate, yielding 6.91 g of almost pure product (mp 171–173 °C). This product was again recrystallized from ethyl acetate (mp 174 °C).

**Trichloro(terpyridine)ruthenium(III), $[Ru(tpy)Cl_3]$.** Terpyridine (1.17 g, 5 mmol) was stirred with absolute ethanol (500 mL) with gentle heating until dissolution. $RuCl_3{\cdot}3H_2O$ (1.31 g, 5 mmol) was added and the solution refluxed for 3 h with stirring. After the mixture was cooled, the brown precipitate was filtered, washed with ethanol and ether, and air-dried (yield 1.83 g, 83%).

**(Bipyridine)chloro(terpyridine)ruthenium(II) Hexafluorophosphate, $[Ru(tpy)(bpy)Cl]PF_6$.** $[Ru(tpy)Cl_3]$ (1.76 g, 3.98 mmol) was added to a warm solution of 2,2′-bipyridine (0.62 g, 4.0 mmol) in 80% aqueous ethanol (500 mL). The mixture was refluxed for 3 h and then reduced in volume (rotory evaporator) to ca. 100 mL. The solution was diluted with distilled water (500 mL) and the complex sorbed on to a column of SP-Sephadex C25 cation exchanger. On elution with 0.2 M NaCl solution, the major brown band was collected, $NH_4PF_6$ added, and the solution extracted with dichloromethane. The organic extract was dried ($Na_2SO_4$), filtered, and evaporated to dryness. The residue was extracted with acetone (ca. 250 mL) and filtered into stirring ether (ca. 700 mL). The precipitate was collected, washed with ether, and dried in vacuo (yield 2.1 g, 83%). Anal. Calcd for $RuC_{25}H_{19}N_5ClPF_6$: C, 44.7; H, 2.85; N, 10.4. Found: C, 44.6; H, 2.99; N, 10.6.

**Chloro(dimethylbipyridine)(terpyridine)ruthenium(II) hexafluorophosphate, $[Ru(tpy)(bpic)Cl]PF_6$,** was prepared in a manner analogous to that for the corresponding bipyridine complex, in 35% yield.

**(Bipyridine)chloro(terpyridine)ruthenium(II) chloride, $[Ru(tpy)(bpy)Cl]Cl$,** was prepared almost quantitatively from the $PF_6^-$ salt by addition of excess tetra-*n*-butylammonium chloride to a solution of the complex in 2-butanone. After the mixture was cooled in ice, the precipitate was collected, washed with 2-butanone and ether, and dried in vacuo.

**Chloro(dimethylbipyridine)(terpyridine)ruthenium(II) chloride, $[Ru(tpy)(bpic)Cl]Cl$,** was obtained from the $PF_6^-$ salt in a manner similar to that for its bpy analogue.

**(Bipyridine)nitro(terpyridine)ruthenium(II) Hexafluorophosphate Hydrate, $[Ru(tpy)(bpy)NO_2]PF_6{\cdot}H_2O$.** [Ru(tpy)(bpy)Cl]Cl (0.72 g) was dissolved in degassed distilled water (140 mL) by stirring and bubbling with nitrogen for 30 min. Excess sodium nitrite (AR, 0.72 g) was added and the solution heated on a steam bath for 2 h under nitrogen. After the solution was cooled to room temperature, ammonium hexafluorophosphate (0.50 g) was slowly added, and the mixture was then cooled in ice before collection of the orange-red precipitate, which was washed with ice-cold water, 4:1 ether/ethanol, and ether and dried in vacuo (yield 0.80 g, 89%).

The crude product (0.80 g) was recrystallized by dissolving in dichloromethane (800 mL) and filtering: the solution was stirred vigorously as petroleum ether (800 mL, X4) was slowly added. Upon settling, the precipitate was collected, washed with petroleum ether, and dried in vacuo (yield 0.69 g, 87% recovery). Anal. Calcd for $RuC_{25}H_{21}N_6O_3PF_6$: C, 42.9; H, 3.03; N, 12.0. Found: C, 42.3; H, 3.05; N, 12.1.

**(Dimethylbipyridine)nitro(terpyridine)ruthenium(II) hexafluorophosphate, $[Ru(tpy)(bpic)NO_2]PF_6$,** was prepared in 70% yield in a manner analogous to that for the corresponding bpy complex, but with three times the volume of water in the reaction mixture.

**(Bipyridine)nitrosyl(terpyridine)ruthenium(II) Hexafluorophosphate, $[Ru(tpy)(bpy)NO](PF_6)_3$.** $[Ru(tpy)(bpy)NO_2]PF_6{\cdot}H_2O$ (0.64 g, 0.91 mmol) was suspended in methanol (75 mL), hexafluorophosphoric acid (70%; 4 mL) added, and the mixture stirred magnetically for 1 h. The solid was then collected, washed with methanol, and dried in vacuo. The product was reprecipitated by dissolving in acetone (ca. 35 mL) and filtering into stirring ether. The precipitate was collected, washed with ether, and air-dried (yield 0.82 g, 94%).

The complex (0.200 g) was recrystallized by dissolving in dry acetone (8 mL) and filtering. To the stirring filtrate was added dry ether (2 mL). After the mixture was cooled with stirring in a closed vessel, the precipitate was collected, washed with ether, and dried in vacuo (yield 0.135 g, 67%). The IR spectrum (KBr disk) showed $\nu_{NO} = 1968$ cm$^{-1}$. Anal. Calcd for $RuC_{25}H_{19}N_6OP_3F_{18}$: C, 31.4; H, 2.00; N, 8.8. Found: C, 31.6; H, 2.28; N, 8.5.

**(Dimethylbipyridine)nitrosyl(terpyridine)ruthenium(II) hexafluorophosphate, $[Ru(tpy)(bpic)NO](PF_6)_3$,** was prepared in a manner analogous to that for the bpy complex, with use of half the volume of methanol (yield 92%). The crude complex was recrystallized twice by dissolving in the minimum volume of dry acetone (6 mL/100 mg of complex), filtering, adding dry ether (40–50% volume), collecting the precipitate, and washing with dry ether.

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**Aqua(bipyridine)(terpyridine)ruthenium(II) hexafluorophosphate, $[Ru(tpy)(bpy)OH_2](PF_6)_2$,** was prepared by suspending $[Ru(tpy)(bpy)NO](PF_6)_3$ (1.464 g, 1.53 mmol) in distilled water (50 mL) and adding a solution of sodium azide (0.0996 g, 1.53 mmol) in distilled water (30 mL) dropwise over 0.5 h and then a further 20 mL of distilled water. The mixture was stirred for a further 3 h. The solid was filtered off, washed with ice-cold water, and dried in vacuo (yield 1.07 g, 88%).

The complex (1.07 g) was recrystallized by dissolving in hot methanol (100 mL) and filtering. To the stirring filtrate was slowly added diethyl ether (ca. 300 mL). Stirring was continued for 30 min in an ice bath. The precipitate was then collected, washed with diethyl ether, and dried in vacuo (yield 1.00 g, 93% recovery).

**Aqua(dimethylbipyridine)(terpyridine)ruthenium(II) hexafluorophosphate, $[Ru(tpy)(bpic)OH_2](PF_6)_2$,** was prepared in a manner analogous to that for the bpy complex in 93% yield.

