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# Redox regulation in ruthenium complexes containing β-diketonate ligands and 2,6-bis(*N*-pyrazolyl)pyridine and its methyl-substituted derivatives

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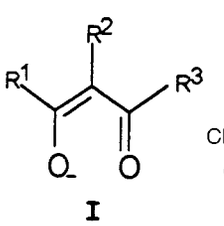
A new family of complexes of the general formula [Ru(Me$_n$bpp)(R$_2$mal)L] has been prepared, where Me$_n$bpp is 2,6-bis(*N*-pyrazolyl)pyridine or a methyl-substituted derivative ($n$ = 0, 2, or 4), R$_2$mal is a 1,3-substituted β-diketonate, and L is chloride or an *N*-heterocycle ligand. The bidentate β-diketonate ligand substantially lowers the Ru(III/II) potentials relative to analogous polypyridyl complexes. The synthetic scheme presented here can be used to prepare a wide variety of complexes for which the Ru(III/II) couple can be systematically and rationally tuned over a range of 600 mV by varying the number of methyl groups on the 2,6-bis(*N*-pyrazolyl)pyridine ligand, and/or the substituents on the β-diketonate ligands. Substitution at the sixth coordination site allows for further synthetic versatility of these complexes, including bridging ligands, such that these complexes may serve as precursors to bimetallic complexes.

## Introduction

The rich redox chemistry of ruthenium complexes is well-documented. In particular, ruthenium(II) complexes have been extensively investigated as redox catalysts[1] and as model complexes for the study of electron-transfer reactions.[2] The choice of ruthenium for these studies is based in part on the extensive methodology which has been developed for the synthesis of these complexes, and much of this work has utilized one of two ligand systems: ammine and polyamine ligands,[3a] or pyridine and polypyridine ligands.[3b]

The chemistry of ruthenium-ammine complexes was largely developed by Taube.[3a] In general, these complexes tend to exhibit reversible Ru(III/II) couples at relatively low potentials, but are hindered by limited stability. The ruthenium-polypyridine complexes are generally more stable than the analogous amine complexes; however, the π-acidity of the polypyridine ligands tends to increase the Ru(III/II) couples relative to amine complexes, which can compromise the utility of these complexes in easily oxidized solvents such as water.

The β-diketonates (Structure I) are a family of anionic,

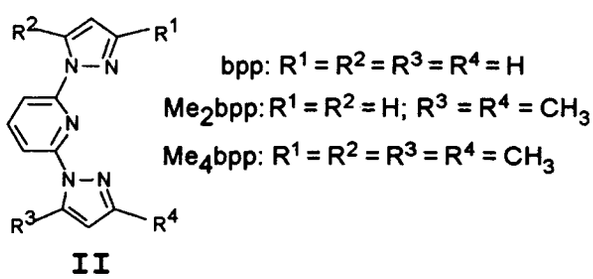


I

$Me_2$mal: $R^1 = R^3 = CH_3$, $R^2 = H$
$Ph_2$mal: $R^1 = R^3 = Ph$, $R^2 = H$
$t$-$Bu_2$mal: $R^1 = R^3 = t$-Bu, $R^2 = H$
$CH_3CF_3$mal: $R^1 = CH_3$, $R^3 = CF_3$, $R^2 = H$
$(CF_3)_2$mal: $R^1 = R^3 = CF_3$, $R^2 = H$

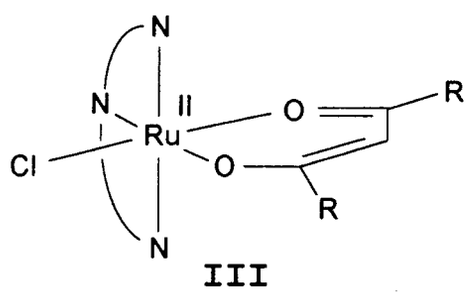
bidentate ligands which form stable chelates with a wide variety of metal ions.[4] The redox potentials of a number of $[Ru(bpy)_n(R_2mal)_{3-n}]^{(n-1)+}$ complexes have been measured and were shown to depend significantly on the substituents of the β-diketonate ligands.[5] In spite of the potential for redox regulation, synthetic procedures for exploiting β-diketonate ligands to attain more versatile ruthenium complexes have been slow to appear.[6]

We have developed a new family of synthetically versatile ruthenium complexes based on β-diketonate ligands and 2,6-bis(*N*-pyrazolyl)pyridine and its methyl-substituted derivatives[7,8] (Structure II). The general structure of these complexes is shown in Structure III, where three coordination sites are occupied by the planar tridentate 2,6-bis(*N*-pyrazolyl)pyridine ligand, and two sites are occupied by the β-diketonate ligand. The complexes exhibit reversible Ru(III/II) couples at low potentials relative to analogous polypyridyl complexes. Furthermore, these complexes are more stable than ruthenium pentaammine complexes due to the chelating nature of the bidentate β-diketonate and tridentate bpp base ligands.



bpp: $R^1 = R^2 = R^3 = R^4 = H$
$Me_2$bpp: $R^1 = R^2 = H$; $R^3 = R^4 = CH_3$
$Me_4$bpp: $R^1 = R^2 = R^3 = R^4 = CH_3$

II



III

The synthetic preparations of complexes with the general formulae Ru(Me$_n$bpp)(R$_2$mal)Cl and [Ru(Me$_n$bpp)(R$_2$mal)L]$^+$ along with their electrochemical and spectroscopic properties are reported. The results suggest that the electron density of the ruthenium center in the Ru(Me$_n$bpp)(R$_2$mal)Cl complexes is strongly influenced by the electron-donating/withdrawing nature of the substituents on both the β-diketonate and the bpp base ligands. Hence, the redox potentials of these complexes can be fine-tuned by varying the ligand substituents. The remaining coordination site is occupied by a chloride ion that can be conveniently substituted by a wide variety of ligands.