**(Amine)(bipyridine)(terpyridine)ruthenium(II) Hexafluorophosphate, $[Ru(tpy)(bpy)_2(NH_2R)](PF_6)_2$, Where $RNH_2$ = Benzylamine ($NH_2Bz$), ($\alpha$-Methylbenzyl)amine ($NH_2$-$\alpha$-MeBz), Isopropylamine ($NH_2CHMe_2$), and Cyclohexylamine ($NH_2$-c-Hx).** $[Ru(tpy)(bpy)(OH_2)](PF_6)$ (200 mg), methanol (3 mL), and the appropriate amine (3 mL) were sealed under $N_2$ in glass ampule and heated at 140 °C for 48 h. When the cooled ampule was opened, methanol was removed by heating and the amine by extraction with ether. The resultant residue was solubilized in water by stirring with Dowex 1-X8 anion-exchange resin (200–400 mesh; $Cl^-$ form) and the cation sorbed on a column of SP-Sephadex C25 cation exchanger. After elution with a 0.1 M sodium acetate/0.01 M sodium hydroxide solution to remove any aqua or chloro species, the amine complex was precipitated by the addition of solid $NH_4PF_6$ washed with ice-cold water and dried in vacuo. Yields were in the range 70–90%. Anal.[12] Calcd for $[Ru(tpy)(bpy)(NH_2Bz)](PF_6)]_2$: C, 43.3; H, 3.18; N, 9.47. Found: C, 42.7; H, 3.24; N, 9.80. Calcd for $[Ru(tpy)(bpy)(NH_2$-$\alpha$-$MeBz)](PF_6)_2$: C, 44.0; H, 3.35; N, 9.32. Found: C, 42.2; H, 3.21; N, 9.78. Calcd for $[Ru(tpy)(bpy)(NH_2CHMe_2)](PF_6)_2$: C, 40.1; H, 3.36; N, 10.0. Found: C, 40.3; H, 3.51; N, 10.0. Calcd for $[Ru(tpy)(bpy)(NH_2$-c-$Hx)](PF_6)_2$: C, 42.3; H, 3.67; N, 9.55. Found: C, 41.8; H, 3.55; N, 9.74.

**(Benzonitrile)(bipyridine)(terpyridine)ruthenium(II) Hexafluorophosphate, $[Ru(tpy)(bpy)(N{\equiv}CPh)](PF_6)_2$.** $[Ru(tpy)(bpy)OH_2](PF_6)_2$ (0.10 g) was dissolved in dry methanol (10 mL), and benzonitrile (2.5 mL) was added. After the mixture was refluxed for 4 h, it was poured into excess stirring ether and cooled in an ice bath. The crude product was then collected by filtration, washed with ether, and dried in vacuo (yield 0.09 g, 81%).

The complex was recrystallized by dissolving in hot absolute ethanol (100 mL) and filtering. The filtrate was cooled slowly to 0 °C, and crystals were allowed to grow for 3 days. The product was then collected, washed with 1:1 ether/absolute ethanol and then with ether, and dried in vacuo (yield 0.04 g, 44% recovery). Anal. Calcd for $RuC_{32}H_{24}N_6P_2F_{12}$: C, 43.5; H, 2.74; N, 9.51. Found: C, 43.5; H, 2.94; N, 9.21.

**(Dimethylbipyridine)(isopropylamine)(terpyridine)ruthenium(II) hexafluorophosphate, $[Ru(tpy)(bpic)(NH_2CHMe_2)](PF_6)_2$,** was prepared and isolated (90%) in a manner similar to that for its bpy analogue.

**(Bipyridine)(isopropylideneamine)(terpyridine)ruthenium(II) Hexafluorophosphate, $[Ru(tpy)(bpy)(NH{=}CMe_2)](PF_6)_2$.** Two methods were used in the synthesis of this species.

(i) $[Ru(tpy)(bpy)(NH_2CHMe_2)](PF_6)_2$ (200 mg) was solubilized in water (5 mL) with use of Dowex 1-X8 anion-exchange resin (200–400 mesh; $Cl^-$ form) and $H_2O_2$ (100 volume; 12 mL) added. The mixture was heated to 60 °C for 30 min with stirring, and the product was precipitated from the filtered solution by $NH_4PF_6$, washed with ice-cold water (slightly acidified with HCl), and dried in vacuo (yield 190 mg, 93%). Anal. Calcd for $RuC_{28}H_{26}N_6P_2F_{12}$: C, 40.2, H, 3.13, N, 10.0; Ru, 12.1. Found: C, 40.8; H, 3.15; N, 10.3; Ru, 12.0.

(ii) $[Ru(tpy)(bpy)NH_2CHMe_2](PF_6)_2$ (0.038 g) in 0.1 M HCl (60 mL) was electrolyzed exhaustively at +0.90 V and then exhaustively at +0.51 V. Solid $NH_4PF_6$ was added to the stirring product solution. The precipitate was collected, washed with acidified ice-cold distilled water, and dried in vacuo (yield 0.028 g, 73%).

The product was redissolved in water and sorbed onto a column of SP-Sephadex C25 cation exchanger. The complex was eluted with 0.5 M NaCl with collection of the first (red) band. Solid $NH_4PF_6$ was added to the stirring eluate, and the resulting precipitate was collected, washed with ice-cold water, and dried in vacuo (79% recovery).

**(Bipyridine)(isopropylideneamido)(terpyridine)ruthenium Hexafluorophosphate, $[Ru(tpy)(bpy)(NCMe_2)](PF_6)_3$.** $[Ru(tpy)(bpy)(NH_2CHMe_2)](PF_6)_2$ (0.10 g) was solubilized in 0.1 M HCl (20 mL) with use of Dowex 1-X8 anion-exchange resin ($Cl^-$). The solution was filtered and electrolyzed exhaustively at +1.00 V ($n$ = 3.8 electrons/Ru). The product was precipitated by the addition of solid $NH_4PF_6$ to the stirring solution. After settling, the precipitate was collected, washed with acidified (HCl) ice-cold distilled water, and dried in vacuo (yield 0.097 g, 83%). Anal. Calcd for $RuC_{28}H_{25}N_6P_3F_{18}$: C, 34.3; H, 2.57; N, 8.56; P, 9.47; F, 34.8. Found: C, 34.0; H, 2.71; N, 8.36; P, 9.10; F, 34.8.

**(Dimethylbipyridine)(isopropylideneamine)(terpyridine)ruthenium(II) hexafluorophosphate, $[Ru(tpy)(bpic)(NH{=}CMe_2)](PF_6)_2$,** was prepared in a manner identical with that detailed for the bpy complex (method ii).