## Experimental

### Materials

Reagent grade solvents and chemicals were used in the synthesis of the ruthenium complexes. Acetonitrile used in electrochemical measurements was distilled from $P_2O_5$ and stored over 4 Å molecular sieves. Tetra-*n*-butylammonium hexafluorophosphate (TBAH) was synthesized by a literature procedure and recrystallized two times from aqueous ethanol.[9] The chromatographic separations were carried out using neutral aluminium oxide 80–200 mesh (Aldrich) and reagent grade solvents.

### Measurements

Electrochemical measurements were obtained on a Princeton Applied Research Model 173 potentiostat equipped with a Model 175 Linear Programmer. Cyclic voltammograms were recorded on a Houston Instrument Model 200 x-y recorder. The working electrodes were a platinum disk electrode (Bioanalytical Systems) for electrochemistry carried out in organic solvents and a glassy carbon electrode for electrochemistry carried out in aqueous conditions. The working electrodes were polished routinely with 0.05 micron alumina micropolish. A platinum wire sealed in a glass tube served as the auxiliary electrode. The half-wave potential was calculated using the equation $E_{1/2} = (E_{p,a} + E_{p,c})/2$, where $E_{p,a}$ and $E_{p,c}$ are the peak anodic and peak cathodic potentials, respectively. Potentials were measured *vs*. a saturated sodium calomel electrode (SSCE). The SSCE reference electrode was periodically checked against the ferrocenium/ferrocene couple.[10] Electronic spectra were measured on a Milton Roy 1201 Spectrophotometer using 1 cm optical cells.

### Syntheses

The ligands bpp, $Me_2$bpp, and $Me_4$bpp, and the complexes Ru(bpp)$Cl_3$, Ru($Me_2$bpp)$Cl_3$, and Ru($Me_4$bpp)$Cl_3$ were prepared by published procedures.[7,8] All of the parent β-diketones were purchased from Aldrich.

**Ru(bpp)(*t*-$Bu_2$mal)Cl.** Ru(bpp)$Cl_3$ (200 mg, 0.49 mmol), triethylamine (0.75 mL, 5.4 mmol), and 2,2,6,6-tetramethyl-3,5-heptanedione (0.81 mL, 3.9 mmol) were combined in 120 mL of absolute ethanol and heated at reflux under $N_2$ for 2 hours. The reaction mixture was allowed to cool, and the solvent was removed by rotary evaporation. The solid residue was redissolved in methylene chloride (120 mL) and filtered to remove insolubles. A portion of the methylene chloride (20%) was removed by rotary evaporation, and hexanes were added; this process was repeated on an alternating basis until the product precipitated, which was isolated by suction filtration. The product was washed with water, washed/dried with anhydrous diethyl ether, and dried under vacuum (119 mg, yield 46%) (Found: C, 48.92; H, 5.22. Calculated for [Ru($C_{11}H_9N_5$)($C_{11}H_{19}O_2$)Cl]·$\frac{1}{2}H_2O$: C, 48.93; H, 5.41%).

**Ru($Me_2$bpp)(*t*-$Bu_2$mal)Cl.** Ru($Me_2$bpp)$Cl_3$ (200 mg, 0.46 mmol), triethylamine (0.70 mL, 5.0 mmol), and 2,2,6,6-tetramethyl-3,5-heptanedione (0.77 mL, 3.7 mmol) were combined in 120 mL of absolute ethanol and heated at reflux under $N_2$ for 3–4 hours. The solid product was isolated from methylene chloride/hexanes as described above for Ru(bpp)(*t*-$Bu_2$mal)Cl. A 90 mg portion of the crude product was dissolved in 20 mL of chloroform and filtered. The filtrate was placed on a rotary evaporator to remove the chloroform. The solid residue was dissolved in 2 mL of methylene chloride and added dropwise to anhydrous diethyl ether with stirring. The product was isolated by suction filtration, dried under vacuum (30 mg) (Found: C, 50.12; H, 5.51. Calculated for [Ru($C_{13}H_{13}N_5$)($C_{11}H_{19}O_2$)Cl]·$H_2O$: C, 49.95; H, 5.94%).

**Ru($Me_4$bpp)(*t*-$Bu_2$mal)Cl.** Ru($Me_4$bpp)$Cl_3$ (400 mg, 0.86 mmol), triethylamine (1.3 mL, 9.4 mmol), and 2,2,6,6-tetramethyl-3,5-heptanedione (1.4 mL, 6.9 mmol) were combined in 120 mL of absolute ethanol and heated at reflux under $N_2$ for 2.5 hours. The solid product was isolated from methylene chloride/hexanes as described above for Ru(bpp)(*t*-$Bu_2$mal)Cl, yielding 460 mg of crude product. A 5 cm plug of alumina was prepared in a 2.5 cm diameter glass column with 1% methanol/methylene chloride. A 0.2 g portion of the crude product was dissolved in 150 mL of methylene chloride and pipetted onto the column. The methanol content of the eluent was gradually increased from 1% to 2%. The first band (brown/maroon) was collected and the solvent was removed by rotary evaporation. The solid residue was redissolved in methylene chloride. The methylene chloride was removed and hexanes added on an alternating basis, precipitating the product, which was isolated by suction filtration. The product was washed/dried with anhydrous diethyl ether and dried under vacuum (80 mg, yield 39%) (Found: C, 53.19; H, 6.17. Calculated for [Ru($C_{15}H_{14}N_5$)($C_{11}H_{19}O_2$)Cl]: C, 53.19; H, 6.18%).

**Ru(bpp)($Me_2$mal)Cl.** Ru(bpp)$Cl_3$ (420 mg, 1.0 mmol), triethylamine (1.5 mL, 11 mmol), and acetylacetone (0.83 mL, 8.0 mmol) were combined in 250 mL of absolute ethanol and heated at reflux under $N_2$ for 2 hours. The solid product was isolated from methylene chloride/hexanes as described above for Ru(bpp)(*t*-$Bu_2$mal)Cl (313 mg, yield 69%) (Found: C, 41.53; H, 3.46. Calculated for [Ru($C_{11}H_9N_5$)($C_5H_7O_2$)Cl]·$H_2O$: C, 41.34; H, 3.90%).

**Ru($Me_2$bpp)($Me_2$mal)Cl.** Ru($Me_2$bpp)$Cl_3$ (210 mg, 0.46 mmol), triethylamine (0.65 mL, 4.8 mmol) and acetylacetone (0.36 mL, 3.5 mmol) were combined in 120 mL of absolute ethanol and heated at reflux under $N_2$ for 2 hours. The solid product was isolated from methylene chloride/hexanes as described above for Ru(bpp)(*t*-$Bu_2$mal)Cl (130 mg, yield 61%) (Found: C, 45.34; H, 3.46. Calculated for [Ru($C_{13}H_{13}N_5$)($C_5H_7O_2$)Cl]: C, 45.52; H, 4.24%).

**Ru($Me_4$bpp)($Me_2$mal)Cl.** Ru($Me_4$bpp)$Cl_3$ (350 mg, 0.70 mmol), triethylamine (1.0 mL, 7.7 mmol), and acetylacetone (0.58 mL, 5.6 mmol) were combined in 110 mL of absolute ethanol and heated at reflux under $N_2$ for 2 hours. The solid product was isolated from methylene chloride/hexanes as described above for Ru(bpp)(*t*-$Bu_2$mal)Cl. A small plug of alumina was prepared in a glass column using 10% acetone/methylene chloride. The crude product was dissolved in 10% acetone/methylene chloride and placed on the column. The first band (maroon) was collected. The 10% acetone/methylene chloride was removed by rotary evaporation and hexanes added on an alternating basis, precipitating the product. The solid was isolated by suction filtration, washed/dried with anhydrous diethyl ether, and dried under vacuum (210 mg, yield 60%) (Found: C, 47.65; H, 4.85. Calculated for [Ru($C_{15}H_{17}N_5$)($C_5H_7O_2$)Cl]: C, 47.76; H, 4.61%).

**Ru(bpp)($Ph_2$mal)Cl.** Ru(bpp)$Cl_3$ (100 mg, 0.24 mmol), triethylamine (0.34 mL, 2.6 mmol), and dibenzoylmethane (430 mg, 1.9 mmol) were combined in 60 mL of absolute ethanol and heated at reflux under $N_2$ for 2 hours. The solid product was isolated from methylene chloride/hexanes as described above for Ru(bpp)(*t*-$Bu_2$mal)Cl (80 mg, yield 58%) (Found: C, 54.63; H, 3.54. Calculated for [Ru($C_{11}H_9N_5$)($C_{15}H_{11}O_2$)Cl]: C, 54.69; H, 3.53%).

**Ru($Me_2$bpp)($Ph_2$mal)Cl.** Ru($Me_2$bpp)$Cl_3$ (100 mg, 0.23 mmol), triethylamine (0.35 mL, 2.5 mmol), and dibenzoylmethane (410 mg, 1.8 mmol) were combined in 60 mL of absolute ethanol and heated at reflux under $N_2$ for 2 hours. The solid product was isolated from methylene chloride/hexanes as

described above for Ru(bpp)(*t*-$Bu_2$mal)Cl (120 mg, yield 87%) (Found: C, 56.02; H, 4.07. Calculated for [Ru($C_{13}H_{13}N_5$)-($C_{15}H_{11}O_2$)Cl]: C, 56.14; H, 4.04%).

**Ru($Me_4$bpp)($Ph_2$mal)Cl.** Ru($Me_4$bpp)$Cl_3$ (110 mg, 0.24 mmol), triethylamine (0.36 mL, 2.6 mmol), and dibenzoylmethane (420 mg, 1.9 mmol) were combined in 60 mL of absolute ethanol and heated at reflux under $N_2$ for 1.5 hours. The solid product was isolated from methylene chloride/hexanes as described above for Ru(bpp)(*t*-$Bu_2$mal)Cl (Found: C, 57.31; H, 4.45. Calculated for [Ru($C_{15}H_{17}N_5$)($C_{15}H_{11}O_2$)Cl]: C, 57.46; H, 4.50%).

**Ru(bpp)(Me,$CF_3$mal)Cl.** Ru(bpp)$Cl_3$ (99 mg, 0.24 mmol), triethylamine (0.36 mL, 2.6 mmol), and 1,1,1-trifluoro-2,4-pentanedione (0.24 mL, 1.9 mmol) were combined in 60 mL of absolute ethanol and heated at reflux under $N_2$ for 3 hours. The solid product was isolated from methylene chloride/hexanes as described above for Ru(bpp)(*t*-$Bu_2$mal)Cl (38 mg, yield 32%) (Found: C, 38.31; H, 2.63. Calculated for [Ru($C_{11}H_9N_5$)($C_5H_4$-$F_3O_2$)Cl]: C, 38.37; H, 2.62%).