**(Dimethylbipyridine)(isopropylideneamido)(terpyridine)ruthenium Hexafluorophosphate, $[Ru(tpy)(bpic)(N{=}CMe_2)](PF_6)_3$.** $[Ru(tpy)(bpic)(NH_2CHMe_2)](PF_6)_2$ (0.081 g) was stirred in 0.1 M HCl with Dowex 1-X8 anion-exchange resin ($Cl^-$ form) until dissolution. After removal of the resin by filtration, the solution was electrolyzed at +0.81 V and the product sorbed on to a column of SP-Sephadex C25 cation exchanger and eluted with an aqueous 0.5 M NaCl/0.1 M HCl solution. The first ca. 95% of the only band visible was collected. Solid $NH_4PF_6$ was added, and after the mixture was stirred for 5 min the precipitate was collected, washed with acidified ice-cold distilled water, and dried in vacuo (yield 0.071 g).

**Structure Determination of the Four-Electron Oxidation Product $[Ru(tpy)(bpy)(NCMe_2)](ClO_4)_3{\cdot}H_2O$. Collection and Reduction of X-ray Data.** A concentrated solution of $[Ru(tpy)(bpy)(NCMe_2)]^{3+}$ was prepared by stirring the $PF_6^-$ salt with Dowex 1-X8 anion-exchange resin ($Cl^-$ form) in 0.1 M HCl. The solution was filtered, excess $NaClO_4$ added, and the mixture kept under vacuum and protected from light for several days. Initially a small amount of an unidentified green product separated (which was removed by filtration), and after ca. 2 weeks orange crystals of the desired salt were obtained from the solution.

A crystal plate of dimensions 0.035 × 0.15 × 0.40 $mm^3$ was mounted on a glass fiber and coated with cyanoacrylate super glue. Lattice parameters at 27 °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 CAD4 four-circle diffractometer employing graphite-monochromated radiation ($\lambda$ = 0.7107 Å). Crystal data for $C_{28}H_{27}N_6Cl_3O_{13}Ru$ (formula weight 863.02): orthorhombic, space group $Pna2_1$, $C_{2v}^9$ (No. 33), with $a$ = 22.034 (13) Å, $b$ = 10.689 (6) Å, and $c$ = 14.251 (9) Å so that $V$ = 3356.42 $Å^3$; $Z = 4$; $\rho_{calcd}$ = 1.688 g $cm^{-3}$; $\mu$(Mo K$\alpha$) = 7.65 $cm^{-1}$; $F(000)$ = 1744 electrons.

Intensity data were collected in the range $1.2 < \theta < 22°$ for the $+h,+k,+l$ octant with use of an $\omega$-$n\theta/3$ scan, where $n$ (=2) was optimized by profile analyses of a typical reflection. The $\omega$ scan angles and horizontal counter apertures employed were $(1.20 + 0.35 \tan\theta)°$ and $(2.40 + 0.5 \tan\theta)$ mm, respectively. Three standard reflections, monitored after every 58 min of data collection, indicated that by completion of the data collection no decomposition had occurred. Data reduction and application of Lorentz and polarization corrections were performed with use of the program SUSCAD.[13] Absorption corrections were applied; the range of transmission factors was from 0.99 to 0.89. Of the 2602 reflections collected, 597 with $I < 2.5\sigma(I)$ 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 one water molecule. In the refinement by full-matrix least squares

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(12) For some complexes in this study, microanalytical figures were persistently low for C and high for N. In such cases, characterization and purity assessment were made on the basis of electrochemical behavior, NMR spectra, and ion-exchange chromatography.

(13) Programs used included SUSCAD and ABSORB ("Data Reduction Programs for the CAD-4 Diffractometer", University of Sydney, 1975), SHELX ("Program for Crystal Structure Determination", G. M. Sheldrick, 1976), and ORTEP (plotting program by G. K. Johnson).

**Table I.** Final Positional Parameters for Non-Hydrogen Atoms in $[Ru(tpy)(bpy)(N{=}C(CH_3)_2)](ClO_4)_3 \cdot H_2O$ (Fractional Coordinates $\times 10^4$ except for Ru ($\times 10^5$))

| atom | *x* | *y* | *z* |
|---|---|---|---|
| C(1) | 2016 (3) | 878 (6) | 1678 (4) |
| C(2) | 2116 (3) | 151 (6) | 2476 (4) |
| C(3) | 1748 (3) | −884 (6) | 2656 (4) |
| C(4) | 1281 (3) | −1191 (6) | 2038 (4) |
| C(5) | 1181 (3) | −464 (6) | 1240 (4) |
| C(6) | 2499 (3) | 3561 (7) | 273 (5) |
| C(7) | 3022 (3) | 3957 (7) | 739 (5) |
| C(8) | 3218 (3) | 3329 (7) | 1541 (5) |
| C(9) | 2892 (3) | 2304 (7) | 1878 (5) |
| C(10) | 2369 (3) | 1908 (7) | 1412 (5) |
| C(11) | 749 (4) | 4242 (9) | 262 (5) |
| C(12) | 476 (4) | 5253 (9) | 716 (5) |
| C(13) | 390 (4) | 5224 (9) | 1685 (5) |
| C(14) | 578 (4) | 4184 (9) | 2201 (5) |
| C(15) | 851 (4) | 3174 (9) | 1748 (5) |
| C(16) | 1527 (3) | 3036 (7) | −1824 (5) |
| C(17) | 1404 (3) | 3928 (7) | −2513 (5) |
| C(18) | 1037 (3) | 4954 (7) | −2304 (5) |
| C(19) | 794 (3) | 5089 (7) | −1406 (5) |
| C(20) | 917 (3) | 4197 (7) | −717 (5) |
| C(21) | 1934 (3) | 1951 (7) | −1867 (4) |
| C(22) | 2308 (3) | 1649 (7) | −2624 (4) |
| C(23) | 2712 (3) | 649 (7) | −2555 (4) |
| C(24) | 2743 (3) | −48 (7) | −1729 (4) |
| C(25) | 2369 (3) | 254 (7) | −972 (4) |
| C(26) | 318 (6) | 398 (13) | −849 (8) |
| C(27) | −333 (6) | 849 (16) | −742 (12) |
| C(28) | 460 (8) | −819 (15) | −1374 (12) |
| Cl(1) | 2951 (2) | 2033 (4) | 4824 |
| Cl(2) | 3965 (2) | 972 (4) | −106 (4) |
| Cl(3) | 4537 (2) | 6351 (4) | 1361 (3) |
| N(1) | 1549 (3) | 570 (6) | 1060 (4) |
| N(2) | 2173 (3) | 2536 (7) | 610 (5) |
| N(3) | 936 (4) | 3203 (9) | 778 (5) |
| N(4) | 1284 (3) | 3171 (7) | −926 (5) |
| N(5) | 1965 (3) | 1254 (7) | −1041 (4) |
| N(6) | 739 (4) | 1010 (9) | −467 (7) |
| O(1) | 3281 (6) | 1263 (14) | 5458 (9) |
| O(2) | 2579 (5) | 2885 (9) | 5341 (7) |
| O(3) | 3333 (7) | 2704 (12) | 4236 (12) |
| O(4) | 2580 (9) | 1275 (15) | 4316 (12) |
| O(5) | 4292 (5) | 1601 (11) | 10611 (7) |
| O(6) | 3534 (8) | 146 (16) | 10304 (9) |
| O(7) | 4347 (6) | 289 (18) | 9355 (11) |
| O(8) | 3620 (6) | 1839 (11) | −642 (10) |
| O(9) | 4696 (7) | 5053 (12) | 1377 (10) |
| O(10) | 4690 (5) | 6930 (11) | 2227 (8) |
| O(11) | 3914 (5) | 6464 (13) | 1142 (11) |
| O(12) | 4912 (6) | 6902 (12) | 657 (9) |
| O(13) | 1245 (7) | 2403 (15) | 3872 (9) |
| Ru | 13913 (4) | 18674 (8) | 31 (12) |