**Ru($Me_2$bpp)(Me,$CF_3$mal)Cl.** Ru($Me_2$bpp)$Cl_3$ (98 mg, 0.22 mmol), triethylamine (0.34 mL, 2.4 mmol), and 1,1,1-trifluoro-2,4-pentanedione (0.21 mL, 1.8 mmol) were combined in 60 mL of absolute ethanol and heated at reflux under $N_2$ for 2 hours. The solid product was isolated from methylene chloride/hexanes as described above for Ru(bpp)(*t*-$Bu_2$mal)Cl. A 12 cm × 1.5 cm alumina column was prepared with methylene chloride. A 30 mg portion of the crude product was dissolved in 80 mL of methylene chloride and transferred to the alumina column. Elution with 0.5% methanol/methylene chloride gave a red/brown band, which was isolated, and the solvent was removed by rotary evaporation. The residue was collected with 3 mL of methylene chloride and added dropwise to anhydrous diethyl ether with stirring, precipitating the product, which was isolated by suction filtration (10 mg) (Found: C, 40.16; H, 3.19. Calculated for [Ru($C_{13}H_{13}N_5$)($C_5H_4F_3O_2$)Cl]·1/2$H_2O$: C, 40.19; H, 3.37%).

**Ru($Me_4$bpp)(Me,$CF_3$mal)Cl.** Ru($Me_4$bpp)$Cl_3$ (100 mg, 0.22 mmol), triethylamine (0.34 mL, 2.4 mmol), and 1,1,1-trifluoro-2,4-pentanedione (0.21 mL, 1.8 mmol) were combined in 60 mL of absolute ethanol and heated at reflux under $N_2$ for 2 hours. The solid product was isolated from methylene chloride/hexanes as described above for Ru(bpp)(*t*-$Bu_2$mal)Cl (54 mg, yield 44%) (Found: C, 43.23; H, 3.81. Calculated for [Ru($C_{15}H_{17}N_5$)($C_5H_4F_3O_2$)Cl]: C, 43.13; H, 3.80%).

**Ru(bpp)(($CF_3$)$_2$mal)Cl.** Ru(bpp)$Cl_3$ (260 mg, 0.63 mmol), triethylamine (0.97 mL, 6.9 mmol), and 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (0.71 mL, 5.0 mmol) were combined in 100 mL of absolute ethanol and heated at reflux under $N_2$ for 2 hours. The solid product was isolated from methylene chloride/hexanes as described above for Ru(bpp)(*t*-$Bu_2$mal)Cl yielding 250 mg. The product was purified by dissolving an 80 mg portion in 0.2% methanol/methylene chloride, which was transferred to a 15 cm × 2.5 cm alumina column prepared with 0.2% methanol/methylene chloride. The eluent was 0.5% methanol/methylene chloride. The first band (purple/maroon) was collected, and the solvent was removed by rotary evaporation. The residue was redissolved in 100 mL of methylene chloride. The methylene chloride was removed by rotary evaporation and hexanes were added on an alternating basis, precipitating the product, which was isolated by suction filtration. The product was washed/dried with anhydrous diethyl ether, and dried under vacuum (52 mg, yield 46%) (Found: C, 34.78; H, 1.85. Calculated for [Ru($C_{11}H_9N_5$)($C_5HF_6O_2$)Cl]: C, 34.64; H, 1.82%).

**Ru($Me_2$bpp)(($CF_3$)$_2$mal)Cl.** Ru($Me_2$bpp)$Cl_3$ (270 mg, 0.60 mmol), triethylamine (0.92 mL, 6.6 mmol), and 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (0.68 mL, 4.8 mmol) were combined in 120 mL of absolute ethanol and heated at reflux under $N_2$ for 2 hours. The solid product was isolated from methylene chloride/hexanes as described above for Ru(bpp)(*t*-$Bu_2$mal)Cl, yielding 260 mg. A 90 mg portion of the crude product was dissolved in 200 mL of 0.1% methanol/methylene chloride and placed on an alumina column (10 cm × 2.5 cm) prepared with 0.1% methanol/methylene chloride. The eluent was 0.4% methanol/methylene chloride. The first band (maroon) was collected, and the solvent was removed by rotary evaporation. The residue was redissolved in methylene chloride. The methylene chloride was removed by rotary evaporation and hexanes were added on an alternating basis, precipitating the product, which was isolated by suction filtration. The product was washed/dried with anhydrous diethyl ether, and dried under vacuum (30 mg, yield 25%) (Found: C, 37.18; H, 2.44. Calculated for [Ru($C_{13}H_{13}N_5$)($C_5HF_6O_2$)Cl]: C, 37.09; H, 2.42%).