**Table II.** Selected Bond Lengths (Å) and Bond Angles (deg) for $[Ru(tpy)(bpy)(N{=}C(CH_3)_2)](ClO_4)_3 \cdot H_2O$

Distances

| | | | |
|---|---|---|---|
| N(1)–Ru | 2.076 (7) | O(3)–Cl(1) | 1.388 (16) |
| N(2)–Ru | 2.055 (6) | O(4)–Cl(1) | 1.361 (18) |
| N(3)–Ru | 2.064 (9) | O(5)–Cl(2) | 1.421 (12) |
| N(4)–Ru | 1.937 (7) | O(6)–Cl(2) | 1.423 (17) |
| N(5)–Ru | 2.060 (7) | O(7)–Cl(2) | 1.353 (17) |
| N(6)–Ru | 1.831 (10) | O(8)–Cl(2) | 1.421 (14) |
| N(6)–C(26) | 1.259 (17) | O(9)–Cl(3) | 1.432 (14) |
| C(26)–C(27) | 1.520 (20) | O(10)–Cl(3) | 1.422 (13) |
| C(26)–C(28) | 1.534 (21) | O(11)–Cl(3) | 1.413 (13) |
| O(1)–Cl(1) | 1.421 (14) | O(12)–Cl(3) | 1.426 (14) |
| O(2)–Cl(1) | 1.429 (11) | | |

Angles

| | | | |
|---|---|---|---|
| N(2)–Ru–N(1) | 77.7 (3) | N(3)–Ru–N(1) | 98.9 (3) |
| N(3)–Ru–N(2) | 86.6 (3) | N(4)–Ru–N(1) | 175.4 (3) |
| N(4)–Ru–N(2) | 98.0 (3) | N(4)–Ru–N(3) | 79.0 (3) |
| N(5)–Ru–N(1) | 102.0 (3) | N(5)–Ru–N(2) | 84.3 (3) |
| N(5)–Ru–N(3) | 154.8 (3) | N(5)–Ru–N(4) | 79.1 (3) |
| N(6)–Ru–N(1) | 93.6 (4) | N(6)–Ru–N(2) | 170.2 (4) |
| N(6)–Ru–N(3) | 99.3 (4) | N(6)–Ru–N(4) | 90.8 (4) |
| N(6)–Ru–N(5) | 93.3 (4) | Ru–N(6)–C(26) | 175.2 (10) |
| C(27)–C(26)–N(6) | 120.7 (13) | C(28)–C(26)–C(27) | 120.7 (13) |
| C(28)–C(26)–N(6) | 120.1 (13) | | |

the bipyridyl and terpyridyl ligands were refined as sets of rigid pyridine rings and with anisotropic temperature factors. Their hydrogen atoms were included in the rigid groups at calculated positions (C–H = 1.00 Å). The other non-hydrogen atoms were also refined anisotropically. The alternative centric symmetric space group, *Pnam*, was considered and rejected as the statistics gave mean $|E^2 - 1|$ values in the range 0.68–0.78 (centric requires 0.97 and noncentric 0.74). Also the perchlorate sites cannot be ordered in the centric space group and no evidence for disorder was found. Refinement converged with $R = 0.0357$, at which stage the largest peak in the final difference map was less than 0.3 e Å$^{-3}$. The absolute configuration of the crystal was tested by repeating the last three cycles of refinement with all coordinates inverted through the origin; the higher corresponding $R$ value of 0.0374 found confirmed the initial configuration. A weighing scheme of the type $w = k/(\sigma_2(F_o) + gF_o^2)$ was refined and converged with $k = 0.82$ and $g = 0.0013$. All scattering factors and anomalous terms were taken from ref 14. The final positional parameters are listed in Table I. The thermal parameters are available as supplementary material, as well as the calculated positional parameters for the hydrogen atoms (except for the methyl hydrogens, which were not found, presumably due to free rotation), and the observed and calculated structure factors. Table II contains selected bond lengths and angles, with values omitted for the rigid pyridine rings in the ligands bpy and tpy (C–C, N–C = 1.395 Å).

## Results and Discussion

The aerial oxidation of $[Ru(NH_3)_5(NH_2Bz)]^{2+}$ has previously been reported by Diamond et al.[4] to yield the benzonitrile complex quantitatively via an observed transient, considered to be the imine species. Evidence for a coordinated imine was also inferred by the same authors from the oxidation of $[Ru(NH_3)_5(NH_2\text{-c-Hx})]^{2+}$, where $[Ru(NH_3)_6]^{3+}$ and cyclohexanone were observed as products, presumably formed by imine hydrolysis.

For the analogous complexes in which the five innocent ligands about the metal center are pyridine-type ligands, the resultant extensive back-bonding substantially shifts the potential for the Ru(III)/Ru(II) couples anodically[3] so that the complexes are no longer oxidized aerobically. A spectrophotometric titration of the oxidation of $[Ru(tpy)(bpy)(NH_2Bz)]^{2+}$ by Ce(IV) in 2 M $H_2SO_4$ indicates a quantitative four-electron process yielding a single product. Cyclic voltammetric studies of this oxidation in acetonitrile solution[15] revealed an irreversible oxidation ($E_{p,a}$ = ca. 1.23 V) on the anodic sweep with a reversible couple at more anodic potentials ($E_{1/2}$ = 1.34 V). Coulometry in the same solvent at 1.27 V resulted in the loss of 3.8 electrons/Ru and the formation of a species that was electrochemically and spectroscopically identical with an authentic sample of [Ru(tpy)(bpy)(benzonitrile)]$^{2+}$ ($E_{1/2}$ = 1.34 V, $\lambda_{max}$ = 449 nm in $CH_3CN$). Similar results were obtained in acidic aqueous solution. No evidence was obtained for the intermediacy of the two-electron oxidation product, the imine.

In an attempt to isolate an imine species, the oxidation of a number of $Ru(tpy)(bpy)^{2+}$ complexes of amines of the type $NH_2CHR^1R^2$ was undertaken (viz. ($\alpha$-methylbenzyl)amine, isopropylamine, and cyclohexylamine), for which the formation of the nitrile is precluded. The results for the three complexes are ostensibly identical, and these are detailed below particularly for the isopropylamine complex, $[Ru(tpy)(bpy)(NH_2CHMe_2)]^{2+}$.

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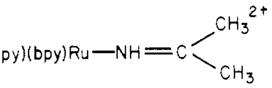
(14) "International Tables for Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. 4, pp 99, 149.

(15) (a) Tetra-*n*-butylammonium hexafluorophosphate used as supporting electrolyte; platinum-bead electrode. (b) Platinum-bead electrode.