**Ru($Me_4$bpp)(($CF_3$)$_2$mal)Cl.** Ru($Me_4$bpp)$Cl_3$ (250 mg, 0.53 mmol), triethylamine (0.81 mL, 5.8 mmol), and 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (0.60 mL, 4.2 mmol) were combined in 120 mL of absolute ethanol and heated at reflux under $N_2$ for 2 hours. The solid product was isolated from methylene chloride/hexanes as described above for Ru(bpp)(*t*-$Bu_2$mal)Cl, yielding 240 mg. A 60 mg portion of the crude product was dissolved in 170 mL of 0.2% methanol/methylene chloride and transferred to an alumina column prepared with 0.2% methanol/methylene chloride. The eluent was 0.5% methanol/methylene chloride. The first band (dark maroon) was collected, and the solvent was removed by rotary evaporation. The solid residue was redissolved in 100 mL of methylene chloride. The methylene chloride was removed by rotary evaporation and hexanes added on an alternating basis, precipitating the product which was isolated by suction filtration. The product was washed/dried with anhydrous diethyl ether, and dried under vacuum (20 mg, yield 33%) (Found: C, 39.46; H, 3.02. Calculated for [Ru($C_{15}H_{17}N_5$)($C_5HF_6O_2$)Cl]: C, 39.32; H, 2.97%).

**[Ru(bpp)($Me_2$mal)(4,4′-bpy)]($PF_6$).** Ru(bpp)($Me_2$mal)Cl (310 mg, 0.69 mmol) and 4,4′-bipyridine (690 mg, 4.4 mmol) were combined in 200 mL of 30% ethanol/water and heated at reflux under $N_2$ for 6 hours. The reaction mixture was allowed to cool. Most of the ethanol was removed from the reaction mixture on a rotary evaporator. Ammonium hexafluorophosphate (500 mg, 3.1 mmol) was dissolved in 3 mL of water and added to the reaction mixture, precipitating the product, which was isolated by suction filtration. The solid was washed with water and washed/dried with anhydrous diethyl ether. The crude product was purified on a neutral alumina column prepared with 1:1 acetonitrile/toluene. The first band (red-orange) was collected, and the solvent was removed by rotary evaporation. The solid residue was dissolved in 4 mL of acetonitrile and added dropwise to anhydrous diethyl ether with stirring, precipitating the product, which was isolated by suction filtration and dried under vacuum (240 mg, yield 49%) (Found: C, 43.81; H, 3.44. Calculated for [Ru($C_{11}H_9N_5$)($C_5H_7O_2$)($C_{10}H_8N_2$)]($PF_6$): C, 43.83; H, 3.40%).

**[Ru(bpp)($Me_2$mal)(ImH)]($PF_6$).** Ru(bpp)($Me_2$mal)Cl (200 mg, 0.45 mmol) and imidazole (190 mg, 2.8 mmol) were combined in 160 mL of 30% ethanol/water and heated at reflux under $N_2$ for 3.5 hours. The reaction mixture was allowed to cool. Approximately ten drops of 60% $HPF_6$ were added, followed by the addition of 300 mg of $NH_4PF_6$ dissolved in minimal water. The resulting precipitate was isolated by suction filtration. The solid was washed with water (acidified with $HPF_6$) and washed/dried with anhydrous diethyl ether. A small plug of acidic alumina was prepared with 0.5% methanol/

methylene chloride. The crude product was dissolved in 0.5% methanol/methylene chloride, and was rapidly passed through the alumina plug while increasing the concentration of methanol to 1%. The first band (maroon) was collected, and the solvent was removed by rotary evaporation. The solid residue was recollected in 4 mL of acetonitrile and added dropwise to anhydrous diethyl ether. The precipitate was isolated by suction filtration and dried under vacuum (100 mg, yield 36%) (Found: C, 36.66; H, 3.27. Calculated for $[Ru(C_{11}H_9N_5)(C_5H_7O_2)(C_3H_4N_2)](PF_6)$: C, 36.55; H, 3.23%).

**[Ru(bpp)(Me$_2$mal)(NCCH$_3$)](PF$_6$).** Ru(bpp)(Me$_2$mal)Cl (100 mg, 0.22 mmol) was added to 50 mL of 20% acetonitrile/water and heated at reflux under $N_2$ for 2 hours. The reaction mixture was allowed to cool. Ammonium hexafluorophosphate (300 mg, 1.8 mmol) was dissolved in 3 mL of water and added to the reaction mixture. The solvent was removed by rotary evaporation. The solid residue was redissolved in 2 mL of acetonitrile and was added dropwise to anhydrous diethyl ether with stirring. The precipitated product was isolated by suction filtration, washed/dried with anhydrous diethyl ether, and dried under vacuum (70 mg, yield 50%) (Found: C, 36.07; H, 3.23. Calculated for $[Ru(C_{11}H_9N_5)(C_5H_7O_2)(C_2H_3N)](PF_6)$: C, 36.19; H, 3.20%).