A spectrophotometric titration of the oxidation of [Ru(tpy)(bpy)($NH_2CHMe_2$)]$^{2+}$ by Ce(IV) in 2 M $H_2SO_4$ indicates an overall four-electron oxidation consisting of two separate two-electron processes, which are consecutive. Spectra taken during exhaustive electrolyses of the amine complex (platinum-gauze electrode) in 0.1 M HCl (at 0.90 V) and acetonitrile (at 1.10 V) indicate similar results. The overall spectrophotometric and coulometric $n$ values were slightly less than 4.0 (typically 3.7–3.8). The second two-electron process could be reversed electrochemically (coulometry at 0.50 V in 0.1 M HCl, 0.55 V in acetonitrile), with $n$ for the reduction being exactly half the value for the overall oxidation. The two- and four-electron products were isolated by precipitation as the hexafluorophosphate salts and could be purified by ion-exchange chromatography on SP-Sephadex.

**Two-Electron Oxidation Product.** The $^1H$ NMR spectrum (in $CD_3CN$) of the two-electron oxidation product revealed two doublets in the aliphatic region centered at 1.12 and 1.62 ppm, with very small coupling (0.73 and 1.56 Hz, respectively). This spectrum is consistent with the imine formulation



$$[(tpy)(bpy)Ru{-}NH{=}C(CH_3)_2]^{2+}$$

with both methyl groups being split by the adjacent NH=C moiety. On addition of a drop of $D_2O$, each doublet collapses to a singlet, following exchange at the imine NH group.

The visible spectrum of this species (MLCT transition) in 2 M $H_2SO_4$ shows $\epsilon_{474}^{max} = 8000$, compared with $\epsilon_{481}^{max} = 8800$ for the parent isopropylamine complex. For complexes of the Ru(tpy)(bpy)$^{2+}$ moiety, the position of the MLCT band in aqueous solution is virtually insensitive to the nature of the sixth ligand unless it is capable of extensive back-bonding.[16] The small blue shift in the visible spectrum on going from the amine to the imine ligand indicates there is a relatively small amount of back-bonding from Ru(II) to the coordinated monodentate imine, compared with the large effect observed for the conjugated $\alpha,\alpha'$-diimine grouping.[3] A similar conclusion is reached from electrochemical studies. The position of the Ru(II) → Ru(III) oxidation in Ru(tpy)(bpy)X$^{2+}$ complexes is also insensitive to X unless it is capable of extensive back-bonding.[17] In cyclic voltammetry, the waves of the anodic sweep corresponding to the Ru(II) → Ru(III) processes are inseparable (see below), consistent with there being little back-bonding in the case of the coordinated imine. This effect has been observed previously, where the difference between the electrode potentials for the Ru(bpy)$_2{}^{2+}$ complexes of 1,2-diamino-1,1-dimethylpropane and its imine is only 0.07 V in acetonitrile,[3] and the cyclic voltammetric waves of 2-(2-aminoethyl)pyridine and its imine product are indistinguishable:[18] in these cases, a monoimine or nonconjugated diimine (respectively) is seen to be only a weak $\pi$-acceptor.

**Four-Electron Oxidation Product.** Microanalytical data showed the product to have the general formula [Ru(tpy)(bpy)($C_3H_6N$)]$_z$($PF_6$)$_{3z}$, and conductance measurements in acetonitrile by Feltham's method[10] showed the molecular complexity $z = 1$, so that the complex is monomeric. When conductance measurements were undertaken, comparisons were made with [Ru(tpy)(bpy)(NO)]($PF_6$)$_3$. The values of $\Lambda_0$, the equivalent conductance at infinite dilution, were 202 ± 9 $\Omega^{-1}$ cm$^2$ equiv$^{-1}$ for [Ru(tpy)(bpy)(NO)]($PF_6$)$_3$ and 211 ± 6 $\Omega^{-1}$ cm$^2$ equiv$^{-1}$ for [Ru(tpy)(bpy)($C_3H_6N$)]($PF_6$)$_3$. The slopes of the Feltham plots were respectively (1.02 ± 0.05) × $10^3$ and (1.07 ± 0.04) × $10^3$ $\Omega^{-1}$ cm$^2$ dm$^{3/2}$ equiv$^{-3/2}$, demonstrating clearly that the complexes are of the same ion type.

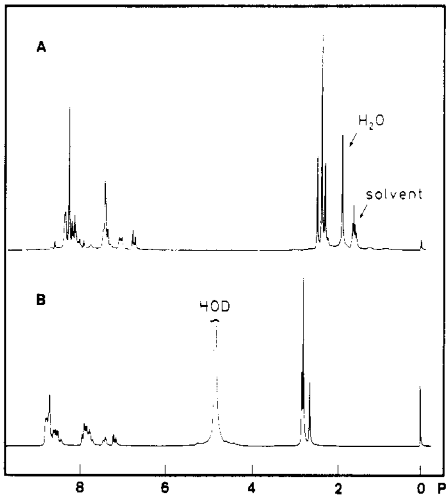


**Figure 1.** $^1H$ NMR (100 MHz) spectra of [Ru(tpy)(bpic)(N=CMe$_2$)]$^{3+}$ in $CD_3CN$ (A) and 0.1 M DCl (B) ($Me_4Si$ external standard).

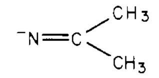
The $^1H$ NMR spectra of the related complex [Ru(tpy)(bpic)($C_3H_6N$)]$^{3+}$ in acetonitrile-$D_3$ and 0.1 M DCl are shown in Figure 1. In the aliphatic region, each spectrum contains a six-proton methyl singlet due to the oxidized isopropylamine ligand ($\delta$ = 2.31 and 2.74, respectively), flanked by two three-proton methyl singlets arising from the dimethylbipyridine ligand.

The complex showed very little absorption in the visible region of the electronic spectrum, consistent with oxidation of the metal center to Ru(III)[19] or Ru(IV).[20] There was significant absorption in the UV region, due primarily to ligand-centered $\pi \rightarrow \pi^*$ transitions, which was sufficiently distinctive to be used as a critical criterion of purity in the synthesis and purification of the complex.

In dry acetonitrile solution, cyclic voltammetric studies showed a reversible couple with $E_{1/2}$ = 0.72 V (Figure 3C).

The magnetic moment measured at 25 °C was $\mu_{eff}$ = 1.2 ± 0.1 $\mu_B$. Since complexes of Ru(II) are invariably diamagnetic, and complexes of Ru(III) and Ru(IV) have generally exhibited magnetic behavior at room temperature consistent with one and two unpaired electrons, respectively,[21] this observation and the cathodic shift in redox potential for these species relative to the potential for the two-electron oxidation product (the isopropylideneamine complex) reflect the unusual nature of the Ru–ligand interaction.

These data were previously interpreted[8] to indicate that the $NCMe_2$ skeleton remained intact during the four-electron oxidation of coordinated isopropylamine and that the most likely structure could be considered (at least in a formal sense) as a Ru(IV) complex containing an N-bound isopropylideneamide anion:



$$^{-}N{=}C(CH_3)_2$$

Consequently, a linear Ru–N–C linkage and Ru–N multiple bonding were predicted.

An X-ray crystal structure analysis has now confirmed that assignment and is discussed below with aspects relating to the unusual magnetic and electrochemical behavior.

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[16] For example, for complexes Ru$^{II}$(tpy)(bpy)X$^{n+}$ in aqueous solution: X = Cl$^-$, $\lambda_{max}$ = 479 nm; $H_2O$, 476 nm; $NH_3$, 482 nm; $NO_2{}^-$, 443 nm; py, 467 nm; benzonitrile, 448 nm.

[17] For example, for complexes Ru(tpy)(bpy)X$^{2+}$ in acetonitrile solution: X = $H_2O$, $E_{1/2}$ = 1.08 V; X = $NH_3$, $E_{1/2}$ = 1.02 V; X = benzonitrile, $E_{1/2}$ = 1.33 V.

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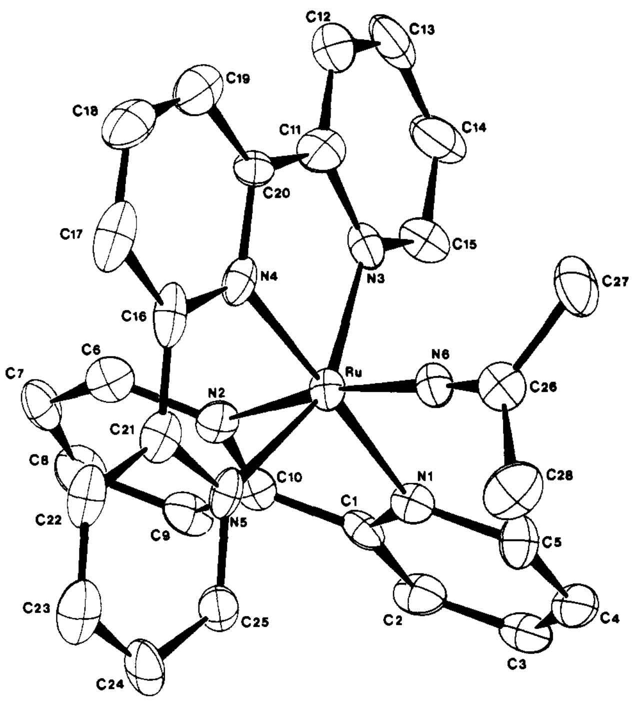

**Figure 2.** ORTEP plot of $[Ru(tpy)(bpy)(N{=}CMe_2)](ClO_4)_3{\cdot}H_2O$ showing atom labeling (25% probability ellipsoids).

**Description of the Structures of the Four-Electron Oxidation Product, $[Ru(tpy)(bpy)(NCMe_2)](ClO_4)_3{\cdot}H_2O$.** A perspective view of the structure of the cation is shown in Figure 2. The cation exhibits metal to pyridyl-type nitrogen ligand distances in the range 2.055–2.076 Å for the bipyridine and noncentral terpyridine rings. These values and the bipyridine chelate bite angles (78.0 (4), 78.5 (5)°) are similar to previous values found for other bipyridine complexes of Ru(II)[22] (where there is $\pi$-back-bonding between a delocalized $\pi^*$(bpy) and $t_{2g}$(Ru) orbitals) and Ru(III)[23] (where there is less extensive $\pi$-overlap[22]). The central ring of the terpyridine ligand has a Ru–N bond length of only 1.937 (7) Å: this contraction of over 0.1 Å of the metal–central N distance is tpy complexes has been noted previously in $Cr(tpy)_2^{3+}$[24] and $Cu(tpy)_2^{2+}$[25] and in mono(terpyridine) complexes of Ga,[26] Zn,[27] and Sn[28] and is presumably due to steric constraint imposed on the ligand by coordination.

The coordinated isopropylideneamide anion has a substantially linear connection to Ru, the angle at N(6) being 175.2 (1.0)°. The angles at the central carbon C(26) sum to exactly 360°, implying $sp^2$ hybridization: the bond length to the nitrogen atom N(6) of 1.259 (17) Å corresponds to a pure C=N double bond.[29] The Ru–N bond length of 1.831 (10) Å is particularly short: while for most Ru(II) complexes the Ru–N distances range from 2.14 Å ($[Ru(NH_3)_6]^{2+}$[30]) to 2.06 Å [$(Ru(bpy)_3]^{2+}$[22]), only for coordinated nitrosyl is a significantly shorter Ru–N bond length observed (average Ru–NO distance 1.74 Å[31]). The analogy between nitrosyl and alkylideneamide anion species is discussed below. In Ru(III) complexes, Ru–N bond lengths are typically ca. 2.10 Å.[23,30]

**The Isopropylideneamido Ligand.** The potential bonding modes of the alkylideneamido (or arylideneamido) ligand, $R_2C{=}N^-$, have been discussed previously.[32] Examples of all possible linkages are known: it may function as a bridging group in polynuclear species,[33] and in mononuclear species, the M–N–C linkage can be either linear[34–36] or bent.[37] The bent linkage requires an $sp^2$-hybridized nitrogen donor atom, whereas for a linear M–N–C assembly, the N may be considered as sp hydridized with considerable $p_\pi(N) \rightarrow d_\pi(M)$ (and possibly $d_\pi(M) \rightarrow \pi^*(C{=}N)$) bonding giving rise to a shortened M–N bond distance. The relative involvements of $p_\pi$–$d_\pi$ and $d_\pi$–$\pi^*$ bonding is often ambiguous,[32] and in most cases the choice of the linear (rather than the bent) linkage could arguably be made by steric requirements.[36]

For the present structure, the nearly linear Ru–N–C linkage and short Ru–N bond indicate multiple bonding. It seems likely this is due to $p_\pi(N) \rightarrow d_\pi(Ru)$ interaction, since there is no indication of the lengthening of the C=N bond arising from $d_\pi \rightarrow \pi^*$ back-donation. Studies with molecular models indicate that the linear linkage would be strongly favored over the bent mode because of steric interaction between the methyl groups and the tpy and bpy rings in the latter case.

The magnetic and electrochemical behaviors of the four-electron oxidation product are consistent with the Ru=N=C formulation. Complexes of Ru(IV) normally exhibit magnetic moments appropriate to two unpaired electrons ($d^4$).[38] For oxoruthenium(IV) species, Moyer and Meyer[20] have rationalized $\mu_{\text{eff}} = 2.94\ \mu_B$ in terms of splitting of the $d_\pi$(Ru) levels into an e* set (destabilized by $p_\pi(O) \rightarrow d_\pi(Ru)$ mixing) and a $b_2$ nonbonding level, assuming approximately $C_{4v}$ symmetry of the $p_\pi$(O) orbitals. For the present complex, only one $p_\pi$(N) orbital overlaps with $d_\pi$(Ru) so that one MO level would be destabilized by $p_\pi(N) \rightarrow d_\pi(Ru)$ mixing, and there would be two essentially nonbonding levels. The complex might therefore be expected to be diamagnetic (as is observed also for Os(IV) complexes of deprotonated ethylenediamine):[39] however, the source of the small residual paramagnetism is unknown.