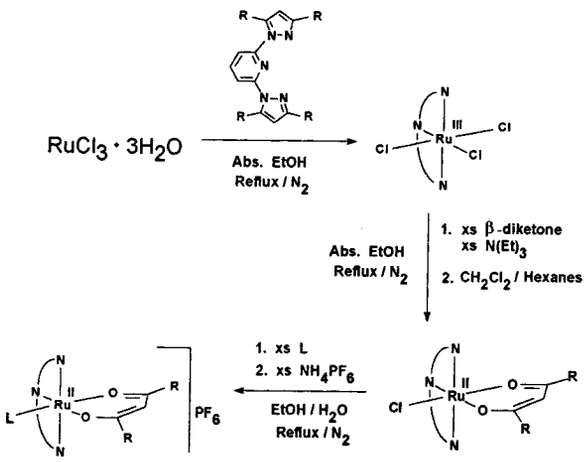
**[Ru(Me$_4$bpp)(Me$_2$mal)(py)](PF$_6$).** Ru(Me$_4$bpp)(Me$_2$mal)Cl (200 mg, 0.38 mmol) and pyridine (0.26 mL, 3.2 mmol) were combined in 110 mL of 30% ethanol/water and heated at reflux under $N_2$ for 3 hours. The reaction mixture was allowed to cool. Ammonium hexafluorophosphate (500 mg, 3.1 mmol) was dissolved in 3 mL of water and added to the reaction mixture. The precipitated product was isolated by suction filtration, washed with water, and washed/dried with anhydrous diethyl ether. The crude product (245 mg) was purified on a 16 cm × 3 cm neutral alumina column prepared and eluted with 1:1 acetonitrile/toluene. The first band (red-orange) was collected, and the solvent was removed on a rotary evaporator. The solid residue was collected with 4 mL of acetonitrile and added dropwise to anhydrous diethyl ether with stirring, precipitating the product, which was isolated by suction filtration. The product was dried under vacuum (160 mg, yield 59%) (Found: C, 43.45; H, 4.27. Calculated for $[Ru(C_{15}H_{17}N_5)(C_5H_7O_2)(C_5H_5N)](PF_6)$: C, 43.42; H, 4.23%).

**[Ru(Me$_4$bpp)(Me$_2$mal)(pyz)](PF$_6$).** Ru(Me$_4$bpp)(Me$_2$mal)Cl (270 mg, 0.54 mmol) and pyrazine (270 mg, 3.4 mmol) were combined in 110 mL of 40% ethanol/water and heated at reflux under $N_2$ for 4 hours. The reaction mixture was allowed to cool. The volume of the reaction mixture was reduced by roughly 1/3 on a rotary evaporator. Approximately 400 mg of $NH_4PF_6$ was dissolved in 3 mL of water and added to the reaction mixture. The precipitated product was isolated by suction filtration, washed with water, and washed/dried with anhydrous diethyl ether. The crude product (150 mg) was purified on a neutral alumina column (17.5 cm × 2.5 cm), which was prepared with 1:1 acetonitrile/toluene. The second band (red-orange) was isolated, and the solvent was removed by rotary evaporation. The solid residue was collected with 4 mL of acetonitrile and added dropwise to anhydrous diethyl ether with stirring, precipitating the product. The product was isolated by suction filtration (110 mg, yield 30%) (Found: C, 41.70; H, 4.07. Calculated for $[Ru(C_{15}H_{17}N_5)(C_5H_7O_2)(C_4H_4N)](PF_6)$: C, 41.62; H, 4.08%).

## Results

### Synthesis

A general scheme for the synthesis of the Ru(Me$_n$bpp)(R$_2$mal)Cl and [Ru(Me$_n$bpp)(R$_2$mal)(L)]$^+$ complexes is shown in Scheme 1. The Ru(Me$_n$bpp)(R$_2$mal)Cl complexes were prepared from the appropriate Ru(Me$_n$bpp)Cl$_3$ and β-diketone. In a typical preparation, Ru(Me$_n$bpp)Cl$_3$ was placed in ethanol with an eight-fold excess of the β-diketone and an eleven-fold excess of triethylamine, and heated at reflux for several hours. The triethylamine serves as a reducing agent toward the Ru(bpp)Cl$_3$ and possibly as a deprotonating agent for the β-diketone. The solvent was removed, and the residual solid was reprecipitated from methylene chloride and hexanes. Product purity was evaluated by cyclic voltammetry and thin-layer chromatography. When necessary, the product was purified by column chromatography on alumina with acetone/methylene chloride or methanol/methylene chloride as the eluent.




**Scheme 1**

The chloride ligand on Ru(Me$_n$bpp)(R$_2$mal)Cl is easily displaced in refluxing ethanol/water, permitting the synthesis of a variety of [Ru(Me$_n$bpp)(Me$_2$mal)L]$^+$ complexes, where L is a neutral ligand such as pyridine, pyrazine, 4,4′-bipyridine, imidazole, or acetonitrile. The pyrazine and 4,4′-bipyridine complexes are of particular interest since they can serve as precursors to bimetallic complexes. In general, the Ru(Me$_n$bpp)(Me$_2$mal)Cl precursors were used without purification for the synthesis of the [Ru(Me$_n$bpp)(R$_2$mal)L]$^+$ complexes, since it is more convenient to purify the latter species by column chromatography, given the relative lability of the chloride. The utility of the Ru(Me$_n$bpp)(R$_2$mal)Cl complexes as starting materials is illustrated here by the complex Ru(Me$_n$bpp)(Me$_2$mal)Cl, which is representative of most of the Ru(Me$_n$bpp)(R$_2$mal)Cl complexes. Only Ru(Me$_n$bpp)((CF$_3$)$_2$mal)Cl proved difficult to use in preparing the analogous [Ru(Me$_n$bpp)((CF$_3$)$_2$mal)L]$^+$ complexes, where reaction with L resulted in formation of a relatively large percentage of the [Ru(Me$_n$bpp)L$_3$]$^{2+}$ complex.