Similarly, the redox potential for the isopropylideneamido complex is considerably cathodic of the Ru(III)/Ru(II) potential for either the isopropylamine or isopropylideneamine analogue. The stabilization of the "Ru(IV)–isopropylideneamido" species is consistent with substantial charge donation from the lone pair on N to the metal center, in a way analogous to that observed for Os(IV) complexes of deprotonated ethylenediamine[39] and the oxoruthenium(IV) species.[20]

An unsuccessful attempt was made to elucidate aspects of the nature of the Ru–N and N–C bonding using infrared and Raman spectroscopy and the complex containing isopropylamine-$^{15}N$.

As noted earlier, the complexes of the alkylideneamide anions described here and nitrosyl complexes of ruthenium exhibit a number of similarities in physical properties, particularly with respect to shortened Ru–N bond lengths, but

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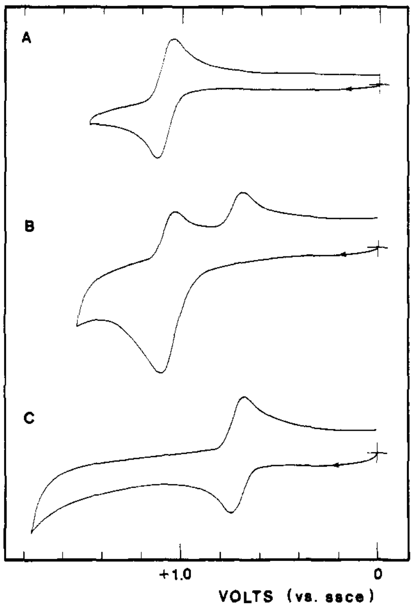

**Figure 3.** Cyclic voltammograms (200 mV/s) of $[Ru(tpy)(bpy)(NH_2CHMe_2)]^{2+}$ (A) and of its two-electron (B) and four-electron (C) oxidation products in acetonitrile solution.[15a]

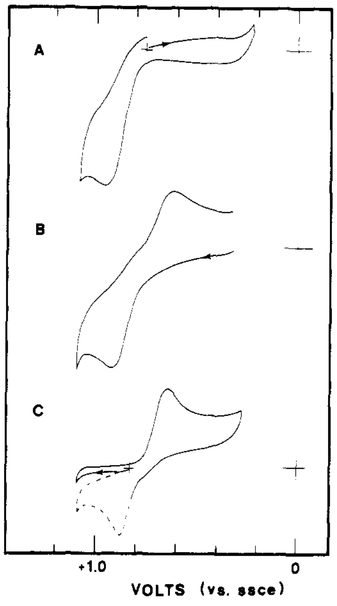

**Figure 4.** Cyclic voltammograms (200 mV/s) of $[Ru(tpy)(bpy)(NH_2CHMe_2)]^{2+}$ (A) and of its two-electron (B) and four-electron (C) oxidation products in 0.1 M HCl.[15b]

also their electronic spectra and redox couples (see below). The simple historical view of nitrosyl complexes as $NO^+$ bound to Ru(II) with extensive metal-to-ligand back-bonding[40] leads to a similar result to the concept of $NCR^1R^2$ bound to Ru(IV) with extensive ligand-to-metal $\pi$-donation. However, as for the nitrosyl complexes where the recognition of extensive covalent interaction has led to the formalism $\{MNO\}^n$ (where $n$ = the total number of electrons associated with the metal d orbitals and $\pi^*$(NO) orbitals),[31] the assignment of oxidation states to the metal and ligating atom for the (alkylideneamido)ruthenium complexes is inappropriate.

**Electrochemical Studies of $[Ru(tpy)(bpy)(NH_2CHMe_2)]^{2+}$ and Its Oxidation Products.** The cyclic voltammograms of $[Ru(tpy)(bpy)(NH_2CHMe_2)]^{2+}$, and of its two- and four-electron oxidation products, are shown in Figures 3 (in acetonitrile) and 4 (in 0.1 M HCl).

In acetonitrile, cyclic voltammetry (200 mV/s) of $[Ru(tpy)(bpy)(NH_2CHMe_2)]^{2+}$ reveals a reversible couple with $E_{1/2}$ = 1.08 V (Figure 3A), associated with the Ru(III)/Ru(II) couple. Under the same experimental conditions, the imine complex shows (Figure 3B) a peak on the anodic sweep ($E_{p,a}$ = 1.10 V), with two peaks ($E_{p,c}$ = 1.03 and 0.69 V) on the subsequent cathodic sweep: the relative magnitudes of these two peaks depended on the sweep rate, the proportion of the peak at more cathodic potential increasing with lower sweep rate. The isopropylideneamido species shows a reversible couple with $E_{1/2}$ = 0.72 V (Figure 3C).

In 0.1 M HCl, the cyclic voltammogram of $[Ru(tpy)(bpy)(NH_2CHMe)]^{2+}$ is completely irreversible with $E_{p,a}$ = 0.90 V, and that of the imine complex is virtually identical (Figure 4A,B). The isopropylideneamido complex shows an irreversible reduction ($E_{p,c}$ = 0.62 V), with an oxidation ($E_{p,a}$ = 0.90 V) on the subsequent anodic sweep (Figure 3C) corresponding to the imine species formed by the initial reduction.

The addition of even small amounts of water to the acetonitrile solutions used in the experiments detailed in Figure 3 gives results consistent with those for aqueous solutions.

Coulometry of the system was identical for the two solvents. Exhaustive oxidation (at 1.10 V in $CH_3CN$; 0.90 V in 0.1 M HCl) showed an overall four-electron oxidation ($n$ = 3.7–3.8). This process consisted of two separate two-electron oxidations (as shown by spectrophotometric analysis during the coulometry), and the second two-electron process could be reversed electrochemically (as discussed earlier).

These electrochemical data reveal that the amine complex exhibits reversible behavior on the cyclic voltammetric time scale consistent with the Ru(III)/Ru(II) couple under anhydrous conditions but that in aqueous solution a rapid subsequent oxidation to the imine species occurs. The amine → imine conversion is irreversible. In aqueous solution, the coordinated imine → isopropylideneamido conversion is rapid and reversible: under anhydrous conditions, the imine complex undergoes ligand oxidation to the isopropylideneamido complex at a rate comparable with the cyclic voltammetric time scale, and although this reaction is reversible, the reverse process is clearly considerably slower. Because of these factors, it is difficult to synthesize electrochemically the imine complex by a two-electron exhaustive electrolysis of the amine species, since their oxidation potentials are very similar and substantial amounts of imine oxidation occur once its concentration builds up. However, since the subsequent two-electron process is reversible, following the four-electron coordinated amine → isopropylideneamide anion oxidation the imine complex may then be regenerated quantitatively by reduction at the appropriate potential.

These observations may be summarized in Scheme I, with the tpy and bpy ligands omitted from the formulas.

**Scheme I**

$$Ru^{II}(NH_2CHMe_2)^{2+} \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} Ru^{III}(NH_2CHMe_2)^{3+} \xrightarrow{-e^-,\,-2H^+}$$

$$Ru^{II}(NH{=}CMe_2)^{2+} \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} Ru^{III}(NH{=}CMe_2)^{3+} \underset{+H^+}{\overset{-H^+\ (fast)}{\rightleftharpoons}}$$

$$Ru^{III}({}^-N{=}CMe_2)^{2+} \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} Ru{=}N{=}CMe_2{}^{3+}$$

The isopropylideneamido complex is relatively stable in acid solution but reverts to the imine under neutral or basic conditions, presumably with concomitant oxidation of water to hydrogen peroxide (no formation of $O_2$ by oxidation of $OH^-$ has been observed). In the presence of oxidizable substrates (particularly alcohols), the isopropylideneamide → isopropylideneamine ligand reduction is relatively rapid. The potential of these cycles in the chemically catalyzed electrochemical oxidation of alcohols, or the formation of $H_2O_2$, may

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be limited however by side reactions to as yet unidentified products.