### Electrochemistry

The Ru(Me$_n$bpp)(R$_2$mal)Cl complexes exhibited single, one-electron Ru(III/II) couples over the range 0.05 to 0.65 V *vs.* SSCE in 0.1 M TBAH/acetonitrile (Table 1). The $\Delta E_p$ between the anodic and cathodic peaks was in the range of 60 to 80 mV. Previous investigations with the complexes [Ru(Me$_n$bpp)$_2$]$^{2+}$ and [Ru(Me$_n$bpp)(Me$_n$bpy)Cl]$^+$ showed that there was a steady decrease in the Ru(III/II) couple as the number of methyl groups was increased, with an average of 24 mV per methyl group.[7] This shift in the redox potential is consistent with the electron-donating nature of the methyl groups. Similar results were obtained with the Ru(Me$_n$bpp)(R$_2$mal)Cl complexes in this study. In Fig. 1, a graph of $E_{1/2}$ for the Ru(III/II) couple *vs.* the number of the methyl groups ($n$) on the Me$_n$bpp for the Ru(Me$_n$bpp)(R$_2$mal)Cl complexes illustrates the control of redox potential that is possible with these ligands. An average slope of 25 mV per methyl group was obtained.

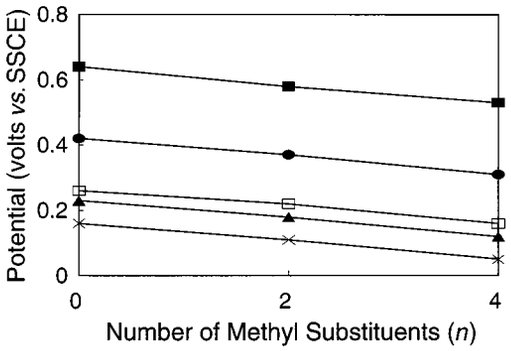



**Fig. 1** A plot of $E_{1/2}$ for the Ru(III/II) couple *vs.* the number of methyl groups on the bpp ligand: (×) = $[Ru(Me_nbpp)(t\text{-}Bu_2mal)Cl]^{+/0}$; (▲) = $[Ru(Me_nbpp)(Me_2mal)Cl]^{+/0}$; (□) = $[Ru(Me_nbpp)(Ph_2mal)Cl]^{+/0}$; (●) = $[Ru(Me_nbpp)(Me,CF_3mal)Cl]^{+/0}$; (■) = $\{Ru(Me_nbpp)[(CF_3)_2mal]Cl\}^{+/0}$. Potentials were measured in 0.1 M TBAH/acetonitrile.

**Table 1** Cyclic voltammetry data for $Ru(Me_nbpp)(R_2mal)Cl$

| Complex | $E_{\frac{1}{2}}$/V [a] |
|---|---|
| $[Ru(bpp)((CF_3)_2mal)Cl]^{+/0}$ | 0.64 |
| $[Ru(Me_2bpp)((CF_3)_2mal)Cl]^{+/0}$ | 0.58 |
| $[Ru(Me_4bpp)((CF_3)_2mal)Cl]^{+/0}$ | 0.53 |
| $[Ru(bpp)(Me,CF_3mal)Cl]^{+/0}$ | 0.42 |
| $[Ru(Me_2bpp)(Me,CF_3mal)Cl]^{+/0}$ | 0.37 |
| $[Ru(Me_4bpp)(Me,CF_3mal)Cl]^{+/0}$ | 0.31 |
| $[Ru(bpp)(Ph_2mal)Cl]^{+/0}$ | 0.26 |
| $[Ru(bpp)(Me_2mal)Cl]^{+/0}$ | 0.23 |
| $[Ru(Me_2bpp)(Ph_2mal)Cl]^{+/0}$ | 0.22 |
| $[Ru(Me_2bpp)(Me_2mal)Cl^{+/0}$ | 0.18 |
| $[Ru(bpp)(t\text{-}Bu_2mal)Cl]^{+/0}$ | 0.16 |
| $[Ru(Me_4bpp)(Ph_2mal)Cl]^{+/0}$ | 0.16 |
| $[Ru(Me_4bpp)(Me_2mal)Cl]^{+/0}$ | 0.12 |
| $[Ru(Me_2bpp)(t\text{-}Bu_2mal)Cl]^{+/0}$ | 0.11 |
| $[Ru(Me_4bpp)(t\text{-}Bu_2mal)Cl]^{+/0}$ | 0.05 |

[a] Potentials measured at a Pt disk electrode *vs.* SSCE in 0.1 M TBAH/acetonitrile.

Substituent effects on metal-based redox couples for β-diketonate ligands are well-documented.[4] Substituent effects within a family of $Ru(Me_nbpp)(R_2mal)Cl$ complexes can be seen in Fig. 1. The Ru(III/II) redox potential shifts in the anodic direction with $R^1$ and $R^3$ in the following order: ($R^1 = R^3 = t$-Bu) < ($R^1 = R^3$ = Me) < ($R^1 = R^3$ = Ph) < ($R^1$ = Me, $R^3 = CF_3$) < ($R^1 = R^3 = CF_3$). Hammett constants, $\sigma_m$, can provide an approximate measure of substituent inductive effects. Fig. 2 shows a linear relationship between $E_{1/2}$ for the Ru(III/II) couples and the sum of the Hammett constants ($\Sigma\sigma_m$) for substituents on the β-diketonate ligand. Holm [5] and Takeuchi [11] and their co-workers have also reported linear relationships for $E_{1/2}$ *vs.* $\Sigma\sigma_m$ with ruthenium tris-β-diketonate complexes.

The Ru(III/II) redox potentials for complexes with the general formula $[Ru(Me_nbpp)(Me_2mal)L]^+$ are listed in Table 2. Comparing the $[Ru(Me_nbpp)(R_2mal)L]^+$ complexes with the corresponding $Ru(Me_nbpp)(R_2mal)Cl$ precursors (Table 1) shows that the substitution of a neutral ligand for the anionic chloride results in an increase in the Ru(III/II) potential for the complex, as expected.

### Electronic spectra

The electronic spectrum of Ru(bpp)($Me_2$mal)Cl shown in Fig. 3 is representative of this family of complexes. The UV region consists primarily of intense ligand-localized $\pi \longrightarrow \pi^*$ transitions, while the visible region is dominated by unresolved overlapping bands which are assigned as metal-to-ligand charge transfer (MLCT) transitions based on their energy and molar absorption coefficients (roughly 8000 $M^{-1}$ $cm^{-1}$ for all complexes in this family). It is difficult to make specific assignments for these MLCT bands since they may involve both

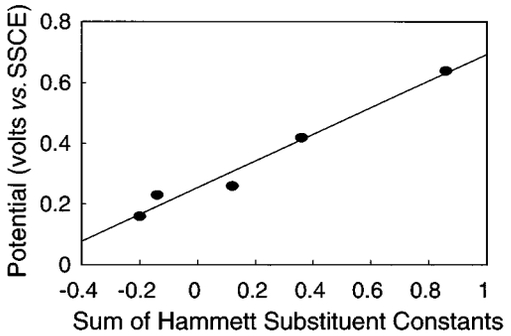



**Fig. 2** A plot of Ru(III/II) redox potential *vs.* the sum of Hammett constants ($\Sigma\sigma_m$) for the $R^1$ and $R^3$ substituents on the Ru(bpp)-($R_2$mal)Cl complexes.

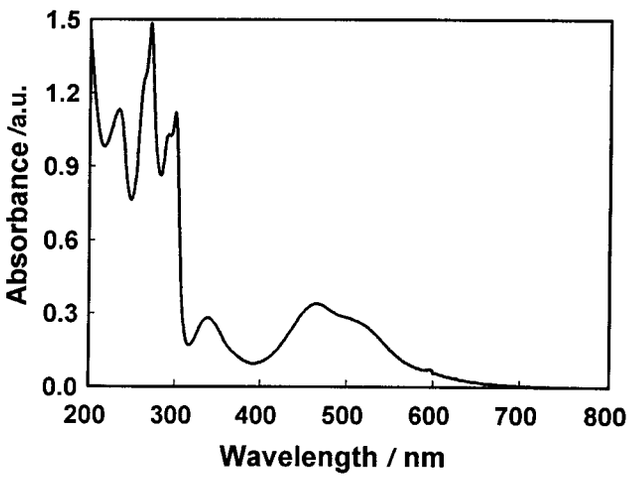



**Fig. 3** UV-Visible spectrum of $5.5 \times 10^{-4}$ M Ru(bpp)($Me_2$mal)Cl in acetonitrile.

**Table 2** Cyclic voltammetry data for $[Ru(Me_nbpp)(R_2mal)L]^+$

| Complex | $E_{\frac{1}{2}}$/V [a] |
|---|---|
| $[Ru(bpp)(Me_2mal)(ImH)]^{2+/+}$ | 0.50 |
| $[Ru(bpp)(Me_2mal)(4,4'\text{-bpy})]^{2+/+}$ | 0.65 |
| $[Ru(bpp)(Me_2mal)(NCCH_3)]^{2+/+}$ | 0.72 |
| $[Ru(Me_4bpp)(Me_2mal)(py)]^{2+/+}$ | 0.52 |
| $[Ru(Me_4bpp)(Me_2mal)(pyz)]^{2+/+}$ | 0.63 |

[a] Potentials measured at a Pt disk electrode *vs.* SSCE in 0.1 M TBAH/acetonitrile.

$Me_n$bpp and $R_2$mal π* orbitals. Given the breadth of these multiple MLCT bands and the comparable molar absorption coefficients for the $Ru(Me_nbpp)(R_2mal)Cl$ complexes, we did not find electronic spectroscopy to be a very useful technique for characterizing these complexes or evaluating product purity.

## Discussion

The synthesis of the $Ru(Me_nbpp)(R_2mal)Cl$ complexes is relatively straightforward, although somewhat complicated by the lability of chloride. The increased lability of the chloride ligand compared to analogous $[Ru(Me_nbpp)(bpy)Cl]^+$ and $[Ru(tpy)(bpy)Cl]^+$ complexes (bpy is 2,2′-bipyridine, and tpy is 2,2′:6′,2″-terpyridine) can be understood in terms of the increase in electron density at the metal center which would be expected to weaken the bonding between ruthenium(II) and the π-donor chloride ligand. Similar explanations have been used to account for the lability of chloride in *cis*- and *trans*-$[Ru(NH_3)_4(L)Cl]^+$ complexes.[12] Given the relative ease with which the chloride ligand can be substituted, a wide variety of complexes may be prepared. In addition to simple monodentate

ligands, the chloride may be replaced by bridging ligands, allowing these complexes to be used as precursors to bimetallic complexes. The synthesis and characterization of bimetallic complexes based on bpp and β-diketonate ligands will be presented in a future paper.

The electrochemical data presented in Table 1 and illustrated in Fig. 1 show that the ruthenium center is strongly influenced by the substituents on both the β-diketonate and bpp base ligands. The linear Hammett relationship in Fig. 2 suggests that the influence of the substituents is largely inductive, at least for the ligand substituents examined here. The extensive control of ligand substituents for these complexes makes it possible to systematically and rationally *fine*-tune the Ru(III/II) couple over a wide potential range. In principle, even finer tuning could be obtained with other existing variations of the $R^1$, $R^2$, and $R^3$ groups on the β-diketonate.[13]

## Acknowledgements

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