**Acknowledgment.** We thank Dr. T. G. Appleton (University of Queensland) for recording the 100-MHz $^1H$ NMR spectra. This research was supported by the Australian Research Grants Scheme.

**Registry No.** $Ru(tpy)Cl_3$, 72905-30-7; $[Ru(tpy)(bpy)Cl]PF_6$, 83572-47-8; $[Ru(tpy)(bpic)Cl]PF_6$, 90412-62-7; $[Ru(tpy)(bpy)Cl]Cl$, 90412-63-8; $[Ru(tpy)(bpic)Cl]Cl$, 90412-64-9; $[Ru(tpy)(bpy)NO_2]PF_6$, 90412-65-0; $[Ru(tpy)(bpic)NO_2]PF_6$, 90412-67-2; $[Ru(tpy)(bpy)NO](PF_6)_3$, 90412-68-3; $[Ru(tpy)(bpic)NO](PF_6)_3$, 90412-70-7; $[Ru(tpy)(bpy)OH_2](PF_6)_2$, 90412-71-8; $[Ru(tpy)(bpic)OH_2](PF_6)_2$, 90412-73-0; $[Ru(tpy)(bpy)(NH_2Bz)](PF_6)_2$, 90412-75-2; $[Ru(tpy)(bpy)(NH_2\text{-}\alpha\text{-}MeBz)](PF_6)_2$, 90412-77-4; $[Ru(tpy)(bpy)(NH_2CHMe_2)](PF_6)_2$, 90412-79-6; $[Ru(tpy)(bpy)(NH_2\text{-c-Hx})](PF_6)_2$, 90412-81-0; $[Ru(tpy)(bpy)(N{\equiv}CPh)](PF_6)_2$, 90412-83-2; $[Ru(tpy)(bpic)(NH_2CHMe_2)](PF_6)_2$, 90412-85-4; $[Ru(tpy)(bpy)(NH{=}CMe_2)](PF_6)_2$, 90412-87-6; $[Ru(tpy)(bpy)(N{=}CMe_2)](PF_6)_3$, 79361-73-2; $[Ru(tpy)(bpic)(NH{=}CMe_2)](PF_6)_2$, 90412-89-8; $[Ru(tpy)(bpic)(N{=}CMe_2)](PF_6)_3$, 90412-91-2; $[Ru(tpy)(bpy)(N{=}CMe_2)](ClO_4)_3{\cdot}H_2O$, 90412-93-4; bpic, 1134-35-6; $NO_2^-$, 14797-65-0; $NH_2\text{-}\alpha\text{-}MeBz$, 98-84-0; $NH_2CHMe_2$, 75-31-0; $NH_2\text{-c-Hx}$, 108-91-8; 4-picoline, 108-89-4.

**Supplementary Material Available:** Thermal parameters 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 (13 pages). Ordering information is given on any current masthead page.

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# Electrochemical and Spectroscopic Study of Isomerization, Cross-Redox, and Self-Exchange Reactions in the $[Cr(CO)_3P_3]^{+/0}$ Redox System

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*Received July 27, 1983*

Homogeneous and heterogeneous aspects of the redox couple $[Cr(CO)_3P_3]^{+/0}$ [P = monodentate phosphorus ligand ($P(OMe)_3$, $P(OPh)_3$, $P(OMe)_2Ph$, $PMe_2Ph$)] have been examined by polarographic, voltammetric, synthetic, magnetic, spectroscopic, and other techniques in dichloromethane solution. The tricarbonyl complexes in each oxidation state can exist in both facial (*fac*$^+$ or *fac*$^0$) and meridional (*mer*$^+$ or *mer*$^0$) forms. Under the electrochemical conditions of polarography or voltammetry, parts of the square reaction scheme

$$\begin{tikzcd}
fac^0 \arrow[r, shift left, "\rightharpoonup" description, phantom] \arrow[r, rightharpoonup, shift left] \arrow[d, rightharpoonup, shift left] & fac^+ + e^- \arrow[l, rightharpoonup, shift left] \arrow[d, rightharpoonup, shift left] \\
mer^0 \arrow[r, rightharpoonup, shift left] \arrow[u, rightharpoonup, shift left] & mer^+ + e^- \arrow[l, rightharpoonup, shift left] \arrow[u, rightharpoonup, shift left]
\end{tikzcd}$$

in addition to the cross-redox reaction *fac*$^+$ + *mer*$^0$ ⇌ *fac*$^0$ + *mer*$^+$, are required to explain the electrode processes at both platinum and mercury electrodes. The heterogeneous rates of electron transfer are relatively fast at either electrode. The homogeneous cross-redox reaction enables generation of *mer*-$Cr(CO)_3P_3$ to occur as an intermediate under conditions of oxidative controlled-potential electrolysis or chemical oxidation of *fac*$^0$ isomers. Ultimately, however, the *mer*$^+$ form is the sole product of these oxidation reactions irrespective of whether *fac*$^0$- or *mer*$^0$-$Cr(CO)_3P_3$ is used as the starting complex. These paramagnetic 17-electron cations can be isolated; they are light and heat sensitive and chemically reactive, readily regenerating the *mer*$^0$ complexes. The electron-transfer reaction *mer*$^{+*}$ + *mer*$^0$ ⇌ *mer*$^{0*}$ + *mer*$^+$ has been shown by ESR and NMR measurements to be faster than the cross-redox reaction *fac*$^+$ + *mer*$^0$ ⇌ *fac*$^0$ + *mer*$^+$.

## Introduction

Compounds of the type $Cr(CO)_3P_3$ (P = phosphorus ligand) can exist in facial or meridional isomeric forms.[3] The isomer formed with standard preparative methods usually depends on the nature of the ligand, although in some cases both isomers can be prepared. One-electron oxidation of the 18-electron $Cr(CO)_3P_3$ complex is expected to produce the 17-electron cation $[Cr(CO)_3P_3]^+$, which could also exist in the facial or meridional forms.

To date, the majority of the redox chemistry of the chromium tricarbonyl derivatives has concerned complexes of polycyclic tridentate (P, S, or N donors) or arene ligands that fix the stereochemistry in the facial form.[4-7] In general, the arene tricarbonyl compounds showed a 1-electron reversible oxidation, and in some cases a second 1-electron reversible couple was also observed.[4-8] In the case of the tridentate ligands two reversible 1-electron oxidation processes were reported.[7] A brief report on the oxidation of $Cr(CO)_3L_3$ (L = nitrogen donor) complexes is also available,[8] but no discussion as to whether structural changes occur on oxidation was given. The mere observation of apparently reversible electrochemical behavior does not prove that there is no structural change accompanying electron transfer as detailed

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